

Molecular Understanding of Structure-Activity Relationships in Co-Catalyzed CO2 and CO Hydrogenation

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Molecular Understanding of Structure-Activity Relationships in Co-Catalyzed CO, and CO Hydrogenation

Roos Krösschell

Molecular Understanding of Structure-Activity Relationships in Co-Catalyzed CO₂ and CO Hydrogenation

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus prof.dr. S.K. Lenaerts, voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op dinsdag 8 april 2025 om 13:30 uur

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Molecular Understanding of Structure-Activity Relationships in Co-catalyzed $\rm CO_2$ and CO Hydrogenation

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1. Introduction

1.1. The energy transition

1.1.1 Climate change

Due to the emission of greenhouse gases by humans, the climate on Earth is changing. Since the mid-20th century, the Earth has been heating up stronger than can be explained by the natural warming and cooling cycles, which have a length of roughly 100.000 years. As greenhouse gases absorb heat from the sun and re-radiate the heat back into the atmosphere, they play a crucial role in maintaining livable temperatures on Earth. With the extra emission of greenhouse gases, the Earth loses the heat to space too slowly and the atmosphere heats up, called the enhanced greenhouse effect.[1] The most relevant greenhouse gases emitted by humans are CO₂, CH₄, N₂O and chlorofluorocarbons (CFCs).[2] The current CO₂ concentration in the atmosphere is 1.5 times higher than it was before the industrial revolution.[1] Anthropogenic CO₂ emissions are mostly due to combustion of fossil fuels and cement production.[1] Methane emissions due to human activities are due to landfills, rice agriculture, biomass burning, livestock animals and leaks from fossil fuel production and transportation. Anthropogenic sources of N₂O are burning fossil fuels and fertilizer production and use. CFCs do not exist in nature and are entirely of industrial origin, used as refrigerants and solvents, and are powerful greenhouse gases due to their ability to trap large amounts of heat.[1,2] Due to the enhanced greenhouse effect, the average global temperature is now more than 1.1 °C above the 1850-1900 pre-industrial average.[1] Rising temperatures can have serious consequences, including more frequent and intense droughts, heatwaves, and heavy rainfall. Higher temperatures lead to the melting of polar ice sheets, which in turn causes sea levels to rise. Due to these consequences, rising temperatures threaten both food security and the availability of drinking water. [2] In 2015, the Paris Agreement was signed by 196 parties at the UN Climate Change Conference to limit global warming. The agreement aims to keep the global average temperature increase well below 2.0 °C above pre-industrial levels and to pursue efforts to limit it to 1.5 °C.[3] To achieve this, significant reductions in anthropogenic greenhouse gas emissions are necessary. To address future energy demands without increasing CO_2 emissions, alternative energy sources like solar, wind, nuclear, geothermal, hydropower, ocean energy, and bioenergy are being adopted. Additionally, effective energy storage solutions play a vital role. For the electricity grid, new

grid-scale storage options besides batteries are needed to manage intermittent electricity generation and usage.[4] In the transport sector, fossil fuels still account for 95% of energy use.[5] Sectors like aviation, shipping, heavy road transport, and the chemical industry cannot rely on batteries but require renewable fuels to become sustainable.[6]

1.1.2 Technologies combating climate change

The transition to a carbon-neutral future requires innovative solutions to integrate renewable energy into all sectors of the economy. Among these, power-to-X technologies have emerged as a promising approach to address the challenges of decarbonization and energy storage. These technologies enable the conversion of renewable electricity into fuels or materials, expanding the applicability of renewable energy beyond the electrical grid. These processes can be categorized as power-to-gas, which produces hydrogen or methane, or power-to-liquid, which generates synthetic fuels such as diesel, gasoline, jet fuel, methanol, or ammonia. A selection among the various power-to-liquid technologies, relevant to this thesis, are shown in Figure 1.1.[7] Though these conversion processes provide a pathway to decarbonize sectors reliant on liquid or gaseous fuels, they face challenges including high initial setup and operational costs as well as significant energy losses during conversion.[8] These challenges spark ongoing research to improve the efficiency and scalability of power-to-X processes.

Power-to-gas specifically involves storing renewable energy in gaseous forms. Hydrogen is produced directly using renewable electricity through water electrolysis, and methane is synthesized through further conversion processes involving CO_2 .[9] The required CO_2 can be captured directly from the atmosphere (direct air capture) or sourced from industrial flue gases. While conventional fossil fuel combustion emits flue gases with a relatively low CO_2 concentration,[10] biomass combustion produces higher concentrations of biogenic CO_2 , which can be utilized to help close the carbon cycle and make the process more sustainable.[11]

Among the power-to-liquid technologies, the Fischer-Tropsch process is the most significant, enabling the production of liquid hydrocarbons which can be refined into fuels such as gasoline, diesel, and kerosene. Alongside Fischer-Tropsch, other power-to-liquid processes focus on the synthesis of chemicals like methanol, dimethyl ether, and formic acid, broadening the scope of renewable energy integration in liquid fuel and chemical production.[12] The Fischer-

Tropsch process utilizes syngas, a mixture of carbon monoxide and hydrogen, as its feedstock which is catalytically converted to longer-chain hydrocarbons, as shown in Figure 1.1.[7] The production of CO from CO_2 is a critical step in the process and is achieved through the reverse water-gas shift (RWGS) reaction, wherein CO_2 reacts with hydrogen to produce CO and H_2O .



Figure 1.1: The production of renewable fuels using Fischer-Tropsch synthesis or methanol synthesis by using renewable H_2 and atmospheric CO_2 (power-to-liquid). Used with permission from [7].

The utilization of renewable feedstocks poses significant challenges due to the inherent stability of the molecules involved. CO_2 represents a formidable obstacle in this context. Thermodynamically, CO_2 resides at the bottom of the energy well, meaning it is highly stable and energetically unfavorable to react with. Its robust C–O bonds require substantial energy input to break, making its activation a key challenge in chemical processes. Catalysts play an essential role in overcoming these barriers by providing alternative reaction pathways with lower energy requirements. Through precise interactions with CO_2 , catalysts can weaken its stable bonds and facilitate its conversion into valuable products such as fuels, chemicals, and materials. By enabling the transformation of CO_2 , catalysts not only address the stability challenge but also open the door to sustainable utilization of this abundant feedstock, contributing to the development of carbon-neutral and circular chemical processes.

1.2. Catalysis

Catalysts play a vital role in everyday life and in industry. Nearly 90% of all chemical processes rely on catalysts, making them crucial contributors to the gross domestic product (GDP) of many developed nations. Without heterogeneous catalysis, the large-scale production of ammonia, essential for intensive agriculture, would be unachievable, jeopardizing the ability to support the current global population. Even within our bodies, catalysts—known as enzymes—drive almost all biological processes. Homogeneous catalysts play an important role in the synthesis of simple and complex molecules, including drug compounds and agrochemicals. It is evident that catalysts are indispensable to both life and society.

1.2.1 Catalytic mechanism

A catalyst is a substance that accelerates chemical reactions by facilitating the breaking and forming of chemical bonds. It achieves this by interacting with reactants, intermediates, and products, thereby reducing the energy barriers for the steps involving bond dissociation and formation. This reduction in activation energy, as shown schematically in Figure 1.2, allows the reaction to proceed at a lower temperature compared to an uncatalyzed reaction. Importantly, a catalyst does not alter the overall energy balance of a reaction, as doing so would violate the first law of thermodynamics, i.e. the conservation of energy. While the formal definition states that a catalyst is both consumed and regenerated during the reaction, suggesting it is not permanently consumed, catalysts in practice can deactivate through various mechanisms. Consequently, they often require regeneration or replacement to maintain their functionality in the process.

1.2.2 Heterogeneous catalysis

Catalysis can be broadly categorized into homogeneous, heterogeneous, and biocatalysis, each distinguished by the nature of the catalyst and its interaction with reactants. Homogeneous catalysis involves catalysts that exist in the same phase as the reactants, typically in solution, enabling uniform interaction at the molecular level. In contrast, heterogeneous catalysis utilizes catalysts in a different phase from the reactants, most commonly solids interacting with gaseous or liquid reactants.[13] This phase separation allows for easy catalyst recovery and reuse but introduces complexities in surface interactions. Biocatalysis, on the other hand, employs biological molecules such as enzymes to catalyze reactions, often with high specificity and under mild conditions. This thesis focuses on nanoparticle catalysis, a branch of heterogeneous catalysis

where catalytic activity arises from the unique properties of nanoparticles. These nanostructures offer high surface-to-volume ratios and tunable surface properties, making them particularly effective in facilitating reactions and an important area of research within the field of heterogeneous catalysis.



Reaction coordinate

Figure 1.2: Reaction energy diagram of catalyzed and uncatalyzed association of A and B. The catalyzed association involves adsorption of reactants A and B, an association step on the catalytic surface and subsequent desorption of AB.

1.2.3 Descriptor-based science

Catalysis is largely a descriptor-based science because it relies on identifying key parameters, or descriptors, that govern catalytic performance, such as activity, selectivity, and stability. These descriptors—often atomic or molecular properties like binding energies, reaction barriers, or electronic structures—serve as simplified representations of complex catalytic systems. By correlating these descriptors with experimental outcomes, scientists can predict the behavior of catalysts, optimize their design, and guide the discovery of new materials. Descriptor-based approaches allow researchers to screen large material libraries efficiently, reducing the need for trial-and-error experimentation and accelerating the development of catalysts for energy, chemical, and environmental applications.

1.2.4 Sabatier principle

The interaction between a catalyst and reactants must strike a balance. If the bond between the catalyst and reactants is too weak, the reactants are insufficiently activated, resulting in minimal or no conversion. Conversely, if the interaction is too strong, the products cannot desorb from the catalyst surface, leading to catalyst poisoning and a halt in activity. This need for an optimal interaction lies at the heart of the so-called Sabatier principle, which defines the fundamental requirement for effective catalysis.[14]

1.3 Length scales in heterogeneous catalysis

The successful implementation of a catalyst hinges on understanding the reaction mechanism and its relationship to the catalyst molecular structure, as well as on various mass and heat transport phenomena. To capture this complexity, catalyst behavior is modeled across multiple length scales, as phenomena at one scale often influence processes at others. Figure 1.3Figure 1.3 illustrates these length scales for a reactor loaded with a typical catalyst consisting of supported metal nanoparticles (NPs).

1.3.1 Active sites

Chemical transformations are facilitated at specific locations known as active sites, which are typically composed of small, ordered arrays of metal atoms. These sites serve as the catalytic centers where reactants are adsorbed and converted into products. Upon adsorption, the internal bonds of the reactants are weakened, a critical step in their activation. The geometry of the active site plays a pivotal role in this process, as it dictates the bonding interaction between the adsorbates and the active site by determining the redistribution of electrons. This influences the extent and manner in which reactants are activated for the catalytic reaction. A particularly notable active site is the B₅ site,[15] known for its exceptional efficiency in cleaving the robust C–O bond. The unique properties and catalytic significance of the B₅ site are explored in greater detail in the following section.

1.3.2 Nanoparticles

The dispersion of the metal phase plays a crucial role in determining the distribution and accessibility of the aforementioned active sites. The dispersion can range from isolated, single supported atoms to nanoparticles spanning hundreds of nanometers. Both the size and shape of the nanoparticles are critical factors that influence the arrangement and properties of active sites, as these structural characteristics dictate the exposure and accessibility of catalytic centers. This topic has been the focus of extensive research, which will be addressed in more detail in the next section.

Beyond size and shape, the specific location of the active site on the nanoparticle is also a key determinant of its reactivity. Active sites near particular geometric features, such as edges, corners, or facets, can exhibit distinct catalytic behaviors due to their unique electronic and structural environments. Recent advances in computational capabilities, particularly in density functional theory (DFT), now allow for the simulation of nanoparticles anchored on supports with unprecedented detail within reasonable time frames. These developments enable researchers to investigate not only isolated active sites but also the broader influence of their surroundings, including neighboring metal atoms and the proximity of a support material, on catalytic activity. This holistic approach provides deeper insights into the complex interplay between nanoparticle structure, active site location, and reactivity.

1.3.3 Catalytic reactor

As mentioned, Figure 1.3 illustrates the various length scales relevant within a catalytic reactor. At the macroscopic scale, support particles, typically around 100 nm to µm scale in size, serve as anchoring structures for smaller metal nanoparticles. To maximize catalytic efficiency and conversion rates, the specific surface area of these supports is enhanced by employing porous structures. Common support materials include refractory oxides such as SiO₂, Al₂O₃, TiO₂, and CeO₂, as well as activated carbon, zeolites, and metal-organic frameworks (MOFs).[16] These porous supports facilitate the movement of reactants through micro-, meso-, and macropores—a process known as intraparticle diffusion— and similarly guide the diffusion of products back into the reactor bulk.



Figure 1.3: Length scales in a catalytic reactor.

The support particles are typically aggregated into millimeter-sized extrudates to fill the reactor, which is designed to accommodate specific reaction requirements. Common catalytic reactor types for methanation processes include fixed-bed reactors and structured reactors featuring microchannel or honeycomb designs, both of which offer controlled flow dynamics and heat transfer. Additionally, fluidized-bed reactors and slurry bubble columns are employed for reactions requiring enhanced mixing and heat management.[17] The choice of reactor type is dictated by the unique demands of the reaction system. With optimal designs, issues such as pressure drops, hot spot formation, inadequate heat removal, and mass transfer limitations, are minimized. These considerations ensure efficient and stable reactor performance, maximizing the overall catalytic activity and product yield.[18]

1.4 Structure sensitivity

Structure sensitivity is a fundamental concept in catalysis, describing how the catalytic performance of a material depends on its structural and topological features at the atomic and nanoscale.[19,20] Unlike structure-insensitive reactions, where catalytic activity remains relatively unchanged regardless of nanoparticle surface characteristics. structure-sensitive reactions are significantly influenced by factors such as nanoparticle size, shape, surface facets, and atomic arrangements.[21,22] These parameters directly affect the availability, abundance, and nature of active sites, which are the specific locations on a catalyst where reactants are converted into products. The origins of structure sensitivity lie in the relationship between catalyst dispersion and reaction rates, a phenomenon first systematically explored by Boudart.[23] His work revealed that variations in particle size and surface structure could lead to pronounced differences in catalytic activity. This concept has since evolved, with contemporary research emphasizing the role of active sites. These active sites often exhibit distinct electronic and geometric properties that are highly sensitive to the atomic environment.

Structure sensitivity is particularly relevant in nanoparticle catalysis, where the interplay between particle size and surface morphology determines the distribution and accessibility of active sites. For instance, smaller nanoparticles often expose a higher fraction of edge and corner sites, which can exhibit unique catalytic properties. Conversely, larger particles may favor terrace sites or specific crystallographic facets, influencing the reaction mechanism and product distribution. Many reactions in heterogeneous catalysis, specifically in nanoparticle catalysis, exhibit strong structure sensitivity relationships. The most well-known examples include ammonia synthesis (Haber-Bosch process), CO₂ methanation (Sabatier reaction), Fischer-Tropsch synthesis, Pt- and Aucatalyzed CO oxidation and ethylene epoxidation. Structure sensitivity exhibits various patterns, as depicted in Figure 1.4.[22,24] In this figure, class-I depicts a structure-insensitive relation, where the turnover frequency (TOF) does not depend on the size of the nanoparticles. This is often observed for hydrogenation

reactions. For some catalytic reactions, an optimal particle size is observed (class-IIIb), whereas for others, activity reaches a plateau, with no further increase or decrease in activity as particle size increases (class-IIIa). These relations are often found for catalytic reactions where the scission of a π -bond is a rate-determining step. Class-II shows a decreasing activity with increasing particle size. This pattern is observed if the cleavage of a σ -bond is rate-determining for the conversion. The following subsections present three specific examples of structure sensitivity that are relevant to this thesis.





1.4.1 Structure sensitivity of CO dissociation

Direct CO dissociation requires breaking of its strong (1072 kJ/mol)[25] triple bond. Blyholder attributed the activation or elongation of the C-O bond when adsorbed perpendicular to the surface (only carbon bonds to the metal) as the result of electron exchange with the surface. CO donates electrons to the surface from its bonding orbitals and receives electrons into its antibonding orbitals, both weakening the C-O bond.[26] However, for this reaction step to proceed with a low energy barrier, specific sites are required on which CO adsorbs parallel to the surface, i.e. oxygen is also bonded to the metal.[27] At these sites, the C–O bond is pre-activated in its adsorbed state, and during the transition state, both the C and O atoms are effectively stabilized, resulting in a small activation energy. This situation is possible on a B_5 site[15] or a B_5 -like site such as a step-edge or pocket site. Only NPs that are large enough can sustain B_5 -like sites,[24,28–30] making direct CO dissociation a structure-sensitive reaction step according to class-IIIb as depicted in Figure 1.4. For CO dissociation in the context of Co-catalyzed Fischer-Tropsch synthesis was found that the optimal NP size for CO cleavage is approximately 6-10 nm.[31–34] Below the optimal particle size, the number of B_5 -sites is limiting, while above the optimum the Co is underutilized. When there are no B_5 -like sites present, CO dissociation on Co is assumed to occur *via* an H-assisted route.[35] The association of a hydrogen atom to either the carbon (CHO) or to the oxygen (COH) atom weakens the C-O bond, resulting in a lower dissociation barrier.

1.4.2 Structure sensitivity of Fischer-Tropsch synthesis

In the Fischer-Tropsch process, syngas (CO + H_2) is converted towards hydrocarbons over a supported Fe, Co, Ru or Ni catalyst. Co and Fe are preferred over Ru and Ni as FT catalyst, because Ru is very expensive, and Ni produces primarily methane.[36] Since the product distribution of the Fischer-Tropsch process follows the Anderson-Schultz-Flory distribution, it is generally accepted that the FT reaction is a polymerization reaction with the *in situ* generation of monomers.[37] C₁ monomers are linked to form hydrocarbons, mostly linear olefins and paraffins. The product distribution ranges from methane to wax molecules. The simplified reaction equation for the FT reaction is as follows:[37]

$$CO + 2 H_2 \rightleftharpoons -CH_2 - + H_2 O \qquad [\Delta H_R^{\Theta} = -165 \text{ kJ/mol}]$$
(1)

The monomer that is added to the growing chain can either be a CO adsorbate (CO-insertion mechanism) or a CH_x (x = 0-3) intermediate (carbide mechanism). In FT synthesis, often the valuable C_{5+} fractions are preferred and methane formation is undesired.[38] Methane formation in FT synthesis proceeds as follows:[17]

$$CO + 3 H_2 \rightleftharpoons CH_4 + H_2 O \qquad [\Delta H_R^{\Theta} = -206 \text{ kJ/mol}]$$
(2)

The FT reaction is observed to be highly structure sensitive. The optimum Co particle size is found to be 6 nm on carbon nanofibers.[31] For SiO₂, Melaet *et al.* found an optimum NP size of 10 nm.[39] For NPs smaller than the optimum size, a decrease in CO conversion and an increase in methane selectivity are observed. This is attributed to the absence of step-edge sites on smaller NPs, which are crucial for facile CO dissociation and chain growth. These sites are therefore essential for achieving significant conversion in FTS.[40] For NPs larger than the optimum size, the activity per surface Co atom remains unchanged. In larger particles, more Co atoms are subsurface atoms and thus not accessible for the

reactants. As a result, an optimum particle size exists that maximizes catalytic performance.

1.4.3 Structure sensitivity of the Sabatier reaction

CO₂ methanation, also known as the Sabatier reaction, proceeds according to the following overall reaction equation:[17]

$$CO_2 + 4 H_2 \rightleftharpoons CH_4 + 2 H_2 O \qquad [\Delta H_R^{\Theta} = -164 \text{ kJ/mol}]$$
(3)

The reaction can be catalyzed by the transition metals Ni, Co, and Ru, often supported on Al_2O_3 or SiO_2 . On these catalysts and under similar conditions, CO can also form *via* the reverse water-gas shift (RWGS) reaction[17]

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad [\Delta H_R^{\Theta} = 41 \text{ kJ/mol}]$$
(4)

which when targeting CH_4 as a final product is an unwanted side-reaction. Although Ni is often preferred for industrial processes due to its low cost, Co is interesting for CO₂ methanation due to its potential low-temperature activity.[41,42] Over both Ni[43] and Co, CO₂ hydrogenation is structure sensitive, and for both metals the structure sensitivity trends are still under debate. Although some studies do not find a particle size effect for CO_2 hydrogenation over Ni[44,45], the majority observes either increasing surfacenormalized activity with increasing particle size, [46] or an optimum particle size. According to these studies this optimum stems from a faster restructuring for larger particles, a different active site distribution for different particle sizes, and a higher electron localization of *d*-electrons for *sub*-2-nm Ni particles.[47,48] There is no consensus regarding the reactivity of small clusters either: both high CH_4 selectivity [47,48] and high CO selectivity [49] have been reported for these structures. Recent work shows that small Ni nanoparticles produce mainly CO due to the absence of step-edge sites needed for facile CO dissociation, and only large nanoparticles are able to produce CH₄.[50] Also for Co, studies report an increasing surface-normalized activity with increasing particle size or an optimum particle size. Guerrero-Ruiz and Rodríguez-Ramos have shown that the specific activity of CO₂ hydrogenation over Co/C decreases with increasing metal dispersion.[51] lablokov *et al.* show that the TOF increases with increasing particle size for SiO₂-supported Co particles between 3 and 10 nm.[52] Parastaev and coworkers find that for a fully reduced Co catalyst supported on ceriazirconia, NPs of 7 - 9 nm are optimal.[53]

1.5 Metal-support interactions

1.5.1 Size and shape of the nanoparticles

The primary function of the support is to stabilize nanoparticles, though some supports are more effective than others in maintaining NP stability and preventing sintering.[54] Consequently, certain metal-support combinations demonstrate superior thermal and chemical stability. The type of support significantly affects the particle size distribution or dispersion of the metal loading. While some supports yield smaller nanoparticles on average, others result in larger nanoparticles.[55–57]

The support impacts not only the size but also the shape of the nanoparticles. Supports with stronger affinity with the metal phase tend to produce more faceted nanoparticles.[58] Small nanoparticles can adopt a flat shape due to strong metal-support interactions.[30,55] When the atomic structures of the support surface and the preferred metal phase are misaligned, lattice strain arises, which can influence the reactivity of the nanoparticles.[59] This effect is more pronounced in smaller nanoparticles.[60] Since the size and shape of nanoparticles directly determine their active sites, these characteristics play a crucial role in catalytic performance.

1.5.2 Extent of reduction, charge transfer and interfacial perimeter

Typically, the fully reduced phase of the active metal is desired in catalysts, but sometimes partially reduced phases have been reported to outperform their fully reduced counterparts. For CO₂ hydrogenation this was found for Co supported on TiO₂[61,62], CoO[63] and ceria-zirconia (CZ)[53]. The catalysts reported in these studies do not obey the structure sensitivity trends established for fully reduced catalysts (*vide supra*). The structure sensitivity of these reactions over fully reduced catalysts was found to follow the trend of class-IIIb as shown in Figure 1.4.[53] Specifically, for CO₂ hydrogenation over Co/CZ, an optimum particle size of 7 - 9 nm was found.[53] The extent of reduction depends not only on the reduction temperature, but on the size of the metal NPs and the support particles as well. Smaller nanoparticles exhibit a stronger interaction with the support, leading to greater resistance against reduction.[64] This effect is also observed when the support particles themselves are smaller.[65]

Charge transfer is the redistribution of electrons between metal atoms and support atoms at the interface, driven by a difference in Fermi level of the NP and

the support. Elevated or lowered atomic charges of support or metal atoms at the interface can potentially alter adsorption and reaction events at the interfacial perimeter. The transfer of electrons only occurs over a few atomic layers of distance.[66–68] These observations align with the concept of the nearsightedness of electronic matter (NEM) proposed by Prodan and Kohn.[69] This concept explains that the electronic structure at a given point is primarily determined by nearby external potentials, with minimal dependence on potentials beyond a certain distance. Beyond this distance, the influence of the external potential, even though the potential is very large, quickly diminishes.[69]

The interfacial perimeter or edges of nanoparticles present a distinct environment, as the atoms in these regions are in direct contact with the support. Charge transfer at the interface can modify the oxidation state of these atoms, while their low coordination (fewer neighboring metal atoms) further influences their properties. Additionally, the presence of support atoms can create unique active site configurations, potentially lowering energy barriers for specific reaction steps. If the support surface can adsorb reactants or intermediates, phenomena such as spillover (the migration of species from the NP to the support) or reverse spillover (migration from the support back to the NP) may occur. Hydrogen spillover, in particular, has been extensively studied, with the extent of hydrogen migration from the NP to the support and the distance it can travel over the support varying significantly across different catalysts.[70,71]

1.6 Scope of this thesis

In this thesis the structure sensitivity of CO and CO_2 methanation over supported cobalt catalysts is investigated, with a focus on the relationship between active site geometries, surrounding environments, and their impact on catalyst activity and selectivity. The research emphasizes key factors such as metal-support interactions and the role of oxygen vacancies in the reaction mechanism. Electron redistribution, encompassing electron donation from the metal to adsorbates and charge transfer between the metal and the support, emerges as a critical descriptor of active site activity. Additionally, adsorbate-induced restructuring of Co atoms, influenced by their immediate coordination environment, significantly affects active site performance. The stability of adsorbates and the transition state also depend on the specific location of the active site on the nanoparticle. To explore these factors, density functional theory (DFT) calculations are employed, incorporating analyses such as density of states (DOS), crystal orbital Hamilton population (COHP), and charge distribution. Genetic algorithms are utilized to generate representative model systems. The insights from DFT calculations are integrated into microkinetic models to simulate intrinsic reaction kinetics of the model catalysts. Structure sensitivity trends are examined using extended surfaces, nanorods supported on Al_2O_3 and TiO_2 , nanoparticles supported on Al_2O_3 , and single atoms and small clusters supported on CoO. The findings are compared with structure sensitivity trends reported in the literature, providing a comprehensive understanding of catalytic behavior.

Chapter 2 covers the theoretical foundations of electronic structure calculations and density functional theory. It provides a brief explanation of density of states and crystal orbital Hamilton population, along with an overview of the fundamental principles of microkinetic modeling.

Chapter 3 focuses on the dissociation of CO over twelve Co sites. The CO dissociation barrier is correlated with the electronic structure of CO. By extracting electronic structure features of adsorbed CO from DOS and COHP analyses we observe how the canonical molecular orbitals of CO change when CO is adsorbed on different active sites. The key factors influencing the activation of the C–O bond are the reduction in electron density within the 1π orbital of CO, the population of the 2π anti-bonding orbitals, and the redistribution of electrons in the 3σ orbital. The origin of the difference in CO activation between flat and step-edge sites, is the enhanced weakening of the 1π orbital on step-edge sites. This is due to a distancing of the 1π orbital with respect to the Co site for five- and sixfold adsorption modes, in order to reduce electron-electron repulsion with the Co *d*-band.

Chapter 4 presents detailed DFT calculations and microkinetic simulations of CO methanation over Co nanorods supported on γ -Al₂O₃(110) and rutile-TiO₂(110), acting as facile computational models representing the edge of Co nanoparticles of several nanometers in size. It was found that interfacial sites exhibit significantly lower CO methanation activity compared to extended surface sites due to the strong adsorption of reaction intermediates, which leads to surface poisoning. The enhanced stability of intermediates was attributed to epitaxial effects, which create coordinatively undersaturated metal atoms at the interface, while charge transfer effects were found to play a minimal role. Additionally, it was observed that CO dissociation at interfacial sites is more challenging, further limiting hydrocarbon chain formation. Overall, interfacial

sites were shown to primarily produce methane, contributing negligibly to chain growth and the catalyst overall activity.

Chapter 5 presents first-principles-based microkinetic models for 1 nm Co nanoparticles supported on Al_2O_3 . Several distinct active sites on these small nanoparticles were examined, including a site on an undercoordinated Co_{20} nanoparticle and three sites on a high-coordinated nanoparticle of approximately 55 atoms: an interfacial site near the support, a top site far from the support, and a pocket site. Strong adsorption on the undercoordinated nanoparticles rendered them inactive, while the inclusion of B₅-like sites enhanced CO hydrogenation activity. However, they remain less active than larger (> 2.0 nm) supported Co nanoparticles. The interfacial site was found to be two orders of magnitude more active than the top site, highlighting the critical role of interfacial sites in driving overall nanoparticle activity in absence of B₅ sites.

Chapter 6 discusses CO_2 methanation over $Co_{1,4,8}/CoO(100)$ models, reporting the DFT simulations of the chemokinetic network from CO_2 to CH_4 , and the microkinetic models based on these data. By using four- and eight-atom clusters generated with genetic algorithms, and a single Co atom on a CoO support, we investigate the reactivity of a partially reduced Co catalyst. This study includes the influence of co-adsorbates on the stability of the stable and transition states. We find that the single Co atom is spatially too constrained to facilitate CO_2 conversion. This site is poisoned with atomic oxygen. The Co_4 and Co_8 clusters are active in the reverse water-gas shift reaction. Water formation is rate-limiting for CO formation. Methane formation is inhibited by high barriers for CO dissociation.

1.7 References

- [1] https://wmo.int/topics/greenhouse-gases, (2024).
- [2] https://science.nasa.gov/, (2024).
- [3] https://unfccc.int/process-and-meetings/the-paris-agreement, (2024).
- [4] S. Vazquez, S.M. Lukic, E. Galvan, L.G. Franquelo, J.M. Carrasco, IEEE Trans. Ind. Electron. 57 (2010) 3881–3895.
- [5] E. Lindstad, T.Ø. Ask, P. Cariou, G.S. Eskeland, A. Rialland, Transp. Res. Part D. 119 (2023) 103713.
- [6] https://www.tno.nl/en/, (2024).
- [7] https://www.efuel-alliance.eu/efuels/what-are-efuels Copyright uniti e.
 V., Icons made by Freepik, Vectors Marker and Pixelperfect from www.flaticon.com., (2024).
- [8] R. Daiyan, I. MacGill, R. Amal, ACS Energy Lett. 5 (2020) 3843–3847.

- [9] R. Tichler, S. Bauer, H. Böhm, in: Storing Energy, Elsevier, 2022, pp. 595–612.
- [10] G. Reiter, J. Lindorfer, J. CO2 Util. 10 (2015) 40–49.
- [11] V. Rodin, J. Lindorfer, H. Böhm, L. Vieira, J. CO2 Util. 41 (2020) 101219.
- [12] C. Panzone, R. Philippe, A. Chappaz, P. Fongarland, A. Bengaouer, J. CO2 Util. 38 (2020) 314–347.
- [13] V. Gold, ed., The IUPAC Compendium of Chemical Terminology: The Gold Book, 4th ed., International Union of Pure and Applied Chemistry (IUPAC), Research Triangle Park, NC, 2019.
- [14] Paul Sabatier, La Catalyse En Chimie Organique, 1913.
- [15] R. Van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189–230.
- [16] U. Hanefeld, L. Lefferts, eds., Catalysis: An Integrated Textbook for Students, Wiley-VCH, Weinheim, 2018.
- [17] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, P. Prabhakaran, S. Bajohr, Fuel 166 (2016) 276–296.
- [18] H.S. Fogler, Elements of Chemical Reaction Engineering, Sixth Edition, Global edition, Pearson, Boston, 2022.
- [19] M. Boudart, J. Mol. Catal. 30 (1985) 27-38.
- [20] C.O. Bennett, M. Che, J. Catal. 120 (1989) 293–302.
- [21] R.A. Van Santen, Acc. Chem. Res. 42 (2009) 57–66.
- [22] M. Che, C.O. Bennett, in: Advances in Catalysis, Elsevier, 1989, pp. 55–172.
- [23] M. Boudart, in: Advances in Catalysis, Elsevier, 1969, pp. 153–166.
- [24] R.A. Van Santen, M. Neurock, S.G. Shetty, Chem. Rev. 110 (2010) 2005– 2048.
- [25] H. Kim, V.D. Doan, W.J. Cho, R. Valero, Z. Aliakbar Tehrani, J.M.L. Madridejos, K.S. Kim, Sci. Rep. 5 (2015) 16307.
- [26] G. Blyholder, J. Phys. Chem. 68 (1964) 2772–2777.
- [27] B. Zijlstra, R.J.P. Broos, W. Chen, I.A.W. Filot, E.J.M. Hensen, Catal. Today 342 (2020) 131–141.
- [28] P. Van Helden, I.M. Ciobîcă, R.L.J. Coetzer, Catal. Today 261 (2016) 48–59.
- [29] R. Agrawal, P. Phatak, L. Spanu, Catal. Today 312 (2018) 174–180.
- [30] M.P.C. van Etten, B. Zijlstra, E.J.M. Hensen, I.A.W. Filot, ACS Catal. 11 (2021) 8484–8492.
- [31] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. Van Dillen, K.P. De Jong, J. Am. Chem. Soc. 128 (2006) 3956–3964.
- [32] J.P. Den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. De Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [33] A.M. Saib, D.J. Moodley, I.M. Ciobîcă, M.M. Hauman, B.H. Sigwebela, C.J. Weststrate, J.W. Niemantsverdriet, J. Van De Loosdrecht, Catal. Today 154 (2010) 271–282.
- [34] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.

- [35] W. Chen, I.A.W. Filot, R. Pestman, E.J.M. Hensen, ACS Catal. 7 (2017) 8061– 8071.
- [36] P.B. Webb, I.A.W. Filot, in: Comprehensive Inorganic Chemistry III (Third Edition), Elsevier, Netherlands, 2023, pp. 354–380.
- [37] J. Van De Loosdrecht, F.G. Botes, I.M. Ciobica, A. Ferreira, P. Gibson, D.J. Moodley, A.M. Saib, J.L. Visagie, C.J. Weststrate, J.W. Niemantsverdriet, in: Comprehensive Inorganic Chemistry II, Elsevier, 2013, pp. 525–557.
- [38] J.G. Speight, in: Handbook of Industrial Hydrocarbon Processes, Elsevier, 2020, pp. 343–386.
- [39] G. Melaet, A.E. Lindeman, G.A. Somorjai, Top. Catal. 57 (2014) 500–507.
- [40] B. Zijlstra, R.J.P. Broos, W. Chen, G.L. Bezemer, I.A.W. Filot, E.J.M. Hensen, ACS Catal. 10 (2020) 9376–9400.
- [41] J. Tu, H. Wu, Q. Qian, S. Han, M. Chu, S. Jia, R. Feng, J. Zhai, M. He, B. Han, Chem. Sci. 12 (2021) 3937–3943.
- [42] J.J.C. Struijs, V. Muravev, M.A. Verheijen, E.J.M. Hensen, N. Kosinov, Angew. Chem. Int. Ed. 62 (2023).
- [43] C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Lu, C.J. Kiely, P.H. Berben, F. Meirer, B.M. Weckhuysen, Nat. Catal. 1 (2018) 163–163.
- [44] A. Karelovic, P. Ruiz, Appl. Catal. B 113–114 (2012) 237–249.
- [45] D. Beierlein, D. Häussermann, M. Pfeifer, T. Schwarz, K. Stöwe, Y. Traa, E. Klemm, Appl. Catal. B 247 (2019) 200–219.
- [46] N.L. Visser, O. Daoura, P.N. Plessow, L.C.J. Smulders, J.W. De Rijk, J.A. Stewart, B.D. Vandegehuchte, F. Studt, J.E.S. Van Der Hoeven, P.E. De Jongh, ChemCatChem 14 (2022) e202200665.
- [47] C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Lu, C.J. Kiely, P.H. Berben, F. Meirer, B.M. Weckhuysen, Nat. Catal. 1 (2018) 127–134.
- [48] C. Vogt, F. Meirer, M. Monai, E. Groeneveld, D. Ferri, R.A. Van Santen, M. Nachtegaal, R.R. Unocic, A.I. Frenkel, B.M. Weckhuysen, Nat. Commun. 12 (2021) 7096.
- [49] H.C. Wu, Y.C. Chang, J.H. Wu, J.H. Lin, I.K. Lin, C.S. Chen, Catal. Sci. Technol. 5 (2015) 4154–4163.
- [50] J.F.M. Simons, T.J. De Heer, R.C.J. Van De Poll, V. Muravev, N. Kosinov, E.J.M. Hensen, J. Am. Chem. Soc. 145 (2023) 20289–20301.
- [51] A. Guerrero-Ruiz, I. Rodríguez-Ramos, React. Kinet. Catal. Lett. 29 (1985) 93–99.
- [52] V. Iablokov, S.K. Beaumont, S. Alayoglu, V.V. Pushkarev, C. Specht, J. Gao, A.P. Alivisatos, N. Kruse, G.A. Somorjai, Nano Lett. 12 (2012) 3091–3096.
- [53] A. Parastaev, V. Muravev, E.H. Osta, T.F. Kimpel, J.F.M. Simons, A.J.F. Van Hoof, E. Uslamin, L. Zhang, J.J.C. Struijs, D.B. Burueva, E.V. Pokochueva, K.V. Kovtunov, I.V. Koptyug, I.J. Villar-Garcia, C. Escudero, T. Altantzis, P. Liu, A. Béché, S. Bals, N. Kosinov, E.J.M. Hensen, Nat. Catal. 5 (2022) 1051–1060.
- [54] J.A. Farmer, C.T. Campbell, Science 329 (2010) 933–936.
- [55] G. Prieto, A. Martínez, P. Concepción, R. Moreno-Tost, J. Catal. 266 (2009) 129–144.

- [56] O. Borg, P. Dietzel, A. Spjelkavik, E. Tveten, J. Walmsley, S. Diplas, S. Eri, A. Holmen, E. Rytter, J. Catal. 259 (2008) 161–164.
- [57] N. Fischer, E. Van Steen, M. Claeys, Catal. Today 171 (2011) 174–179.
- [58] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsøe, Science 295 (2002) 2053–2055.
- [59] T. Nilsson Pingel, M. Jørgensen, A.B. Yankovich, H. Grönbeck, E. Olsson, Nat. Commun. 9 (2018) 2722.
- [60] N. Shibata, A. Goto, K. Matsunaga, T. Mizoguchi, S.D. Findlay, T. Yamamoto, Y. Ikuhara, Phys. Rev. Lett. 102 (2009) 136105.
- [61] G. Melaet, W.T. Ralston, C.-S. Li, S. Alayoglu, K. An, N. Musselwhite, B. Kalkan, G.A. Somorjai, J. Am. Chem. Soc. 136 (2014) 2260–2263.
- [62] I.C.T. Have, J.J.G. Kromwijk, M. Monai, D. Ferri, E.B. Sterk, F. Meirer, B.M. Weckhuysen, Nat. Commun. 13 (2022) 324.
- [63] K. Zhao, M. Calizzi, E. Moioli, M. Li, A. Borsay, L. Lombardo, R. Mutschler, W. Luo, A. Züttel, J. Energy Chem. 53 (2021) 241–250.
- [64] R.C. Reuel, C.H. Bartholomew, J. Catal. 85 (1984) 78–88.
- [65] A. Parastaev, V. Muravev, E. Huertas Osta, A.J.F. Van Hoof, T.F. Kimpel, N. Kosinov, E.J.M. Hensen, Nat. Catal. 3 (2020) 526–533.
- [66] G. Pacchioni, Phys. Chem. Chem. Phys. 15 (2013) 1737.
- [67] A. Ruiz Puigdollers, P. Schlexer, S. Tosoni, G. Pacchioni, ACS Catal. 7 (2017) 6493–6513.
- [68] G. Pacchioni, H.-J. Freund, Chem. Soc. Rev. 47 (2018) 8474–8502.
- [69] E. Prodan, W. Kohn, Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 11635–11638.
- [70] W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, J.A. Van Bokhoven, Nature 541 (2017) 68–71.
- [71] W.C. Conner, J.L. Falconer, Chem. Rev. 95 (1995) 759–788.

2. Theory and Methods

2.1 Introduction

Advancements in computational chemistry have transformed our ability to model and analyze complex chemical systems with unprecedented precision. Central to these developments is the integration of quantum-chemical methods, such as density functional theory (DFT), which enables the detailed exploration of electronic structures and reaction mechanisms in diverse systems. This chapter outlines the theoretical foundations and practical methodologies employed in this study, including DFT and its variants, electronic structure analysis, and microkinetic modeling. Emphasis is placed on the principles, approximations, and computational strategies that underpin these techniques, with a focus on their application to molecular systems and catalytic processes. Where applicable, there will be a focus on implementation details relevant to the Vienna Ab Initio Simulation Package (VASP)[1,2], Local Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER)[3–6] for electronic structure analysis, and MKMCXX[7] for microkinetic modeling.

In this document, we adhere to the following notational conventions for clarity and consistency:

- Matrices are denoted by uppercase bold letters, e.g. **A** or **F**.
- Vectors are represented using the arrow notation, e.g. \vec{r} or \vec{k} .
- Scalars are written as non-bold, lowercase or uppercase letters, e.g. *x*, *E*.
- Operators are indicated with a hat symbol, e.g. \hat{H} for the Hamiltonian operator.
- Sets are represented using curly braces, e.g. $\{x_1, x_2, \dots, x_n\}$.
- Unless otherwise specified, an unbounded integral is understood to be over the complete configuration space of the system.
- The following symbols represent commonly used sets:
 - C: the set of complex numbers.
 - \mathbb{R} : the set of real numbers.
 - \mathbb{Z} : the set of integers.

2.2 Quantum-chemical methods

Quantum chemical methods, such as density functional theory, are employed to investigate the electronic structure of complexes bonded to catalysts. These methods address the Schrödinger equation by incorporating a series of approximations. This section introduces the fundamental electronic structure problem and outlines the approximations used to solve it.

2.2.1 The electronic structure problem

Central to the description of a quantum-chemical system is the non-relativistic, time-independent Schrödinger equation as given by[8]

$$\widehat{H}\Psi = E\Psi \tag{1}$$

Here, \hat{H} represents the Hamiltonian operator, Ψ the wavefunction, and E the energy of the system. For a system with N electrons and M nuclei, the Hamiltonian operator in atomic units is given by

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{\alpha=1}^{M} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^{2} - \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{\alpha=1}^{M} \sum_{\beta>\alpha}^{M} \frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}}$$
(2)

In this context, i, j refer to the electrons, and α, β refer to the nuclei. M_{α} represents the mass of nucleus α . The distances r_{ij} , $r_{i\alpha}$, and $r_{\alpha\beta}$ correspond to the separations between electrons i and j, electron i and nucleus α , and nuclei α and β , respectively. Lastly, Z_{α} denotes the charge of nucleus α . The terms in the Hamiltonian represent, in order: the kinetic energy of the electrons, the kinetic energy of the nuclei, the electron-nucleus interaction energy, the electron-electron interaction energy, and the nucleus-nucleus repulsion energy.

Due to the significant mass difference between nuclei and electrons, nuclear motion induces only a negligible delay in electronic redistribution. This allows the decoupling of nuclear and electronic motion, an approach known as the Born-Oppenheimer approximation.[9] Under this approximation, the Hamiltonian simplifies to the electronic Hamiltonian given by

$$\widehat{H}_{\text{elec}} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$$
(3)

In this form, the electronic structure problem depends only parametrically on the nuclei, which provide a fixed attractive potential for the electrons and a constant repulsive term for nucleus-nucleus interactions.

The electronic Hamiltonian operates on a many-electron wavefunction, which, to account for quantum statistics, is expressed as a Slater determinant provided by[10]

$$\Psi(r_1, r_2, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(r_1) & \chi_2(r_1) & \cdots & \chi_N(r_1) \\ \chi_1(r_2) & \chi_2(r_2) & \cdots & \chi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(r_N) & \chi_2(r_N) & \dots & \chi_N(r_N) \end{vmatrix}$$
(4)

Here, χ_i are spin-orbitals, which combine spatial and spin wavefunctions, and are assumed, without loss of generality, to form an orthonormal set.

This determinant formulation elegantly captures key quantum properties:

- 1. **Indistinguishability:** Electrons cannot be uniquely identified, as all permutations of spin-orbitals are included.
- 2. **Exchange antisymmetry**: Swapping two electrons inverts the determinant sign, reflecting their fermionic nature.
- 3. **Pauli exclusion principle**: If two electrons occupy the same spin-orbital, the determinant becomes zero due to linear dependence, representing a physically invalid solution.[11]

Thus, the Slater determinant framework inherently enforces the indistinguishability of electrons, exchange antisymmetry, and exclusion principles, accurately modeling electron behavior in many-electron systems.

2.2.2 Hartree-Fock approximation

Although the Hartree-Fock approximation is not directly used in this thesis, it serves as a crucial foundation for understanding density functional theory. The Hartree-Fock formalism provides valuable insights into electronic interactions and approximations that underpin modern quantum chemical methods. Furthermore, its expressions are utilized in this work to elaborate on the concept of self-interaction error, highlighting its relevance in the context of DFT.

The Slater determinant is an eigenfunction of the electronic Hamiltonian, with the electronic energy of the system as its eigenvalue. Applying the electronic Hamiltonian, as given in Equation 3, to a Slater determinant, as defined in Equation 4, results in an energy expression involving sums over one-electron and two-electron integrals

$$E = \langle \Psi | \hat{H}_{elec} | \Psi \rangle = \sum_{i=1}^{N} \langle \chi_i(r_1) | \hat{h}_1 | \chi_i(r_1) \rangle$$

+ $\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \chi_i(r_1) \chi_j(r_2) | r_{12}^{-1} | \chi_i(r_1) \chi_j(r_2) \rangle$
- $\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \chi_i(r_1) \chi_j(r_2) | r_{12}^{-1} | \chi_i(r_2) \chi_j(r_1) \rangle$ (5)

where the first term, related to the one-electron integrals, corresponds to the kinetic energy and the Coulombic attraction between the electrons and nuclei as given by

$$h_i = -\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1}^M \frac{Z_\alpha}{r_{i\alpha}}$$
(6)

The second and third terms, associated with two-electron integrals, represent the electron-electron repulsion J_{ij} and exchange K_{ij} energies, respectively. The exchange term, unique to quantum mechanics, has no classical electrostatic counterpart. It arises from the quantum statistics of (fermionic) electrons. This term is negative, suggesting a seemingly favorable interaction between electrons. However, it is better interpreted as a correction due to the Pauli exclusion principle, which prevents two electrons from occupying the same space. This spatial restriction arises from the ability of two electrons of same spin to switch orbitals to reduce repulsion, and mitigates part of the electron-electron repulsion between same spin electrons.[12]

Within the Hartree-Fock approximation, the optimal ground-state wavefunction is determined by finding the set of spin-orbitals that minimizes the total energy.[13,14] Since the spin-orbitals must remain orthonormal, this minimization involves a constrained optimization, typically achieved using the Lagrange method of undetermined multipliers.[15] This approach leads to a set of one-electron equations given by

$$\left[\hat{h}_{1} + \sum_{j=1}^{N} \int \langle \chi_{j}(x_{2}) | r_{12}^{-1} | (1 - \hat{P}_{12}) \chi_{j}(x_{2}) \rangle \right] \chi_{i}(x_{1}) = \epsilon_{ji} \chi_{j}(x_{1})$$
(7)

The form of Equation 7 differs from the canonical representation of the Hartree-Fock equations. This is because there is not a single unique Slater determinant that minimizes Equation 5 rather, an infinite set of such determinants exists, related through unitary transformations.[16] This property arises from the fact that the product of two determinants is the determinant of the products. If the spin-orbitals inside Equation 4 are represented by a matrix **A**, then the Slater determinant itself (ignoring here for simplicity the normalization constant) is given by

$$\Psi = \det(\mathbf{A}) \tag{8}$$

A unitary transformation among the spin-orbitals can then be represented by

$$\mathbf{A}' = \mathbf{U}\mathbf{A} \tag{9}$$

where each new spin-orbital is essentially a linear combination of the old spinorbitals. The unitary transformation, represented by **U**, ensures that the orthonormality condition of the spin-orbitals remains conserved. Since

$$det(\mathbf{U}\mathbf{A}) = det(\mathbf{U}) det(\mathbf{A}) \tag{10}$$

and

$$\det(\mathbf{U}) = 1 \tag{11}$$

this implies that a unitary transformation among the spin-orbitals eventually yields the same many-electron wave function and thus the same electronic energy. To establish a unique solution, the standard convention in electronic structure calculations is to choose the Slater determinant such that $\epsilon_{ij} = 0$ when $i \neq j$.[12] Under this constraint, Equation 7 simplifies to

$$\left[\hat{h}_{1} + \sum_{j=1}^{N} \int \langle \chi_{j}(x_{2}) | r_{12}^{-1} | (1 - \hat{P}_{12}) \chi_{j}(x_{2}) \rangle \right] \chi_{i}(x_{1}) = \epsilon_{i} \chi_{i}(x_{1})$$
(12)

For systems with non-degenerate states, this approach ensures a unique solution. However, for degenerate states, there is still freedom to choose among the degenerate subsystems, while the eigenvalues remain fixed. This behavior, known from linear algebra, allows an infinite set of new eigenvectors to be constructed from a basis of eigenvectors sharing the same eigenvalue.[17] In practice, the ambiguity in choosing among degenerate eigenvectors is not a problem because physical properties depend only on eigenvalues, not the specific eigenvectors.

The solutions found through this formalism typically correspond to delocalized wavefunctions, reflecting irreducible representations of the molecular point group, extending over many atoms in the system.[12] Nevertheless, other solutions, related via unitary transformations among occupied spin-orbitals, can be useful for interpreting the electronic structure. For instance, localized solutions, which maximize the squared centroid of molecular orbitals, align more closely with the intuitive concept of chemical bonding and can often be directly associated to Lewis structures.

The energy expression within Hartree-Fock as given in Equation 5 can be rewritten as

$$E_{\rm HF} = \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (J_{ij} - K_{ij})$$
(13)

where h_i is the one-electron integral representing the kinetic energy and nuclear attraction for electron *i*, J_{ij} is the Coulomb integral representing the electron-electron repulsion between electrons *i* and *j*, and K_{ij} is the exchange integral arising from the antisymmetry of the wavefunction.

The Coulomb integral for an electron *i* interacting with itself is given by

$$J_{ii} = \int \chi_i^*(\mathbf{r}_1) \frac{1}{|r_1 - r_1|} \chi_i(r_1) \, dr_1 \to \infty \tag{14}$$

which is physically meaningless as it implies infinite self-repulsion. However, the exchange integral for the same electron exactly cancels this term as can be seen by

$$K_{ii} = \int \chi_i^*(r_1)\chi_i(r_1) \frac{1}{|r_1 - r_1|} \chi_i^*(r_1)\chi_i(r_1) dr_1 = J_{ii}$$
(15)

Thus, for the self-interaction case, the total contribution of the Coulomb and exchange terms is

$$J_{ii} - K_{ii} = 0 (16)$$

This exact cancellation of self-interaction terms ensures that the Hartree-Fock method is free from self-interaction error. However, this property does not hold for density functional approximations, where the exchange-correlation functional may not fully account for the self-interaction, leading to an unphysical interaction of an electron with itself.[18] This limitation of density functional

theory, not present in Hartree-Fock, will be revisited upon the explanation of the Hubbard *U*-term (*vide infra*).

2.2.3 Roothaan equations

Although Equation 12 represents a condition that needs to be met to obtain the best approximation of the electronic ground state, it does not provide an algorithm to achieve this solution. The next step is to introduce a known set of functions, called a basis set, that are used to produce a linear approximation of the spatial part ψ of the spin-orbitals χ , as given by

$$\psi(r) = \sum_{j=1}^{N} c_j \phi_j(r) \tag{17}$$

The set of *N* functions $\{\phi_j\}$ represents the basis set. Many basis sets are available in the literature. The most well-known are the localized Gaussian- and Slater-type orbitals and the delocalized plane waves. Throughout this work, we primarily use plane waves, and the motivation for this choice, along with their benefits, will be discussed later in this chapter.

Inserting Equation 17 into Equation 12, and assuming for simplicity a spinrestricted system where all spin-up electrons align with spin-down electrons, leads to the following equation

$$\sum_{j=1}^{N} c_{jk} \langle \phi_i | \hat{f}_i | \phi_j \rangle = \epsilon_k \sum_{j=1}^{N} c_{jk} \langle \phi_i | \phi_j \rangle$$
(18)

This equation, when considering all molecular orbitals ψ_i , can be further condensed into a single matrix equation, known as the Roothaan equation[18]

$$FC = SCE \tag{19}$$

Here, **F** is the Fock matrix, **C** the coefficient matrix, **E** the energy matrix, and **S** the overlap matrix. The elements of the Fock and overlap matrices are defined as

$$F_{ij} = \langle \phi_i | \hat{f} | \phi_j \rangle \tag{20}$$

and

$$S_{ij} = \langle \phi_i | \phi_j \rangle \tag{21}$$

where the Fock operator is given by

$$\hat{f}_{i} = \hat{h}_{i} + \sum_{j=1}^{N} (J_{ij} - K_{ij})$$
(22)

From the definition of Equation 17, it is evident that the elements of the Fock matrix depend on the solution ψ_i . Thus, Equation 18 represents a set of integrodifferential equations.

The physical interpretation of this situation is that the Fock operator depends on the electron density distribution, as the electrons are repelled by the averaged field of all electrons. However, the electron density distribution is precisely what we aim to calculate. In other words, this creates the infamous "chicken-and-egg" problem, necessitating an iterative procedure to find the best approximation of the ground state.

In practice, the process starts with a well-chosen initial guess for the electron density and progressively updates it. To avoid instabilities during the iterative procedure, one can use simple linear mixing, where the old solution is partially incorporated into the new one, or a more advanced technique, such as direct inversion of the iterative subspace (DIIS).[19]

2.2.4 Post-Hartree-Fock methods

From Equation 12, it is evident that electrons are approximated to experience an averaged potential due to the field of the nuclei and all the other electrons. In other words, the Hartree-Fock method is fundamentally an independentelectron approach. The major drawback of this approximation is that the correlation in the movement of electrons is neglected. However, exchange interactions are treated exactly. These limitations prevent the method from accurately describing instantaneous electron-electron repulsion, leading to poor representation of dispersion and van der Waals interactions within this theory.

Many post-Hartree-Fock methods have been developed to account for electronelectron correlation. Notable examples include the Configuration Interaction (CI) method, which uses a linear combination of Slater determinants instead of a single one.[20] Møller-Plesset perturbation theory incorporates electron correlation via perturbation theory,[21–23] while the Coupled Cluster method handles it using so-called cluster operators.[24]

Although these methods provide chemically accurate descriptions of electronic structure, their application is limited by their computational scaling with the number of basis functions, N. Hartree-Fock scales as N^4 , second-order Møller-

Plesset perturbation theory scales as N^5 , coupled cluster with single and double excitations scales as N^6 , and Configuration Interaction can scale as high as N^9 . Due to this scaling behavior, these approaches are generally restricted to relatively small systems. In practice, they are applicable to systems with less than 50 atoms.

2.2.5 Density functional theory

A different approach to approximating solutions to the Schrödinger equation is provided by density functional theory. Remarkably, the groundwork for DFT was laid by Thomas[25] and Fermi[26] in the 1920s, but its formal development came roughly forty years later in the landmark paper by Hohenberg and Kohn.[27] In this work, Hohenberg and Kohn proved, using a *reductio ad absurdum* argument, that the electron density uniquely determines the external potential up to a constant. This implies that instead of solving a complex wave function, the electron density itself can be utilized as the central property to address the electronic structure problem. Analogous to Equation 5, the energy equation in DFT is given by

$$E[\rho] = T[\rho] + V[\rho] + U[\rho]$$
(23)

where *T* corresponds to the kinetic energy, *V* the energy due to the external potential generated by the nuclei acting on the electrons and *U* the energy due to the interaction of the electrons among each other. All these terms are explicit functionals of the electron density $\rho(\vec{r})$ as given by

$$\rho(\vec{r}) = |\Psi|^2 \tag{24}$$

with Ψ being the many-electron wave function. Determining the electron density that resolves the electronic structure problem involves finding the density that minimizes the energy relation of Equation 23, i.e.

$$E_0 = \min_{\rho} (T[\rho] + V[\rho] + U[\rho])$$
(25)

subject to the constraint that the number of electrons remains conserved. Hohenberg and Kohn showed that any electron density that does not correspond to the ground state electron density will be higher in energy than the ground state electron density, showing that the outcome of a minimization procedure will be the best approximation of the true ground state solution. To this aim, it is advantageous to define a universal functional $F[\rho(\vec{r})]$ by means of rewriting Equation 23 such that

$$E[\rho(\vec{r})] = -\int v_{\text{ext}}(\vec{r})\rho(\vec{r})d\vec{r} + F[\rho(\vec{r})]$$
(26)

wherein the universal functional $F[\rho(\vec{r})]$ is defined as

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{\rm X}[\vec{r}]$$
(27)

and where the first term corresponds to the kinetic energy, the second term to the classical electron-electron repulsion and the third term to the exchange energy of the electrons. The universality of $F[\rho(\vec{r})]$ lies in the fact that the functional is invariant with respect to the system under study. Inserting the universal functional into the original energy expression yields

$$E[\rho(\vec{r})] = T[\rho(\vec{r})] - \int v_{\text{ext}}(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} \, d\vec{r}' + E_{\text{X}}[\vec{r}]$$
(28)

An actual implementation of Equation 28 remains elusive as an explicit expression for the kinetic energy and the exchange energy in terms of the electron density remains unknown. It should be emphasized that an exact expression for the exchange term is known for the many-electron wave function from Hartree-Fock theory, as already seen in Equation 5. To tackle this problem, Kohn and Sham proposed to model a system of interacting electrons using a proxy system of non-interacting electrons for which the kinetic energy T_s can be determined from their one-electron wave functions[28]

$$T_{\rm s}[\rho] = -\sum_{i}^{N} \langle \psi_i \left| -\frac{1}{2} \nabla^2 \right| \psi_i \rangle \tag{29}$$

Equation 29 requires careful interpretation. While the electron density can be directly derived from the one-electron wave functions, there is an infinite number of possible sets of one-electron wave functions related via Equation 9 that can produce the same electron density and the same total kinetic energy. Consequently, it cannot be asserted that a definitive expression for the non-correlated kinetic energy as a function of the electron density exists; a specific set of one-electron wave functions remains necessary. Since the actual system consists of interacting electrons, the error introduced by this approximation is incorporated into a correlation term, which is then combined with the exchange term to form the exchange-correlation energy yielding the following energy expression
$$E[\rho(\vec{r})] = T_{\rm s}[\rho(\vec{r})] - \int v_{\rm ext}(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} \, d\vec{r}' + E_{\rm XC}[\vec{r}] \quad (30)$$

Minimization of Equation 30 subject to the constraint that the one-electron wave functions remain orthonormal with respect to each other yields, very much akin to Equation 12, the following set of one-electron eigenfunction equations

$$\left\{-\frac{1}{2}\nabla^2 + \nu_{KS}\right\}\psi_i = \epsilon_i\psi_i \tag{31}$$

wherein the Kohn-Sham potential $v_{\rm KS}$ is defined as

$$\nu_{\rm KS}(\vec{r}) = \sum_{j} -\frac{Z_j}{\left|\vec{r} - \vec{R}_j\right|} + \int \frac{\rho(\vec{r}')}{\left|\vec{r} - \vec{r}'\right|} d\vec{r}' + \frac{\delta E_{\rm XC}[\rho(\vec{r})]}{\delta\rho(\vec{r})}$$
(32)

The last term in the above expression corresponds to the functional derivative of the exchange-correlation energy towards the electron density. In turn, the electron density itself can be obtained via

$$\rho = \sum_{i \in \text{ occ.}} |\psi_i|^2 \tag{33}$$

2.2.5.1 Exchange-correlation functional

While the equations above may appear convoluted, they essentially represent a reformulation of the original electronic structure problem within the DFT framework into an independent-electron approximation, consolidating all unknown terms into a single exchange-correlation energy functional. The functional derivative of this term defines the exchange-correlation potential.

Rearranging terms does not address the fundamental challenge that no explicit expressions exist for the exchange and correlation energy as functions of the electron density. However, reasonable approximations have been developed. The earliest of these approximations is based on the homogeneous electron gas. Using the quantum Monte Carlo approach of Ceperley and Alder,[29] Vosko, Wilk, and Nusair[30] devised a correlation functional for the correlation interaction through Padé approximant interpolation. Additionally, an expression for the exchange component, also derived from the homogeneous electron gas, was introduced in the paper by Hohenberg and Kohn.[27] Combining these two descriptions, i.e. for the exchange and correlation interactions, yields what is known as the local density approximation (LDA). Some authors, more precise in their terminology, refer to it as SVWN5, where "S" denotes the Slater-type exchange and "VWN5" refers to the fifth equation in the work of Vosko, Wilk, and Nusair.[30]

Although the local density approximation produced reasonable results, particularly for metals, it was soon recognized that its predictions fell short of achieving chemical accuracy. This outcome is intuitive, as the LDA assumes a locally uniform electron density which is often invalid for chemically significant systems. A natural progression from LDA is the inclusion of the electron density gradient $\nabla \rho(\vec{r})$ (more specifically, the magnitude of that gradient), a method known as the generalized gradient approximation (GGA). Various forms of GGA-type exchange-correlation functionals have been developed. In this work, we employed the GGA functional introduced by Perdew, Burke, and Ernzerhof, commonly referred to as the PBE exchange-correlation functional.[31] PBE strikes a balance between accuracy and computational efficiency, making it suitable for a broad range of materials and molecular systems. It provides improved treatment of exchange and correlation effects, offering better predictions for properties like bond energies, geometries, and reaction barriers compared to LDA, while maintaining simplicity and robustness.

A modified version of the PBE functional, known as revised PBE (RPBE), was developed to address specific errors in the original PBE functional.[32] While RPBE improves the description of certain systems, its broader applicability remains uncertain. For example, as highlighted in the original RPBE paper, it successfully resolves the issue of CO adsorption site preferences, where PBE incorrectly identifies the favored position.[32] However, this improvement comes at the expense of accuracy in other cases, such as the prediction of the CO adsorption energy on Rh surfaces, where RPBE performs worse than PBE. This trade-off highlights the context-dependent nature of functional performance and the inherent challenges in achieving universal accuracy within density functional theory. As the broader applicability and accuracy of RPBE is less consistent compared to PBE, RPBE is not used in this thesis.

2.2.5.2 Jacob's ladder

Jacob's ladder of density functional approximations organizes functionals by their complexity and accuracy in describing electronic interactions.[33] At the base, the local density approximation assumes a uniform electron density, offering simplicity but limited accuracy. The second rung, occupied by generalized gradient approximation functionals, incorporates the gradient of the electron density to enhance predictions. Meta-GGA functionals, on the third rung,

include the second derivative of the electron density (Laplacian) for further accuracy, while hybrid functionals combine GGA with exact exchange, offering higher precision, but at higher computational costs.

In this thesis, which investigates numerous elementary reaction steps in systems containing more than 100 atoms, computational feasibility necessitated the use of approximations. Consequently, all calculations were performed using generalized gradient approximation (GGA) functionals, corresponding to the second rung of Jacob's ladder. This choice reflects the limitations imposed by the size of the systems studied, as higher-rung functionals would have been computationally prohibitive.

2.2.5.3 Dispersion corrections

Grimme dispersion corrections are an often-used enhancement DFT for accurately capturing long-range dispersion interactions, such as van der Waals forces, which are inadequately described by standard functionals like GGA. These interactions play a significant role in non-covalent bonding, molecular conformations, and adsorption processes, particularly in large and complex systems. The DFT-D3 method developed by Grimme introduces an empirical correction that is added to the standard DFT energy, accounting for dispersion effects efficiently without significantly increasing computational costs.[34] In this method, the dispersion energy is given by

$$E_{\rm disp} = -\frac{1}{2} \sum_{i=1}^{N_{\rm at}} \sum_{j=1}^{N_{\rm at}} \sum_{\vec{n}} \left(f_{\rm d,6}(r_{ij,\vec{n}}) \frac{C_{6ij}}{r_{ij,\vec{n}}^6} + f_{\rm d,8}(r_{ij,\vec{n}}) \frac{C_{8ij}}{r_{ij,\vec{n}}^8} \right)$$
(34)

where N_{at} is the number of atoms, $r_{ij,\vec{n}}$ represents the distance between atoms *i* and *j* considering periodic images \vec{n} , and C_{6ij} and C_{8ij} are dispersion coefficients for the atom pair (i, j). The prime on the summation indicates that terms with i = j are excluded when $\vec{n} = \vec{0}$. The functions $f_{d,6}$ and $f_{d,8}$ are damping functions that modulate the dispersion interaction at short interatomic distances to prevent singularities. In this thesis, we use Becke-Johnson (BJ) damping for which the damping functions are given by[35]

$$f_{d,n}(r_{ij}) = \frac{s_n r_{ij}^n}{r_{ij}^n + (a_1 R_{0ij} + a_2)^n}$$
(35)

where *n* corresponds to the order of the dispersion term (e.g., 6 or 8), s_n is a scaling factor (with $s_6 = 1$), a_1 and a_2 are adjustable parameters, and R_{0ij} is a

reference distance between atoms *i* and *j*. This damping function ensures a smooth transition between the dispersion-corrected and conventional DFT energies. The inclusion of Grimme dispersion corrections is critical for achieving a balanced treatment of both short- and long-range interactions, ensuring robust and chemically meaningful results.

2.2.5.4 Hubbard U-term

The self-interaction error (SIE) is a well-known limitation in DFT that arises due to the incomplete cancellation of the self-Coulomb and self-exchange interactions, particularly in systems with delocalized electronic states. For a hypothetical one-electron system, the exact total electronic energy can be described using only the kinetic energy T_s , the attraction energy by the nuclei E_{ext} and the nucleus-nucleus repulsion E_{nn} . With reference to Equation 30, and under the assumption of a one-electron system, the third term, representing the classical electron-electron repulsion E_J , and the fourth term, representing the exchange-correlation energy E_{XC} , should cancel each other out as

$$E_{\rm J}[\rho_1] = -E_{\rm XC}[\rho_1] \tag{36}$$

Violation of these conditions will lead to the self-interaction error energy, $E_{\rm SI}$ as given by

$$E_{\rm SI}[\rho_1] = E_{\rm J}[\rho_1] + E_{\rm XC}[\rho_1]$$
(37)

This error leads to incorrect predictions for properties such as ionization potentials, band gaps, and charge localization. To address the SIE, one can apply the Perdew-Zunger self-interaction correction (PZ-SIC),[36] which explicitly removes self-interaction terms for each electron. Alternatively, SIE can be mitigated, though not entirely removed, by progressing up Jacob's ladder of density functionals: starting from the local density approximation, moving to generalized gradient approximations, meta-GGAs, and finally hybrid functionals that incorporate a fraction of exact exchange. While this progression reduces SIE, it remains inherently present to some degree.

Another approach to reduce, though not completely remove, the self-interaction error (SIE) is the application of a Hubbard U correction,[37] which adds an onsite Coulomb interaction term to better account for localized states, offering a practical solution for systems with strongly correlated electrons. The Hubbard U-term is particularly useful when applied to GGA functionals in DFT, especially for systems containing strongly localized electrons, such as those found in transition metal d-orbitals or rare earth f-orbitals. While GGA functionals are

effective for many systems, they often fail to accurately capture the strong on-site electron-electron interactions characteristic of these localized states. As shown above, this failure stems from the tendency of GGAs to over-delocalize electron densities, leading to incorrect predictions of electronic and magnetic properties, band gaps, and energetics in materials with significant correlation effects.

The Hubbard *U*-term addresses this deficiency by explicitly penalizing energetically unfavorable electron configurations, enforcing a more accurate localization of electrons. In practice, this correction modifies the electronic Hamiltonian to include an on-site Coulomb interaction term for localized orbitals via

$$E_{\rm DFT+U} = E_{\rm DFT} + E_{\rm U} - E_{\rm DC}$$
(38)

where the first term is the canonical DFT energy, the second term the Hubbard U correction and the third term a double-counting correction term. The Hubbard correction term is defined as

$$E_{\rm U} = \frac{U}{2} \sum_{i} \sum_{\sigma} \sum_{m,m'} \left(n_{mm'}^{i,\sigma} n_{m'm}^{l,\sigma} - n_{mm}^{i,\sigma} n_{m'm'}^{i,\sigma} \right)$$
(39)

where *U* is the Hubbard parameter, representing the strength of the on-site Coulomb interaction, *i* denotes the atomic site index, σ is the spin index, *m* and *m*' are the orbital indices, and $n_{mm'}^{i,\sigma}$ represents the density matrix for localized orbitals at site *i*.

The double-counting term is given by

$$E_{\rm DC} = \frac{U}{2} \sum_{i} \sum_{\sigma} N_i^{\sigma} (N_i^{\sigma} - 1)$$
(40)

where

$$N_i^{\sigma} = \sum_m n_{mm}^{i,\sigma} \tag{41}$$

is the total number of electrons in localized orbitals at site *i* with spin σ .

By introducing the parameter U, representing the strength of the on-site interaction, the GGA+U method selectively corrects the underestimation of electronic localization without significantly altering the GGA framework for other regions of the system. This correction improves the prediction of

properties such as band gaps, magnetic moments, and phase stability in materials where GGA alone is insufficient.

Within this thesis, we make use of the simplified (rotationally invariant) approach to the DFT+*U* formalism as established by Dudarev *et al.*[38] In this approach, the Hubbard *U* and exchange *J* parameters are combined into an effective parameter $U_{\text{eff}} = U - J$.

The total energy in the simplified DFT+U approach is given by:

$$E_{\rm DFT+U} = E_{\rm DFT} + E_{\rm U} \tag{42}$$

where E_{DFT} is the standard DFT energy and E_{U} is the Hubbard correction term.

The Hubbard correction term in the simplified approach is then given by

$$E_{\rm U} = \frac{U_{\rm eff}}{2} \sum_{I} \sum_{\sigma} ({\rm Tr}[n_{\sigma}^{I}(1-n_{\sigma}^{I})])$$
(43)

where $U_{\text{eff}} = U - J$ is the *effective* on-site Coulomb interaction, and n_{σ}^{I} is the occupation matrix for localized orbitals at site *I* with spin σ . The occupation matrix n_{σ}^{I} is computed as

$$n_{mm'}^{I,\sigma} = \sum_{k} f_{k}^{\sigma} \langle \psi_{k\sigma} | \phi_{m}^{I} \rangle \langle \phi_{m'}^{I} | \psi_{k\sigma} \rangle$$
(44)

where f_k^{α} is the occupation number of the Kohn-Sham orbital $|\psi_{k\sigma}\rangle$, $|\phi_m^I\rangle$ are the localized atomic-like orbitals at site *I*, and *m*, *m'* are orbital indices.

The correction to the Kohn-Sham potential Equation 32 in the simplified DFT+U is derived from the derivative of E_U with respect to the occupation matrix:

$$V_{mm'}^{I,\sigma} = U_{\rm eff} \left(\frac{1}{2} \delta_{mm'} - n_{mm'}^{I,\sigma}\right) \tag{45}$$

The effective *U* combines the Coulomb *U* and exchange *J* interactions to simplify the parametrization. Additionally, this formalism maintains rotational invariance of the occupation matrix, ensuring that the energy correction is independent of the choice of the localized orbital basis. This approach is computationally efficient while improving the description of strongly correlated systems compared to standard DFT.

2.2.5.5 Plane-wave basis set

Plane waves are a widely used basis set in electronic structure calculations, particularly in systems with periodic boundary conditions, such as crystalline materials. Unlike Gaussian or Slater-type orbitals, which are localized and centered around individual atoms, plane waves are delocalized and span the entire periodic unit cell of the system. The general expression of a (normalized) plane wave corresponds to

$$\phi(\vec{G},\vec{r}) = \frac{1}{\sqrt{\Omega}} \exp(\mathrm{i}\vec{G}\cdot\vec{r}) \tag{46}$$

where \vec{G} is the reciprocal lattice vector and Ω the volume of the unitcell. The set of plane-wave vectors $\{\vec{G}\}$ are chosen such that the plane waves form an orthonormal basis set as given by

$$\left\langle \phi(\vec{G}) \middle| \phi(\vec{G}') \right\rangle \ge \delta_{\vec{G},\vec{G}'} \tag{47}$$

where $\boldsymbol{\delta}$ is the Kronecker delta given by

$$\delta_{ij} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \end{cases}$$
(48)

Provided that

$$\exp(i\vec{G}\cdot\vec{R}) = 1 \tag{49}$$

the plane waves are naturally periodic, as demonstrated by the relation:

$$\phi(\vec{G}, \vec{r} + \vec{R}) = \frac{1}{\sqrt{\Omega}} \exp\left(\mathrm{i}\vec{G} \cdot \left(\vec{r} + \vec{R}\right)\right)$$
(50)

$$= \frac{1}{\sqrt{\Omega}} \exp(i\vec{G} \cdot \vec{r}) \exp(i\vec{G} \cdot \vec{R})$$
(51)

Here, \vec{R} represents one of the fundamental lattice vectors that define the unit cell. The periodicity condition is satisfied by choosing the reciprocal lattice vector \vec{G} such that

$$\vec{G} \cdot \vec{R} = 2\pi n, \ n \in \mathbb{Z}$$
(52)

Plane waves thus respect the translational symmetry of the lattice, meaning that shifting by a lattice vector \vec{R} , which is one of the constituting vectors of the unit cell, does not change their form.

Any arbitrary function $u(\vec{r})$ that resides inside the unit cell that meets the condition

$$u(\vec{r}) = u\left(\vec{r} + \vec{R}\right) \tag{53}$$

can be represented by a plane wave expansion in the sense that

$$u(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{u}(\vec{G}) \exp(i\vec{G} \cdot \vec{r})$$
(54)

where $\tilde{u}(\vec{G}) \in \mathbb{C}$ act as the plane wave expansion coefficients. In the above expansion, the plane waves $\phi(\vec{G}, \vec{r})$ thus act as basis functions. To find the plane wave expansion coefficients $\tilde{u}(\vec{G})$, consider the integral $\langle \phi(\vec{G}', \vec{r}) | u(\vec{r}) \rangle$, which by application of Equations 47 and 54 yields

$$\left\langle \phi\left(\vec{G}',\vec{r}\right) \middle| u(\vec{r}) \right\rangle = \int_{\Omega} d\vec{r} \; \frac{1}{\Omega} \sum_{\vec{G}} \tilde{u}\left(\vec{G}\right) \exp\left(i\left(\vec{G} - \vec{G}'\right) \cdot \vec{r}\right) \tag{55}$$

$$=\sum_{\vec{G}}\tilde{u}(\vec{G})\delta_{\vec{G},\vec{G}},\tag{56}$$

$$=\tilde{u}(\vec{G}') \tag{57}$$

As can be seen, the above integral provides a mathematical recipe for finding the plane wave expansion coefficients $\tilde{u}(\vec{G})$ for any vector \vec{G} , exploiting the orthonormality relationship among the plane waves.

Although Equation 55 provides a straightforward recipe to find the $\tilde{u}(\vec{G})$, when one is tasked to find the set { $\tilde{u}(\vec{G})$ } it turns out that there is a significantly more efficient numerical recipes available, known as the fast Fourier transform (FFT).[39] Uniquely, the FFT tactically exploits common operations in the evaluation of the integrals for plane waves within the same set (e.g. those spanned from the same unit cell) such that in contrast to the typical N^3 scaling observed in numerical integration, one obtains a mere $N \log N$ scaling.[40] Mathematically, the FFT is a mapping from real space to reciprocal space, as given by

$$\left\{\tilde{u}\left(\vec{G}\right)\right\} = \hat{\mathcal{F}}_{\mathsf{PW}}[\left\{u(\vec{r})\right\}] \tag{58}$$

One of the most salient features of the plane wave basis set is its ability to drastically simplify the computation of the classical electron-electron repulsion,

$$E_{\rm J} = \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} \, d\vec{r}' \tag{59}$$

which is a computationally expensive convolution operation in real space, as can be readily seen from the double integral. In the plane wave framework, this complexity is mitigated by leveraging a fundamental property of Fourier transforms: a convolution in real space translates to a simple multiplication in reciprocal space. By representing the electron density and potential in reciprocal space, the evaluation of the electron-electron repulsion reduces to straightforward pointwise multiplication, eliminating the need for complex integration routines.

Given a charge density function $\rho(\vec{r})$, the electrostatic potential $\varphi(\vec{r})$ can be readily calculated by solving Poisson's equation

$$\nabla^2 \varphi(\vec{r}) = -4\pi \rho(\vec{r}) \tag{60}$$

Suppose that we expand the charge density via Equation 54 giving

$$\rho(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} \tilde{\rho}(\vec{G}) \exp(\mathrm{i}\vec{G} \cdot \vec{r})$$
(61)

Insertion of Equation 61 into Equation 60 provides the following second-order differential equation

$$\nabla^2 \varphi(\vec{r}) = -\frac{4\pi}{\sqrt{\Omega}} \sum_{\vec{G}} \nabla^2 \tilde{\rho}(\vec{G}) \exp(i\vec{G} \cdot \vec{r})$$
(62)

which can be readily solved, yielding

$$\varphi(\vec{r}) = -\frac{4\pi}{\sqrt{\Omega}} \sum_{\vec{G}} \frac{\tilde{\rho}(\vec{G})}{\left|\vec{G}\right|^2} \exp(i\vec{G}\cdot\vec{r})$$
(63)

The $\vec{G} = 0$ term in the summation of Equation 63 can be ignored because, although it leads to a divergence due to the denominator $|\vec{G}|^2$ becoming zero, this term does not contribute to the final potential as it cancels out with similar divergent terms arising from the electron-nucleus interaction and the Ewald sum. In most physical systems, charge neutrality is assumed, meaning the net

charge density $\rho(\vec{r})$ integrates to zero over the unit cell, causing $\tilde{\rho}(\vec{G} = 0)$ to vanish. Even for non-neutral systems, this term corresponds to a uniform potential shift that is unphysical and does not affect observable quantities such as forces or energies, which depend only on potential differences. Therefore, while the $\vec{G} = 0$ term is not entirely ignored, its contribution cancels out with other terms, making it irrelevant in practical calculations allowing Equation 63 to be rewritten as

$$\varphi(\vec{r}) = -\frac{4\pi}{\sqrt{\Omega}} \sum_{\vec{G}\neq\vec{0}} \frac{\tilde{\rho}(\vec{G})}{\left|\vec{G}\right|^2} \exp(\mathrm{i}\vec{G}\cdot\vec{r})$$
(64)

Exploiting the numerically efficient FFT, Equation 64 is equivalent to

$$\varphi(\vec{r}) = \hat{\mathcal{F}}_{PW}^{-1} \left[-\frac{4\pi}{\left| \vec{G} \right|^2} \hat{\mathcal{F}}_{PW}[\rho(\vec{r})] \right]_{\vec{G} \neq \vec{0}}$$
(65)

Finally, from Equation 65, we can readily find E_{I} by means of

$$E_{\rm J} = \int_{\Omega} \varphi(\vec{r}) \cdot \rho(\vec{r}) d\vec{r} \tag{66}$$

This procedure is also applied in the evaluation of the nuclear attraction. However, in this case, only a single FFT back-transform is performed, as a straightforward analytical solution is available for a set of point charges. Starting from the set of point charges, we find that

$$\left\langle \phi\left(\vec{G},\vec{r}\right) \middle| u(\vec{r}) \right\rangle = \frac{1}{\sqrt{\Omega}} \int_{\Omega} d\vec{r} \sum_{\vec{G}} \exp\left(\mathrm{i}\vec{G}\cdot\vec{r}\right) \cdot \delta\left(\vec{r}-\vec{R}_{j}\right) \tag{67}$$

$$=\frac{1}{\sqrt{\Omega}}\exp(\mathrm{i}\vec{G}\cdot\vec{R}_{j}) \tag{68}$$

Generalizing these results, we find

$$\hat{\mathcal{F}}_{PW}\left[\sum_{j}q_{j}\delta(\vec{r}-\vec{R}_{j})\right] = \frac{1}{\sqrt{\Omega}}\sum_{\vec{G}}\sum_{j}\exp(\mathrm{i}\vec{G}\cdot\vec{R}_{j})$$
(69)

Thus, the nuclear attraction potential can be found according to

$$\nu_{\text{ext}} = -\frac{4\pi}{\sqrt{\Omega}} \hat{\mathcal{F}}_{PW}^{-1} \left[\sum_{\{\vec{G}\neq\vec{0}} |\vec{G}|^{-2} \sum_{j} \exp(\mathbf{i}\vec{G}\cdot\vec{R}_{j}) \right]$$
(70)

and the nuclear attraction energy can be found, very much akin to Equation 66 to be

$$E_{\rm ext} = \int_{\Omega} v_{\rm ext}(\vec{r}) \cdot \rho(\vec{r}) d\vec{r}$$
(71)

As can be readily seen, the use of plane waves as a basis set offers significant computational advantages, enabling the efficient modeling of relatively large systems despite the inherently computationally expensive nature of density functional theory. The delocalized and periodic nature of plane waves aligns naturally with the symmetry of periodic systems, simplifying many aspects of the calculations. For instance, operations like the evaluation of the kinetic energy operator (not shown here) and electron-electron interactions are particularly streamlined in reciprocal space, where complex convolutions transform into simple multiplications. These features, combined with the availability of highly optimized algorithms such as the fast Fourier transform, reduce the computational overhead, making it feasible to study large-scale systems while maintaining the accuracy and robustness of DFT.

2.2.5.6 k-point sampling

In computational materials science, k-points refer to points in the Brillouin zone used to sample the electronic wave vectors in periodic systems. Accurate k-point sampling is crucial for calculating properties such as total energy, electronic structure and density of states. k-point sampling approximates integrals over the Brillouin zone by summing over a finite set of discrete points, reducing computational cost while maintaining sufficient accuracy.

In VASP, several schemes are available for generating *k*-points:

- **Monkhorst-Pack grids.**[41] The Monkhorst-Pack scheme generates uniform grids of *k*-points in the Brillouin zone, ensuring symmetry in sampling. It is widely used for periodic systems.
- **Gamma-centered grids.** This scheme centers the grid at the Γ-point (the origin of the reciprocal lattice). It is particularly useful for systems with symmetry around Γ or for non-metallic systems.

• Automatic mesh generation. VASP can automatically generate *k*-point grids based on the number of subdivisions along each reciprocal lattice vector, as specified in the KPOINTS file.

The density of k-points directly affects the accuracy of the calculations. Metallic systems require finer grids to capture the details of the Fermi surface, while coarser grids may suffice for insulators or large systems. To ensure reliable results, proper convergence testing is essential.

k-point convergence testing involves systematically increasing the density of k-points used to sample the Brillouin zone and monitoring the resulting changes in key calculated properties, such as total energy, band structure, or forces. The process typically begins with a coarse k-point grid, which is gradually refined by increasing the number of divisions along each reciprocal lattice vector. At each refinement step, the property of interest is computed, and the results are compared to determine if the changes fall below a predefined threshold, indicating convergence. Once convergence is achieved, the smallest k-point grid that satisfies the accuracy requirements is selected for further calculations, ensuring reliable results while minimizing computational cost.

In this thesis, the unit cells used are typically fairly large. For such systems, the electronic states vary slowly in reciprocal space and using only the Γ -point (the origin of the reciprocal lattice) often suffices to achieve accurate results.

2.2.5.7 Electron smearing

Electron smearing is a technique used in DFT calculations to improve convergence for systems with partially occupied electronic states, such as metals or systems with small band gaps. In these cases, the discrete nature of *k*-point sampling can lead to numerical instabilities or slow convergence due to abrupt changes in the occupation of electronic states near the Fermi level. Smearing methods address this issue by introducing a nonzero finite electronic temperature, spreading the occupation of states around the Fermi level and smoothing the electronic density of states. In VASP, several smearing methods are available, including the Methfessel-Paxton scheme,[42] Gaussian smearing,[43] and the tetrahedron method with Blöchl corrections.[44] The choice of smearing method and width depends on the system under investigation. For metals, Methfessel-Paxton or Gaussian smearing is commonly used, while the tetrahedron method is preferred for insulators and semiconductors where accurate total energies are critical. After the calculation, the electronic temperature can be extrapolated to zero to recover the groundstate properties of the system.

2.2.5.8 Projector augmented wave method

Besides a number of advantages shown above, plane waves also carry a number of disadvantages when used in electronic structure calculations which have to be mitigated. Due to the highly oscillatory nature of core orbitals, an extremely large number of plane waves would be required to accurately describe them. This would result in the majority of computational resources being spent on modeling the core electron density, which has minimal relevance to most chemical properties. To address this, the core electrons are typically not explicitly modeled, and instead, the frozen-core approximation is employed. In this thesis, the projector augmented wave (PAW) method, introduced by Blöchl,[45,46] is used to describe the core electrons, while the valence electrons are explicitly modeled using a plane wave basis set. This approach, implemented as a key feature in the VASP simulation package, has been used throughout this work.

2.2.6 Electronic structure analysis

From a user perspective, an electronic structure calculation provides the electronic energy of a system based on the specified nuclear positions within a unit cell and the total number of electrons. While many practitioners primarily focus on the resulting energy values, delving into the underlying electron structure offers significant insights.

2.2.6.1 Electron density

Examining the electron density, both as a function of spatial position and energy, can reveal valuable information about chemical processes and interactions. The electron density is fundamentally a scalar field that describes the probability of finding an electron at a given point in space. This scalar field can be effectively visualized using contour plots or isosurfaces. Contour plots provide a two-dimensional representation by projecting the electron density onto a plane. Alternatively, isosurfaces offer a three-dimensional perspective, where surfaces of constant electron density are rendered, allowing for an intuitive visualization of spatial features such as bonding regions, charge accumulation, and voids. Spatial analysis of the electron density helps elucidate how reaction mechanisms lead to electron density redistribution. This analysis can encompass overall electron density changes or more specific partial (band-decomposed) charge densities. For instance, differences in activation energies between elementary

reaction steps can often be rationalized by studying the initial electron density redistribution upon the adsorption of a reactant onto a catalyst.

2.2.6.2 Density of states

Another powerful approach to studying electron density is through a density of states (DOS) analysis. The DOS method is a cornerstone in condensed matter physics and materials science, used to describe the distribution of energy states available to particles within a solid-state system. This analysis provides vital insights into the electronic properties of materials, including metals, semiconductors, and insulators. Fundamentally, the DOS calculates the number of electronic states available at each energy level within a material. The results are often depicted as a plot of the number of states per unit energy interval versus the energy level, resembling a molecular orbital diagram in concept.

2.2.6.3 Crystal orbital Hamilton population analysis

Interpreting the contribution of specific features in the DOS towards the stability of a complex can be extremely challenging, and in many cases, even impossible. The DOS provides information about the distribution of energy states but does not directly indicate whether a particular contribution is bonding, antibonding, or non-bonding between a specific pair of atoms. This ambiguity makes it difficult to connect electronic structure features to the stability or bonding nature of a system. To address this, one can employ the crystal orbital Hamilton population (COHP) method.[4] COHP decomposes the electronic structure into bonding, antibonding, and non-bonding interactions for specific atom pairs, offering a more detailed and intuitive understanding of the electronic contributions to the system stability.

A limitation of the plane wave basis set is that it represents Kohn-Sham states in a fully delocalized manner, making it impossible to directly associate basis functions with specific atoms. While this delocalization is beneficial for modeling periodic systems, it complicates the attribution of contributions from individual Kohn-Sham states to particular atoms. To analyze atomic contributions effectively, the Kohn-Sham states must be projected onto a localized basis set.

Projecting the Kohn-Sham states onto a localized basis set, along with applying a corresponding transformation to the Hamiltonian matrix, allows us to define the interaction strength between any two atoms in the system, as expressed by

$$\eta_{k,A-B} = o_k \sum_{i \in A} \sum_{j \in B} C_{ik} C_{jk} H_{ij}$$
(72)

where k corresponds to the Kohn-Sham state, i and j to local basis functions and A and B to distinct atoms in the system. o_k is the occupancy factor of the Kohn-Sham state, C_{ik} and C_{jk} the linear expansion coefficients in the localized basis with respect to Kohn-Sham state k and H_{ij} an (off-diagonal) element of the transformed Hamiltonian matrix.

The summation in Equation 72 considers only the basis functions *i* located on atom *A* and basis functions *j* located on atom *B*. The resulting value η can be interpreted as follows: a negative value indicates a bonding interaction, a positive value indicates an antibonding interaction, and a value of zero indicates a non-bonding interaction. For example, Equation 72 predicts that core orbitals—molecular orbitals associated with atomic core orbitals—are non-bonding. This is because core orbitals contribute non-zero values either for *i* or *j*, but not both, which causes the summation to result in zero. The same reasoning applies to lone-pair orbitals, which are non-bonding due to symmetry restrictions.

The projection utilized allowing for Equation 72 may not fully capture the representation quality of the original plane wave basis set. In practical terms, some information can be lost during the projection process. This reduction in representativeness is typically measured by a loss ratio, which quantifies the relative amount of electron density lost upon projection. To ensure the reliability of the analysis, it is important to keep this loss below 5%. In this thesis, the LOBSTER program has been employed to perform the projections and carry out the subsequent electronic structure analysis.[3–6]

The total electronic energy of a system remains constant under a unitary transformation among the occupied Kohn-Sham states (per Equation 9). As a result, the specific COHP result is not unique and can vary with different unitary transformations. The energy invariance under a unitary transformation also implies that the integrated COHP value converges to the same result at the Fermi level, regardless of the transformation. In this thesis, the canonical solution is consistently presented: the COHP analysis is based on the set of Kohn-Sham states that diagonalize the Hamiltonian matrix in the chosen basis.

Leveraging the rotational symmetry of the SO(3) group, it is possible to mix the localized orbitals on the same atom and that share the same angular momentum quantum number l using Wigner *D*-matrices.[47] This approach allows the orbital corresponding to m = 0 (e.g., p_z , d_{z^2} , f_{z^3}) to always align with the bonding axis between atoms *A* and *B*. The SO(3) symmetry ensures that such rotations preserve the orthonormality of the basis functions and conserve the

total angular momentum. By aligning the m = 0 orbital along the bonding axis, the COHP analysis becomes more intuitive and directly correlated with the spatial geometry of the system. Specifically for studying linear molecules such as CO, this approach has been applied in this thesis.

2.3 Evolutionary searches

Nanoparticles can adopt a wide range of morphologies, such as pyramidal, cuboctahedral, or highly irregular structures, depending on their composition, size, and interaction with the substrate. The complexity is further compounded by the influence of surface chemistry, as the interaction between the nanoparticle and the substrate can significantly alter the nanoparticle shape and stability. Traditional optimization methods struggle to efficiently navigate this extensive energy landscape. Evolutionary searches are an ideal tool to identify the optimal nanoparticle configuration.

The genetic algorithm developed by the Hammer group addresses the challenge of exploring the vast configurational space of metal nanoparticles adsorbed on surfaces.[48] The algorithm begins by generating an initial population of candidate nanoparticle configurations. These configurations may be created randomly or based on prior knowledge, such as simple geometric shapes. Each candidate represents a specific arrangement of atoms in the nanoparticle adsorbed on the surface. The fitness of each configuration is then evaluated, typically based on its total energy computed using Density Functional Theory (DFT) or empirical potentials. The fitness function is designed to favor lowerenergy structures, aligning with the objective of identifying the most stable or desirable configuration.

Once the fitness of the population is assessed, a subset of configurations is selected for reproduction. Configurations with lower energy are more likely to be selected, following the principle of survival of the fittest. These selected configurations undergo crossover (recombination), where pairs of configurations are combined to produce offspring. For nanoparticles, this process may involve mixing atomic positions or structural motifs from two parent configurations, such as swapping segments of their atomic arrangements. This step introduces diversity into the population and allows the algorithm to explore new structural configurations.

To further enhance diversity and prevent the algorithm from getting trapped in local minima, random mutations are applied to the offspring. These mutations might involve moving atoms to new positions, adding or removing atoms, or rearranging atomic configurations within the nanoparticle or at its interface with the surface. The resulting offspring then replace less fit configurations in the population, ensuring that the overall quality of the population improves over successive generations. This iterative process of fitness evaluation, selection, crossover, and mutation continues for a predefined number of generations or until the population converges to an optimal configuration.

A key feature of this genetic algorithm is its explicit consideration of the interaction between the nanoparticle and the adsorbing surface. This ensures that the optimization captures both the nanoparticle shape and its chemical interaction with the substrate, which are critical for applications such as catalysis. The algorithm also incorporates parallelization, enabling multiple configurations to be evaluated simultaneously, which accelerates convergence. Additionally, the fitness function can be customized to include criteria beyond energy minimization, although not explicitly used in this thesis, such as stability under reaction conditions or catalytic activity, making the algorithm highly versatile for different applications.

Within this thesis, we have used an in-house modified variant of this algorithm, specifically catered to the supercomputer architecture employed.[49] These modifications include tailored parallelization strategies that leverage the computational resources of the supercomputer to evaluate multiple candidate configurations simultaneously, significantly enhancing efficiency and scalability. Additionally, the algorithm has been optimized to handle system-specific constraints, such as accommodating the particular interaction models between nanoparticles and surfaces and managing the memory and processing requirements unique to the computational setup.

2.4 Microkinetic modeling

Microkinetic modeling is widely used to describe intricate chemo-kinetic networks by representing them as a collection of elementary reaction steps. The construction of such models requires a thorough analysis of the reaction network, which can be derived from experimental data or obtained through *ab initio* methods such as DFT calculations. To study the time-dependent behavior of the chemical system, a series of ordinary differential equations (ODEs) is solved over time.

In this section, the establishment of microkinetic parameters through firstprinciples calculations will be explained first. Then, the derivation of a set of ODEs from a sequence of elementary reaction steps will be demonstrated. Finally, the process of solving these ODEs and the application of sensitivity analysis to extract valuable insights from microkinetic simulations will be discussed.

2.4.1 Parameter evaluation for microkinetic modeling

Microkinetic modeling involves constructing a detailed representation of chemokinetic networks by breaking them down into elementary reaction steps. To establish a microkinetic model, accurate determination of the rate constants for these elementary steps is essential. These rate constants can be derived using DFT calculations, which optimize the electronic structures of the initial, transition, and final states of the relevant reaction steps. The absolute electronic energy is then calculated, enabling the determination of the electronic activation energy in both forward and backward directions. Incorporating the zero-point energy (ZPE) correction is critical, as neglecting it can yield erroneous results, particularly for hydrogenation reactions.

The harmonic transition state theory is employed to calculate the rates of elementary reaction steps under the following assumptions:

- The transition state is in thermal equilibrium with the initial state, characterized by a thermal equilibrium constant.
- The transition from the transition state to the final state is considered irreversible.
- Crossing the transition state occurs with a specific velocity or frequency over the hyperdimensional potential energy surface.
- The transmission coefficient is assumed to be unity, and other trajectories are not sampled.

Under these assumptions, the rate constant for an elementary reaction step is determined using the Eyring equation[50]

$$k = \frac{k_{\rm B}T}{h} \frac{Q^{\rm TS}}{Q^{\rm IS}} \exp\left(-\frac{\Delta E_{\rm act}^{\rm elec}}{k_{\rm B}T}\right)$$
(73)

where k is the reaction rate, $k_{\rm B}$ and h are Boltzmann's and Planck's constants, T is the temperature, $Q^{\rm IS}$ and $Q^{\rm TS}$ are the partition functions of the initial and transition states, and $\Delta E_{\rm act}^{\rm elec}$ is electronic activation energy.

Within theoretical heterogeneous catalysis, three fundamental types of elementary reaction steps are distinguished:

- Reactions over the catalytic surface.
- Adsorption of reactants onto the surface.
- Desorption of products from the surface.

For reactions over the catalytic surface, it is typically assumed that the partition functions Q^{IS} and Q^{TS} are purely vibrational. Furthermore, contributions from the adsorbate are considered dominant due to the significant mass disparity between the metal atoms and adsorbates. Under these assumptions, the overall partition function for the initial state is expressed as the product of 3N vibrational partition functions, where N is the number of atoms in the adsorbate

$$q_{\rm vib} = \prod_{i=1}^{3N} \frac{\exp(-\frac{h\nu_i}{2k_{\rm B}T})}{1 - \exp(-\frac{h\nu_i}{k_{\rm B}T})}$$
(74)

The vibrational frequencies v_i in Equation 74 are obtained from electronic structure calculations by constructing a Hessian matrix, whose elements are given by

$$H_{ij} = \frac{\partial^2 E}{\partial x_i \,\partial x_j} \tag{75}$$

The values for H_{ij} in Equation 75 are approximated using a four-point finite difference stencil as given by

$$H_{ij} = \frac{1}{2} \left(\frac{\left(\frac{\partial E}{\partial x_i}\right)_{j+\frac{1}{2}\Delta x_j} - \left(\frac{\partial E}{\partial x_i}\right)_{j-\frac{1}{2}\Delta x_j}}{\Delta x_j} + \dots + \frac{\left(\frac{\partial E}{\partial x_j}\right)_{i+\frac{1}{2}\Delta x_i} - \left(\frac{\partial E}{\partial x_i}\right)_{i-\frac{1}{2}\Delta x_i}}{\Delta x_i} \right)$$
(76)

The matrix **H** is subsequently mass-weighted according to

$$H_{ij}^{\text{mass-weighted}} = \frac{H_{ij}}{\sqrt{m_i m_j}}$$
(77)

Diagonalizing this matrix yields 3N eigenvectors and eigenvalues, representing the normal modes and vibrational energies, respectively. These are used in the vibrational partition function.

In Equation 73, 3*N* frequencies are used for Q^{IS} , while 3N - 1 frequencies are used for Q^{TS} , as one frequency corresponds to the reaction coordinate, resulting in an imaginary value. This imaginary frequency is accounted for in the Eyring

equation and is excluded from the transition state partition function. For surface reactions, typical pre-exponential factors in Equation 73 are on the order of 10^{13} s⁻¹. Adsorption and desorption steps, however, involve significant entropy changes, leading to deviations in pre-exponential values.

To model adsorption reactions, the reactant in the gas phase is assumed to possess three translational degrees of freedom and either 0, 2, or 3 rotational degrees of freedom, depending on whether it is an atom, linear molecule, or nonlinear molecule, respectively. Translational and rotational partition functions can be readily derived from statistical thermodynamic principles. The translational partition function is given by

$$q_{\text{trans,3D}} = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \tag{78}$$

where m is the mass of the particle, $k_{\rm B}$ is the Boltzmann constant, T is the temperature, h is Planck's constant, and V is the volume of the container. This expression accounts for the contribution of translational motion to the overall partition function of a system.

For rotational motion, the partition function depends on whether the molecule is linear or nonlinear. For a linear molecule, the rotational partition function is:

$$q_{\rm rot,lin} = \frac{T}{\sigma \Theta_{\rm rot}} \tag{79}$$

where σ is the symmetry number of the molecule, Θ_{rot} is the rotational temperature, and *T* is the temperature. For a nonlinear molecule, the rotational partition function becomes:

$$q_{\rm rot,nonlin} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{T^3}{\Theta_{\rm A} \Theta_{\rm B} \Theta_{\rm C}} \right)^{1/2} \tag{80}$$

where Θ_A , Θ_B , and Θ_C are the rotational temperatures about the principal axes of the molecule, and σ accounts for the symmetry.

For adsorption, a single translational partition function is converted into a vibrational one. Assuming that quotients in vibrational partition functions are negligible relative to other terms, the adsorption rate constant is

$$k^{\rm ads} = \frac{k_{\rm B}T}{h} \frac{q_{\rm vib}^{\rm TS} q_{\rm rot}^{\rm TS} q_{\rm trans,2D}^{\rm TS}}{q_{\rm vib}^{\rm gas} q_{\rm trans,3D}^{\rm gas} q_{\rm rot}^{\rm gas}}$$
(81)

$$=\frac{k_{\rm B}T}{h}\frac{PA_{\rm st}}{\sqrt{2\pi mk_{\rm B}T}}$$
(82)

where A_{st} is the effective adsorption area, m is the molar mass, and P is the partial pressure. The desorption rate constant is derived from the adsorption equilibrium constant

$$K_{\rm ads} = \frac{k_{\rm ads}}{k_{\rm des}} = \exp\left(-\frac{\Delta H_{\rm ads}}{RT} + \frac{\Delta S_{\rm ads}}{R}\right)$$
(83)

which by insertion into Equation 82 yields

$$k_{\rm des} = \frac{k_{\rm B}T}{h} \frac{PA_{\rm st}}{\sqrt{2\pi m k_{\rm B}T}} \exp\left(\frac{\Delta H_{\rm ads}}{RT} - \frac{\Delta S_{\rm ads}}{R}\right)$$
(84)

Using the partition function of the adsorbed complex, the adsorption entropy is calculated from

$$\Delta S_{\rm ads} = R \ln Q^{\rm IS} - S^0 \tag{85}$$

wherein S^0 can be found via the Shomate equation[51]

$$S^{0} = A\ln(T) + B \cdot T + \frac{C \cdot T^{2}}{2} + \frac{D \cdot T^{3}}{3} - \frac{E}{2 \cdot T^{2}} + G$$
(86)

with parameters tabulated in the NIST Chemistry Webbook.[52] Alternatively, one can also establish S^0 by means of Equations 78 and 80.

Insertion of Equation 85 into Equation 84 yields

$$k_{\rm des} = \frac{PA_{\rm st}}{\sqrt{2\pi mk_{\rm B}T}} \exp\left(-\frac{\Delta H_{\rm des}}{RT}\right) \frac{\exp\left(\frac{S^0}{R}\right)}{Q_{\rm ads}}$$
(87)

Assuming that the adsorbed complex only has vibrational degrees of freedom, under the harmonic approximation Q^{IS} can be calculated from the vibrational frequencies via

$$Q^{\rm IS} = \prod_{i} \frac{1}{1 - \exp\left(-\frac{h\nu_i}{k_{\rm B}T}\right)} \tag{88}$$

The zero-point energy contribution of the vibrational frequencies is omitted in the above equation as it corresponds to a component of ΔH_{des} in Equation 87.

Using Equations 73, 83 and 87, the set of differential equations governing all surface reactions can be constructed. The rate expression for an elementary reaction step *j* is formulated as

$$r_j = k_j \prod_i \theta_i^{\nu_{ij}} \tag{89}$$

wherein k is the reaction rate constant as calculated by the Eyring equation, θ_i the concentration of reactant i in elementary reaction step j on the surface and v_j the stoichiometric coefficient of reactant i in elementary reaction step j. It should be noted that in Equation 89, we only treat the elementary reaction step in one direction, thus for each elementary reaction step, two rate expressions as shown in Equation 89 are obtained.

2.4.2 Solving systems of ordinary differential equations

The set of rate expressions corresponding to Equation 89 can be assembled into a system of time-dependent ODEs. To create this set of ODEs, we define a series of elementary reaction steps R, each associated with specific rate constants. As a result, the system contains 2R elementary reaction equations involving N compounds. For each compound, the change in its surface concentration over time can be expressed as

$$\frac{d\theta_i}{dt} = \sum_{j=1}^{2R} \left(\nu_{i,j} k_j \prod_q \theta_q^{\nu_{q,j}} \right)$$
(90)

where θ_i is the concentration of species *i* on the surface, $v_{i,j}$ is the stoichiometric coefficient of compound *i* in reaction *j*, k_j is the rate constant of reaction *j*, θ_q is the concentration of compound *q* in reaction *j*, and $v_{q,j}$ is the stoichiometric coefficient of compound *q* in reaction *j*. By integrating these equations over time, it is possible to calculate the kinetic properties of the reaction, such as the overall reaction rate and the surface coverages. The set of ODEs is solved iteratively until a steady-state solution is reached for all species *i*.

The equations involved in chemical systems are often categorized as stiff equations. Stiffness refers to the requirement of extremely small time steps for stable and accurate numerical integration. In this thesis, a multistep backward differentiation formula (BDF) method, as implemented in the Sundials library,[53] is used to integrate the set of ODEs.

In this method, the derivative of a function is approximated as a linear combination of the function values at previous time steps. For a first-order ODE given by

$$\frac{dy}{dt} = f(y,t) \tag{91}$$

the BDF method calculates the solution at the next time step, t_{n+1} , using the following implicit equation

$$\sum_{k=0}^{m} \alpha_k y_{n-k} = \Delta t f(y_{n+1}, t_{n+1})$$
(92)

where *m* is the order of the method, α_k are the method-specific coefficients, Δt is the time step, and y_{n-k} are the solution values at previous time steps. A distinguishing feature of the BDF method is its implicit formulation, which requires evaluating $f(y_{n+1}, t_{n+1})$ at the new time step. This typically involves solving a nonlinear system of equations but provides exceptional stability for stiff problems, allowing the use of larger time steps compared to explicit methods.

The order of the method m is dynamically adjusted between one and five based on the steepness of the solution. To assess steepness, the Jacobian matrix is evaluated. While an analytical Jacobian can be supplied, it is often more practical to compute this matrix numerically using a finite difference approximation, which simplifies implementation without compromising accuracy.

2.4.3 Kinetic sensitivity analysis

In microkinetic modeling, the goal is to obtain kinetic properties such as reaction rates and surface coverages under transient and steady-state conditions. By performing a kinetic sensitivity analysis, we can calculate observables that relate to experimental data, providing valuable insights for the rational design of new catalysts or interpreting experimental results for existing catalytic materials.

2.4.3.1 Reaction orders

The reaction order quantifies the relative change in the reaction rate with respect to a relative change in the partial pressure of gas-phase compounds (either reactants or products). It offers a way to investigate the influence of reactants and products on the reaction rate.

To illustrate this, consider a generic bimolecular reaction

$$\begin{array}{c} A+B \rightleftarrows C \\ 51 \end{array} \tag{93}$$

The rate of this forward reaction r^+ can be expressed as:

$$r^{+} = k[A]^{n_{A}}[B]^{n_{B}}$$
(94)

or equivalently:

$$r^+ = k P_{\rm A}^{n_{\rm A}} P_{\rm B}^{n_{\rm B}} \tag{95}$$

where $n_{\rm A}$, $n_{\rm B}$, and $n_{\rm C}$ are the reaction orders of components A, B, and C, respectively.

The reaction order for a given component *i* is mathematically defined as

$$n_i = P_i \frac{\partial \ln r^+}{\partial P_i} \tag{96}$$

where n_i is the reaction order for component *i*, r^+ is the forward reaction rate, and P_i is the partial pressure of component *i*. Reaction orders can be determined experimentally by changing the partial pressure of a reactant or product by a small amount and measuring the resulting change in the reaction rate.

2.4.3.2 Apparent activation energy

The apparent activation energy is used to probe the influence of temperature on the reaction rate. In other words, it represents the kinetic sensitivity of the reaction rate to temperature. The apparent activation energy is mathematically expressed as

$$\Delta E_{\rm act}^{\rm app} = RT^2 \frac{\partial \ln r^+}{\partial T} \tag{97}$$

where ΔE_{act}^{app} is the apparent activation energy, *R* is the universal gas constant, *T* is the temperature, and r^+ is the forward reaction rate.

A positive value of ΔE_{act}^{app} indicates that the overall reaction rate increases with increasing temperature. Conversely, a negative value implies that the reaction rate decreases as the temperature increases. The apparent activation energy is an experimentally accessible quantity, similar to reaction orders, and is typically determined by fitting the temperature dependence of the reaction rate or rate constant to the Arrhenius equation.

2.4.3.2 Degree of rate and selectivity control

In analytical modeling of chemical kinetics, the so-called rate-determining step (RDS) assumption is considered a highly useful concept. Under this assumption,

it is assumed that a single elementary reaction step is so slow that it entirely determines the overall reaction rate. However, in practice, the overall rate can potentially be controlled by multiple elementary reaction steps. To account for this, sensitivity analysis on the activation energy of all elementary reaction steps is performed in microkinetic simulations. This approach is referred to as degree of rate control (DRC) analysis. This method was originally developed by Kozuch and Shaik[54] and was later popularized by Campbell.[55] In this work, sensitivity analysis with respect to the activation energy for all elementary reaction steps is conducted.

For each elementary reaction step *j*, a DRC coefficient is calculated by evaluating the following differential

$$\chi_{\mathrm{DRC},j} = \frac{k_j}{r} \left(\frac{\partial r}{\partial k_j}\right)_{k_i \neq j, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_j}\right)_{k_i \neq j, K_i}$$
(98)

where $\chi_{DRC,j}$ is the DRC coefficient for step j, k_j and K_j are the forward rate and equilibrium constants for step j, respectively, and r is the overall reaction rate. The differential in Equation 98 is used to evaluate the relative effect of the reaction rate by changing the activation energy of step j by an infinitesimal amount, while keeping the rate constants of all other steps fixed and maintaining the overall thermodynamics of the reaction.

A positive value of $\chi_{DRC,j}$ indicates that the overall reaction rate increases when the barrier of the elementary reaction step decreases, implying that the step is rate-limiting. Conversely, a negative coefficient indicates that lowering the activation energy of a given elementary reaction step decreases the overall reaction rate, implying that the step is rate-inhibiting. If a single elementary step has a DRC coefficient of 1, that step is referred to as the rate-determining step in the context of Langmuir-Hinshelwood-Hougen-Watson kinetics.

When zero conversion is assumed (i.e., under initial conditions), the sum of DRC coefficients is conserved, as expressed by

$$\sum_{j} \chi_{\text{DRC},j} = 1 \tag{99}$$

Analogous to the degree of rate control, the degree of selectivity control (DSC) coefficient is used to determine the influence of a particular elementary reaction step on the selectivity of the overall reaction.

The DSC coefficient is evaluated using the following equation

$$\chi_{\text{DSC},j,c} = \eta_c \left(\chi_{\text{DRC},j,c} - \chi_{\text{DRC},j,r} \right)$$
(100)

where η_c represents the selectivity of compound *c* with respect to some reference compound *r*. $\chi_{DRC,j,c}$ is the DRC coefficient for compound *c*, and $\chi_{DRC,j,r}$ is the DRC coefficient for the reference compound *r*.

From Equation 99, it can be deduced that the sum of DSC coefficients is zero

$$\sum_{j} \chi_{\text{DSC},j,c} = 0 \tag{101}$$

where $\chi_{DSC,j,c}$ is the DSC coefficient of product *c* due to a change in the kinetics of elementary reaction step *j*.

2.4.4 Lateral interactions

Lateral interactions refer to the interactions between adsorbates on a catalytic surface, which can influence the adsorption energies and reaction barriers. These interactions play a critical role in determining the overall kinetics of catalytic processes, particularly at high coverages where adsorbates are in close proximity. In microkinetic modeling, the accurate representation of lateral interactions is essential to capture the effects of coverage on reaction rates and selectivity. Lateral interactions can include through-space electrostatic or Van der Waals forces, as well as chemical interactions such as bond formation or strain effects. Implementing these interactions must be calculated for all pairs or groups of adsorbates, especially in heterogeneous systems.

In this thesis, a simplified model is implemented to represent lateral interactions. Instead of building a detailed lateral interaction potential based on a matrix of cross-interactions, the lateral interaction is modeled on a per-atom basis. For hydrocarbon catalysis, the lateral interaction is defined based on the number of C and H species in each adsorbate, rather than specifying the interactions between each type of CH_x adsorbate.

The simplified model assumes that through-space lateral repulsion is based on the total coverage, rather than the sum of individual contributions from partial coverages. For a given element x, the lateral interaction potential is described by the equation

$$E_x^{\text{lat}} = E_x^{\theta = \theta_{\text{total}}} \frac{\left(101^{\theta_{\text{lat}}} - 1\right)}{100}$$
(102)

This equation implies that when the total coverage is zero $\theta_{lat} = 0$, the lateral interaction potential also vanishes.

It is assumed that all species contribute equally to the lateral interaction potential, except for H, due to its significantly smaller size. Additionally, a mapping of the lateral interaction potential to a specific coverage range is introduced by defining lower and upper bounds, θ_{LB} and θ_{UB} . The overall equation for θ_{lat} is given by

$$\theta_{\text{lat}} = \frac{\left(\theta_{\text{total}} - \theta_* - \frac{1}{2}\theta_{\text{H}}\right) - \theta_{\text{LB}}}{\theta_{\text{UB}} - \theta_{\text{LB}}}$$
(103)

For example, by setting $\theta_{\text{LB}} = 0.25$ ML (monolayer) and $\theta_{\text{UB}} = 0.75$ ML, the lateral interaction coverage is zero below a coverage of 0.25 ML. The penalty increases exponentially, reaching $E_x^{\theta=\theta_{\text{total}}}$ at a coverage of 0.75 ML CO, or at 0.5 ML CO + 0.5 ML H.

2.5 References

- [1] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251–14269.
- [2] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15–50.
- [3] R. Dronskowski, P.E. Bloechl, J. Phys. Chem. 97 (1993) 8617–8624.
- [4] V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Phys. Chem. A 115 (2011) 5461–5466.
- [5] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Comput. Chem. 34 (2013) 2557–2567.
- [6] R. Nelson, C. Ertural, J. George, V.L. Deringer, G. Hautier, R. Dronskowski, J. Comput. Chem. 41 (2020) 1931–1940.
- [7] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [8] E. Schrödinger, Phys. Rev. 28 (1926) 1049–1070.
- [9] M. Born, R. Oppenheimer, Ann. Phys. 389 (1927) 457-484.
- [10] J.C. Slater, Phys. Rev. 34 (1929) 1293–1322.
- [11] W. Pauli, Z. Physik 31 (1925) 765–783.
- [12] Szabo, A., Ostlund, N. S., Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, Dover Publications, New York, 1996.
- [13] D.R. Hartree, Math. Proc. Camb. Phil. Soc. 24 (1928) 111–132.
- [14] V. Fock, Z. Physik 61 (1930) 126–148.

- [15] R.A. Adams, Calculus: A Complete Course, 8. ed, Pearson Education, Toronto, 2014.
- [16] J.M. Foster, S.F. Boys, Rev. Mod. Phys. 32 (1960) 300–302.
- [17] D.C. Lay, S.R. Lay, J.J. McDonald, Linear Algebra and Its Applications, 5. edition, global edition, Pearson, Boston, 2016.
- [18] J.L. Bao, L. Gagliardi, D.G. Truhlar, J. Phys. Chem. Lett. 9 (2018) 2353–2358.
- [19] P. Pulay, Chem. Phys. Lett. 73 (1980) 393–398.
- [20] C. David Sherrill, H.F. Schaefer, in: Advances in Quantum Chemistry, Elsevier, 1999, pp. 143–269.
- [21] M. Marsman, A. Grüneis, J. Paier, G. Kresse, J. Chem. Phys. 130 (2009) 184103.
- [22] T. Schäfer, B. Ramberger, G. Kresse, J. Chem. Phys. 146 (2017) 104101.
- [23] T. Schäfer, B. Ramberger, G. Kresse, J. Chem. Phys. 148 (2018) 064103.
- [24] J. Čížek, J. Chem. Phys. 45 (1966) 4256–4266.
- [25] L.H. Thomas, Math. Proc. Camb. Phil. Soc. 23 (1927) 542-548.
- [26] E. Fermi, Rend. Accad. Naz. Lincei. 6 (1927) 602–607.
- [27] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864–B871.
- [28] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133-A1138.
- [29] D. Ceperley, B. Alder, Science 231 (1986) 555-560.
- [30] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200–1211.
- [31] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865-3868.
- [32] B. Hammer, L.B. Hansen, J.K. Nørskov, Phys. Rev. B 59 (1999) 7413–7421.
- [33] J.P. Perdew, in: AIP Conference Proceedings, AIP, Antwerp (Belgium), 2001, pp. 1–20.
- [34] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132 (2010) 154104.
- [35] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 32 (2011) 1456–1465.
- [36] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048–5079.
- [37] V.I. Anisimov, M.A. Korotin, J. Zaanen, O.K. Andersen, Phys. Rev. Lett. 68 (1992) 345–348.
- [38] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Phys. Rev. B 57 (1998) 1505–1509.
- [39] J.W. Cooley, J.W. Tukey, Math. Comp. 19 (1965) 297–301.
- [40] W.H. Press, ed., Numerical Recipes: The Art of Scientific Computing, 3rd ed, Cambridge University Press, Cambridge, UK ; New York, 2007.
- [41] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188–5192.
- [42] M. Methfessel, A.T. Paxton, Phys. Rev. B 40 (1989) 3616–3621.
- [43] C.-L. Fu, K.-M. Ho, Phys. Rev. B 28 (1983) 5480–5486.
- [44] P.E. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 16223–16233.
- [45] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953–17979.
- [46] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758–1775.
- [47] E.P. Wigner, Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra, Expanded and improved ed, Academic Press, New York, 1959.
- [48] L.B. Vilhelmsen, B. Hammer, J. Chem. Phys. 141 (2014) 044711.

- [49] M.-W. Chang, L. Zhang, M. Davids, I.A.W. Filot, E.J.M. Hensen, J. Catal. 392 (2020) 39–47.
- [50] H. Eyring, J. Chem. Phys. 3 (1935) 107–115.
- [51] C.H. Shomate, J. Phys. Chem. 58 (1954) 368–372.
- [52] M. Chase, NIST-JANAF Thermochemical Tables, 4th ed, American chemical society, Washington, D.C, 1998.
- [53] A.C. Hindmarsh, P.N. Brown, K.E. Grant, S.L. Lee, R. Serban, D.E. Shumaker, C.S. Woodward, ACM Trans. Math. Softw. 31 (2005) 363–396.
- [54] S. Kozuch, S. Shaik, J. Am. Chem. Soc. 128 (2006) 3355–3365.
- [55] C.T. Campbell, ACS Catal. 7 (2017) 2770–2779.

3. Unravelling CO Activation on Flat and Stepped Co Surfaces: A Molecular Orbital Analysis

Abstract

Structure sensitivity in heterogeneous catalysis dictates the overall activity and selectivity of a catalyst whose origins lie in the atomic configurations of the active sites. We explored the influence of the active site geometry on the dissociation activity of CO by investigating the electronic structure of CO adsorbed on twelve different Co sites and correlating its electronic structure features to the corresponding C-O dissociation barrier. By including the electronic structure analyses of CO adsorbed on step-edge sites, we expand upon the current models that primarily pertain to flat sites. The most important descriptors for activation of the C–O bond are the decrease in electron density in CO's 1π orbital, the occupation of 2π anti-bonding orbitals and the redistribution of electrons in the 3σ orbital. The enhanced weakening of the C–O bond that occurs when CO adsorbs on sites with a step-edge motif as compared to flat sites is caused by a distancing of the 1π orbital with respect to Co. This distancing reduces the electron-electron repulsion with the Cod-band. These results deepen our understanding of the electronic phenomena that enable the breaking of a molecular bond on a metal surface.



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3.1 Introduction

Structure sensitivity is a phenomenon encountered in heterogeneous catalysis where the reaction rate strongly depends on the size of the nanoparticle. The contemporary view is that the size of the nanoparticles determines the abundance and stability of sites required for the activation of a critical bond in a reactant or intermediate. This concept was pioneered a little over half a century ago by van Boudart.[1] Not only the abundance and geometry of the active sites determine the reactivity of the nanoparticle with adsorbates, but also the coordination number of the metal atoms that make up the active site. Nørskov et al.[2] showed that a decreasing coordination number leads to a decrease of the *d*-band width and an increase of the *d*-band center. This can result in strong molecular chemisorption on metal atoms with a low coordination number, e.g. on very small nanoparticles, at the metal-support interface, or on step sites. Several important reactions in heterogeneous catalysis show a strong structure sensitivity relationship. For example, for steam methane reforming it is found that decreasing the nanoparticle size improves the activity of this reaction as smaller particles expose more kink and corner sites which are instrumental in the activation of the C-H σ -bond.[3–5] In contrast, for ammonia synthesis[6–8], Fischer-Tropsch synthesis[9–14] and CO₂ methanation[15–18], it is found that the turnover frequency (TOF) increases with increasing nanoparticle size. For these reactions, the activation of a π -bond is critical, because it requires the availability of step-edge or B₅ sites (as defined by Van Hardeveld *et al.*[19]), whose abundance increases with increasing particle size.

The structure sensitivity relationship as found in heterogeneous catalysis already points out to the fact that the specific topology of an active site plays a crucial role in the activation of chemical bonds. Consequently, vast differences in activation energies are observed as function of the active site configuration.[20] In this study, we aim to understand the underlying electronic factors by which the active site topology controls the activation of π -bonds. We specifically focus here on the CO molecule as CO dissociation plays a central role in processes such as Fischer-Tropsch synthesis (FTS)[21,22] and CO₂ methanation.[23] For these processes, CO dissociation is not only a major rate-controlling step, but its barrier also determines the selectivity between CH₄ and longer hydrocarbons in FTS[24], and between CH₄ and CO formation in CO₂ methanation.[25] Facile CO dissociation is observed over the transition metals Fe, Ru, Co, and Ni[26], for which nanoparticles can be supported on metal oxides like alumina, silica, titania, and magnesia.[26] Depending on the active site, CO dissociation occurs

either in a direct fashion or in an H-assisted manner via intermediates such as HCO, H_2CO or COH.

The C-O bond is very strong (1072 kJ/mol)[27] and its scission requires the presence of a catalyst. The redistribution of electron density upon CO adsorption on a transition metal destabilizes the CO triple bond, providing access to a more facile dissociation pathway. Over the past decades, many models have been constructed to describe this process. The most well-known model is from Blyholder[28] who applied the theories of Orgel[29,30], Ballhausen[31], and Richardson[32] about the bonding of a carbonyl as a ligand to a metal center to CO adsorption on extended transition metal surfaces. Using Hückel molecular orbital theory, Blyholder constructed a semi-quantitative description on the nature of the metal-CO bond. The model predicts that electron donation from CO to the metal atom occurs by the interaction of the lone electron pair that resides on the C-terminus of CO with the metal. This donation results in a large negative charge on the metal atom, giving rise to a backdonation from the metal to CO. This backdonation involves electrons from the d-orbitals of the metal, which are transferred to the antibonding π -orbitals of CO. Later, the term 'Blyholder model' was used in a more general sense for models where only the frontier orbitals of CO, i.e. the HOMO and the LUMO, are involved in the bonding with the metal.[33] According to this HOMO-LUMO model, CO chemisorption is the interaction of the 5σ orbital (HOMO) and 2π orbital (LUMO) with the *d*-orbitals of the metal. This interaction consists of CO donating electrons from the 5σ orbital to the metal *d*band, called σ -donation, and the metal *d*-band donating electrons into 2π , referred to as π -backdonation. Within the HOMO-LUMO model, both σ -donation and π -backdonation strengthen the metal-CO bond and weaken the C-O internal bond.

With advances in both computational resources as well as improved electronic structure models, several contributions were made to further refine upon the Blyholder model. Bagus *et al.*[34,35] performed self-consistent-field (SCF) calculations for CO adsorbed on Na, Mg and Al surfaces. They found that the electron donation from the 5σ orbital to the *d*-band is in fact very little, and that the 5σ orbital is slightly antibonding for the metal-CO bond. This is because the metal σ -electrons move away from CO to reduce the Pauli repulsion with the electron donation from the 5σ orbital. They state that the metal-CO bond mainly consists of electron donation from the metal into the 2π orbital.

Föhlisch, Pettersson, Nilsson *et al.*[36,37] performed X-ray emission spectroscopy (XES) measurements in conjunction with density functional theory

(DFT) calculations to understand CO bonding patterns on Cu and Ni surfaces. They found that after rehybridization of the 4σ and 5σ orbitals of CO with the d_{σ} orbitals of the metal, a σ -interaction exists that is repulsive for the metal-CO bond. This σ -interaction however strengthens the internal C-O bond. As a counteracting effect, the 1π and 2π orbitals mix with the d_{π} orbitals of the metal and this π -interaction results in a weakening of the internal C-O bond and a strengthening of the metal-CO bond. The net result of these two counteracting effects determines the adsorption strength of CO and its activation. More recent DFT studies on CO adsorption on Ni and Cu surfaces are executed by Gameel et al.[38,39] In their contributions, they unravel the role of the active site configuration and study the frontier molecular orbitals and charge redistribution. They suggest that the σ -interaction is indeed repulsive for Ni-CO. but partially repulsive and partially attractive for the Cu-CO bond. Furthermore, they found that C-O bond activation does not depend on the adsorption strength of CO, but is strongly correlated with the coordination number of the metalcarbon interaction.

The previously mentioned studies focus primarily on one-, two-, three- and fourfold adsorbed CO, yet it has been shown that five- and sixfold adsorbed CO give rise to far lower CO dissociation barriers.[24] Because both the carbon and the oxygen bind to the surface, orbital overlap is enhanced, potentially allowing for an increased electron transfer between CO and the metal. In a previous work, we have shown by alloying Rh with Fe that increased electron transfer can result in a lower dissociation barrier. The lower electronegativity of Fe gives rise to enhanced charge transfer from the metal to CO, resulting in increased occupation of antibonding orbitals, leading to a reduced CO dissociation barrier in comparison to a pure Rh surface[40].

In this contribution, we expand upon the previously constructed models for CO adsorption and bond activation by considering active site configurations that allow for five- and sixfold adsorbed CO. We studied electron redistribution and orbital hybridization by means of detailed density of states, crystal orbital Hamilton population and DDEC6 charge analyses. The role of the σ - and π -systems in the bond (de)stabilization is explored and rationalized. We revisit the conclusions of the Blyholder model and place our observations into perspective with previous models developed in the open literature. The interpretation of the topology and local chemical environment of the active site towards modulating the dissociation barrier by the rearrangement of the molecular orbitals is crucial for the rational design of novel catalyst formulations.

3.2 Methods

3.2.1 DFT

Plane-wave density functional theory calculations were performed using the Vienna Ab Initio Simulation Package (VASP)[41,42] that employs the projectoraugmented wave (PAW) method to describe the core electrons.[43,44] The Perdew-Burke-Ernzerhof (PBE) functional[45] is used to describe electron exchange and correlation. PBE and its revised version by Hammer et al.[46] (RPBE) were both considered. Note that no Van der Waals corrections were applied as after thorough testing we found that the calculations with and without Van der Waals correction vielded similar results due to cancellation effects. An elaborate discussion can be found in Section A.1. Solutions to the Kohn-Sham equations were calculated using a plane wave basis set with a cut-off of 400 eV. For all calculations, spin polarization was included. The initial guess for the magnetic moment of each atom was set to 3.0 for the Co bulk, the Co slab, and the TiO₂-supported Co models to ensure the systems converge to the magnetic ground state. For the Al₂O₃-supported Co models, the initial guess for the magnetic moment of each atom was set to 1.0, since for these systems this value was sufficient for convergence to the magnetic ground state. We used the first order Methfessel-Paxton method to apply smearing to the electrons, with a smearing width of 0.2 eV. Exception to this is the simulation of CO in gas phase, for which we used Gaussian smearing with a smearing width of 5×10^{-4} eV. A discussion about the type of smearing and the smearing width can be found in Section A.2. The Co FCC and HCP bulk phases were computed in unit cells of 3.51 \times 3.51 \times 3.51 Å³ and 2.49 \times 2.49 \times 4.02 Å³, respectively. For both bulk cells, kpoint convergence was reached with a mesh of $11 \times 11 \times 11 k$ -points (criterion of 1 meV/atom). For the extended surfaces, a k-point mesh of $5 \times 5 \times 1$ is used to sample the Brillouin zone. The dimensions of the surface cells are 10.54 × 10.54 × 21.27 Å³ for Co(100), 9.94 × 10.54 × 22.21 Å³ for Co(110), 9.96 × 9.96 × 22.02 Å³ for Co(0001), and 8.64 × 9.47 × 21.55 Å³ for Co(11 $\overline{2}$ 1). For the supported nanoclusters and -rods, a *k*-point mesh of $1 \times 1 \times 1$, i.e. only the Γ -point, is used. The dimensions of these cells are $16.14 \times 16.79 \times 25.00$ Å³ for the Co₅₅/Al₂O₃ nanocluster and for the Co_{84}/Al_2O_3 nanorod, and 17.74 × 19.55 × 26.49 Å³ for the Co_{54}/TiO_2 nanocluster and for the Co_{81}/TiO_2 nanorod. We optimized the stable states and the transition states using an ionic convergence criterion of 1×10^{-4} eV and an electronic convergence criterion of 1×10^{-5} eV. It was verified that all residual forces are less than 0.05 eV/Å for the adsorbate atoms in each cartesian direction. All energies are corrected for the vibrational zero-point energy (ZPE).

We obtained bulk Co-Co distances of 2.48 Å and 2.26 Å for FCC and HCP, respectively. These values are in good agreement with the reported experimental values of 2.51 Å[47] and 2.29 Å for cobalt FCC and HCP, respectively.[48] For a discussion on the performance of PBE on the cohesive energy of FCC and HCP Co, see Section A.3. We searched for transition states with the nudged elastic band (NEB) method as implemented in VASP. We verified that the optimized transition states show one imaginary frequency in the direction of the reaction coordinate. For the optimized stable states, we verified that the frequencies are non-imaginary.

3.2.2 Models

We placed Co(0001) (HCP), Co(11 $\overline{2}1$) (HCP), Co(100) (FCC), and Co(110) (FCC) slabs at the center of the supercell. A vacuum slab of at least 15 Å was added to avoid spurious interactions between the adsorbates. The Co(0001) and Co(100) models consist of four layers, the Co(11 $\overline{2}1$) and Co(110) models consist of six layers. None of the layers in the slabs are frozen.

The supported nanoclusters and -rods were created as follows. As supports for the nanoclusters and nanorods we used γ -Al₂O₃(110) and rutile-TiO₂(110) surfaces because these are reported to be thermodynamically the most stable.[8,49] Four layers of the support material were placed in a supercell, the bottom two layers were frozen. After adding the nanocluster or nanorod, we enlarged the vacuum space above the slab to accommodate adsorbates leaving a distance of at least 12 Å between neighboring supercells. The Co_{55}/Al_2O_3 nanocluster model is based on the Ni₅₅ cluster on the γ -Al₂O₃(110) surface of Silaghi, Comas-Vives and Copéret[50], where the Ni was replaced by Co. Starting from the hemispherical cobalt cluster of the Co_{55}/Al_2O_3 model, three cobalt atoms were removed to create a pocket site with a B_5 motif for the Co_{52}/Al_2O_3 model. The Co_{54}/TiO_2 model was based on the latter but with two additional cobalt atoms at the base of the nanocluster to make it adhere to the TiO_2 support. The continuous nanorods were built by starting with bare supports and adding one layer of cobalt atoms at the time, allowing the atoms to relax in between. On both Co_{84}/Al_2O_3 and Co_{81}/TiO_2 nanorods, B₅-like sites close to the metal-support interface were created by adding an extra layer of cobalt atoms on top of the existing nanorod. By covering the nanorod only partially with the extra layer, several stepped sites emerged. The stability of the nanoclusters and nanorods was assessed by calculating the energy corresponding to one Co atom detaching from the nanocluster and migrating to the Al₂O₃ or TiO₂ support.[51] A detailed discussion on the stability of the models can be found in Section A.4. Due to the

use of sufficiently large vacuum slabs, no dipole corrections were applied. A vacuum slab is confirmed to be sufficiently large when the charge density between the neighboring cells decreases to below $1 \times 10^{-5} e/Å^3$. Furthermore, we verified that adding a dipole correction indeed did not change the results. These tests are shown in Section A.5.

3.2.3 DOS, COHP, and DDEC6 charges

We performed single-point calculations of the optimized pristine and initial states with VASP. The LOBSTER software [52–56] was used to perform crystal orbital Hamilton population (COHP) and density of states (DOS) analyses. The number of bands in VASP and the number of local basis functions in LOBSTER were both set to the sum of the valence orbitals of all atoms present in the system. We used the pbeVaspFit2015 basis set[55,57,58] with the basis functions [2s, 2p] for C and O, [3s, 3p] for Al, and [4s, 3p, 3d] for Ti and Co. For the DOS calculations, the basis functions were rotated in such way that the x-axis is parallel to the C-O internal bond (using the "autorotate" keyword). For the COHP calculations, this was done for each atom-atom pair interaction to always align the bond axis with the global *x*-axis of the basis functions. We computed the COHP in an orbitalwise fashion. The absolute charge spilling was below 4.0% (average of the two spin channels) for all calculations. This means that at least 96% of the occupied wave function was projected onto the local basis functions. The absolute charge spilling could not be lowered by employment of more basis functions. The Chargemol program version 3.5 was used to calculate the DDEC6 atomic charges.[59,60]

3.2.4 Research data

Relevant input and output files for all calculations, necessary for facile reproduction of the results, are shared via a Zenodo repository.[61] This repository also includes the set of Python scripts that have been used to parse the output files and to produce the graphs.

3.3 Results and discussion

3.3.1 Models

To unravel the electronic structure of CO bonding and activation on Co sites, a diverse set of model systems was studied including flat and stepped extended surfaces as well as nanoparticles and -rods supported on Al_2O_3 and TiO_2 . The set of model systems exposes a variety of active sites configurations, including planar threefold and fourfold configurations, which give rise to one-, two-, three-
and fourfold CO adsorption, as well as B₅ type step-edges, which can facilitate five- and sixfold CO adsorption. To investigate the influence of a metal-support interface, the supports TiO_2 and Al_2O_3 are chosen to include both a reducible and a non-reducible metal oxide, respectively. In Figure 3.1, an overview is given of the twelve models, showing CO adsorbed in its predissociation state. Although some of our models provide top or bridge sites at which CO can easily adsorb, we discard top and bridge sites when studying CO dissociation. This is because CO would migrate from a top or bridge site to a three- or fourfold site prior to the dissociation of the C-O bond in order to provide a stable transition state. It also offers a more stable final state for the C atom, since we have found that on the Co nanorods and nanoparticles, C prefers a three- or fourfold coordination with Co over a top or bridge site. On the Co(0001) surface, the preferred adsorption site of carbon is a threefold site [76], on Co(1121) a fourfold site. [77] We also initiated CO adsorption configurations different from the configurations shown in Figure 3.1, such as side-on adsorption on three- and fourfold sites, and O-end adsorption, but none of these attempts resulted in stable states.

In Figure 3.1a-f, the six extended surface models are shown. Figure 3.1a displays the corrugated Co($11\overline{2}1$) surface where CO adsorption occurs in a threefold mode within a B₅ site. Figure 3.1b and c depict FCC and HCP sites on the closely packed Co(0001) surface, respectively. Figure 3.1d and e show the (quasi)fourfold adsorption modes of CO on the open Co(110) and Co(100) surfaces, respectively. Lastly, Figure 3.1f pertains to a Co($11\overline{2}1$) surface and displays a sixfold adsorption. Herein, C is fourfold coordinated to Co and O interacts with the two Co atoms at the upper edge of the B₅ site. While the active site configurations on the extended surfaces as shown in Figure 3.1a-f have been thoroughly studied in the past, we reiterate these calculations to establish a benchmark for comparing results obtained for the supported nanoclusters and - rods. A comparative analysis of our findings and the CO dissociation barriers that are previously reported for these sites is presented in Table A.9.



Figure 3.1: Geometry of the active site in the initial state of CO dissociation. NC and NR refer to nanocluster and nanorod, respectively. Activation energies for direct CO dissociation are reported including ZPE correction.

The supported nanoclusters and -rods allow us to investigate active sites close to the metal-support interface. Herein, we vary the type of active site, its distance to the support interface as well as the type of the support. The nanoclusters are approximately 1 nm in diameter at the base. Both nanorods are continuous in one direction and represent the interfacial perimeter of larger nanoparticles. Figure 3.1g-i shows the Al_2O_3 -supported nanoclusters. In Figure 3.1g and h, CO is adsorbed in a threefold configuration either at the top of the nanoparticle, which is relatively far away from the interfacial perimeter (Figure 3.1g), or at a threefold site bordering the support (Figure 3.1h). The cobalt atoms of the threefold sites in Figure 3.1g,h have a lower coordination number than in Figure 3.1a-c. Figure 3.1i-l show B₅-like sites, similar to the B₅ site in Figure 3.1f. Figure 3.1i and j are B₅-like sites on an Al_2O_3 -supported nanocluster and nanorod, respectively. Figure 3.1k and l are B₅-like sites on a TiO₂-supported nanocluster and nanorod, respectively.

3.3.2 CO dissociation pathways and energetics

Here, we discuss the mode of CO adsorption, the CO dissociation pathway, and the corresponding reaction energetics for the twelve model systems as shown in Figure 3.1. The values reported are based on the PBE exchange-correlation functional. We compared these results with the RPBE exchange-correlation functional as shown in Section A.6 and we did not find any significant differences for the barriers. The reaction energetics and the coordination numbers are provided in Table 3.1. The geometries of the transition and final states are shown in Figure A.9 and A.10, respectively. We discuss the geometry of CO dissociation on the twelve active sites elaborately in Section A.7. Below we discuss the two reaction steps on the Co($11\overline{2}1$) surface, since we discuss the DOS and COHP of these steps in more detail in Section 3.3.4.

In Figure 3.1a, CO adsorbs on a threefold site as exposed on the Co($11\overline{2}1$) surface. The adsorption energy is -166 kJ/mol. In the transition state, the oxygen moiety migrates to a neighboring active site and is bonded to the surface in a quasi-threefold configuration. The carbon atom remains in the threefold site. In the transition state, C and O share two Co atoms. In the final state, the oxygen atom continues to migrate away from the carbon atom and adsorbs at an adjacent threefold site. Only a single Co atom is shared between C and O. This elementary reaction step has an activation energy of 242 kJ/mol and is endothermic by 112 kJ/mol.

Table 3.1: CO adsorption energies (ΔE_{ads}), forward ($\Delta E_{act,for}$) and backward ($\Delta E_{act,back}$) energies for CO dissociation, and CO coordination in the initial state (IS) and transition state (TS) on the twelve Co sites. NC and NR refer to nanocluster and nanorod, respectively. Activation energies for direct CO dissociation are reported including ZPE correction.

Model	ΔE_{ads}	$\Delta E_{act,for}$	$\Delta E_{act,back}$	Coordination	Coordination
	[kJ/mol]	[kJ/mol]	[kJ/mol]	in IS	in TS
Co(1121)	-166	242	130	C: 3; 0: -	C: 3; 0: 3
3f					
Co(0001)	-158	229	110	C: 3; 0: -	C: 3; 0: 2
FCC					
Co(0001)	-160	222	135	C: 3; 0: -	C: 3; 0: 2
НСР					
Co(110)	-135	116	105	C: 4; 0: -	C: 4; 0: 2
Co(100)	-175	125	168	C: 4; 0: -	C: 4; 0: 2
Co(1121)	-163	82	101	C: 4; 0: 2	C: 4; 0: 2
B ₅					
Co_{55}/Al_2O_3	-169	201	165	C: 3; 0: -	C: 3; 0: 3
NC top					
Co_{55}/Al_2O_3	-180	206	155	C: 3; 0: -	C: 3; 0: 2
NC					
interface					
Co_{52}/Al_2O_3	-152	75	80	C: 4; 0: 2	C: 4; 0: 2
NC					
Co_{84}/Al_2O_3	-156	121	138	C: 4; 0: 1	C: 4; 0: 2
NR					
Co_{54}/TiO_2	-158	78	96	C: 4; 0: 2	C: 4; 0: 2
NC					
Co_{81}/TiO_2	-152	100	111	C: 4; 0: 1	C: 4; 0: 3
NR					

Figure 3.1f displays the Co($11\overline{2}1$) surface, which possesses a B₅ site that accommodates a sixfold adsorption of CO, with carbon and oxygen atoms bonding to the metal in a fourfold and twofold configuration, respectively. Notably, carbon and oxygen atoms do not share any cobalt atoms in this initial state, and the adsorption energy is -163 kJ/mol. The transition state exhibits an elongated C-O bond due to the movement of O away from C while C remains stationary, with an activation energy of 82 kJ/mol. Subsequently, oxygen moves further between two cobalt atoms to bond with a third cobalt atom in the final

state, where C and O atoms continue to not share any cobalt atoms. This CO dissociation process is slightly exothermic, with an energy release of 19 kJ/mol.

3.3.3 Approximating orbital overlap between CO and Co

The adsorption mode of CO and the proximity of CO to the Co atoms is correlated with the extent of orbital overlap. To understand how these factors affect the CO dissociation barrier, three metrics are introduced whose correlation with the dissociation barrier are studied. These three metrics are considered because they are based solely on the positions of the atoms in the initial state, and not (directly) on the electron density. Other metrics that could have been considered are the Co *d*-band height, the Co *d*-band width, and the charge on the CO adsorbate. More complex and potentially better performing metrics could be found when considering the electron density of the metal surface site or of the adsorbate. However, evaluation of these metrics requires more input data and are thus not as facile and swift as metrics based on the atomic positions only. The three metrics considered correspond to the number of Co atoms the CO species is bonded to (CO coordination number), the distance between the C,O and Co atoms, and the amount of overlap of probe electron density functions placed on CO and Co.

To examine the coordination number dependency of the dissociation barriers, in Figure 3.2 the CO dissociation barriers for the various active sites are shown. The active sites are ordered from high to low dissociation barrier and they are color-coded by the CO coordination number in the predissociation state. We consider two atoms to be bonded when the distance between them is less than 2.0 Å. From Figure 3.2, it is clear that a higher coordination of CO in the predissociation state coincides with a lower energy barrier for CO dissociation. This result is in line with Hammond's postulate, which states that when the molecular structures of the predissociation state and the transition state resemble each other, the energies of these states will resemble each other as well.[62] For five- and sixfold coordinated sites, O is already attached to Co. For these sites, the predissociation state of CO resembles the transition state more than for the three- and fourfold coordinated sites, resulting in a lower reaction barrier.

Although the use of coordination numbers is an established procedure to describe chemical bonding[63], another approach was also considered. Rather than a predetermined cut-off radius that determines the coordination number, we considered the distance metric μ_1 , a sum of modified interatomic distances d_{ij} between the atoms as given by

$$\mu_1 = \sum_{i \in Co, j \in C, 0} d_{ij}^{-\alpha} \tag{1}$$

wherein *i,j* loops over all the Co-C and Co-O distances and α (non-negative) is a power. Alternatively, we considered the overlap metric μ_2 , where we placed exponentially decaying functions on the Co, C and O atoms and determined the overlap between these functions as given by

$$\mu_2 = \sum_{i \in \text{Co}, j \in \text{C}, \text{O}} \langle \phi_i | \phi_j \rangle \tag{2}$$

with $\phi(r) = \exp(-\alpha \cdot r)$ or $\phi(r) = \exp(-\alpha \cdot r^2)$, wherein $\phi_i(r), \phi_j(r)$ are functions centered at Co, C, or O. To find the best correlations, we optimized the fitting parameters α for μ_1 and μ_2 . More details on the procedure can be found in Section A.8.



Figure 3.2: CO dissociation barriers ordered from high to low barrier, colored by the coordination of CO in the predissociation state.

Among all options considered, the best metric for the CO dissociation barrier corresponds to an overlap function μ_2 (Equation 2) wherein $\phi(r) = \exp(-\alpha \cdot r^2)$. This probe function mimics the electron density exponentially decaying with increasing distance to the atom. The correlation between overlap and CO dissociation barrier is shown in Figure 3.3. The other correlations are shown in

Figure A.11. The Pearson correlation coefficient for the optimized correlation in Figure 3.3 is -0.96 and its coefficient of determination R^2 is 0.92. This exponential function shows a better correlation with CO dissociation barrier than the coordination number, even though it is also only based on the distance between the C, O and Co atoms. This shows that the activation of CO highly depends on the distance between CO and the metal. The rationale is that the electron transfer between CO and the metal depends on the electron density overlap, which in turn depends on the distance. The degree of electron transfer determines the activation of the C-O bond.



Figure 3.3: Correlation between CO dissociation barrier and the electron density overlap between CO and Co in the predissociation state. The overlap is computed as $\mu_2 = \sum_{i \in Co, j \in C, o} \langle \phi_i | \phi_j \rangle$ where the electron density ϕ is modelled as Gaussian $\phi(r) = \exp(-\alpha \cdot r^2)$ with $\alpha = 0.97$ for C, O, and $\alpha = 0.75$ for Co. The Pearson correlation coefficient is -0.96.

3.3.4 Electronic structure analysis of CO molecular orbitals

To understand in more detail the mechanism of the bonding of CO to a cobalt site and its subsequent activation, an extensive electronic structure analysis using a *lm*-decomposed projected DOS (*lm*-pDOS) analysis, DDEC6 charge analysis and COHP analysis is conducted. We will first present this analysis for two cases: the threefold and sixfold adsorption sites as exposed on the Co(1121) surface. These two situations have been chosen as they represent sufficiently distinct adsorption configurations and show a large difference in the CO dissociation barrier (242 kJ/mol and 82 kJ/mol, respectively). Thereafter, we generalize our observations for all model systems to establish correlations with the activation energy for CO dissociation.

3.3.4.1 Density of States

In Figure 3.4, the DOS for CO adsorbed in the threefold (Figure 3.4b) and sixfold (Figure 3.4c) adsorption sites are shown. As a reference, in Figure 3.4a the DOS of CO in the gas phase is included. All figures use the same reference energy, i.e. the zero of energy corresponding to the Fermi level of CO in the gas phase such that the peak positions can be readily compared. The molecular orbitals (MOs) are labelled based on their canonical names.[64] In Figure 3.4a-c, the features are marked by horizontal black lines on opposite sides and the area under the DOS curve is integrated to obtain the number of states per feature. In Figure 3.4d-f, the outcomes obtained from Figure 3.4a-c are combined to generate separate DOS profiles for the σ -network, encompassing the 3σ , 4σ , and 5σ molecular orbitals, and the π -network, consisting of the 1π and 2π molecular orbitals. The sum of the number of electrons in the σ - and π -network corresponds to the integrated DOS (IDOS).

From Figure 3.4a-c, we observe that upon adsorption the number of electrons associated with CO increases from 10.0 (valence) electrons in the gas phase to 10.69 and 11.08 (valence) electrons for the threefold and sixfold adsorbed configurations, respectively. The increase in electron density according to the DOS analysis is in good agreement with the charge of adsorbed CO according to the DDEC6 analysis, as shown in Figure A.12. The number of electrons associated with adsorbed CO correlates well with the CO dissociation barrier, as shown in Figure A.13. The 3σ and 4σ orbitals remain narrow upon adsorption in line with their confined and localized nature due to their seemingly limited interaction with the metal *d*-band. Consequently, the corresponding peaks display only subtle deviations from the gas phase situation. The 3σ peak undergoes an upward energy shift compared to the gas phase, indicative of increased electronelectron repulsion stemming from closer proximity to the surface. Similarly, the 1π peak also undergoes an upward shift. In contrast, the 4σ , 5σ , and 2π peaks display a downward energy shift upon adsorption. This downward shift of the 2π orbital facilitates its partial filling, as it now resides below the Fermi level. Consequently, the adsorption-induced shift in the 2π orbital leads to its altered occupancy. Distinct from the behavior of the 3σ and 4σ orbitals, the 1π , 5σ , and formerly unoccupied 2π orbitals exhibit significant mixing with the Co *d*-states, resulting in peak broadening. The profoundness of this mixing is especially visible for the 1π and 5σ orbitals whose states overlap in terms of energy.



Figure 3.4: *lm*-pDOS analysis of CO gas phase (a,d), CO adsorbed on Co(11 $\overline{2}$ 1) threefold site (b,e), and CO adsorbed on Co(11 $\overline{2}$ 1) B₅ (c,f). Subfigures a-c show the total and integrated DOS for CO, whereas subfigures d-f show the σ - and π -contributions. All plots use the same reference energy, corresponding to the Fermi level of CO in the gas phase. The IDOS at Fermi level is shown above the black line at zero energy (a-c), or near the red and blue dots (d-f). The values next to the peaks pertain to the area under the curves. The dashed lines show the integrated σ - and π -contributions (I σ and I π).

Differentiating between these two states is however possible by segregation of the σ - and π -contributions. As shown in Figure 3.4d-f, through the utilization of the *lm*-pDOS, we can attribute all 2s and 2p_x contributions to σ -bonding and thus the 5 σ orbital, while the 2p_y and 2p_z contributions correspond to π -bonding and thus the 1 π orbitals. From the same figures it can be readily observed that upon adsorption, the σ -system loses electrons with respect to the gas phase whereas the π -system gains electrons. In the case of threefold adsorption, the π -system is comparatively lower than in the case of sixfold adsorption.

The previous analysis is executed for all twelve model systems and the results are collected in Figure 3.5. Based on the analysis presented in this figure, it becomes evident that the process of CO adsorption from the gas phase has a negligible impact on the number of electrons in the 3σ orbital, regardless of the specific adsorption mode or site under consideration. Regarding the 4σ and 5σ orbitals, it is observed that for each roughly half an electron is transferred from CO to the metal, irrespective of the adsorption mode.

In contrast, the behavior of the 1π and 2π orbitals regarding electron migration is contingent upon the topological characteristics of the active site. Specifically, the 1π orbitals exhibit an initial occupancy of 4.0 electrons in the gas phase, which, upon adsorption, results in a donation of approximately 0.6 to 1.0 electron from CO to the metal. Similarly, the unoccupied 2π orbitals in the gas phase acquire approximately 1.6 to 2.5 electrons following adsorption.

The shifts in electron density within the 1π and 2π orbitals demonstrate a strong correlation with the dissociation barriers, as evidenced by Pearson correlation coefficients of 0.949 and -0.947, respectively. Conversely, the correlation between electron density in the 3σ , 4σ and 5σ states and the dissociation barrier appears to be comparatively weaker, exhibiting Pearson correlation coefficients of -0.112, -0.567, and 0.819, respectively.

Hence, the quantification of electron loss from the 1π orbital of CO and the corresponding electron gain in the 2π orbital emerges as a highly informative parameter to characterize the C-O dissociation barrier and, consequently, the extent of C-O activation. Remarkably, a substantial alteration in electron density within CO's π -bond accompanies CO activation, exhibiting a strong correlation. In contrast, a comparatively minor shift in electron density, less significantly correlated, is observed during CO activation within the σ -bond.

It is noteworthy that although the Pearson correlation coefficients and integrated DOS or COHP values are both quantitative measurements, combining the two to assess which MO modulation is most influential remains qualitative in nature as the two individual measurements cannot be combined into a single meaningful quantitative model predicting dissociation barriers.



Figure 3.5: Molecular orbital DOS integrals for the various adsorption configurations of CO (upper left plot) and their corresponding reaction barriers (upper right plot). Pearson correlation coefficients for the correlation between the DOS integrals and the reaction barriers (lower plot).

3.3.4.2 COHP

The rearrangement of the electron density among the orbitals leads to a destabilization of the C-O bond. The COHP method is an effective procedure to quantitatively assess this destabilization. By projection of the Kohn-Sham states onto local atomic orbitals, the interaction strength between any two atoms can be probed. The COHP analysis for gaseous and adsorbed CO on the Co(11 $\overline{2}$ 1) 3f and B₅ sites is visualized in Figure 3.6a-c. Akin to the procedure shown in Figure 3.4d-f, in Figure 3.6d-f the COHP is split into σ - and π -contributions to distinguish between these networks.



Figure 3.6: COHP as function of the energy of the Kohn-Sham states of CO in the gas phase (a,d), CO adsorbed on Co($11\overline{2}1$) threefold site (b,e), and CO adsorbed on Co($11\overline{2}1$) B₅ (c,f). Subfigures a-c show the total and integrated COHP for CO, whereas subfigures d-f show the σ - and π -contributions. All plots use the same reference energy, corresponding to the Fermi level of CO in the gas phase. The ICOHP at Fermi level is shown above the black line at zero energy (a-c), or near the red and blue dots (d-f). The values next to the peaks pertain to the area under the curves. The dashed lines show the integrated σ - and π -contributions (I σ and I π).

In Figure 3.6a, we observe that for CO in gas phase, the 3σ , 4σ , and 1π orbitals are bonding for the molecule, whereas the 5σ and unoccupied 2π orbitals are

antibonding. For adsorbed CO in Figure 3.6b and c, it appears the orbitals largely retain their bonding or antibonding character. While the DOS analysis indicates a minimal impact of the surface topology on the occupancy of the 3σ state. Figure 3.6 reveals a more pronounced influence on its corresponding integrated COHP (ICOHP) value. Despite the 3 σ state exhibiting limited interference with the Co *d*band preventing orbital mixing, the enhanced electron-electron repulsion arising from its closer proximity to the *d*-electrons leads to an electron redistribution such that the bonding character is severely diminished. Opposite to 3σ , the 4σ orbital increases in bonding character for C-O upon adsorption. This increase is small and rather constant for all adsorptions and moreover shows no correlation with the activation energy for C-O bond scission. Although the 4σ MO has a minor contribution to the C-O bond strength, it plays a large and consistent role in binding CO to the Co site. From Figure A.14 and A.15, which show the COHP of the Co-CO bond, it can be seen that the 4σ MO contributes between approximately 25% to 35% to the total Co-CO bonding. Figure A.16 shows a very small spread for the 4σ orbital, thus this bonding contribution is constant for all adsorptions and thus independent of the adsorption mode.

Upon CO adsorption, the bonding character of the 1π orbital clearly decreases with respect to the value found for gas phase CO. The 5σ orbital, which is slightly antibonding in the gas phase, remains slightly antibonding for the 3f adsorption site. For the B₅ adsorption site however, no σ -states are to be found in the vicinity of E = -5 eV. As already eluded upon in the DOS analysis, the strong mixing of the 5σ and 1π orbitals with the *d*-states of Co results in the formation of a set of new states with σ - and π -character. The availability of coordinatively unsaturated Co atoms in the B₅ adsorption site leads to the formation of new stable states with σ -character that in contrast to the gas phase lie lower in energy as compared to the states with π -character. As a result, these states have a slight bonding character. Finally, the unoccupied 2π molecular orbitals in the gas phase descend below the Fermi level upon CO adsorption and thus become occupied. These states are antibonding irrespective of the adsorption site, though for the B₅ site more electrons occupy these states and hence these states exhibit a higher (more antibonding) COHP character.

Again, we can generalize these results for all the systems that were studied. The collective data for all systems is visualized in Figure 3.7. We already established that the 3σ molecular orbital does not readily mix with *d*-states due to its compactness, though it increases in energy with respect to the Fermi level upon adsorption. This increase in energy is caused by electron-electron repulsion

which is more pronounced the shorter the distance between C,O and the Co atoms (see also Figure 3.3). The COHP coefficients for the 3σ orbital clearly show this trend wherein a higher COHP value (less bonding) value is found as function of decreasing C-O scission barrier. A Pearson correlation coefficient of -0.760 confirms this inverse trend, though this correlation should not be interpreted as that the 3σ plays an important role in the bonding and activation of CO. It is rather that the COHP character of this molecular orbital serves as a proxy to characterize the proximity of CO with the metal surface. The 4σ orbital, whose electron distribution is somewhat more diffuse as compared to the 3σ orbital, is less affected by the decrease in the distance between CO and the metal atoms. Consequently, we observe that its COHP character only marginally varies with changes in the site topology as shown by a relatively poor Pearson correlation coefficient of 0.562. Stronger correlations are found for the 5σ and 1π orbitals as indicated by their Pearson correlation coefficients of 0.862 and -0.914, respectively. These molecular orbitals strongly interact with the Co *d*-band. This interaction has a profound effect on their (anti)bonding character. For the 5σ molecular orbitals, it is observed that its COHP values decrease, i.e. that the MO becomes more bonding, with decreasing reaction barrier. Conversely, for the 1π orbital it is seen that its COHP value increases, thus becoming less bonding with decreasing reaction barrier. The variations in the character of the COHP for the 1π and 2π orbitals can be rationalized based on the electron occupancy assigned to these states. Considering the presence of a nodal plane along the bonding axis, the 1π atomic orbitals inherently possess a bonding character. The reduction in the integrated COHP pertaining to these states merely reflects their diminished occupancy, as depicted in Figure 3.5. A parallel rationale applies to the 2π states, which exhibit not only a nodal plane along the bonding axis but also a perpendicular plane intersecting the C-O bond. Consequently, these states inherently manifest an antibonding character. When more electrons are donated into these states, simultaneously the overall integrated COHP increases and the reaction barrier decreases.

For the 5σ orbital, a change from antibonding to bonding is observed upon a decrease of the reaction barrier indicating that the bonding character of the 5σ orbital shows an opposite trend with respect to the overall strength of the bond. To understand this behavior, we need to consider the electron density associated with 5σ bond, which is hindered by the fact that the 5σ and 1π states overlap in energy. In Figure 3.8, contour plots of the electron density corresponding to the region of interest for the Co(11 $\overline{2}1$) 3f and Co(11 $\overline{2}1$) B₅ systems are shown. For reference, also the contour plots for the 5σ and 1π molecular orbitals in gaseous

CO are shown. The energy intervals used to construct these contour plots are indicated by the hashed rectangles in the DOS graph in the center of the figure. These energy intervals have been chosen such that they allow for a qualitative analysis.



Figure 3.7: Molecular orbital COHP integrals for the various adsorption configurations of CO (five upper left plots) and their corresponding reaction barriers (upper right plot). Pearson correlation coefficients for the correlation between the COHP integrals and the reaction barriers (lower left plot). Pearson correlation coefficients for correlations between the COHP integrals (lower right plot).

We can readily observe that the contour plots of the 5σ states and 1π regions for Co(11 $\overline{2}$ 1) 3f show a striking similarity. Upon adsorption, the electron density in the 5σ MO shifts from its predominant presence around the carbon atom to the oxygen atom. This shift alleviates the unfavorable electron-electron repulsion with the electron density on the cobalt surface. Despite this redistribution of electron density, we can observe the preservation of two nodal planes perpendicular to the bonding axis upon adsorption. Consequently, this preservation results in a minor antibonding molecular orbital, akin to the situation in the gas phase, consistent with the COHP values. Similarly, the nodal characteristics of the 1π molecular orbital remain intact after adsorption, leading to an overall bonding character.

The analysis of the Co(11 $\overline{2}$ 1) B₅ system is more intricate due to the overlapping nature of the 5 σ and 1 π states. In the region where these states overlap, the

electron density reveals a slight decrease in electron density close to the C atom and similar to the Co(11 $\overline{2}$ 1) 3f system a migration of electron density to the O atom. Our interpretation of the situation is that when compared to the Co(11 $\overline{2}$ 1) 3f system, the 5 σ states exhibit a reduced antibonding character, primarily attributed to the disappearance of the two nodal planes perpendicular to the bonding axis.



Figure 3.8: Electron density plots corresponding to characteristic energy regions of the DOS for the Co(11 $\overline{2}$ 1) 3f system (center two contour plots) and Co(11 $\overline{2}$ 1) B₅ system (rightmost two contour plots). In the DOS graph, red shows the σ - and blue shows the π -contribution. For comparison purposes, the electron density associated with the 5 σ and 1 π molecular orbitals for gaseous CO are shown as well (leftmost two contour plots). The characteristic energy regions are shown by the hatched rectangles in the DOS graph. On opposite sides of the DOS graph a schematic depiction is provided how the contour plane is oriented with respect to the unit cell.

Given the similar features observed in the DOS for both the σ - and π -systems in this region of interest, we infer that the electron density as shown in the contour plot is also characteristic for the 1π states. For the 1π molecular orbital in the gas phase as well as the 1π states for the $Co(11\overline{2}1)$ 3f system we observe that the electron density is almost symmetrically distributed around the C-O bonding axis, resulting in a favorable interaction as evidenced by the negative COHP values. In contrast, due to the close proximity of the CO molecule with respect to the catalytic surface for the $Co(11\overline{2}1)$ B₅ system, the electron density is redistributed to mitigate unfavorable electron-electron repulsion. Consequently,

the electron density resides predominantly at the opposite side of the C-O bond with respect to the surface. This rather asymmetrical electron density distribution is less favorable for the C-O bonding and thus an increase in the COHP value (i.e. more antibonding) is observed for the 1π states in the Co($11\overline{2}1$) B₅ system as compared to the Co($11\overline{2}1$) 3f system or the gas phase.

Based on the results discussed, we are now able to perform a qualitative assessment of which changes in shape and occupation of the canonical molecular orbitals have the largest influence on the dissociation barrier. Note that for this assessment, we cannot solely rely on using the Pearson correlation coefficients as these only measure the extent of linear correlation between the samples and not the relative impacts of the different orbitals on the CO dissociation barrier (i.e. the slopes). The slope of the linear relationship can be readily assessed by considering the absolute changes in the iCOHP values. Here we find that the largest changes in iCOHP for the MOs that show a negative correlation with the reaction barrier are ranked as $3\sigma > 1\pi > 2\pi$. Since the changes for 3σ show a somewhat weaker correlation with the barriers than 1π (Pearson correlation coefficient of 3σ is 0.760), we conclude that changes to the 1π orbital (Pearson correlation barrier, closely followed by changes in 3σ and to a lesser extent by the occupation of the 2π MO.

3.3.5 Comparison with literature models

The original paper from Blyholder[28] primarily focusses on π -backdonation from the metal to CO, resulting in a weakening of the C-O bond. Similar to these results, we find a net transfer of electron density from the metal to CO. The formerly empty 2π -orbitals receive electron density from Co. In contrast to that, the 1π orbitals donate electron density to the metal. Electron donation from the 1π -orbitals and backdonation to the 2π -orbitals both strengthen the M-CO bond while weakening the internal C-O bond. Like the Blyholder model, we find that the σ -interactions play a less dominant role.

Föhlisch *et al.*[36,37] proposed a chemisorption model for Cu-CO and Ni-CO where the π - and σ -interactions have opposed effects. The former interaction strengthens the metal-CO bond while weakening the internal C-O bond, whereas the latter does the opposite. For the π -interaction, our findings are in line with this result. However, for the σ -interaction we do not find a counteracting effect, yet we predict it has a similar effect as the π -interaction though to a lesser extent. Although the electron redistribution in the highest lying σ -orbitals, i.e. the 4σ and

 5σ MOs, result in a strengthening of the C-O bond upon adsorption, the C-O destabilization caused by the 3σ MO is of a greater magnitude.

More recently, Gameel *et al.*[38] examined the electronic structure of CO adsorbed on Cu, and later also on Ni[39]. They draw similar conclusions for CO on Ni and Cu as we do for Co. When metal-CO coordination increases, more electron density is transferred to the 2π orbitals, and the C-O bond is weakened. Similar to our findings, they do not observe a correlation between the CO adsorption energy and C-O bond activation. The authors examine the 3σ and 1π orbitals in detail, rationalizing orbital destabilization based on an increase in energy of the eigenvalues of the Kohn-Sham states and broadening of the density of states. Our results for CO on Co show the same upshift for 3σ and broadening of 1π . Gameel *et al.* also conclude that the broadening of 1π has a larger effect on the C-O bond destabilization than the alterations in the 3σ orbital. Our observation that the electron loss in the 1π orbitals and the electron redistribution in the 3σ orbital are the most important factors for C-O bond weakening are in agreement with their results. We thus conclude that a high similarity exists for CO activation for these three late transition metals.

3.4 Conclusions

We investigated the electronic structure of CO adsorbed on various Co sites, displaying vast differences in the CO dissociation barrier. Geometric analysis of the adsorbate-site topology reveals that a probe electron density overlap between M-C and M-O acts as an accurate descriptor for the CO dissociation barrier. To understand the underlying electronic effects of this observation, detailed density of states, crystal orbital Hamilton population, and DDEC6 charge analyses were conducted to rationalize the changes in activation energies based on orbital hybridization and charge transfer.

For each of the canonical molecular orbitals in CO, we identified the trends between weakly and strongly activating active site configurations, based on their charge and bonding characteristics. We found that the 3σ orbital retains its total charge upon adsorption, however the electron density redistributes to reduce electron-electron repulsion with the *d*-band. This results in a blueshift of the 3σ orbital, weakening the C-O bond.

The 4σ and 5σ orbitals both lose a constant amount of electron density upon adsorption, independent of the adsorption mode and corresponding to a total of about 0.9 electrons with respect to the gas phase. This loss in electron density and the redistribution of the electron density of these orbitals results for both orbitals in a strengthening of the C-O bond. This effect is rather small for the 4σ molecular orbital, yet more pronounced for the 5σ orbital. For three- and fourfold adsorption modes, we attribute the small increase in bond strength of 5σ to the migration of electron density from C towards the O terminus, leading to a loss of nodal plane character perpendicular to the C-O bonding axis present in the 5σ orbital of gaseous CO. For five- and sixfold adsorption modes, the increase in bond strength is larger because these perpendicular nodal planes disappear altogether, manifesting in an overall bonding characteristic of the 5σ orbital for these configurations.

For the 1π orbital, it is found that a significant amount of electron density is donated to Co upon adsorption, a feature which is strongly correlated to the CO dissociation barrier. Like the 5σ orbital, we assign this observation to the changes that occur in the nodal planes. For three- and fourfold adsorption modes, the 1π molecular orbital retains its nodal plane alongside the C-O bonding axis and thus its bonding character. Therefore, loss of electron density in the 1π orbital leads to a weakening of the C-O bond. For five- and sixfold adsorption modes, the enhanced electron-electron repulsion results in a further distancing of the 1π orbital with respect to the Co atoms, leading to a shift of the 1π nodal plane away from the Co surface. This weakens the C-O bond. The 2π orbital, which is unoccupied for CO in the gas phase, gains up to 2.5 electrons upon adsorption. Both the increase in electron density as well as the increase in antibonding character of the 2π orbital portray strong correlations with the CO dissociation barrier.

When we distinguish between σ - and π -systems, we observe that, in total, both systems are strengthening the Co-CO bond and weakening the C-O bond upon adsorption. The individual components of the σ -system play different roles. 4σ shows a constant C-O bond strengthening independent of the adsorption mode, while 5σ contributes more to strengthening the C-O bond upon more activated adsorption. The 3σ bond weakens the C-O bond upon adsorption and is more weakening for more activated adsorptions. The π -system has a critical role in the activation of CO, both 1π and 2π largely contributing to this. Both the electron donation from 1π to the *d*-band and the backdonation into 2π become more pronounced upon more activated adsorption.

In this work, we provided an electronic structure level understanding of how geometrical and charge-transfer factors modulate the CO dissociation barrier. We identified changes to the 3σ and 1π molecular orbitals to be most influential in affecting the barrier, a process that can be induced by facilitating an active site

configuration that allows for a tilted CO adsorption such as a B_5 motif. This understanding can inspire new experimental avenues towards novel catalyst nanoparticle formulations exposing specific highly active site configurations leading to more active and selective catalyst materials.

3.5 References

- [1] M. Boudart, in: Advances in Catalysis, Elsevier, 1969, pp. 153–166.
- [2] A. Nilsson, L.G.M. Pettersson, J.K. Nørskov, eds., Chemical Bonding at Surfaces and Interfaces, 1. ed, Elsevier, Amsterdam, 2008.
- [3] D.A.J.M. Ligthart, R.A. Van Santen, E.J.M. Hensen, J. Catal. 280 (2011) 206–220.
- [4] J. Wei, J. Catal. 225 (2004) 116–127.
- [5] A. Parmaliana, F. Arena, F. Frusteri, S. Coluccia, L. Marchese, G. Martra, A.L. Chuvilin, J. Catal. 141 (1993) 34–47.
- [6] N. Spencer, J. Catal. 74 (1982) 129–135.
- [7] K. Honkala, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Nørskov, Science 307 (2005) 555–558.
- [8] J. Yang, H. Wang, X. Zhao, Y.L. Li, W.L. Fan, RSC Adv. 6 (2016) 40459–40473.
- [9] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. van Dillen, K.P. de Jong, J. Am. Chem. Soc. 128 (2006) 3956– 3964.
- [10] J. Kang, S. Zhang, Q. Zhang, Y. Wang, Angew. Chem. Int. Ed. 48 (2009) 2565– 2568.
- [11] J.M.G. Carballo, J. Yang, A. Holmen, S. García-Rodríguez, S. Rojas, M. Ojeda, J.L.G. Fierro, J. Catal. 284 (2011) 102–108.
- [12] J.P. Den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. De Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [13] E. Iglesia, J. Catal. 137 (1992) 212–224.
- [14] A. Tuxen, S. Carenco, M. Chintapalli, C.-H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A.P. Alivisatos, G. Thornton, W.-F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, J. Am. Chem. Soc. 135 (2013) 2273–2278.
- [15] N.L. Visser, O. Daoura, P.N. Plessow, L.C.J. Smulders, J.W. De Rijk, J.A. Stewart, B.D. Vandegehuchte, F. Studt, J.E.S. Van Der Hoeven, P.E. De Jongh, ChemCatChem 14 (2022) e202200665.
- [16] J.K. Kesavan, I. Luisetto, S. Tuti, C. Meneghini, G. Iucci, C. Battocchio, S. Mobilio, S. Casciardi, R. Sisto, J. CO2 Util. 23 (2018) 200–211.
- [17] Y. Guo, S. Mei, K. Yuan, D.-J. Wang, H.-C. Liu, C.-H. Yan, Y.-W. Zhang, ACS Catal. 8 (2018) 6203–6215.
- [18] G. Melaet, A.E. Lindeman, G.A. Somorjai, Top. Catal. 57 (2014) 500–507.
- [19] R. Van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189–230.
- [20] M.P.C. van Etten, B. Zijlstra, E.J.M. Hensen, I.A.W. Filot, ACS Catal. 11 (2021) 8484–8492.

- [21] W. Chen, B. Zijlstra, I.A.W. Filot, R. Pestman, E.J.M. Hensen, ChemCatChem 10 (2018) 136–140.
- [22] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.
- [23] J.J.C. Struijs, V. Muravev, M.A. Verheijen, E.J.M. Hensen, N. Kosinov, Angew. Chem. Int. Ed. 62 (2023).
- [24] B. Zijlstra, R.J.P. Broos, W. Chen, I.A.W. Filot, E.J.M. Hensen, Catal. Today 342 (2020) 131–141.
- [25] E.B. Sterk, A.-E. Nieuwelink, M. Monai, J.N. Louwen, E.T.C. Vogt, I.A.W. Filot, B.M. Weckhuysen, JACS Au 2 (2022) 2714–2730.
- [26] U. Hanefeld, L. Lefferts, eds., Catalysis: An Integrated Textbook for Students, Wiley-VCH, Weinheim, 2018.
- [27] H. Kim, V.D. Doan, W.J. Cho, R. Valero, Z. Aliakbar Tehrani, J.M.L. Madridejos, K.S. Kim, Sci. Rep. 5 (2015) 16307.
- [28] G. Blyholder, J. Phys. Chem. 68 (1964) 2772–2777.
- [29] C.A. Coulson, Nature 191 (1961) 1233-1234.
- [30] L.E. Orgel, Inorg. Chem. 1 (1962) 25–29.
- [31] C.J. Ballhausen, M.A. Weiner, J. Electrochem. Soc. 110 (1963) 97C.
- [32] N.G. Gaylord, R.E. Dessy, J. Polym. Sci. 55 (1961) S3–S4.
- [33] R.A. van Santen, ed., Catalysis: An Integrated Approach, 2., rev.enlarged ed., 2. impression, Elsevier, Amsterdam, 2000.
- [34] P.S. Bagus, C.J. Nelin, C.W. Bauschlicher, Phys. Rev. B 28 (1983) 5423–5438.
- [35] P.S. Bagus, K. Hermann, Phys. Rev. B 33 (1986) 2987–2991.
- [36] A. Föhlisch, M. Nyberg, P. Bennich, L. Triguero, J. Hasselström, O. Karis, L.G.M. Pettersson, A. Nilsson, J. Chem. Phys. 112 (2000) 1946–1958.
- [37] A. Föhlisch, M. Nyberg, J. Hasselström, O. Karis, L.G.M. Pettersson, A. Nilsson, Phys. Rev. Lett. 85 (2000) 3309–3312.
- [38] K.M. Gameel, I.M. Sharafeldin, A.U. Abourayya, A.H. Biby, N.K. Allam, Phys. Chem. Chem. Phys. 20 (2018) 25892–25900.
- [39] K.M. Gameel, I.M. Sharafeldin, N.K. Allam, Phys. Chem. Chem. Phys. 21 (2019) 11476–11487.
- [40] I.A.W. Filot, F. Fariduddin, R.J.P. Broos, B. Zijlstra, E.J.M. Hensen, Catal. Today 275 (2016) 111–118.
- [41] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251–14269.
- [42] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15–50.
- [43] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953–17979.
- [44] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758–1775.
- [45] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [46] B. Hammer, L.B. Hansen, J.K. Nørskov, Phys. Rev. B 59 (1999) 7413–7421.
- [47] M. Wuttig, X. Liu, Ultrathin Metal Films, Springer Berlin Heidelberg, Berlin, Heidelberg, 2004.
- [48] C. Kittel, Introduction to Solid State Physics, 8th ed, Wiley, Hoboken, NJ, 2005.
- [49] S. Kanungo, Y. Su, M.F. Neira d'Angelo, J.C. Schouten, E.J.M. Hensen, Catal. Sci. Technol. 7 (2017) 2252–2261.

- [50] M.-C. Silaghi, A. Comas-Vives, C. Copéret, ACS Catal. 6 (2016) 4501–4505.
- [51] Y.-Q. Su, J.-X. Liu, I.A.W. Filot, E.J.M. Hensen, Chem. Mater. 29 (2017) 9456– 9462.
- [52] R. Dronskowski, P.E. Bloechl, J. Phys. Chem. 97 (1993) 8617–8624.
- [53] V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Phys. Chem. A 115 (2011) 5461–5466.
- [54] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Comput. Chem. 34 (2013) 2557–2567.
- [55] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Comput. Chem. 37 (2016) 1030–1035.
- [56] R. Nelson, C. Ertural, J. George, V.L. Deringer, G. Hautier, R. Dronskowski, J. Comput. Chem. 41 (2020) 1931–1940.
- [57] T. Koga, K. Kanayama, S. Watanabe, A.J. Thakkar, Int. J. Quant. Chem. 71 (1999) 491–497.
- [58] T. Koga, K. Kanayama, T. Watanabe, T. Imai, A.J. Thakkar, Theor. Chem. Acc. 104 (2000) 411–413.
- [59] T.A. Manz, N.G. Limas, RSC Adv. 6 (2016) 47771–47801.
- [60] N.G. Limas, T.A. Manz, RSC Adv. 6 (2016) 45727–45747.
- [61] R.D.E. Krösschell, E.J.M. Hensen, I.A.W. Filot, (2023).
- [62] G.S. Hammond, J. Am. Chem. Soc. 77 (1955) 334–338.
- [63] F. Calle-Vallejo, D. Loffreda, M.T.M. Koper, P. Sautet, Nature Chem. 7 (2015) 403–410.
- [64] W.L. Jorgensen, L. Salem, The Organic Chemist's Book of Orbitals, Academic Press, New York, 1973.
- [65] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132 (2010) 154104.
- [66] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 32 (2011) 1456–1465.
- [67] V.A. De La Peña O'Shea, I.D.P.R. Moreira, A. Roldán, F. Illas, J. Chem. Phys. 133 (2010) 024701.
- [68] A. Taylor, J. Inst. Met. 77 (1950) 585–594.
- [69] P.J. Feibelman, B. Hammer, J.K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, J. Dumesic, J. Phys. Chem. B 105 (2001) 4018–4025.
- [70] M. Mohamad, B. Ul Haq, R. Ahmed, A. Shaari, N. Ali, R. Hussain, Mater. Sci. Semicond. Process. 31 (2015) 405–414.
- [71] T. Saelee, P. Apichoksiri, M. Rittiruam, C. Wangphon, P. Khajondetchairit, S. Praserthdam, P. Praserthdam, Chemosphere 340 (2023) 139842.
- [72] M.P.C. Van Etten, M.E. De Laat, E.J.M. Hensen, I.A.W. Filot, J. Phys. Chem. C 127 (2023) 15148–15156.
- [73] J. Wellendorff, T.L. Silbaugh, D. Garcia-Pintos, J.K. Nørskov, T. Bligaard, F. Studt, C.T. Campbell, Surf. Sci. 640 (2015) 36–44.
- [74] Q. Ge, M. Neurock, J. Phys. Chem. B 110 (2006) 15368–15380.
- [75] C. Chen, Q. Wang, R. Zhang, B. Hou, D. Li, L. Jia, B. Wang, Appl. Catal. A 523 (2016) 209–220.
- [76] Z. Zhang, S. Liu, X. Hou, L. Qi, W. Li, J. Mol. Model. 26 (2020) 134.
- [77] L. Liu, Y. Shi, J. Rong, Q. Wang, M. Zhong, Molecules 29 (2024) 4760.

A. Appendix

Section A.1: Comparison with and without Van der Waals correction

For four sites, we compare the electronic density of CO adsorption and dissociation over that site with no Van der Waals correction, the Van der Waals correction DFT-D3 method of Grimme with zero-damping function[65] and the Van der Waals correction DFT-D3 method of Grimme with Becke-Johnson damping function.[66] To apply no Van der Waals correction DFT-D3 method of Grimme with zero-damping function for the Van der Waals correction DFT-D3 method of Grimme with zero-damping function. To apply no Van der Waals correction DFT-D3 method of Grimme with zero-damping function and IVDW = 12 for the Van der Waals correction DFT-D3 method of Grimme with Becke-Johnson damping function. For the sake of brevity, the labels IVDW0, IVDW11 and IVDW12, respectively, are used in this section to distinguish between these three cases.

The CO adsorption and CO dissociation energies are compared for the different Van der Waals corrections in Table A.1-A.4 for four representative active sites. The DOS and COHP plots that correspond to CO in predissociation state on these sites are shown in Figure A.5-A.8. On top of the qualitative comparison of the DOS and COHP plots, we have computed the average absolute deviation per data point for DOS and COHP with respect to the calculation that has no Van der Waals correction applied. The average absolute deviation per data point is calculated for the data points up to Fermi level. These values are listed in the Table A.1-A.4 in the last two columns.

The CO adsorption energy is significantly affected by a Van der Waals correction. Generally, we see that CO adsorption becomes more stable when a Van der Waals correction is applied. The only case where this is not true is for the Co_{52}/Al_2O_3 NC site for the Van der Waals correction with zero-damping (IVDW11), where CO adsorbs 2 kJ/mol less stable than without correction. The largest difference between uncorrected and Van der Waals corrected values for CO adsorption is the Co_{81}/TiO_2 NR site for the Van der Waals correction with Becke-Johnson damping (IVDW12), with 29 kJ/mol.

For CO dissociation, the difference between uncorrected and Van der Waals corrected energies are not significant. In general, the difference is 1-2 kJ/mol. The largest difference is found for the Co(0001) HCP site, with a difference of 7 kJ/mol for IVDW12.

The DOS and COHP plots are very similar. The total DOS and COHP values deviate very little from each other, whether a Van der Waals correction was applied or

not. The individual peaks are very similar as well and differ from each other by a maximum of 0.03 for the DOS peaks and 0.05 for the COHP peaks. Also, the average absolute deviation per data point is very small for each geometry. The largest value for DOS is 3.95×10^{-2} (for Co_{52}/Al_2O_3 NC site) and the largest value for COHP is 1.05×10^{-1} (for $Co(11\overline{2}1)$ B₅ site) for this metric.

From this detailed comparison we conclude that the electronic structure analyses that we have performed regarding the electronic density of CO on several Co sites and the corresponding CO dissociation energy barrier are not significantly affected by whether a Van der Waals correction is applied or not.

Table A.1: CO adsorption and CO dissociation energies on Co(0001) HCP site with and without Van der Waals correction.

Co(0001) HCP site								
Van der	CO	CO	CO	DOS	СОНР			
Waals	adsorption	dissociation	dissociation	average	average			
correction	energy	energy	energy	absolute	absolute			
	[kJ/mol]	forward	backward	deviation	deviation			
		[kJ/mol]	[kJ/mol]	per data	per data			
				point	point			
IVDW0	-163	226	140	0.00E+00	0.00E+00			
IVDW11	-183	222	143	8.79E-03	1.92E-02			
IVDW12	-190	219	144	1.64E-02	3.13E-02			

Table A.2: CO adsorption and CO dissociation energies on Co(11 $\overline{2}$ 1) B₅ site with and without Van der Waals correction.

Co(11 $\overline{2}$ 1) B ₅ site									
Van der	CO	CO	CO	DOS	СОНР				
Waals	adsorption	dissociation	dissociation	average	average				
correction	energy	energy	energy	absolute	absolute				
	[kJ/mol]	forward	backward	deviation	deviation				
		[kJ/mol]	[kJ/mol]	per data	per data				
				point	point				
IVDW0	-158	83	102	0.00E+00	0.00E+00				
IVDW11	-170	82	103	3.70E-02	1.05E-01				
IVDW12	-181	82	103	3.94E-02	9.39E-02				

Table A.3: CO adsorption and CO dissociation energies on Co_{52}/Al_2O_3 NC site with and without Van der Waals correction.

Co ₅₂ /Al ₂ O ₃ NC site								
Van der	CO	CO	CO	DOS	СОНР			
Waals	adsorption	dissociation	dissociation	average	average			
correction	energy	energy	energy	absolute	absolute			
	[kJ/mol]	forward	backward	deviation	deviation			
		[kJ/mol]	[kJ/mol]	per data	per data			
				point	point			
IVDW0	-156	79	83	0.00E+00	0.00E+00			
IVDW11	-154	80	99	2.63E-02	3.27E-02			
IVDW12	-165	81	100	3.95E-02	5.07E-02			

Table A.4: CO adsorption and CO dissociation energies on Co_{81}/TiO_2 NR site with and without Van der Waals correction.

Co ₈₁ /TiO ₂ NR site								
Van der	CO	CO	CO	DOS	СОНР			
Waals	adsorption	dissociation	dissociation	average	average			
correction	energy	energy	energy	absolute	absolute			
	[kJ/mol]	forward	backward	deviation	deviation			
		[kJ/mol]	[kJ/mol]	per data	per data			
				point	point			
IVDW0	-152	103	115	0.00E+00	0.00E+00			
IVDW11	-166	104	109	2.25E-02	4.68E-02			
IVDW12	-181	102	108	2.89E-02	5.90E-02			



Figure A.1: DOS plots of predissociation state of CO on Co(0001) HCP site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).



Figure A.2: COHP plots of predissociation state of CO on Co(0001) HCP site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).



Figure A.3: DOS plots of predissociation state of CO on Co($11\overline{2}1$) B₅ site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).



Figure A.4: COHP plots of predissociation state of CO on Co($11\overline{2}1$) B₅ site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).



Figure A.5: DOS plots of predissociation state of CO on Co_{52}/Al_2O_3 NC site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).



Figure A.6: COHP plots of predissociation state of CO on Co_{52}/Al_2O_3 NC site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).



Figure A.7: DOS plots of predissociation state of CO on Co_{81}/TiO_2 NR site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).



Figure A.8: COHP plots of predissociation state of CO on Co_{81}/TiO_2 NR site without Van der Waals correction (left), with DFT-D3 zero-damping correction (middle), and with DFT-D3 Becke-Johnson damping correction (right).

Section A.2: Type of smearing and smearing width

To investigate the effect of the type of smearing and the smearing width on the Al_2O_3 and TiO_2 supports, we simulated the bare Al_2O_3 and TiO_2 supports, the Co nanocluster (NC) on Al_2O_3 , and the Co nanorod (NR) on TiO_2 with both Gaussian smearing, and first order method of Methfessel-Paxton smearing. For Gaussian smearing, a smearing width of smearing width of 0.05 eV was used. For the first order method of Methfessel-Paxton smearing width of 0.2 eV was used. Since Al_2O_3 and TiO_2 are both insulators, Gaussian smearing would be the recommended choice to simulate pure Al_2O_3 and TiO_2 . The differences in energy between the simulations with Gaussian smearing, and first order method of Methfessel-Paxton smearing, and first order method of Methfessel-Paxton smearing, and first order method of Methfessel-Paxton smearing, and TiO_2. The differences in energy between the simulations with Gaussian smearing, and first order method of Methfessel-Paxton smearing are shown in Table A.5. These differences are extremely small. Therefore, we conclude that the influence of the smearing widths on the results for the Al_2O_3 and TiO_2 supports is negligible.

Model	Absolute energy difference between different smearing settings [eV]
γ-Al ₂ O ₃ (110)	0.015
Co_{52}/Al_2O_3 NC	0.010
rutile-TiO ₂ (110)	0.017
Co ₈₁ /TiO ₂ NR	0.001

Table A.5: Absolute energy difference between different smearing settings.

Section A.3: Performance of PBE on the cohesive energy of FCC and HCP Co

PBE and other GGA's are reported to perform poorly on predicting the cohesive energy of the FCC and HCP Co bulk phases.[67] We computed a cohesive energy of 5.17 and 5.19 eV/atom for Co bulk FCC and HCP, respectively. In experiments, a cohesive energy of 4.39 eV/atom is reported.[68] This difference might affect adsorption energies, however it is well-known that such adsorption energies are poorly predicted by PBE to begin with.[69] Despite the poor prediction of Co bulk energies, we assume that such errors cancel in the calculation of dissociation barriers, similar to when using different exchange-correlation functionals or inclusion of a VdW correction. Regarding the performance of PBE on γ -Al₂O₃[71] are well described by the PBE functional.

Section A.4: Assessment of stability of supported Co nanoclusters and nanorods

For the $C_{055}/Al_2O_3(110)$ nanocluster model, we took the $Ni_{55}/Al_2O_3(110)$ model from Silaghi *et al.*[50] The authors of this work calculated the binding energy per atom and the metal-support interaction (both defined on page S2 of the Supporting Information of the work from Silaghi *et al.*[50]) for several Ni₅₅ clusters on a γ -Al₂O₃(110) support, and they found the Ni₅₅ Marks nanocluster to be the most stable cluster of 55 Ni atoms on a γ -Al₂O₃(110) support. They employed velocity scaled ab initio molecular dynamics to investigate the behavior of this nanoparticle at 1000 K and this confirmed their DFT findings. Co and Ni are next to each other in the periodic table and often show similar behavior. Therefore, we expect a Co_{55} Marks nanocluster on a γ -Al₂O₃(110) support to be stable as well. To confirm this, we performed calculations of one Co atom leaving the nanocluster and migrating over the Al_2O_3 support (detachment). For completeness, we performed these calculations for the nanocluster on the TiO_2 support as well, as for both nanorods on Al_2O_3 and TiO_2 . The results are shown in Table A.6. The energies in Table A.6 show that an event where a Co atom detaches from the nanoclusters or nanorods is endothermic. The Co detachment energies are quite high, indicating that this is not likely to happen. We observe that a Co atom is more stabilized on the bare TiO_2 support than on the bare Al_2O_3 support in line with known strong metal-support interactions[72], giving rise to lower Co detachment energies for the nanocluster and nanorod on the TiO₂ support. For both supports, the Co detachment energy for the nanocluster is lower than for the nanorod.

Model	Co detachment energy [kJ/mol]
Co ₅₅ /Al ₂ O ₃ nanocluster	317
Co ₈₄ /Al ₂ O ₃ nanorod	554
Co ₅₄ /TiO ₂ nanocluster	90
Co ₈₁ /TiO ₂ nanorod	106

Table A.6: Co detachment energy of supported Co nanoclusters and nanorods.

Section A.5: Dipole correction.

For the Co slabs, we added a large vacuum layer of at least 15 Å to avoid dipole interactions between the adsorbates. For the supported Co nanorods and nanoclusters, where the vacuum layers are smaller than 15 Å (but larger than 12 Å), we tested whether applying a dipole correction resulted in different

adsorption and dissociation energies. For the Co/Al_2O_3 nanocluster and the Co/TiO_2 nanorod, we computed the differences in CO adsorption energy, forward and backward CO dissociation energy. The results are shown in Table A.7. The differences are found to be sufficiently small to discard the use of dipole corrections for these systems.

Table A.7:	Absolute	energy	difference	between	calculations	with	and	without
dipole corr	ection.							

Model	Difference in CO	Difference in CO	Difference in CO	
	adsorption	dissociation	dissociation	
	energy [eV]	energy forward	energy	
		[eV]	backward [eV]	
Co ₅₂ /Al ₂ O ₃ pocket	0.00	0.01	0.00	
site				
Co ₈₁ /TiO ₂ pocket	0.02	0.04	0.05	
site				

Section A.6: Comparison between PBE and RPBE

As mentioned in the Methods section, we use the PBE functional for the exchange-correlation in our DFT calculations. Literature shows that the CO adsorption energy is highly dependent on the choice of exchange-correlation functional.[73] To assess the dependence of our results on the choice of exchange-correlation functional, we calculated a few systems with the revised PBE from Hammer *et al.*[46] The results are summarized in Table A.8. The difference in adsorption energies between PBE and RPBE are very large: approximately 140 kJ/mol. It is known that PBE overestimates the CO adsorption energy.[73] For the barriers, the difference between PBE and RPBE is much smaller. The absolute differences between the barriers computed with PBE and RPBE lie between 1 and 4 kJ/mol. This is well within accuracy limit of DFT (10 kJ/mol). The backward dissociation barrier for Co_{54}/TiO_2 NC shows a difference of 16 kJ/mol between PBE and RPBE. Thus, the forward CO dissociation barriers are likely to be independent of the used exchange-correlation functional.

Table A.8: Comparison of CO adsorption energies, forward and backward energies for CO dissociation between PBE and revised PBE from Hammer *et al*. The states and barriers are not corrected for zero-point energy.

	CO adsorption			CO dissociation			CO dissociation			
	energy	[kJ/mol]		barrie	barrier forward			energy backward		
				[kJ/mol]			[kJ/mol]			
Model	PBE	RPBE	Δ	PBE	RPBE	Δ	PBE	RPBE	Δ	
Co(1121)	-158	-22	136	83	88	4	102	97	-5	
B ₅										
Co_{52}/Al_2O_3	-155	-17	139	79	80	1	83	90	7	
NC										
Co ₅₄ /TiO ₂	-167	-24	142	91	89	-2	144	160	16	
NC										



Figure A.9: Geometry of transition state of CO dissociation on twelve Co sites.



Figure A.10: Geometry of final state of CO dissociation on twelve Co sites.

Section A.7: Description of initial, transition and final states of CO dissociation

First, we compare the six extended surfaces. In Figure 3.1a, CO adsorbs on a threefold site as exposed on the Co($11\overline{2}1$) surface. The adsorption energy is -166 kJ/mol. In the transition state (Figure A.9a), the oxygen moiety migrates to a neighboring active site and is bonded to the surface in a quasi-threefold configuration. The carbon atom remains in the threefold site. In the transition state, C and O share two Co atoms. In the final state (Figure A.10a), the oxygen atom continues to migrate away from the carbon atom and adsorbs at an adjacent threefold site. Only a single Co atom is shared between C and O. This elementary reaction step has an activation energy of 242 kJ/mol and is endothermic by 112 kJ/mol.

In Figure 3.1b, the initial state of CO adsorbed on an FCC site on the Co(0001) is shown. This state has an adsorption energy of -158 kJ/mol. CO dissociation proceeds by the CO moiety bending towards the surface by which O adsorbs in a bridge configuration (Figure A.9b). In this configuration, the C and O atoms share a single Co atom. In the final state, the oxygen atom has migrated to an adjacent FCC site and resides in a threefold configuration. Like the transition state, also in the final state only a single Co atom is shared between C and O (Figure A.10b). The dissociation reaction has a barrier of 229 kJ/mol and is endothermic by 119 kJ/mol.

Figure 3.1c shows CO adsorbed on an HCP site on the Co(0001) surface, in a threefold fashion. The adsorption is exothermic by 160 kJ/mol. As on the Co(0001) FCC site, in transition state the oxygen adsorbs in a bridged manner on the surface, while the carbon remains in its place (Figure A.9c). One cobalt atom is shared with carbon in this state. In the final state, the C and O occupy two neighboring HCP threefold sites, while sharing one cobalt atom (Figure A.10c). This dissociation step has an energy barrier of 222 kJ/mol and is endothermic by 87 kJ/mol.

In Figure 3.1d, CO adsorbs on the Co(110) surface with an adsorption energy of -135 kJ/mol. In the adsorbed state, carbon is bonded to four cobalt atoms. In the transition state, the oxygen attaches in a bridged manner to two cobalt atoms (Figure A.9d). One cobalt atom is shared between oxygen and carbon. Carbon remains at its fourfold position. The oxygen moves further between the two cobalt atoms until it can bond to a third cobalt atom in the final state (Figure
A.10d). One cobalt atom is shared by C and O. The energy barrier associated with this reaction step is 116 kJ/mol. This step is endothermic by 11 kJ/mol.

Figure 3.1e displays CO adsorbed at a fourfold site on the Co(100) surface, which corresponds to an energy of -175 kJ/mol. To dissociate, oxygen moves to a bridged position between two cobalt atoms (Figure A.9e). Both these cobalt atoms are also bonded to carbon. Carbon stays in its original place in the transition state. In the final state, O is adsorbed at a fourfold site next to the adsorption site of C (Figure A.10e). The energy barrier of this step is 125 kJ/mol, and the reaction step is exothermic by 43 kJ/mol.

Figure 3.1f displays the Co($11\overline{2}1$) surface, which possesses a B₅ site that accommodates a sixfold adsorption of CO, with carbon and oxygen bonding to the metal in a fourfold and twofold configuration, respectively. Notably, carbon and oxygen atoms do not share any cobalt atoms in this initial state, and the adsorption energy is -163 kJ/mol. The transition state exhibits an elongated C-O bond due to the movement of O away from C while C remains stationary, with an activation energy of 82 kJ/mol (Figure A.9f). Subsequently, oxygen moves further between two cobalt atoms to bond with a third cobalt atom in the final state, where C and O atoms continue to not share any cobalt atoms (Figure A.10f). This CO dissociation process is slightly exothermic, with an energy release of 19 kJ/mol.

Next, we compare the six supported nanoclusters and -rods. Figure 3.1g depicts a threefold top site on a Al_2O_3 -supported nanocluster of 55 cobalt atoms. The energy of adsorption on this site is -169 kJ/mol. Because of the low coordination numbers of the Co atoms, they are relatively mobile. Upon CO dissociation, this enhanced mobility allows for the emergence of an adjacent threefold site accepting the oxygen moiety in the transition state (Figure A.9g). In this configuration, one Co is shared between C and O. As oxygen moves further away from carbon, the cobalt atoms perturb again in such a way that a fourfold site harboring the carbon is formed (Figure A.10g). Oxygen is positioned at the adjacent threefold site in the final state. One cobalt atom is bonded to both C and O. This elementary reaction step has an activation energy of 201 kJ/mol and is endothermic by 36 kJ/mol.

In Figure 3.1h, CO is adsorbed on a threefold site close to the support of the Co_{55}/Al_2O_3 model. One of the three cobalt atoms of the threefold site is attached directly to the support. CO adsorbs on this site with -180 kJ/mol. Oxygen moves away from carbon until it is positioned in a bridged fashion between two cobalt

atoms (Figure A.9h). One of these cobalt atoms is also bonded to carbon. In the final state, the oxygen also bonds to a third Co atom that is not bonded to carbon (Figure A.10h). The Co atoms do not perturb as extensively as observed for the Co_{55}/Al_2O_3 system. This reaction has a barrier of 206 kJ/mol and is endothermic by 50 kJ/mol.

Figure 3.1i shows the adsorption of CO on a pocket site of the Co_{52}/Al_2O_3 model. Both carbon (fourfold) and oxygen (twofold) bond to the metal in the initial state very much akin to the fourfold adsorption mode found for the Co(1121) B₅ site (Figure 3.1f). The adsorption energy is -152 kJ/mol. No cobalt atoms are shared between C and O. The transition state resembles the initial state, but with an increased C-O bond distance (Figure A.9i). In the final state, the C-O distance increases further, and O adsorbs in a threefold mode to a site neighboring the fourfold site on which carbon is still adsorbed (Figure A.10i). No cobalt atoms are shared between oxygen and carbon in this final state. The barrier for this dissociation is 75 kJ/mol and the dissociation is slightly exothermic by 4 kJ/mol. Notably, this barrier is lower in comparison to the situation found for the similar situation on the extended Co(1121) model.

The Al₂O₃-supported nanorod in Figure 3.1j exhibits a site close to the support on which CO can adsorb in a fivefold manner. Carbon bonds in a fourfold manner, oxygen bonds to a single cobalt atom that is not shared with carbon. The adsorption energy is -156 kJ/mol. Oxygen moves towards a bridged position between the cobalt atom to which it was attached in initial state and a cobalt atom that carbon bonds to (Figure A.9j). In this transition state, carbon remains fourfold bonded to cobalt. In the final state, oxygen bonds in a bridged manner between two cobalt atoms that are not shared with carbon (Figure A.10j). The barrier for this dissociation is 121 kJ/mol. The dissociation is exothermic by 17 kJ/mol.

In Figure 3.1k, CO adsorbs in a sixfold manner in a pocket site on a TiO_2 supported nanocluster. The adsorption energy is -158 kJ/mol. The initial, transition and final states are similar to the initial, transition (Figure A.9k) and final states on the Al_2O_3 -supported pocket site. A noticeable difference is the higher mobility of the cobalt atoms for the TiO_2 -supported nanocluster. In the final state, the cobalt atoms have a different configuration than in the initial state, with carbon's fourfold and oxygen's threefold neighboring sites shifted with respect to each other (Figure A.10k). The barrier that belongs to this elementary reaction step is 78 kJ/mol. The reaction is exothermic by 18 kJ/mol. Figure 3.1l shows CO on a TiO₂-supported nanorod. The initial state is like the Al_2O_3 -supported nanorod, with an adsorption energy of -152 kJ/mol. Also, the transition states on both nanorods are alike, but on the TiO₂-supported NR, oxygen bonds to an extra Co atom (Figure A.9I). This Co atom does not bond to C. The final state resembles that of the Al_2O_3 -supported nanorod as well, but instead of only bonding bridged between two Co atoms that are not shared with C, O bonds also to a third Co atom which is shared with C (Figure A.10I). The activation energy for this CO dissociation is 100 kJ/mol and the reaction energy is -10 kJ/mol.

Model	CO dissociation	CO dissociation	Source	
	barrier forward	energy backward		
	[kJ/mol]	[kJ/mol]		
Co(1121) 3f	242	130	This work	
Co(0001) FCC	229	110	This work	
Co(0001) HCP	222	135	This work	
Co(110)	116	105	This work	
Co(100)	125	168	This work	
$Co(11\bar{2}1) B_5$	82	101	This work	
Co(0001)	225	158	[24]	
Co(0001)	233	-	[74]	
Co(0001)	235	190	[75]	
Co(110)	135	-	[20]	
Co(100)	133	-	[20]	
Co(100)	131	199	[75]	
$Co(11\bar{2}1) B_5$	100	102	[24]	

Table A.9: Forward and backward CO dissociation energies for the extended surface models and the values reported in the literature.

Section A.8: Approximating orbital overlap between CO and Co

Using the atom positions from the DFT-optimized predissociation states, we calculated the electron density overlap between CO and Co as if the electron densities of these atoms were only radially dependent. We computed the overlap μ_2 as defined in Equation 2 with $\phi(r) = \exp(-\alpha \cdot r)$ (Figure A.11c) and $\phi(r) = \exp(-\alpha \cdot r^2)$ (Figure A.11d). This was done by placing a Lebedev quadrature grid on the carbon and oxygen atoms. By looping over all cobalt atoms, the overlap for each cobalt atom and the carbon or oxygen atom was determined

according to the formula for ϕ . The sum of the overlap equals the overlap metric μ_2 . To find the best correlation for this dataset of twelve states, the fitting parameter α was optimized for both $\phi(r)$ functions. This was done by minimizing the Pearson correlation coefficient with the Nelder-Mead method.



Figure A.11: Correlation between CO dissociation barrier and the electron density overlap between CO and Co in the predissociation state. Distance and overlap metrics are computed with $\mu_1(d) = \sum_{i \in Co, j \in C, 0} d_{i,j}^{-3}$, with a Pearson correlation coefficient of -0.91 (a); $\mu_1(d) = \sum_{i \in Co, j \in C, 0} d_{i,j}^{-\alpha}$ with $\alpha = 4.9$ for C-Co distances and $\alpha = 6.4$ for O-Co distances, with a Pearson correlation coefficient of -0.93 (b); $\mu_2 = \sum_{i \in Co, j \in C, 0} \langle \phi_i | \phi_j \rangle$ with $\phi(r) = \exp(-\alpha \cdot r)$ with $\alpha = 2.0$ for C and O, and $\alpha = 5.4$ for Co, with a Pearson correlation coefficient of -0.95 (c); $\mu_2 = \sum_{i \in Co, j \in C, 0} \langle \phi_i | \phi_j \rangle$ with $\phi(r) = \exp(-\alpha \cdot r^2)$ with $\alpha = 0.97$ for C, O, and $\alpha = 0.75$ for Co, with a Pearson correlation coefficient of -0.96 (d).



Figure A.12: Correlation between IDOS at Fermi level and the DDEC6 charge of adsorbed CO. The Pearson correlation coefficient for this correlation is -0.93.



Figure A.13 Correlation between CO dissociation barrier and IDOS at Fermi level. The Pearson correlation coefficient for this correlation is -0.91.



Figure A.14: COHP as function of the energy of the Kohn-Sham states of the Co-CO bond for CO adsorbed on Co(11 $\overline{2}$ 1) 3f (a,c), and CO adsorbed on Co(11 $\overline{2}$ 1) B₅ (b,d). Subfigures a and b show the total and integrated COHP for CO, whereas subfigures c and d show the σ - and π -contributions. All plots use the same reference energy. The integrated COHP at Fermi level is shown above the black line at zero energy (a,b), or near the red and blue dots (c,d). The values next to the peaks pertain to the area under the curves. The dashed lines show the integrated σ - and π -contributions (I σ and I π).



Figure A.15: σ - and π -contributions of the COHP as function of the energy of the Kohn-Sham states of the Co-CO bond for CO adsorbed on Co(11 $\overline{2}$ 1) 3f (a), and CO adsorbed on Co(11 $\overline{2}$ 1) B₅ (b). All plots use the same reference energy. The integrated COHP at Fermi level is shown above the black line at zero energy.



Figure A.16: Boxplot of the COHP values of the Co-CO interactions.

4. Interfacial Reactivity in Fischer-Tropsch Synthesis: A DFT Study of Co Nanorods on Al₂O₃ and TiO₂

Abstract

This study investigates the reactivity of the metal-support interface in Fischer-Tropsch synthesis (FTS) using density functional theory (DFT) simulations, using continuous Co nanorods on Al_2O_3 and TiO_2 supports. The results reveal that interfacial sites exhibit low CO conversion, predominantly yielding methane, even in the presence of highly active B_5 sites. Microkinetic simulations attribute this low activity to the poisoning of active sites at the interface by reaction intermediates, which are more stable here than on extended surface sites. This stability is linked to the support's influence on nanoparticle structure, leading to coordinatively undersaturated Co atoms. The high CO dissociation barriers at interfacial sites result in minimal C_{2+} species production. While charge transfer occurs between the Co nanorods and the supports, it primarily impacts the Co atoms directly bonded to the support. These atoms acquire either a positive or negative charge, depending on their proximity to oxygen or Al/Ti atoms. However, this effect diminishes rapidly, leaving most interfacial active sites unaffected and having minimal influence on overall reactivity.



4.1 Introduction

Fischer-Tropsch synthesis (FTS), developed in the 1920s, has remained a crucial process since, and continues to be significant in the context of the ongoing energy transition. In the Fischer-Tropsch (FT) reaction, a mixture of CO and H_2 produced from the gasification of coal or biomass, or natural gas reforming, is converted

into valuable products. FT catalysts can also convert CO_2 and H_2 , making the FT process interesting for carbon capture and utilization (CCU).[1,2] In CCU processes, CO_2 is captured, generally from industrial point sources, and converted into fuels and chemical feedstock in order to reduce carbon emissions.

The FT reaction can be viewed as a polymerization reaction with the *in situ* production of CH_x monomers, which are linked to form hydrocarbon chains. A low selectivity towards methane and specifically a high C_{5+} selectivity is often desired, as further processing to a fuel requires liquids and waxes instead of gaseous products.[3] Co and Fe are preferred over Ru and Ni as FT catalyst, because Ru is very expensive, and Ni primarily produces methane.[4] Fe is extensively studied for CO_2 -FT conversion[2], because it facilitates the (reverse) water-gas-shift (WGS) reaction, but Co is investigated for CO_2 -FT as well.[5] Fe provides some advantages over Co; it can convert feedstocks with higher C/H ratios, making this metal more suitable to convert coal-based syngas than Co, and it is one of the most abundant elements in the Earth's crust. However, Co is more resistant to catalyst deactivation and produces less olefins and oxygenates.[6] Typical operating conditions for Co-catalyzed FT are 225 °C and 20-40 bar.[7] Often Al₂O₃ (alumina) or TiO₂ (titania) is used to support the Co nanoparticles.[8–11]

Experiments have shown that in FTS, the product distribution depends strongly on the composition and morphology of the catalyst, a phenomenon known as structure sensitivity.[12,13] The term structure sensitivity was introduced by Boudart to explain the commonly observed correlation between catalytic rate and the dispersion of catalytically active particles.[14] Although this effect is observed at the mesoscale, in essence the nanoscale structure of the catalyst, i.e. the distribution of active sites, determines the activity and selectivity.[15] Decades of research on the structure-activity dependence of FT catalysts shows that with increasing Co site density C_{5+} selectivity increases [16] and methane formation decreases.[17] It has also been established that smaller metal particles (< 6 nm) produce relatively more methane and that larger metal particles, which host so-called B₅ or step-edge sites, are necessary for chain growth.[12,18–20] This is linked to the observations that CO dissociates more efficiently on larger than on smaller particles[21], and that a facile CO dissociation increases the probability of chain growth.[22] Furthermore, kinetic experiments have shown that on small Co nanoparticles, carbon and oxygen surface species bind very strongly, which poisons the active sites and inhibits methanation.[23] However, when examining particle size and morphology, the

support must be considered as well, since different supports can induce different reactivities via metal-support interactions. It has been shown that catalyst performance can be optimized by controlling these metal-support interactions, e.g. by modifying the metal dispersion and the extent of reduction of the active phase. As smaller metal particles exhibit a stronger affinity with the support, they are more difficult to reduce.[24] Reuel and Bartholomew correlated a higher dispersion with a lower degree of reduction, which led to lower CO hydrogenation activity and higher selectivity towards CO₂ for Co catalysts on various supports.[25] They ascribed this effect to an oxide phase being present at the surface of the well-dispersed, poorly reduced samples, with the oxide phase catalyzing the WGS reaction. Mejía et al. demonstrated how Co catalysts supported by reducible metal oxides can be tuned *via* a reduction-oxidationreduction treatment which increases the cobalt surface area and FT activity.[26] Parastaev et al. varied the particle size of ceria-zirconia support particles and used this to synthesize a Co catalyst that enables oxygen spillover, which boosts conversion.[24] Other factors that influence the structure sensitivity of a Co FT catalyst that are (partially) influenced by the support, are the size of the metal nanoparticle[27-32], nanoparticle morphology[33], charge transfer[34], the chemical composition of the metal and the support[35], whether strong metalsupport interactions (SMSI) occur[36], and the reactivity of the interfacial perimeter, i.e. synchronized reactions.[37] Investigating the interplay between metal-support interactions and structure sensitivity is very complex. Multiple phenomena influence each other and often these phenomena cannot easily be disentangled in experiments.[37] Modelling supported catalysts with DFT is challenging as the inclusion of both the active metal and the support leads to computationally expensive systems. To overcome this, an inverse catalyst could be modelled, where a support-like ligand is placed on a metal surface. The work of Van Heerden *et al.* shows that when the OAl(OH)₂ ligand is present on an FCC Co(111) surface, CO will interact strongly with the ligand, making CO dissociation feasible.[38] Also Zhang et al. showed with an inverse model of $Ti_4O_8/Co(0001)$ that CO preferentially adsorbs at interfacial sites over a site on the extended surface site.[39] A disadvantage of inverse models however is that they assume a perfect crystalline surface for the Co at the metal-support interface, while it is known that metal-support interactions can change the arrangement of the atoms of the nanoparticle close to the interface.[38,40] With increasing computational power resources, it is now feasible to simulate larger systems with DFT, where the support and the nanoparticle are both explicitly modelled as such.

This study seeks to explore how support materials impact the activity and selectivity of interfacial active sites in the Fischer-Tropsch synthesis reaction through charge transfer and epitaxial effects. Due to differences in electronegativity, the support can donate or withdraw electrons from the active site, affecting its capacity to inject electron density into the anti-bonding orbitals of the adsorbate, thereby altering reaction barriers. While charge transfer effects modify the electronic properties without changing the active site's topology. epitaxial effects influence reaction barriers by altering the geometry of active sites such that it favors a specific alignment with the support structure. To study these effects, we constructed two Co nanorod models deposited on the y- $Al_2O_3(110)$ and rutile-TiO₂(110) supports. These nanorods are continuous in one direction and serve as a proxy for nanoparticle edges. To compare active sites located at the nanoparticle-support interface with those farther from the edge, we also investigate a B_5 site present on the extended Co(1121) surface that has been studied earlier by Zijlstra et al.[41] For each of these active site configurations, DFT calculations are performed to elucidate the reaction energetics for CO hydrogenation to methane. Based on these energetics, microkinetic models are built and used to elucidate the reaction mechanism. By means of a lumped kinetic model, we also investigate the capacity of these active sites to produce long-chain hydrocarbons under CO hydrogenation conditions.

Our findings indicate that the interface of a nanoparticle is a locus for undesirable methane production, albeit at a much lower rate compared to active sites farther from the edge. That the interface exhibits a high selectivity towards methane is inferred from the kinetic model of Van Santen and Markvoort[83,84] shows that under typical FTS conditions the CO dissociation rate must be sufficiently high for a high chain-growth probability, which is required for the production of C₂₊ species. For the nanorod models, the CO dissociation rate is too low to produce significant amounts of products other than methane. The reduced CO conversion at the nanoparticle interface is mainly due to the significantly increased stability of reaction intermediates, which leads to the deactivation of these sites. Additionally, the higher barriers for CO dissociation at the interface, compared to the extended surface, result in a negligible selectivity for long-chain hydrocarbon formation, causing CO hydrogenation to primarily yield methane. Analysis of the electronic structure shows that charge transfer between the Al_2O_3 - and TiO₂-supports and the Co nanoparticle affects only the Co atoms in direct contact with the support. For active sites located more than one atomic layer away, no support-induced electronic effects are observed. Since relevant active site configurations, i.e. those that have a step-edge like topology, can only manifest at least one atomic layer away from the interface, we assign the differences in reactivity between the nanorods and the extended surface to epitaxial effects. Despite the nanoparticle-support interface contributing to undesirable methane formation, we conclude such sites to be poisoned by C, O or H and thus these sites provide a negligible contribution to the overall methane production in conventional FTS.

4.2 Methods

4.2.1 DFT

Plane-wave density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP)[42,43] that employs the projector-augmented wave (PAW) method to describe the core electrons.[44,45] The Perdew-Burke-Ernzerhof (PBE) functional[46] is used to describe electron exchange and correlation. The DFT-D3 method of Grimme with Becke-Johnson damping was used to correct for the Van der Waals forces.[47] Solutions to the Kohn-Sham equations were calculated using a plane wave basis set with a cutoff of 400 eV. For all calculations, spin polarization was included. For facile convergence towards the magnetic ground state, an initial magnetic moment of 3.0 was set for each atom. We used the first order Methfessel-Paxton method to apply smearing to the electrons, with a smearing width of 0.2 eV. For gas phase calculations, a smearing width of 5×10^{-4} eV was applied. A dipole correction normal to the surface was applied to correct for the dipole moment of the adsorbates. For gas phase calculations, a dipole correction was applied in all directions.[48,49] For the supported nanorods, a *k*-point mesh of $1 \times 1 \times 1$, i.e. the Γ -point, is used. With this sampling, *k*-point conversion was reached, such that an increase in the number of *k*-points resulted in energy differences of less than 1 meV/atom. The dimensions of the nanorod cells are 16.14 × 16.79 × 25.00 $Å^3$ for the Al₂O₃-supported Conanorod, and 17.74 × 19.55 × 26.49 Å³ for the TiO₂supported Conanorod. The gas phase molecules were placed in cells of 10.00 × 10.00×10.00 Å³. We optimized the stable states and the transition states using an ionic convergence criterion of 1×10^{-4} eV and an electronic convergence criterion of 1×10^{-5} eV. It was verified that all residual forces are less than 0.1 eV/Å for the adsorbate atoms. All energies are corrected for the vibrational zeropoint energy (ZPE). We searched for transition states with the nudged elastic band (NEB) method as implemented in VASP. We verified that the optimized transition states show one imaginary frequency in the direction of the reaction coordinate.

The generation of the supported nanorods is described in an earlier work, where these models were used to study CO dissociation over several Co sites.[50] For convenience, we will reiterate on the most salient details of the procedure here. Images of the nanorods can be found in Figure B.2-B.3. The support consists of four layers, of which the bottom two layers are frozen. Co atoms were added on top of the support, layer by layer, to create the nanorods. The atoms were allowed to relax after each successive addition of a layer of atoms. The step-edge sites were created by adding only half the number of atoms as normally required to form a full layer. Where this partial layer ends, the stepped sites appear. An assessment of the stability of the nanorod models is reported in the previous study (in its Supporting Information or in Appendix A of this thesis).[50] For both nanorods we calculated the Co detachment energy, i.e. the required energy to migrate a Co atom from the nanorod to a remote site on the Al_2O_3 or TiO_2 support. Given typical catalytic operating conditions for these materials, the detachment energies found are prohibitively high to assume these nanorods to be thermally stable.

4.2.2 Microkinetic simulations

Microkinetic simulations were conducted using MKMCXX.[20] This software solves a set of ordinary differential equations describing adsorption, reaction and desorption events by performing time integration. The absolute and relative tolerances were set to 1×10^{-9} . It was verified that the simulations were time-converged at all temperatures.

The net adsorption rate r_i of gas phase species i is modelled as

$$r_i = k_{i, \text{ ads}} \theta_* p_i - k_{i, \text{ des}} \theta_i \tag{1}$$

where $k_{i, ads}$ and $k_{i, des}$ are the temperature-dependent adsorption and desorption rate constants, respectively, θ_* the fraction of free sites at the catalytic surface, p_i the partial pressure of species *i*, and θ_i the fraction of sites occupied by species *i*. The temperature-dependent adsorption rate constant of gas molecules, that in their transition state for adsorption lose one translational degree of freedom, is described by

$$k_{i, \text{ ads}} = S \frac{A}{\sqrt{2\pi m_i k_{\text{B}} T}}$$
(2)

where *S* is the sticking coefficient that is set to unity, *A* the area of the adsorption site, m_i the mass of the adsorbate *i*, k_B the Boltzmann constant and *T* the

temperature. The desorption rate of adsorbates is calculated from $k_{i, ads}$ and the equilibrium constant for adsorption, which yields

$$k_{i, \text{des}} = S \frac{A}{\sqrt{2\pi m k_{\text{B}} T}} \exp\left(\frac{\Delta H_{\text{ads}}}{RT}\right) \exp\left(\frac{S_{\text{gas}}}{R}\right) \frac{1}{Q_{\text{ads}, \text{v}}}$$
(3)

where $Q_{ads,v}$ is the product of the vibrational partition functions of the adsorbate in the adsorbed state, S_{gas} the entropy in the gas phase as calculated using the Shomate equation (*vide infra*), *R* the gas phase constant, and ΔH_{ads} is the adsorption enthalpy as given by

$$\Delta H_{\rm ads} = \Delta E_{\rm elec} + \Delta E_{\rm zpe} + \frac{NRT}{2} \tag{4}$$

with ΔE_{elec} the electronic adsorption energy, ΔE_{zpe} the difference in the zeropoint energy (ZPE) between the adsorbed and gas phase state, and *N* the total number of rotational and translational degrees of freedom in the gas phase. To incorporate the entropic contribution in the adsorption and desorption rate, the gas phase entropy is calculated using the Shomate equation for CO, H₂, H₂O and CH₄.[51]

The reaction rate for surface reactions is given by

$$k_{\text{react}} = \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q} \exp\left(\frac{-\Delta E_{\text{act}}}{k_{\text{B}}T}\right)$$
(5)

where Q^{\ddagger} and Q are the partition functions of the activated complex and the corresponding initial state, respectively, and ΔE_{act} is the energy needed to activate the reaction.

For elementary reaction steps with very low barriers, the application of the zeropoint energy correction sometimes results in negative barriers. Cleary, such barriers are in disagreement with transition state theory as the rates associated with such barriers will decrease with increasing temperature. On top of that, negative (or otherwise very low) barriers cause numeric instabilities in the ordinary differential equation solver of MKMCXX. To correct this undesirable behavior, any barriers found that are lower than 5 kJ/mol are adjusted. This adjustment involves increasing both the forward and backward barrier by the same value such that the lowest of the two barriers corresponds to 5 kJ/mol. The systematic adjustment of both the forward and the backward barrier ensures that the equilibrium constant for the elementary reaction step is not affected by the correction, ensuring invariance of overall reaction thermodynamics.

To account for the effect of lateral interactions, a lateral interaction potential was introduced as described in a previous work.[41] Lateral interactions can result in a significant decrease in adsorption rate or increase in desorption rate as the surface coverage increases. This is due to a decrease in available electrons at the catalytic surface and an increase in repulsion from other adsorbates. In our simulations, no penalty was applied for adsorption below ¼ coverage. Between ¼ and ¾ coverage, the penalty increases exponentially with increasing coverage. A typical adsorption energy penalty $E_{i,pen}^{lat}$ of species *i* at coverage θ_{lat} is given by

$$E_{i,\text{pen}}^{\text{lat}} = E_{i,\text{pen}}^{\theta = \theta_{\text{total}}} \frac{101^{\theta_{\text{lat}}} - 1}{100}$$
(6)

where $E_{i,\text{pen}}^{\theta=1}$ is the maximum adsorption energy penalty of species *i*, i.e. the penalty applied at maximum coverage.

For the simulations in this work, between ³/₄ and full coverage, the penalty was set to the maximum value. The fraction of the maximum penalty that is applied as a function of surface coverage is plotted in Figure B.1. Due to its small size, adsorbed H only counts as half an adsorbate in calculating the coverage

$$\theta_{\text{lat}} = \theta_{\text{total}} - \theta_* - 0.5 \,\theta_{\text{H}} \tag{7}$$

Sensitivity analysis towards pressure, temperature and barriers is conducted in MKMCXX by evaluating the reaction order, the apparent activation energy and the degree of rate control, respectively. The reaction orders are calculated according to

$$n_i = p_i \frac{\partial \ln r^+}{\partial p_i} \tag{8}$$

where n_i is the reaction order of species *i*, p_i is the partial pressure of species *i* and r^+ is the forward rate of the product of interest. The apparent activation energy is evaluated *via*

$$\Delta E_{\rm act}^{\rm app} = RT^2 \frac{\partial \ln r^+}{\partial T} \tag{9}$$

where r^+ is the forward rate of the product of interest. The degree of rate control X of elementary reaction step i is defined as[52]

$$X_{i} = \left(\frac{\partial \ln r}{\partial \ln k_{i}}\right)_{k_{j\neq i},K_{j}}$$
(10)

where r is the net rate of the product of interest, and where all the equilibrium constants K_j and the rate constants k of all other reaction steps except i are held constant. All the above quantities are evaluated numerically by means of a five-point centered finite difference stencil.[53]

4.2.3 Charge analysis

The computation of the atomic charges was done with the Chargemol program to calculate DDEC6 charges[54,55] and the Bader method to calculate Bader charges.[56] For these electronic structure calculations, the number of Kohn-Sham orbitals *N* used was set such that

$$N \ge 1.2 \cdot \max\left(\frac{N_{\text{elec}} + N_{\text{ion}}}{2}, \frac{5N_{\text{elec}}}{3}\right) \tag{11}$$

where N_{elec} is the number of valence electrons in the system and N_{ion} the number of ions. The charges visualized in this work are the average of the charges obtained by the Bader and DDEC6 methods.

4.3 Results and discussion

4.3.1 Models

To study interfacial effects of the support material on the rate of methane formation in Co-catalyzed FTS, we compare three active site motifs. Two of these correspond to active sites located in the vicinity of the metal-support interface, while the third, acting as a reference, represents a site at a significant distance from any interface. The models are visualized in Figure 4.1. In Figure B.2-B.4, top, front and side views of the models are shown. In all three scenarios, step-edge sites are chosen as these allow for facile CO activation, a necessary requirement for producing longer hydrocarbons under FTS conditions.[41] To model the metal-support interfaces, one-dimensionally extended Co nanorods are used which mimic the catalyst nanoparticle perimeter without incurring the computational cost of simulating large Co nanoparticles. These nanorods are placed on γ -Al₂O₃(110) and rutile-TiO₂(110), which are the most stable surface terminations for these two support materials.[57,58] Both these support materials are commonly used in FTS[59], and are known to have similar affinity with Co atoms[60,61], which is an important factor for the morphology of the Co nanoparticle.[62] The nanorods were constructed to expose a step-edge site configuration as indicated by the darker shaded atoms in Figure 4.1. The interfacial active sites are compared to a B_5 site on the extended Co(11 $\overline{2}$ 1) surface (Figure 4.1c), as explored previously by Zijlstra *et al.*[41] This site will act as the reference where there is no influence from the support on the reactivity.



Figure 4.1: (a) Al_2O_3 -supported Co nanorod, (b) TiO_2 -supported Co nanorod, and (c) Co($11\overline{2}1$) DFT models. For each model, the Co atoms of one step-edge site are colored dark blue.

The distance from the center of the step-edge site to the nearest atom of the support surface is 4.62 Å for the Al₂O₃-supported Co nanorod and 5.66 Å for the TiO₂-supported Co nanorod. Attempts to construct step-edge site configurations with a B₅ motif closer to the interface failed due to unfavorable stacking of the Co atoms. To quantify the similarity in the geometry of the active sites, we calculated the minimized Hilbert-Schmidt (mHS) norm[63,64] (details are provided in Section B.1) between the sites explored in this work as shown in Table 4.1. If two sites are equivalent, their mHS norm will be zero as can be readily seen from the zero entries on the diagonal of Table 4.1. As a reference, a terrace site on Co(0001) (as visualized in Figure B.5) is included. The mHS between $(11\overline{2}1)$ and (0001) is 5.72, which is significantly higher than the mHS values between the step-edge sites. Based on the low mHS values between the step-edge sites, it can be concluded that active site geometries are sufficiently similar by which effects caused by the local stacking of the metal atoms in the active sites can be considered negligible, allowing for an effective comparison between the three active site configurations.

mHS norms	γ-Al ₂ O ₃ (110)	r-TiO ₂ (110)	(1121)	(0001)
γ-Al ₂ O ₃ (110)	0.00	1.09	0.68	5.20
r-TiO ₂ (110)	1.09	0.00	0.74	5.90
(1121)	0.68	0.74	0.00	5.72
(0001)	5.20	5.90	5.72	0.00

Table 4.1: Minimized Hilbert-Schmidt norms among the three B_5 active site configurations explored in this work.

4.3.2 Reaction energetics

All elementary reaction steps relevant to CO methanation were explored for the three active site configurations. Pathways for C-O bond scission include both direct as well as hydrogen-assisted routes *via* HCO and COH. O removal was considered *via* twofold direct hydrogenation of O as well as by disproportionation of two adjacent hydroxyl species. In Figure 4.2, the reaction energetics for CO methanation are shown. The corresponding images of the geometries of stable and transition states are provided in Figure B.6-B.9. For comparison purposes, in Figure 4.2c the reaction energies over Co(11 $\overline{2}$ 1) as reported earlier by Zijlstra *et al.*[41] are shown as well. Barriers that are lower than 5 kJ/mol were adjusted according to the procedure as described in the Methods section. All barriers are migration corrected, i.e. they are calculated with respect to the most stable adsorption site of the corresponding intermediates.

4.3.2.1 Adsorption and desorption

It was found that H₂ readily dissociates upon adsorption on the nanorods due to the strong Co-H interaction and that this adsorption step only involves an entropic adsorption barrier owing to a loss of degrees of freedom. In comparison to Co(11 $\overline{2}$ 1), where an adsorption energy of 85 kJ/mol was found, elevated H₂ adsorption energies of 132 and 116 kJ/mol were observed for the Al₂O₃ and TiO₂ systems, respectively. Similarly, for CO and H₂O it was also found that they bind stronger to the nanorods as compared to the extended surface. CO adsorption energies of 205 and 219 kJ/mol are observed for the Al₂O₃ and TiO₂ systems in comparison to 171 kJ/mol for Co(11 $\overline{2}$ 1). H₂O is associated with adsorption energies of 71 and 80 kJ/mol for the Al₂O₃ and TiO₂ systems, whereas Co(11 $\overline{2}$ 1) provides an H₂O adsorption energy of 53 kJ/mol. Finally, whereas CH₄ can adsorb weakly on Co(11 $\overline{2}$ 1) with an adsorption energy of 6 kJ/mol, CH₃ hydrogenation to form CH₄ on the nanorods results in the immediate desorption of CH₄.



Figure 4.2: Reaction energy networks of CO methanation over (a) the Al_2O_3 supported Co nanorod, (b) the TiO₂-supported Co nanorod, and (c) Co(11 $\overline{2}1$). The values are given in kJ/mol and include the ZPE correction. The arrows indicate the direction of the forward barrier for proceeding from one reaction intermediate to another. Values for Co(11 $\overline{2}1$) are adapted from Zijlstra *et al.*[41]

4.3.2.2 Thermodynamic assessment

Based on the DFT-computed gas phase electronic energies and frequencies, we computed the zero-point energy corrected electronic reaction energy, the reaction enthalpy and the reaction Gibbs free energy, of which the latter two were compared to experimental data. The experimental reaction enthalpy and Gibbs free energy were obtained by means of the Shomate equation and tabulated values for the reactants and products.[51,65] Details of the procedure are provided in Section B.2.

The zero-point energy corrected electronic reaction energy for CO methanation was found to be -229 kJ/mol, fully consistent with the earlier calculations of Zijlstra and coworkers.[41] The reaction enthalpy and Gibbs free energy were both computed at T = 225 °C and p = 1 atm, corresponding to typical reaction conditions.[66] At the DFT/PBE+D3 level of theory, a reaction enthalpy of $\Delta_R H_{225^\circ C} = -252$ kJ/mol in comparison to the experimental value of $\Delta_R H_{225^\circ C} = -215$ kJ/mol is found. For the Gibbs free reaction energy, a value of $\Delta_R G_{225^\circ C} = -126$ kJ/mol was found in comparison to the experimental value of $\Delta_R G_{225^\circ C} = -97$ kJ/mol. Clearly, the DFT/PBE+D3 results are in relatively poor agreement with experimental values. We attribute this deviation to inaccuracies of the harmonic approximation used in determining the vibrational modes as well as the application of the ideal gas approximation.

Because the calculated enthalpy and entropy corrections based on statistical thermodynamics are in poor agreement with experimental values, as shown in the previous paragraph, enthalpy and entropy corrections for the microkinetic models are based on experimental results and computed by means of the Shomate equation (vide supra). Moreover, to ensure that the overall thermodynamics of the reaction is adequately reproduced by the microkinetic models, we apply the same correction as done earlier by Zijlstra *et al.* to the CO adsorption energy.[41] The reaction enthalpy at the standard reference state is $\Delta_{\rm R}H_{25^{\circ}\rm C}$ = -206 kJ/mol. PBE is known to overestimate CO adsorption on metal surfaces[67–69] and we therefore apply a correction to the CO adsorption energy of +22.72 kJ/mol with respect to the values shown in Figure 4.2. This value is the difference between the computed reaction enthalpy of -229 kJ/mol and the reaction enthalpy known from experiment of -206 kJ/mol. This correction ensures that in the microkinetic models, the thermodynamics of the chemokinetic network are correct. By inserting the correct reaction enthalpy $\Delta_{\rm R}H_{25^{\circ}\rm C}$ = -206 kJ/mol as a reference and the Shomate parameters for the reactants and products in gas phase into the microkinetic model, MKMCXX can calculate the gas phase enthalpy and entropy at higher (reaction) temperatures as well. This ensures that also at reaction temperature, the thermodynamics of the simulations correspond to the experimental values. The reaction energy diagrams including this correction can be found in Figure B.11-B.14.

4.3.2.3 Surface reactions

CO dissociation

Direct CO dissociation barriers were computed earlier for the nanorods[50] and correspond to 148 and 129 kJ/mol for the Al_2O_3 and TiO_2 systems, respectively. The CO dissociation barrier over Co($11\overline{2}1$) corresponds to 100 kJ/mol, significantly lower compared to the barriers found for the nanorods. The Al₂O₃ system shows a higher dissociation barrier than observed for the TiO₂ system. We assign this difference to a subtle variation in the dissociation pathway, as can be derived from the geometries shown in Figure B.7 and B.9. Whereas oxygen is only coordinated to two Co atoms in the transition state (TS) for the Al₂O₃ system, it coordinates to three Co atoms in the TS for the TiO₂ system. The latter more intimate pathway of CO bond scission for the TiO₂ nanorod results in a lowering of the TS in comparison to the Al₂O₃ nanorod, resulting in a more facile CO dissociation. For hydrogen-assisted CO dissociation routes over step-edges, higher effective barriers are typically found in comparison to the direct route.[41,70,71] Indeed, whereas C-O bond scission over the Al₂O₃-supported nanorod involves a barrier of 148 kJ/mol, the effective dissociation barrier for the HCO and COH pathways correspond to 198 and 192 kJ/mol, respectively. For the TiO₂-nanorod, effective barriers for these latter two pathways correspond to 177 and 220 kJ/mol which are both higher than the barrier of 129 kJ/mol found for direct dissociation.

CH_x hydrogenation

After C-O bond scission, methane formation proceeds by the sequential hydrogenation of CH_x (x = 0-3) intermediates. The transition states associated with these elementary reaction steps are visualized in Figure B.7, B.9 and B.10. From Figure 4.2, it can be seen that hydrogenation of carbonaceous species involves slightly higher barriers on the nanorods as compared to the extended surface. The effective barriers for C hydrogenation to CH_4 are 247, 156 and 120 kJ/mol for the Al_2O_3 -supported nanorod, the TiO_2 -supported nanorod and $Co(11\overline{2}1)$, respectively. These differences between the nanorods and the extended surface are predominantly caused by the high stability of C on the nanorods as these systems offer a fourfold adsorption site close to the interface. In addition to the fourfold site being an excellent adsorption site for C[72], the

Co atoms at the support interface are also more coordinatively unsaturated, further enhancing the stability of C.[73]

CH formation is associated with activation energies of 79, 43 and 65 kJ/mol for the Al_2O_3 and TiO_2 -supported systems and $Co(11\overline{2}1)$, respectively. For the three systems considered, the hydrogenation of C proceeds in a very similar pattern; carbon is adsorbed in a fourfold site and the hydrogenation event proceeds *via* a migration of an H species from an adjacent site through a bridged configuration. In all three transition states, two Co atoms are shared between C and H. Consequently, fairly similar barriers are observed. H species are slightly less stable on the TiO₂-nanorod resulting in a somewhat lower barrier compared to the Al_2O_3 -nanorod.

The hydrogenation of CH to form CH₂ was found to be more difficult on the supported nanorods ($\Delta E_{act} = 92 \text{ kJ/mol}$ and 110 kJ/mol for the Al₂O₃- and TiO₂- supported systems, respectively) in comparison to the extended Co(1121) surface (47 kJ/mol). On the extended surface, CH is positioned at a threefold site, with H approaching over a single Co atom that is highly undercoordinated. For the TS of the TiO₂-system, CH is also positioned at a threefold site, but H is bonded in a threefold configuration rather than in a top mode. For the TS on Al₂O₃, CH is at a fourfold site and H is at a bridge site. The lower barrier observed for the extended surface is attributed to its TS exploiting a highly undercoordinated Co atom at the step-edge, which are known to be excellent sites for σ -bond formation.[74–76] It should be noted that alternative active site configurations were sought. However, despite our best efforts more stable transition states, where H is bonded atop to a highly undercoordinated Co atom, were not found. For completeness, the alternative geometries of the TSs explored for the TiO₂ system are provided in Figure B.15.

CH₂ hydrogenation to form CH₃ has an activation energy of 85, 60, and 41 kJ/mol for the Al₂O₃- and TiO₂-supported systems and Co(11 $\overline{2}$ 1), respectively. Whereas H is bonded in a bridged orientation in the TS of the extended surface, hydrogenation over the nanorods proceeds by H approaching the CH₂ moiety from a top position. According to the same reasoning as for CH₂ formation, the lower barrier observed for the extended surface is attributed to these highly undercoordinated Co atoms at the step-edge being excellent sites for σ -bond formation.[74–76] Whereas such a motif can be present on the extended surface, we found that it is unstable on the nanorods.

Finally, CH₄ formation is associated with a high barrier on the Al₂O₃-supported nanorod (112 kJ/mol) compared to the TiO₂-supported nanorod and the $Co(11\overline{2}1)$ extended surface (61 and 76 kJ/mol, respectively). Whereas CH₃ is adsorbed on a single Co atom in a top configuration for the TiO₂-nanorod and for $Co(11\overline{2}1)$, for the Al₂O₃-nanorod it is adsorbed in a bridged manner. The higher activation energy of the TS on the Al_2O_3 -supported nanorod can be explained by the concept of bond order conservation. According to this principle, the total binding capability of a single atom with its surrounding atoms remains constant.[73,77,78] When applying this principle to a surface Co atom, it suggests that a Co atom bonded to multiple adsorbates distributes its binding power among them, leading to weaker individual chemical bonds compared to a Co atom bonded to a single adsorbate. Consequently, since CH₃ and H share only one of the two Co atoms that H is bonded to in the transition state on the TiO₂supported nanorod and on the extended surface, but both Co atoms that H is bonded to on the Al₂O₃-supported nanorod, the transition state on the Al₂O₃supported nanorod is less stabilized, leading to a higher activation energy. In line with the bond order conservation principle, this rationalizes the higher barrier observed for the Al₂O₃-system.

H₂O formation

On the nanorods, the elementary reaction steps towards H_2O formation show higher barriers compared to those on Co(1121). Hydroxyl formation is activated by 151 and 149 kJ/mol for the Al₂O₃- and TiO₂-nanorods, whereas the barrier found for the extended surface is 89 kJ/mol. Because there is no Co atom shared between O and H in the TS of Co(1121), this is a relatively stable TS, following the bond order conservation principle. This favorable configuration on Co(1121) is enabled by the existence of two parallel rows of low-coordinated atoms at just the right distance for O-H bond formation (Figure B.10). Conversely, the Al₂O₃and TiO₂-nanorods provide only TS configurations where a Co atom is shared between O and H.

The barriers for hydroxyl hydrogenation by a hydrogen adatom (direct hydrogenation of OH) are 192, 101 and 123 kJ/mol for Al_2O_3 , TiO_2 and $Co(11\overline{2}1)$, respectively. The comparatively high barrier for the Al_2O_3 -supported system is caused by the sharing of a single Co atom in its TS, while the other two systems involve TSs without sharing any atoms.

The formation of H_2O can also proceed *via* the disproportionation of two adjacent hydroxyl species and appears more favorable than direct

hydrogenation for all three systems. Water formation from two hydroxyl species is associated with barriers of 99, 85 and 61 kJ/mol. In contrast to direct OH hydrogenation, in the OH-OH disproportionation reaction H is bonded to O rather than Co, the former being a weaker bond. This provides a more facile pathway but requires the formation of two hydroxyl species first. We anticipate that the preferred pathway under catalytic conditions depends on the surface coverage of OH, which in turn is governed by the ease of its formation.

4.3.3 Microkinetic simulations

To assess the activity and preferred mechanism for CO hydrogenation to methane for the three candidate systems, we performed microkinetic simulations based on the reaction energetics presented in the previous sections. All simulations were conducted in the temperature range of 120-520 °C with intervals of 10 °C and at a pressure of 1 bar. This is a typical operating pressure Co-catalyzed methanation studies.[79]



Figure 4.3: Intrinsic activity for CH_4 production of the Al_2O_3 - and TiO_2 -nanorods and the Co(1121) extended surface.

Figure 4.3 shows the CH₄ production rates for the three catalyst systems. The highest activity was observed for Co($11\overline{2}1$), which shows a turnover frequency (TOF) of 7.69 s⁻¹. Significantly lower rates are observed for the supported nanorods. Compared to the dual-site microkinetic model of Zijlstra *et al.*, which is composed of the linked kinetic networks corresponding to Co(0001) and Co($11\overline{2}1$) in a 10:1 active site ratio[41], our single-site Co($11\overline{2}1$) model is about an order of magnitude more active. This difference arises from the high barrier for CO dissociation on the Co(0001) surface. Our microkinetic model for the

Co($11\overline{2}1$) surface shows a two orders of magnitude difference in activity compared to experimental data.[12,79] Experimentally determined reaction rates are typically normalized to the number of exposed surface atoms, which can be determined using chemisorption studies or approximated through microscopy. In the microkinetic model normalization is instead based on a single active site configuration, which leads to an overprediction because the catalytic surface is not exclusively composed of this active site motif. Although it is possible to correct for the overprediction by multiplying the calculated rates by a surface abundancy factor[40,80], we continue using the original numbers since our primary interest is comparing the activity between different active site motifs.

In Figure 4.4, the molar fluxes for all three catalyst systems are shown. The molar rates for the transformations between the reaction intermediates are provided at T = 230 °C. The dominant pathway corresponding to the highest rates linking the reactants and products is highlighted in green. For all catalyst systems, direct CO dissociation is preferred over the hydrogen-assisted routes. This is in agreement with the lowest effective barrier for CO scission corresponding to the direct pathway for all three catalysts, and aligns with the experimental work of Chen *et al.*[79]

Water formation proceeds *via* OH-OH disproportionation over Co($11\overline{2}1$) and the Al₂O₃-supported nanorod, and *via* direct hydroxyl hydrogenation over the TiO₂-supported nanorod. Despite OH-OH disproportionation showing a lower barrier for all catalytic systems than direct hydroxyl hydrogenation, the preferred pathway also depends on the rate of hydroxyl formation, which is a strongly endothermic reaction step on the nanorods. For TiO₂-supported nanorod, OH-OH disproportionation presents an effective barrier of 217 kJ/mol, while the direct route has a significantly lower effective barrier of 167 kJ/mol, making it the favored pathway. Conversely, for the Al₂O₃-supported nanorod the effective barriers for the direct and OH-OH disproportionation pathways stand at 243 kJ/mol and 202 kJ/mol respectively, favoring OH-OH disproportionation.



Figure 4.4: Molar flux diagrams of CO methanation at 230 °C on (a) Al_2O_3 supported Co nanorod, (b) TiO₂-supported Co nanorod, and (c) Co(1121) in s⁻¹. The green arrows show the dominant reaction pathways at this temperature.

In Figure 4.5, the surface coverage and degree of rate control (DRC) analyses are presented for the three catalysts. The reaction orders and apparent activation energies are provided in Figure B.16-B.19. From Figure 4.5, Figure B.16 and B.18, it can be seen that Co(1121) and the Al₂O₃-supported nanorod show the same qualitative trends. In the low temperature regime, the surface is mainly covered by co-adsorbed CO and H. CO dissociation is difficult as indicated by this step being strongly rate-determining. With increasing temperature, there is sufficient thermal energy available in the system to overcome the CO dissociation barrier as can be seen by the gradual decrease in its DRC coefficient. Furthermore, the dissociation reaction benefits from a higher number of available surface sites, which increases with temperature. As the DRC coefficient for CO dissociation decreases, there is a corresponding increase in the DRC coefficient for CH₃ hydrogenation. The scarcity of empty sites at intermediate temperature and a comparatively low rate for oxygen removal causes CO dissociation to become a rate-inhibiting step as it results in the deposition of O, which reduces the availability of active sites required for other reaction steps such as H_2 adsorption. At elevated temperature, this form of rate-inhibition remains present although it is now caused by the OH-OH disproportionation reaction which despite leading to H₂O formation, does not vet decrease the number of available sites in this elementary reaction step. Comparing the DRC analyses of $Co(11\overline{2}1)$ and the Al₂O₃-supported nanorod shows that the latter exposes larger absolute values for its DRC coefficients at intermediate temperature. This result is directly linked to the strong adsorption of reactants observed for the Al₂O₃-supported nanorod in comparison to Co($11\overline{2}1$). A significantly smaller part of the surface hosts free active sites as a consequence of the strong binding of the reactants and intermediates to the nanorod. Compared to the extended surface, this leads to a significantly greater inhibition of the CO dissociation rate (which reduces the number of free sites) and a stronger rate control of methane formation (which creates free sites).

For Co(11 $\overline{2}$ 1) and the Al₂O₃-supported nanorod, the reaction orders in CO and H₂ (Figure B.16 and B.18) are in line with these observations. At low temperature, a near-zero reaction order in CO and a negative reaction order in H₂ is observed. As CO dissociation is limited by the number of available sites, increased H₂ adsorption is unfavorable, reflected in a negative order in H₂. With increasing temperature, the order in CO becomes negative whereas the order in H₂ becomes positive. As the CO dissociation rate is higher at intermediate temperatures, adsorption of CO would lead to more surface poisoning by C and O, resulting in a negative reaction order in CO. For the extended surface, surface

poisoning by C and O is less pronounced because more free sites are available at lower temperature. At intermediate temperatures, CH₃ hydrogenation becomes rate limiting and more H₂ adsorption would benefit the overall reaction rate as it increases the rate of CH₃ hydrogenation. At elevated temperatures, surface poisoning by C or O becomes negligible owing to the increased abundance of free sites. This effect is also visible in the apparent activation energy ΔE_{act}^{app} (Figure B.19), which for the Al_2O_3 -supported nanorod shows a minimum at 260 °C after which ΔE_{act}^{app} increases again. The apparent activation energy of the extended surface is approximately 0 kJ/mol at temperatures above 300 °C, indicating that at these temperatures the adsorption, desorption and reaction events are wellbalanced, and the optimal production rate is reached. The high reaction orders in H₂ and the high DRC coefficients observed for CH₃ hydrogenation are in accordance with transient kinetic experiments that show that at 260 °C, the CH₄ formation rate is to be controlled mainly by CH_x hydrogenation rather than CO dissociation.[79] The impact of the hydrogen coverage on the activity is in line with experimental results.[81]

Compared to the Al_2O_3 -supported nanorod, on the TiO₂-supported nanorod CO dissociation proceeds more easily. As the barrier for water formation is relatively high compared to that for CO dissociation, a high surface coverage of O and H is observed at low temperature. The DRC analysis reflects this situation. At low temperature, all elementary reaction steps associated with water formation are rate-controlling with hydroxyl hydrogenation showing the largest value. The DRC coefficient for hydroxyl hydrogenation increases with increasing temperature at the expense of direct CO dissociation, which becomes a rateinhibiting step owing to the deposition of hard-to-remove oxygen species. A further increase in temperature results in a decrease of the DRC coefficient of hydroxyl hydrogenation and an increase of the DRC coefficient corresponding to methyl hydrogenation. From the surface abundance as function of temperature as well as the DRC analysis, it appears that the TiO₂-supported nanorod has a weakened hydrogenation capability compared to $Co(11\overline{2}1)$, which is not only reflected in its low rate of oxygen hydrogenation at low temperature, but also in an increase of carbonaceous species (C and CH) with increasing temperature. Indeed, the significantly higher barrier for CH hydrogenation (110 kJ/mol) limits efficient CH₄ formation from surface carbon. This also shows in the positive order in H₂ and negative order in CO (Figure B.17) over the entire temperature range. H₂ adsorption favors oxygen and CH_x hydrogenation, while more CO adsorption leads to more C and O that need to be hydrogenated. The apparent activation energy for the TiO_2 -supported nanorod (Figure B.19) decreases only slowly with increasing temperature, in line with the strong adsorption of the reactants.



Figure 4.5: (a,c,e) Surface coverages and (b,d,f) degree of rate control (DRC) analyses for CO methanation on (a,b) Al_2O_3 -supported Co nanorod, (c,d) TiO₂-supported Co nanorod, (e,f) and Co(11 $\overline{2}1$).

We observe that the TiO₂-supported nanorod exhibits lower effective barriers for CO dissociation, CH_x hydrogenation and H_2O formation than the Al_2O_3 supported nanorod. This results in a methanation rate of two to four orders of magnitude higher on TiO₂ than on Al_2O_3 , depending on the operating temperature. Comparing the three models, it is evident from Figure 4.4 and 4.5 that the lower activity of the nanorods compared to the extended surface is directly linked to the number of available sites these surfaces expose under operating conditions. In line with the Sabatier principle[82], the nanorods bind too strongly with the reaction intermediates leading to partial poisoning and a reduced activity in comparison to Co(11 $\overline{2}1$).

4.3.4 Active sites at the interface versus extended surface

From the previous section it is apparent that surface sites located at the metalsupport interface, as modelled by the nanorod systems, are significantly less active than those present at further distance from that interface, as modelled by the extended surfaces. To unravel the underlying factors behind this activity difference, we investigate three possible causes: (1) increased adsorption strength of reactants at the interface, (2) heightened CO dissociation barriers at the interfacial sites and (3) interfacial metal-support charge transfer effects.

4.3.4.1 Adsorption and desorption at the interface

From the reaction energy diagram of the three catalyst systems (Figure B.14 and Figure 4.2), it can be seen that significantly larger adsorption energies for CO and H₂ are observed on the nanorods than on Co(11 $\overline{2}$ 1). To assess the impact of the adsorption strength on the overall activity of the catalyst system, the microkinetic models based on the DFT-derived energetics were modified. In this modification, uniformity among the surface barriers for all elementary reaction steps between the three models, with exception of the steps involving adsorption and desorption, was imposed. Adsorption and desorption steps remained in line with the barriers seen in the original models. For the surface reaction steps, all forward barriers were set to 80 kJ/mol whereas all backward barriers were set to 37.3 kJ/mol for the Al₂O₃-supported nanorod, 43.4 kJ/mol for the TiO₂-supported nanorod and 60.4 kJ/mol for the Co(11 $\overline{2}$ 1) surface, the latter three sets of barriers ensuring a consistent reaction energy for all three models. The corresponding potential energy diagrams are shown in Figure B.20.

Variation in CH₄ formation rates for these models remains within four orders of magnitude across all temperatures (Figure B.21), whereas the original models displayed a maximum difference exceeding seven orders of magnitude (Figure 4.3). Although in Figure B.21 a smaller difference in CH₄ formation rate between the extended surface and the nanorods is observed than for the original models, at a typical FTS reaction temperature of T = 230 °C the extended surface still shows a two orders of magnitude higher production. This demonstrates that

under typical operation conditions the increased stability of the reactants at the interface results in a significantly lower activity.

4.3.4.2 Enhanced CO dissociation at the interface

Next, we modify the CO dissociation TS for the nanorods so that the forward barrier is the same as that found for the Co(11 $\overline{2}$ 1) extended surface (ΔE_{act} = 99 kJ/mol). By only modifying the TS height, the overall thermodynamics of the reaction is kept consistent. The activity as function of temperature is shown in Figure B.22; for both nanorods a decreased activity is observed at *T* > 180 °C, compared to the original simulations. For the TiO₂-supported nanorod CO dissociation is rate-inhibiting and lowering of its barrier results in decreased activity owing to enhanced poisoning by O; this is in line with the results of Figure 4.5d. For the Al₂O₃-supported nanorod, the decreased activity is caused by enhanced surface poisoning by C species whose surface abundance is significantly increased as a result of more facile CO dissociation. These results show that a facile CO dissociation barrier does not improve the CO TOF but rather leads to active site poisoning by strongly adsorbed C and O.

As CO dissociation was found to be rate-inhibiting for the TiO₂-supported nanorod as a consequence of inefficient removal of the oxygen produced from the dissociation reaction, we also explored a scenario where this rate-inhibition is removed by lowering the barriers for O and OH hydrogenation. Under this condition, multiple elementary reaction steps become rate-controlling, at 230 °C H₂O desorption having the largest DRC coefficient (as shown in Figure B.23). Although the TOF increases by about an order of magnitude with respect to the original model, the activity for the TiO₂-supported nanorods remains at least two orders of magnitude less active than the Co(11 $\overline{2}1$) surface (Figure B.24).

4.3.4.3 Charge transfer effects at the interface

Cobalt atoms at the interface that are in contact with the support exchange electrons with the support atoms. To understand the extent of this charge transfer, we studied the effective nuclear charges *via* Bader and DDEC6 charge analyses (Figure 4.6). As there is no clear consensus in the literature which method is more accurate, the average between the two was used, noting that both methods produce qualitatively the same trends. The highest variations in atomic charge are observed for the lowest layer of each of the nanorods, i.e. the layer in direct contact with the support (Figure 4.6a (Al₂O₃) and e (TiO₂)). The charges on the Co atoms range between -0.4 and 0.4 *e* for both nanorods. From Figure 4.6e, we can readily see that the Co charges in the bottom layer of the TiO₂

nanorod portray an ordered structure, commensurate with their stacking on the support. The Co atoms in direct contact with the oxygen atoms of the support effectively donate electron density to those oxygen atoms, in line with the higher electronegativity of the oxygen atoms as compared to Co. For the Co atoms in contact with Ti, electron density is gained due to Co being more electronegative than Ti. These effects rapidly diminish with increasing distance of the Co atoms from the support; for the second, third and fourth layers (Figure 4.6f-h), significantly lower deviations from the neutral charge, i.e. Co⁰, are observed.



Figure 4.6: Atomic charges in *e* of the Co nanorod supported by (a-d) Al_2O_3 and (e-h) TiO₂. From left to right, each subfigure shows the next layer of the nanorod, while retaining previous visualized layers. For example, the second column (b,f) shows the first and second layer of each of the nanorods. The Co atoms are colored depending on their charge, which is the average of the Bader charge and DDEC6 charge. Red atoms correspond to O, grey atoms correspond to Al or Ti.

For the nanorod on Al_2O_3 , no clear ordered pattern is observed as the γ - $Al_2O_3(110)$ surface does not offer a favorable alignment to accommodate the packing of the Co atoms. Here, the same observation is made as for the TiO₂ nanorod, i.e. the Co atoms that are in direct contact with the oxygen atoms from the support donate electron density and the Co atoms in direct contact with Al, which is less electronegative than Co, gain electron density. The unfavorable alignment of the first layer means that some Co atoms in the second layer (Figure 4.6b) still expose relatively large deviations from the neutral charge, depending on their contact with either Al or O. As seen from Figure 4.6c and d, the third and fourth layers on the Al_2O_3 nanorod do not carry large excess charges, in line with their relatively large distance from the support. The charge analysis thus shows that only Co atoms that directly bond to the Al_2O_3 or TiO_2 supports show significant charge differences. For reference, the atomic charges of $Co(11\overline{2}1)$ are visualized in Figure B.25.

Table 4.2: Total, average, minimum and maximum Bader and DDEC6 charges of the Co atoms of the step-edge sites on the Al_2O_3 -supported Co nanorod (Co_{NR}/Al_2O_3), TiO₂-supported Co nanorod (Co_{NR}/TiO_2), and Co(1121).

System	Bader charge [<i>e</i>]			DDEC6 charge [e]				
	Total	Average	Min.	Max.	Total	Average	Min.	Max.
Co_{NR}/Al_2O_3	-0.06	-0.01	-0.06	0.03	-0.08	-0.02	-0.12	0.11
(5 Co)								
Co_{NR}/TiO_2	0.03	0.01	-0.04	0.04	0.01	0.00	-0.10	0.05
(5 Co)								
Co(1121)	-0.03	0.00	-0.04	0.02	0.07	0.01	-0.11	0.14
(6 Co)								

Table 4.2 shows the total, average, minimum and maximum charges of the Co atoms that make up the $B_5(-like)$ sites on the Al_2O_3 - and TiO_2 -supported Co nanorods and on the Co(1121) extended surface. Since the nanorod active sites lie at the second or third layer of the nanorod as displayed in Figure 4.6, the absolute charges on the Co atoms are relatively small with respect to Co⁰. Furthermore, these charges are very similar to those found for the B_5 site on the Co(1121) surface, although the Al_2O_3 -supported nanorod shows slightly larger deviations owing to the irregular structure of its first layer.

Despite the vacant active site showing only a marginal difference in charge with respect to Co⁰, adsorption of a strongly electronegative reaction intermediate might still induce a different charge transfer effect between the different active sites. To assess this, we conducted an additional charge analysis for CO adsorbed on the three active site configurations (Section B.3). The charge accumulation on CO after adsorption on the three active sites is found to be fairly similar (see Table B.1). Moreover, there is no systematic trend between the total or average charge on the Co atoms in the vacant configuration and the charge accumulation

of CO upon its adsorption. We thus infer that the charge accumulation on CO is predominantly induced by the specific active site topology and experiences a negligible influence by the support. These findings are in line with our earlier work.[50] A single layer of Co atoms already provides a strong shielding effect, and the charge transfer effect is thus very local in nature.

4.3.5 Epitaxial effect

The charge transfer effects induced by the support rapidly diminish as the distance from the interface increases. Therefore, charge transfer cannot explain the observed differences in reactant stability and methanation activity between the nanorods and the extended surface. The additional microkinetic simulations described in section 4.3.4.1, which differ only by the adsorption energy of reactants and products, suggest that the stability of the species on the surface primarily determines the methanation activity of these active sites. To understand the causes of the differences in adsorption strength between the nanorods and the extended surface, we examine the geometries of the most stable adsorption sites for the reactants and intermediates, as shown in Figure B.6 and B.8. Typically, the species are adsorbed at or near the active site configuration. Since the active site topologies are highly similar, as indicated by their low mHS norms, this cannot explain the differences in stability. However, when examining the first coordination shell of the active site, we observe significant differences. For the extended surface, the first coordination shell corresponds to the HCP stacking of the bulk. In contrast, for the supported nanorods the stacking of cobalt atoms in the first coordination shell is strongly influenced by the surface topology of the support, as shown in Figure B.27. Due to the alignment with the support's top layer structure, an active site topology with a B₅ motif required for a facile CO dissociation comes at the expense of creating coordinatively undersaturated metal atoms which, in contrast to atoms in extended surfaces, give rise to very strong metal-adsorbate interactions. This explains how the epitaxial effect contributes to the reduced activity of the interfacial sites.

4.3.6 Methane formation at the Co/Al_2O_3 and Co/TiO_2 interface

The epitaxial effect has important implications for the activity and selectivity under Fischer-Tropsch synthesis conditions. From Figure 4.5, it was seen that at a typical operating temperature of 200 °C, CO dissociation controls the overall activity for the Al_2O_3 -supported nanorod and the extended Co(1121), whereas for the TiO₂-supported nanorod the rate is predominantly controlled by OH hydrogenation to H₂O. As such, the former two catalytic surfaces operate under a CO dissociation limited kinetic regime whereas the latter surface operates in an oxygen removal limited regime. [20,83,84] For the extended Co($11\overline{2}1$) surface, the production of long-chain hydrocarbons under typical CO hydrogenation conditions was observed, both experimentally as well as *via* microkinetic simulations.[41,85,86] Using the lumped kinetics model of Van Santen and Markvoort[83,84], we can establish the expected chain-growth probability α under typical FTS conditions based on the rates of CO activation and oxygen removal. This model was obtained by a first-principles microkinetic study of the FT reaction and can be used to estimate the FT selectivity based on activation energies.[83,84] The authors lumped the hydrogenation steps together with other reaction steps, rather than considering all elementary reaction steps explicitly. Using this model, the authors show that high CO activation barriers lead to low chain growth and predominantly methane formation.[84] Oxygen removal and CO dissociation are kinetically linked via the O species, and so the barriers for the CO dissociation reaction and oxygen hydrogenation to water are lumped together in a single effective dissociation reaction rate constant k_{diss} .



Figure 4.7: Chain-growth parameter α as function of the (effective) dissociation rate constant k_{diss} using the lumped kinetics model of Van Santen and Markvoort.[83,84]
The results of the kinetic model displayed in Figure 4.7 reveal that the effective rate constant for CO dissociation for the Al_2O_3 - and TiO_2 -supported nanorods is respectively five and three orders of magnitude smaller than that observed for $Co(11\overline{2}1)$ at T = 200 °C. Assuming the most ideal situation where the nanorods would exhibit a facile C+C coupling step similar to $Co(11\overline{2}1)$, the lumped kinetics model predicts a chain-growth probability of approximately 0.1 for the TiO_2 -supported nanorod and nearly zero for the Al_2O_3 -supported nanorod. Clearly, the low rates for CO dissociation and oxygen removal on the nanorods result in a near-negligible selectivity towards longer hydrocarbon chains and almost exclusive production of methane, albeit at a very low rate.

4.4 Conclusions

In this study, we investigated the impact of support materials on the activity and selectivity in Fischer-Tropsch synthesis (FTS) of active sites located at the nanoparticle-support interface by examining charge transfer and epitaxial effects. Charge transfer, induced by differences in electronegativity, alters the electronic properties of active sites and in turn the reaction barriers, without changing the site geometry. In contrast, epitaxial effects change the geometry of active sites to align with the support structure, directly influencing reaction energy barriers. We used two Co nanorod models on γ -Al₂O₃(110) and rutile-TiO₂(110) supports to explore these effects and compared the results with the extended Co(11 $\overline{2}1$) surface.

It was found that the metal-support interfaces of Co/Al₂O₃ and Co/TiO₂ exhibit significantly lower CO methanation activity compared to active sites located farther from the interface. Despite these interfaces showing similar reaction barriers due to the availability of a step-edge site, this reduced activity is primarily caused by the high stability of reaction intermediates at the interface, leading to surface poisoning by H, O, C, and to a lesser extent by CO. The enhanced stability of these intermediates at the interface is attributed to epitaxial effects, where alignment with the support induces coordinatively undersaturated metal atoms in the proximity of the active site. Our findings indicate that this difference in adsorbate stability is not driven by charge transfer effects. While charge transfer significantly alters the atomic charges of Co atoms directly bonded to the support, the atomic charges of Co atoms further away do not differ more than the typical variations seen for extended surfaces. This observation is consistent for both supports. The Co atoms directly bonded to the support exhibit either a positive or negative charge, depending on their proximity to oxygen atoms or Al/Ti atoms in the support.

Additionally, we find that CO dissociation is more challenging at the interfacial sites than on the extended surface. When disregarding the high stability of intermediates at the interface and assuming efficient C+C coupling, the rate of hydrocarbon chain formation at the interface remains negligibly low due to the relatively high CO dissociation and oxygen removal barriers at these sites.

In conclusion, this study demonstrates that while the nature of the support plays a crucial role in influencing the activity and selectivity of Fischer-Tropsch synthesis by e.g. tuning the dispersion and reduction properties of catalytic nanoparticles, its influence on interfacial active sites is consistent among the supports studied in this work. Due to the presence of coordinatively undersaturated metal atoms originating from the alignment of the crystal structures of the active material and the support, interfacial sites exhibit very strong adsorption energies. This results in those sites mainly producing methane, not participating in chain-growth and providing an almost negligible contribution to the overall particle's catalytic activity.

4.5 References

- [1] C. Schmidt, S. Kureti, Chem. Ing. Tech. 94 (2022) 1747–1755.
- [2] D.D. Suppiah, W.M.A.W. Daud, M.R. Johan, Energy Fuels 35 (2021) 17261– 17278.
- [3] J.G. Speight, in: Handbook of Industrial Hydrocarbon Processes, Elsevier, 2020, pp. 343–386.
- [4] P.B. Webb, I.A.W. Filot, in: Comprehensive Inorganic Chemistry III (Third Edition), Elsevier, Netherlands, 2023, pp. 354–380.
- [5] D. Chakrabarti, A. De Klerk, V. Prasad, M.K. Gnanamani, W.D. Shafer, G. Jacobs, D.E. Sparks, B.H. Davis, Ind. Eng. Chem. Res. 54 (2015) 1189–1196.
- [6] J. Van De Loosdrecht, F.G. Botes, I.M. Ciobica, A. Ferreira, P. Gibson, D.J. Moodley, A.M. Saib, J.L. Visagie, C.J. Weststrate, J.W. Niemantsverdriet, in: Comprehensive Inorganic Chemistry II, Elsevier, 2013, pp. 525–557.
- [7] M. Corral Valero, P. Raybaud, Catal. Lett. 143 (2013) 1–17.
- [8] T.O. Eschemann, J.H. Bitter, K.P. De Jong, Catal. Today 228 (2014) 89–95.
- [9] T.O. Eschemann, K.P. De Jong, ACS Catal. 5 (2015) 3181–3188.
- [10] C.E. Kliewer, S.L. Soled, G. Kiss, Catal. Today 323 (2019) 233–256.
- [11] L.M. Van Koppen, A. Iulian Dugulan, G. Leendert Bezemer, E.J.M. Hensen, J. Catal. 420 (2023) 44–57.
- [12] J.P. Den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. De Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [13] E. Iglesia, J. Catal. 137 (1992) 212–224.
- [14] M. Boudart, in: Advances in Catalysis, Elsevier, 1969, pp. 153–166.
- [15] G.A. Somorjai, J. Carrazza, Ind. Eng. Chem. Fund. 25 (1986) 63–69.
- [16] E. Iglesia, Appl. Catal. A 161 (1997) 59–78.

- [17] N. Fischer, E. Van Steen, M. Claeys, J. Catal. 299 (2013) 67–80.
- [18] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. Van Dillen, K.P. De Jong, J. Am. Chem. Soc. 128 (2006) 3956–3964.
- [19] A.M. Saib, D.J. Moodley, I.M. Ciobîcă, M.M. Hauman, B.H. Sigwebela, C.J. Weststrate, J.W. Niemantsverdriet, J. Van De Loosdrecht, Catal. Today 154 (2010) 271–282.
- [20] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [21] A. Tuxen, S. Carenco, M. Chintapalli, C.-H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A.P. Alivisatos, G. Thornton, W.-F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, J. Am. Chem. Soc. 135 (2013) 2273–2278.
- [22] R.A. Van Santen, I.M. Ciobîcă, E. Van Steen, M.M. Ghouri, in: Advances in Catalysis, Elsevier, 2011, pp. 127–187.
- [23] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Langmuir 26 (2010) 16558–16567.
- [24] A. Parastaev, V. Muravev, E. Huertas Osta, A.J.F. Van Hoof, T.F. Kimpel, N. Kosinov, E.J.M. Hensen, Nat. Catal. 3 (2020) 526–533.
- [25] R.C. Reuel, C.H. Bartholomew, J. Catal. 85 (1984) 78-88.
- [26] C. Hernández Mejía, T.W. van Deelen, K.P. de Jong, Nat. Commun. 9 (2018) 4459.
- [27] A. Barbier, A. Tuel, I. Arcon, A. Kodre, G.A. Martin, J. Catal. 200 (2001) 106– 116.
- [28] G.-Z. Bian, N. Fujishita, T. Mochizuki, W.-S. Ning, M. Yamada, Appl. Catal. A 252 (2003) 251–260.
- [29] G. Prieto, A. Martínez, P. Concepción, R. Moreno-Tost, J. Catal. 266 (2009) 129–144.
- [30] O. Borg, P. Dietzel, A. Spjelkavik, E. Tveten, J. Walmsley, S. Diplas, S. Eri, A. Holmen, E. Rytter, J. Catal. 259 (2008) 161–164.
- [31] N. Fischer, E. Van Steen, M. Claeys, Catal. Today 171 (2011) 174–179.
- [32] A. Martínez, J. Rollán, M.A. Arribas, H.S. Cerqueira, A.F. Costa, E.F. S.-Aguiar, J. Catal. 249 (2007) 162–173.
- [33] M.P.C. Van Etten, M.E. De Laat, E.J.M. Hensen, I.A.W. Filot, J. Phys. Chem. C 127 (2023) 15148–15156.
- [34] G. Pacchioni, H.-J. Freund, Chem. Soc. Rev. 47 (2018) 8474–8502.
- [35] T.W. Van Deelen, J.J. Nijhuis, N.A. Krans, J. Zečević, K.P. De Jong, ACS Catal. 8 (2018) 10581–10589.
- [36] G. Prieto, M.I.S. De Mello, P. Concepción, R. Murciano, S.B.C. Pergher, A. Martínez, ACS Catal. 5 (2015) 3323–3335.
- [37] T.W. van Deelen, C. Hernández Mejía, K.P. de Jong, Nat. Catal. 2 (2019) 955– 970.
- [38] T. Van Heerden, E. Van Steen, Faraday Discuss. 197 (2017) 87–99.

- [39] R. Zhang, M. Athariboroujeny, G. Collinge, V. Iablokov, K.D. Shumilov, L. Kovarik, A.N. Alexandrova, N. Kruse, J.-S. McEwen, ACS Catal. 10 (2020) 14722–14731.
- [40] M.P.C. van Etten, B. Zijlstra, E.J.M. Hensen, I.A.W. Filot, ACS Catal. 11 (2021) 8484–8492.
- [41] B. Zijlstra, R.J.P. Broos, W. Chen, G.L. Bezemer, I.A.W. Filot, E.J.M. Hensen, ACS Catal. 10 (2020) 9376–9400.
- [42] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251–14269.
- [43] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15–50.
- [44] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953-17979.
- [45] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758–1775.
- [46] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [47] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 32 (2011) 1456–1465.
- [48] G. Makov, M.C. Payne, Phys. Rev. B 51 (1995) 4014–4022.
- [49] J. Neugebauer, M. Scheffler, Phys. Rev. B 46 (1992) 16067–16080.
- [50] R.D.E. Krösschell, E.J.M. Hensen, I.A.W. Filot, J. Phys. Chem. C 128 (2024) 8947–8960.
- [51] M. Chase, NIST-JANAF Thermochemical Tables, 4th ed, American chemical society, Washington, D.C, 1998.
- [52] C.T. Campbell, ACS Catal. 7 (2017) 2770–2779.
- [53] M. Abramowitz, I.A. Stegun, Handbook of Mathematical Functions: With Formulas, Graphs, and Mathematical Tables, Dover Publications, 1965.
- [54] T.A. Manz, N.G. Limas, RSC Adv. 6 (2016) 47771–47801.
- [55] N.G. Limas, T.A. Manz, RSC Adv. 6 (2016) 45727-45747.
- [56] M. Yu, D.R. Trinkle, J. Chem. Phys. 134 (2011) 064111.
- [57] J. Yang, H. Wang, X. Zhao, Y.L. Li, W.L. Fan, RSC Adv. 6 (2016) 40459–40473.
- [58] S. Kanungo, Y. Su, M.F. Neira d'Angelo, J.C. Schouten, E.J.M. Hensen, Catal. Sci. Technol. 7 (2017) 2252–2261.
- [59] G. Jacobs, T.K. Das, Y. Zhang, J. Li, G. Racoillet, B.H. Davis, Appl. Catal. A 233 (2002) 263–281.
- [60] I.C.T. Have, J.J.G. Kromwijk, M. Monai, D. Ferri, E.B. Sterk, F. Meirer, B.M. Weckhuysen, Nat. Commun. 13 (2022) 324.
- [61] C. Qiu, Y. Odarchenko, Q. Meng, P. Cong, M.A.W. Schoen, A. Kleibert, T. Forrest, A.M. Beale, Chem. Sci. 11 (2020) 13060–13070.
- [62] L. Ji, J. Lin, H.C. Zeng, J. Phys. Chem. B 104 (2000) 1783–1790.
- [63] W.F. Reinhart, A.W. Long, M.P. Howard, A.L. Ferguson, A.Z. Panagiotopoulos, Soft Matter 13 (2017) 4733–4745.
- [64] I.A.W. Filot, M.P.C. Van Etten, D.W.J.G. Trommelen, E.J.M. Hensen, JOSS 8 (2023) 5710.
- [65] C.H. Shomate, J. Phys. Chem. 58 (1954) 368–372.
- [66] J. W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, 1st ed., Wiley, 2003.
- [67] P.J. Feibelman, B. Hammer, J.K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, J. Dumesic, J. Phys. Chem. B 105 (2001) 4018–4025.

- [68] F. Abild-Pedersen, M.P. Andersson, Surf. Sci. 601 (2007) 1747–1753.
- [69] J. Wellendorff, T.L. Silbaugh, D. Garcia-Pintos, J.K. Nørskov, T. Bligaard, F. Studt, C.T. Campbell, Surf. Sci. 640 (2015) 36–44.
- [70] S. Shetty, A.P.J. Jansen, R.A. Van Santen, J. Am. Chem. Soc. 131 (2009) 12874–12875.
- [71] I.A.W. Filot, R.J.P. Broos, J.P.M. Van Rijn, G.J.H.A. Van Heugten, R.A. Van Santen, E.J.M. Hensen, ACS Catal. 5 (2015) 5453–5467.
- [72] A. Banerjee, V. Navarro, J.W.M. Frenken, A.P. Van Bavel, H.P.C.E. Kuipers, M. Saeys, J. Phys. Chem. Lett. 7 (2016) 1996–2001.
- [73] R.A. Van Santen, M. Neurock, Catal. Rev. 37 (1995) 557-698.
- [74] D.A.J.M. Ligthart, R.A. Van Santen, E.J.M. Hensen, J. Catal. 280 (2011) 206– 220.
- [75] J. Wei, J. Catal. 225 (2004) 116–127.
- [76] A. Parmaliana, F. Arena, F. Frusteri, S. Coluccia, L. Marchese, G. Martra, A.L. Chuvilin, J. Catal. 141 (1993) 34–47.
- [77] R.A. Santen, ed., Modern Heterogeneous Catalysis: An Introduction, 1st ed., Wiley, 2017.
- [78] Van Santen, R. A., Zonnevylle, M.C., Jansen, P.J., Phil. Trans. R. Soc. Lond. A 341 (1992) 269–282.
- [79] W. Chen, R. Pestman, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen, ACS Catal. 7 (2017) 8050–8060.
- [80] E.B. Sterk, A.-E. Nieuwelink, M. Monai, J.N. Louwen, E.T.C. Vogt, I.A.W. Filot, B.M. Weckhuysen, JACS Au 2 (2022) 2714–2730.
- [81] J. Yang, Y. Qi, J. Zhu, Y.-A. Zhu, D. Chen, A. Holmen, J. Catal. 308 (2013) 37– 49.
- [82] P. Sabatier, Ber. Dtsch. Chem. Ges. 44 (1911) 1984–2001.
- [83] A.J. Markvoort, R.A. van Santen, P.A.J. Hilbers, E.J.M. Hensen, Angew. Chem. Int. Ed. 51 (2012) 9015–9019.
- [84] R.A. Van Santen, A.J. Markvoort, M.M. Ghouri, P.A.J. Hilbers, E.J.M. Hensen, J. Phys. Chem. C 117 (2013) 4488–4504.
- [85] W. Chen, I.A.W. Filot, R. Pestman, E.J.M. Hensen, ACS Catal. 7 (2017) 8061– 8071.
- [86] B. Zijlstra, R.J.P. Broos, W. Chen, I.A.W. Filot, E.J.M. Hensen, Catal. Today 342 (2020) 131–141.
- [87] R.A. Horn, C.R. Johnson, Matrix Analysis, 23. print, Cambridge Univ. Press, Cambridge, 2010.

B. Appendix



Figure B.1: Lateral interactions penalty.



Figure B.2: (upper left) Top, (upper right) front, (lower left) back, and (lower right) side views of the Al_2O_3 -supported Co nanorod.



Figure B.3: (upper left) Top, (upper right) front, (lower left) back, and (lower right) side views of the TiO_2 -supported Co nanorod.



Figure B.4: (left) Top, (middle) front and (right) side views of Co($11\overline{2}1$).

Section B.1: Hilbert-Schmidt norm

To compare the geometry of two sites, we calculate the minimized Hilbert-Schmidt (mHS) norm[63,87], which can be used as a measure of similarity. If two sites are equal, their mHS norm will be zero. To calculate the mHS norm for two sites, for each site we produce a distance matrix wherein each matrix element represents the distance between two atoms of that site. Upon comparison of two sites, the distance matrices of the two sites are subtracted from each other, resulting in the difference matrix $\|\mathbf{A}\|_{HS}$. Since different labelling of the atoms of the site results in different difference matrices, all possible difference matrices are calculated. For all these matrices, the Hilbert-Schmidt norm is calculated according to:

$$\|\mathbf{A}\|_{HS} = \sqrt{\sum_{i,j} a_{ij}^2}$$

The lowest Hilbert-Schmidt norm is the minimized Hilbert-Schmidt norm.



Figure B.5: Top view of Co(0001).



Figure B.6: Stable state geometries of the Al₂O₃-supported Co nanorod.



Figure B.7: Transition state geometries of the Al₂O₃-supported Co nanorod.



Figure B.8: Stable state geometries of the TiO₂-supported Co nanorod.















Figure B.9: Transition state geometries of the TiO₂-supported Co nanorod.



Figure B.10: Transition state geometries of $Co(11\overline{2}1)$.[41]

Section B.2: Shomate equation

The enthalpy and Gibbs free energy of the gas phase species involved in CO methanation at several temperatures were calculated using tabulated values and the Shomate equation.[51,65]

The gas phase enthalpy H_T^0 at temperature *T* is calculated as follows:

$$H_T^0 - H_{298.15}^0 = A \cdot t + \frac{1}{2} \cdot B \cdot t^2 + \frac{1}{3} \cdot C \cdot t^3 + \frac{1}{4} \cdot D \cdot t^4 - \frac{E}{t} + F - H$$
(1)

where $H_{298.15}^0$ is the standard enthalpy in kJ/mol at 298.15 K, *T* the temperature in K and t = T/1000.

The gas phase entropy S_T^0 at temperature *T* is calculated with:

$$S_T^0 = A \cdot \ln t + B \cdot t + \frac{1}{2} \cdot C \cdot t^2 + \frac{1}{3} \cdot D \cdot t^3 - \frac{E}{2 \cdot t^2} + G$$
(2)



Figure B.11: Reaction energy diagram of the dominant reaction pathway at 230 °C for the Al_2O_3 -supported Co nanorod.



Figure B.12: Reaction energy diagram of the dominant reaction pathway at 230 $^{\circ}$ C for the TiO₂-supported Co nanorod.



Figure B.13: Reaction energy diagram of the dominant reaction pathway at 230 °C for Co($11\overline{2}1$).



Figure B.14: Reaction energy diagram of the dominant reaction pathways at 230 °C for the three models.



Figure B.15: Alternative transition states for CH_2 formation on the TiO_2 -supported Co nanorod.



Figure B.16: Reaction orders for the Al₂O₃-supported Co nanorod.



Figure B.17: Reaction orders for the TiO₂-supported Co nanorod.



Figure B.18: Reaction orders for $Co(11\overline{2}1)$.







Figure B.20: Reaction energy diagram of CO methanation with adapted barriers.



Figure B.21: Production rate of CH₄ with adapted barriers.



Figure B.22: Production rate of CH₄ with adapted CO dissociation barrier.



Figure B.23: DRC for CO methanation on TiO_2 -supported Co nanorod with adapted OH and O hydrogenation barriers.



Figure B.24: Production rate of CH_4 with adapted O and OH hydrogenation barriers.

Section B.3: Electron donation to adsorbed CO

We computed the electron density that is donated to CO when adsorbed on the three step-edge sites. These charges can be found in Table B.1. CO is adsorbed fivefold on the nanorods and sixfold on the extended surface. Images of these geometries are shown in Figure B.26. The charge of CO differs only a little for both nanorods. CO on Co($11\overline{2}1$) contains an increased electron density compared to the nanorods. This higher electron density is located at the C atom, while the O atomic charges are very similar. We suggest that this difference between the extended surface and the nanorods is due to the sixfold instead of fivefold adsorption on the extended surface. Upon sixfold adsorption, there is one extra Co atom that donates electron density to CO. We hypothesize that this is the cause for the small increase in electron density of CO on the extended surface, because the atomic charges of the empty sites are much alike.

	Bader charge [e]	DDEC6 charge [e]
Al ₂ O ₃ -supported nanorod	-0.82	-0.20
TiO ₂ -supported nanorod	-0.79	-0.21
Co(1121)	-0.93	-0.25

Table B.1: Bader and DDEC6 charges of CO adsorbed on the step-edge sites.



Figure B.25: Atomic charges of Co($11\overline{2}1$). The average of the Bader charge and DDEC6 charge [*e*] is visualized, with (a) the same charge range as Figure 4.6 for comparison with the nanorods, and (b) a smaller range to visualize the local differences. A darker color means that more electron density is present at that atom.



Figure B.26: CO adsorbed on step-edge sites. CO adsorbed on (left) Al_2O_3 -supported Co nanorod, (middle) TiO_2 -supported Co nanorod, and (right) Co(11 $\overline{2}$ 1).



Figure B.27: Co atoms of first coordination shell of step-edge sites on (left) the Al_2O_3 -supported nanorod, and (right) the TiO_2 -supported nanorod. The step-edge site is colored darker blue, the first coordination shell is colored lighter blue.

5. First-principles Modelling of CO Methanation over Small Cobalt Nanoparticles Supported on Al₂O₃

Abstract

In Co-catalyzed Fischer-Tropsch synthesis (FTS), smaller nanoparticles typically exhibit lower turnover frequencies (TOF) and increased methane selectivity. To elucidate these experimental trends, we employ density functional theory (DFT) to investigate 1 nm Co nanoparticles supported on $Al_2O_3(110)$. Three nanoparticle models are considered: a highly undercoordinated Co₂₀ nanoparticle (NP), a hemispherical Co_{55} NP, and a Co_{52} NP featuring a B₅-like pocket site. Microkinetic simulations reveal that the Co₂₀ nanoparticle is catalytically inactive due to poisoning of active sites by CO and H, which bind extremely strongly to this nanoparticle. This suggests that undercoordinated active sites on very small nanoparticles, like Co₂₀, are prone to poisoning, rendering them ineffective for catalysis. Comparing the reactivity of the Co₅₅ NP with extended Co surface models containing B₅ sites, we observe a three-ordersof-magnitude lower TOF for the Co₅₅ NP. This confirms that the absence of a B₅like site significantly impacts reactivity. The Co₅₂ NP model with a B₅-like pocket site demonstrates that these sites are crucial not only for efficient CO scission, but also for facilitating C and O hydrogenation. Interfacial active sites at the nanoparticle-support boundary of the Co₅₅ NP show much higher activity than sites located further away from the interface, identifying interfacial sites as the predominant contributors to methane formation. The rate determining step, CHO dissociation, has a lower barrier on the interfacial site than on the top site. Electronic structure analysis reveals that this enhanced interfacial activity is caused by an enhanced adsorbate induced restructuring of the interfacial active site, resulting in a higher coordination number of CHO and a more stable adsorption state. This leads to an increased electron donation to CHO, leading to a higher C-O bond activation and a more facile scission. These findings provide critical insights into the performance limitations of sub-optimal-sized nanoparticles in structure-sensitive catalytic reactions.

5.1 Introduction

Nanoparticle catalysis represents a key area in heterogeneous catalysis, offering the advantage of high metal exposure and increased catalytic activity when supported metal nanoparticles (NPs) are employed.[1] Controlling NP size serves as a powerful synthetic strategy to tailor nanoparticle morphology and optimize catalytic performance.[2,3] The design and development of supported NP catalysts is often guided by a descriptor-based approach, linking measurable properties to catalytic activity.[4–7] A critical aspect of NP catalysts is their potential structure-sensitivity, where reactivity is dictated by the nature and distribution of active sites, which are inherently influenced by the catalyst structural characteristics, particle size being the most important one.

The Haber-Bosch process, the Sabatier reaction and Fischer-Tropsch synthesis (FTS) are prime examples of reactions where catalytic activity depends on nanoparticle size. [2,3,8] Understanding structure-sensitivity in these processes is vital for optimizing operations and advancing technologies like CO₂-based FTS and CO₂ hydrogenation to CH₄ using renewable H₂. Among these systems, the particle size dependency in FTS has been a particular focus of extensive experimental studies. Iglesia et al. showed that for nanoparticles between 10 and 200 nm, turnover frequency (TOF) is size-independent.[9] Bezemer et al. demonstrated that for carbon nanofiber-supported Co catalysts with NPs between 2.6 and 27 nm, particles smaller than 6 nm exhibit lower CO hydrogenation activity and higher CH₄ selectivity. They attributed this partly to CO-induced surface reconstruction observed via EXAFS under reaction conditions.[2] Similarly, Melaet et al. found that SiO₂-supported Co NPs smaller than 10 nm display reduced CO hydrogenation activity and increased CH₄ selectivity, linked to a relatively higher hydrogenation activity compared to the CO dissociation rate in smaller particles.[10] These trends are corroborated across various supports, including carbon nanotubes [11], γ -Al₂O₃[12,13], α -Al₂O₃[14], TiO₂[15], δ - $/\theta$ -Al₂O₃[16], carbon spheres[17], and SiO₂.[18,19]

Figure 5.1 provides a comprehensive summary of experimental studies, showcasing TOF data from multiple investigations. [2,11-13,15,17,18,20-23] An optimal NP size of 6–10 nm is widely recognized, as smaller particles appear to be less active per exposed Co atom, while larger NPs underutilize cobalt atoms since here a lower fraction of the Co atoms is exposed. Multiscale studies provide further insight, revealing that only sufficiently large NPs exhibit a high surface abundancy of B₅-like active sites. [24-26] These sites provide significantly lower CO dissociation barriers than flat surface sites, allowing for high FTS activity, which explains the observed trend. [27-30]



Figure 5.1: CO turnover frequency (TOF) of Co catalysts with varying particle size. The dashed line serves to guide the eye. Data obtained from references [78,2,11–13,15,17,18,20–23].

While the role of larger nanoparticles in FTS is relatively well understood, the role of smaller nanoparticles remains less clear. Small Co NPs lack the step-edge or B₅-like sites essential for high activity, as such sites require layered terraces for their stability.[31,32] For smaller particles, CO-induced blocking of active edge or corner sites has been observed[33], as well as particle flattening, which increases the number of Co-SiO₂ interfacial sites that possess a lower activity.[21] In situ studies reveal that under methanation conditions small NPs remain metallic but may undergo structural changes due to C adatoms from CO.[2,10,22] Oxidation by water vapor significantly reduces activity in Co/SiO_2 NPs under certain conditions[19], while partial oxidation improves performance on TiO₂-supported NPs.[10] Hindered H₂ dissociation on small particles further limits methanation.[22] CO dissociation, a critical reaction step for FTS[27], has been extensively studied. [27,34,35] How determining CO dissociation is for the overall conversion, depends on catalyst structure and operating conditions.[36] Smaller NPs facilitate a hydrogen-assisted CO dissociation route[37], whereas larger particles enable direct dissociation.[36]

Understanding the reactivity of small nanoparticles is essential not only to clarify their specific contributions but also because their interfacial sites can act as

proxy for analogous sites on larger NPs. Small Co nanoparticles possess distinctive characteristics, including high interface-to-bulk ratios and low coordination. Consequently, their role cannot be accurately studied with extended surface models, instead detailed simulations of small, supported nanoparticles are required. Here, we investigate CO methanation on 1 nm Co NPs supported on Al_2O_3 using density functional theory (DFT) calculations and microkinetic simulations. Three nanoparticle models are considered: a highly undercoordinated Co_{20} nanoparticle (average coordination number of CN = 4.7(of exposed Co atoms)), a hemispherical Co_{55} nanoparticle, and a Co_{52} nanoparticle featuring a B₅-like active site, the latter two having higher coordination numbers (CN = 7.1-7.6). This study compares the reactivity of these NPs with results from extended surfaces, which act as a proxy for larger nanoparticles.[38] We find that low-coordinated NPs are inactive due to poisoning. High-coordinated NPs in absence of a B₅ site exhibit lower activity compared to > 6 nm NPs, showing the importance of such sites in facilitating CO scission and C and O hydrogenation. In absence of B₅-like sites, CO dissociation occurs via CHO. Interfacial sites near the Al_2O_3 support exhibit conversion rates two orders of magnitude higher than sites further distanced from the interface, which arises from easier C-O bond breaking in CHO species near the support. The higher activation of the C-O bond in CHO at the interface stems from an adsorbate-induced restructuring of the interfacial site, which results in a more stable adsorption and more electron donation to CHO, weakening its internal C-0 bond. The turnover frequency of interfacial sites on the 1 nm NP aligns well with experimental TOF values for 2.6 nm Co NPs, suggesting that methane production in small Co NPs primarily originates from these interfacial sites.

5.2 Methods

5.2.1 DFT

Plane-wave density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP)[39,40]. The projectoraugmented wave (PAW) method was employed to describe the core electrons.[41,42] The Perdew-Burke-Ernzerhof (PBE) functional[43] is used to describe electron exchange and correlation. To correct for the Van der Waals forces, the DFT-D3 method of Grimme with Becke-Johnson damping was used.[44] Due to its robustness across the periodic table, this method is suitable for large systems.[45] Solutions to the Kohn-Sham equations were calculated using a plane wave basis set with a cut-off of 400 eV. For all calculations, spin polarization was included. For facile convergence towards the magnetic ground state, an initial magnetic moment of 3.0 was set for each atom. We used the first order Methfessel-Paxton method to apply smearing to the electrons, with a smearing width of 0.2 eV. For gas phase calculations, a smearing width of 5×10^{-10} ⁴ eV was applied. A dipole correction normal to the surface was applied to correct for the dipole moment of the adsorbates. For gas phase calculations, a dipole correction was applied in all directions. [46,47] For the supported nanoparticles, a k-point mesh of $1 \times 1 \times 1$, i.e. the Γ -point, is used. With this sampling, k-point conversion was reached, such that an increase in the number of *k*-points resulted in energy differences of less than 1 meV/atom. The dimensions of the Co_{20} nanoparticle cell are $16.14 \times 16.79 \times 20.00$ Å³, the Co₅₂ and Co₅₅ nanoparticles are placed in a $16.14 \times 16.79 \times 25.00 \text{ Å}^3$ cell. The gas phase molecules were placed in cells of $10.00 \times 10.00 \times 10.00$ Å³. We optimized the stable states and the transition states using an ionic convergence criterion of 1×10^{-4} eV and an electronic convergence criterion of 1×10^{-5} eV. It was verified that all residual forces are less than 0.1 eV/Å for the adsorbate atoms. All energies are corrected for the vibrational zero-point energy (ZPE). We searched for transition states with the nudged elastic band (NEB) method as implemented in VASP. We verified that the optimized transition states show an imaginary frequency in the direction of the reaction coordinate.

The generation of the supported nanoparticles is described in earlier work, where these models were used to study CO dissociation over several Co sites.[48] For convenience, we will reiterate on the most salient details of the procedure here. Images of the nanoparticles can be found in Figure C.1-C.3. As supports for the nanoparticles we used γ -Al₂O₃(110) because this is reported to be thermodynamically the most stable termination.[49] Four layers of the support material were placed in a supercell, the bottom two layers were frozen. After adding the nanoparticle, we enlarged the vacuum space above the slab to accommodate adsorbates leaving a distance of at least 12 Å between neighboring super cells. The Co₅₅/Al₂O₃ nanoparticle model is based on the Ni₅₅ particle on the γ -Al₂O₃(110) surface of Silaghi, Comas-Vives and Copéret[51], where the Ni was replaced by Co. Starting from the hemispherical cobalt particle of the Co_{55}/Al_2O_3 model, three cobalt atoms were removed to create a pocket site with a B₅-site resembling motif for the Co_{52}/Al_2O_3 model. The Co_{20}/Al_2O_3 model was created by removing 35 Co atoms from the hemispherical Co₅₅/Al₂O₃ nanoparticle. The twenty Co atoms that are left form a flat pancake-like shape, with at most two Co atoms on top of each other. An assessment of the stability of the nanoparticle models is reported in a previous study (in its Supporting Information or in Appendix A of this thesis). [48] For the Co₅₅/Al₂O₃ nanoparticle we calculated the Co detachment energy, i.e. the required energy to migrate a Co atom from the nanorod to a remote site on the Al_2O_3 support. Given typical catalytic operating conditions for these materials, the detachment energy is sufficiently high so we can assume that this nanoparticle is thermally stable.

5.2.2 Microkinetic simulations

Microkinetic simulations were conducted using MKMCXX.[52] This software solves a set of ordinary differential equations describing adsorption, reaction and desorption events by performing time integration. The absolute and relative tolerances were set to 1×10^{-9} . It was verified that the simulations were time-converged at all temperatures.

The net adsorption rate r_i of gas phase species *i* is modelled as

$$r_i = k_{i, \text{ ads}} \theta_* p_i - k_{i, \text{ des}} \theta_i \tag{1}$$

where $k_{i, ads}$ and $k_{i, des}$ are the temperature-dependent adsorption and desorption rate constants, respectively, θ_* the fraction of free sites at the catalytic surface, p_i the partial pressure of species *i*, and θ_i the fraction of sites occupied by species *i*. The temperature-dependent adsorption rate constant of gas molecules, that in their transition state for adsorption lose one translational degree of freedom, is described by

$$k_{i, \text{ ads}} = S \frac{A}{\sqrt{2\pi m_i k_{\text{B}} T}}$$
(2)

where *S* is the sticking coefficient that is set to unity, *A* the area of the adsorption site, m_i the mass of the adsorbate *i*, k_B the Boltzmann constant and *T* the temperature. The desorption rate of adsorbates is calculated from $k_{i, ads}$ and the equilibrium constant for adsorption, which yields

$$k_{i, \text{ des}} = S \frac{A}{\sqrt{2\pi m k_{\text{B}} T}} \exp\left(\frac{\Delta H_{\text{ads}}}{RT}\right) \exp\left(\frac{S_{\text{gas}}}{R}\right) \frac{1}{Q_{\text{ads}, \text{v}}}$$
(3)

where $Q_{ads,v}$ is the product of the vibrational partition functions of the adsorbate in the adsorbed state, S_{gas} the entropy in the gas phase as calculated using the Shomate equation (*vide infra*), *R* the gas phase constant, and ΔH_{ads} is the adsorption enthalpy as given by

$$\Delta H_{\rm ads} = \Delta E_{\rm elec} + \Delta E_{\rm zpe} + \frac{NRT}{2} \tag{4}$$

with ΔE_{elec} the electronic adsorption energy, ΔE_{zpe} the difference in the zeropoint energy (ZPE) between the adsorbed and gas phase state, and *N* the total number of rotational and translational degrees of freedom in the gas phase. To incorporate the entropic contribution in the adsorption and desorption rate, the gas phase entropy is calculated using the Shomate equation for CO, H₂, H₂O and CH₄.[53]

The reaction rate for surface reactions is given by

$$k_{\text{react}} = \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q} \exp\left(\frac{-\Delta E_{\text{act}}}{k_{\text{B}}T}\right)$$
(5)

where Q^{\ddagger} and Q are the partition functions of the activated complex and the corresponding initial state, respectively, and ΔE_{act} is the energy needed to activate the reaction.

For elementary reaction steps with very low barriers, the application of the zeropoint energy correction sometimes results in negative barriers. Cleary, such barriers are in disagreement with transition state theory as the rates associated with such barriers will decrease with increasing temperature. On top of that, negative (or otherwise very low) barriers cause numeric instabilities in the ordinary differential equation solver of MKMCXX. To correct this undesirable behavior, any barriers found that are lower than 5 kJ/mol are adjusted. This adjustment involves increasing both the forward and backward barrier by the same value such that the lowest of the two barriers corresponds to 5 kJ/mol. The systematic adjustment of both the forward and the backward barrier ensures that the equilibrium constant for the elementary reaction step is not affected by the correction, ensuring invariance of overall reaction thermodynamics.

To account for the effect of lateral interactions, a lateral interaction potential was introduced as described in a previous work.[54] Lateral interactions can result in a significant decrease in adsorption rate or increase in desorption rate as the surface coverage increases. This is due to a decrease in available electrons at the catalytic surface and an increase in repulsion from other adsorbates. In our simulations, no penalty was applied for adsorption below ¼ coverage. Between ¼ and ¾ coverage, the penalty increases exponentially with increasing coverage. A typical adsorption energy penalty $E_{i,pen}^{lat}$ of species *i* at coverage θ_{lat} is given by

$$E_{i,\text{pen}}^{\text{lat}} = E_{i,\text{pen}}^{\theta=1} \frac{101^{\theta_{\text{lat}}} - 1}{100}$$
(6)

where $E_{i,\text{pen}}^{\theta=1}$ is the maximum adsorption energy penalty of species *i*, i.e. the penalty applied at maximum coverage.

For the simulations in this work, between $\frac{3}{4}$ and full coverage, the penalty was set to the maximum value. Due to its small size, adsorbed H only counts as half an adsorbate in calculating the coverage

$$\theta_{\text{lat}} = \theta_{\text{total}} - \theta_* - 0.5 \,\theta_{\text{H}} \tag{7}$$

Sensitivity analysis towards pressure, temperature and barriers is conducted in MKMCXX by evaluating the reaction order, the apparent activation energy and the degree of rate control, respectively. The reaction orders are calculated according to

$$n_i = p_i \frac{\partial \ln r^+}{\partial p_i} \tag{8}$$

where n_i is the reaction order of species i, p_i is the partial pressure of species i and r^+ is the forward rate of the product of interest. The apparent activation energy is evaluated *via*

$$\Delta E_{\rm act}^{\rm app} = RT^2 \frac{\partial \ln r^+}{\partial T} \tag{9}$$

where r^+ is the forward rate of the product of interest. The degree of rate control X of elementary reaction step i is defined as[55]

$$X_{i} = \left(\frac{\partial \ln r}{\partial \ln k_{i}}\right)_{k_{j\neq i}, K_{j}}$$
(10)

where r is the net rate of the product of interest, and where all the equilibrium constants K_j and the rate constants k of all other reaction steps except i are held constant. All the above quantities are evaluated numerically by means of a five-point centered finite difference stencil.[56]

5.2.3 COHP

We performed single-point calculations of optimized states VASP. The LOBSTER software[57–61] was used to perform crystal orbital Hamilton population (COHP) analyses. The number of bands in VASP and the number of local basis functions in LOBSTER were both set to the sum of the valence orbitals of all atoms present in the system. We used the pbeVaspFit2015 basis set[60,62,63] with the basis functions (1s) for H, (2s, 2p) for C and O, (3s, 3p) for Al, and (4s,

3p, 3d) for Co. For the COHP calculations, the basis functions were rotated in such way that the *x*-axis is parallel to the C-O internal bond (using the "autorotate" keyword). We computed the COHP in an orbitalwise fashion. The absolute charge spilling was below 4.0% (average of the two spin channels) for all calculations. This means that at least 96% of the occupied wave function was projected onto the local basis functions. The absolute charge spilling could not be lowered by employment of more basis functions.

5.3 Results and discussion

5.3.1 Models

To study the reactivity of small Co nanoparticles (NPs) on an alumina support, we have created three Co nanoparticle models, which are shown in Figure 5.2ac. These models were created based on the Ni₅₅/Al₂O₃ model of Silaghi *et al.*[51] To study the reactivity of a Co nanoparticle consisting of low-coordinated Co atoms, we created a flat nanoparticle of twenty Co atoms by removing 35 Co atoms from the 55 atoms particle (Figure 5.2a). This resulted in a flat nanoparticle of 9.7 \times 7.0 \times 1.9 Å³ size. In Table 5.1, the average coordination numbers (*CN*) of the active sites as defined in Figure 5.2 are tabulated. Two Co atoms are considered to be coordinated if the distance between them is less than 3.0 Å. The average coordination number of the Co atoms in the Co₂₀ NP equals 4.7, which is relatively low. The Co_{55}/Al_2O_3 nanoparticle, as shown in Figure 5.2b, is a high-coordinated nanoparticle of 9.9 \times 8.3 \times 6.3 Å³ size. The average coordination number of the top site (green site in Figure 5.2b) is 7.6, and for the site near the support (yellow site in Figure 5.2b) this is 7.1. Although these are low numbers compared to CN = 9.0 for a surface Co on Co(0001), these values are high compared to CN = 4.7 for Co₂₀, and therefore we refer to the Co₅₅ NP as high-coordinated and to Co₂₀ as low-coordinated. The Co₅₅/Al₂O₃ particle predominantly exhibits threefold sites like those on the Co(0001) extended surface, but with a higher curvature with respect to each other and featuring numerous (small) irregularities. The absence of step-edge sites is in line with expectation for such a small particle, since previous studies have shown that the number of step-edge sites increases with increasing particle size and that small particles do not exhibit step-edge sites. [26] The Co₂₀ nanoparticle exhibits besides threefold sites also a fourfold and a pocket-like site. On the Co₅₅/Al₂O₃ nanoparticle, two active sites are explored; one located on top of the nanoparticle (Figure 5.2b green site) and another close to the support (Figure 5.2b yellow site). Besides subtle differences in the local stacking of the Co atoms, these active sites predominantly differ in their distance to the support interface.



Figure 5.2: Geometries of the models (a) Co_{20}/Al_2O_3 , (b) Co_{55}/Al_2O_3 , (c) Co_{52}/Al_2O_3 , and (d) Co(0001). The active sites are colored green for the top site (Co_{55}/T), yellow for the near support site (Co_{55}/NS), and purple for the pocket site (Co_{52}/P). For the Co_{20}/Al_2O_3 nanoparticle and the Co(0001) surface (no coloring of active sites), the entire nanoparticle or slab surface was used.

As the Co_{55}/Al_2O_3 system only exhibits threefold sites which are associated with relatively high C-O bond scission barriers, three atoms were removed to create a B₅-like site (Figure 5.2c purple site).[64] It was verified by means of geometry optimization that this pocket site is stable. Side-on perspectives of the three models are provided in Figure C.1-C.3. The CO methanation activity of these small nanoparticles is compared with the activity of the extended Co(0001) surface, whose geometry is shown in Figure 5.2d. This surface exhibits only FCC and HCP (hollow) threefold sites and was studied in detail in the work of Zijlstra *et al.*[54]

Active site	Average coordination number of active site atoms CN [-]
Co ₂₀	4.7
Co ₅₅ /NS	7.1
Co ₅₅ /T	7.6
Co(0001)	9.0
Co ₅₂ /P	7.3
$Co(11\bar{2}1)/B_5$	8.2

Table 5.1: Average coordination number per active site.

The threefold sites on the Co₂₀ and Co₅₅ particles exhibit a similar geometry as the threefold sites on the Co(0001) extended surface. This can be quantitatively shown using the minimized Hilbert Schmidt (mHS) norm.[65] A detailed description of how this metric is constructed can be found in Section B.1. In short, if two sites show a low mHS value, this indicates a higher degree of similarity, a value of zero implying that the two sites are (locally) identical. In Table 5.2, the mHS norms among all active sites considered in this study are shown. As a reference, we included the B₅ site of Co(11 $\overline{2}1$) (Co(11 $\overline{2}1$)/B₅). For Co(11 $\overline{2}1$)/B₅ and Co_{52}/P we used three Co atoms of the fourfold site that is part of the B₅ or pocket site for calculating the mHS norm. Among all threefold sites, the mHS values are below 0.42, indicating a high degree of similarity. The mHS values show that the threefold sites themselves are much alike for Co₂₀ and Co₅₅, however their surroundings differ. The proximity to the support and the arrangement of the Co atoms in their first coordination shell, the latter dictated by epitaxial effects of the support, are distinct. The mHS norm between Co₅₂/P and Co $(11\overline{2}1)/B_5$ is 0.23, which indicates a high similarity as expected. The mHS values between any threefold site and Co_{52}/P or $Co(11\overline{2}1)/B_5$ are at least 0.93, reflecting the low geometric resemblance between threefold and pocket sites.

Table 5.2: Minimized Hilbert-Schmidt (mHS) norms among all active sites considered in this study.

mHS norms	Co ₂₀	Co ₅₅ /NS	Co ₅₅ /T	Co(0001)	Co ₅₂ /P	Co(1121)/B ₅
Co ₂₀	0.00	0.31	0.30	0.42	1.15	1.37
Co ₅₅ /NS	0.31	0.00	0.20	0.18	1.10	1.30
Co ₅₅ /T	0.30	0.20	0.00	0.16	0.93	1.15
Co(0001)	0.42	0.18	0.16	0.00	0.96	1.17
Co ₅₂ /P	1.15	1.10	0.93	0.96	0.00	0.23
Co(1121)/B ₅	1.37	1.30	1.15	1.17	0.23	0.00

5.3.2 Reaction energetics

In Figure 5.3, the computed reaction energetics for CO methanation are shown. All elementary reaction steps relevant to CO methanation were explored for the Co₂₀ (Figure 5.3a), Co₅₅/NS (Figure 5.3b), and Co₅₅/T (Figure 5.3c) sites. The corresponding images of the geometries of stable and transition states (TS) are provided in Figure C.4-C.10. Pathways for C-O bond scission include both direct as well as hydrogen-assisted routes, the latter *via* CHO and COH intermediates. O removal proceeds by twofold direct hydrogenation of O or *via* the exchange of a proton between two adjacent hydroxyl species. For comparison purposes, in Figure 5.3d the reaction energies over Co(0001) as reported by Zijlstra *et al.*[54] are shown as well. For the Co₅₂/P and Co(11 $\overline{2}1$)/B₅ site, only direct CO dissociation is explored (Figure 5.3e,f). Barriers that are lower than 5 kJ/mol after application of the ZPE correction were adjusted according to the procedure as described in the Methods section. All barriers are reported with respect to the most stable configuration of the adsorbates present in their initial and final states.

5.3.2.1 Adsorption and desorption

 H_2 adsorbs in a dissociative manner on all active sites. For the Co_{20}/Al_2O_3 system, a substantially higher adsorption energy was observed (325 kJ/mol) compared to the other three models (102, 97, and 99 kJ/mol for the Co_{55}/NS , Co_{55}/T and Co(0001) sites, respectively). Similarly, for CO it was found that it adsorbs with a significantly higher adsorption energy on the Co₂₀ nanoparticle (302 kJ/mol) as compared to the other systems. CO adsorption on the Co₅₅ nanoparticle is associated with adsorption energies of 194 kJ/mol and 175 kJ/mol for the NS and T threefold sites, respectively. For the extended Co(0001) surface, the lowest CO adsorption energy among the considered systems was found, corresponding to 164 kJ/mol. The H₂O adsorption strength follows the same pattern as found for CO: the Co₂₀ particle exhibits the highest adsorption energy (198 kJ/mol), followed by the Co₅₅/NS (62 kJ/mol) and the Co₅₅/T sites (49 kJ/mol) and finally the extended surface (24 kJ/mol). On the Co nanoparticles, it was found that CH_3 hydrogenation results in immediate desorption of CH_4 . In contrast, on Co(0001) it turns out that CH₄ is weakly adsorbed with 2 kJ/mol. The higher stability of H, CO and H_2O on the three nanoparticle sites compared to Co(0001) can be ascribed to the lower coordination number of the Co atoms of the nanoparticle. Lower coordination numbers are associated with a higher *d*-band center and a narrower *d*-band width.[66] Assuming similar molecular orbital overlap and a similar site geometry, the higher *d*-band center for the more coordinatively unsaturated sites results in stronger metal-adsorbate bonds.[66] Another explanation is that the stronger adsorption on the NP sites is due to adsorbate induced site restructuring. The Co atoms of the NP active sites are more mobile than the Co atoms of extended surfaces. The increased mobility can result in more stable adsorption, as it allows the system to maximize electron overlap by selecting the most favorable atomic configuration from a broader range of possibilities, compared to the more limited options available for more rigid active sites.

5.3.2.2 Thermodynamic assessment

To ensure thermodynamic consistency with experimental results for our microkinetic models, we calculated the reaction enthalpy ($\Delta_R H$) and Gibbs free energy ($\Delta_R G$) using standard statistical thermodynamic approaches.[67] The experimental reaction energies ($\Delta_R H$ and $\Delta_R G$) were computed by means of the Shomate equation utilizing tabulated values.[53,68] Details of the procedure are provided in the previous chapter in Section B.2.

The zero-point energy corrected electronic reaction energy for CO methanation was found to be -229 kJ/mol, fully consistent with the earlier calculations of Zijlstra and coworkers.[54] The enthalpy and Gibbs free energy were both computed at T = 225 °C and p = 1 atm, corresponding to typical reaction conditions.[69] At the DFT/PBE+D3 level of theory, a reaction enthalpy of $\Delta_R H_{225^\circ C} = -252$ kJ/mol in comparison to the experimental value of $\Delta_R H_{225^\circ C} = -215$ kJ/mol is found. For the Gibbs free reaction energy, a value of $\Delta_R G_{225^\circ C} = -126$ kJ/mol was found in comparison to the experimental value of $\Delta_R G_{225^\circ C} = -97$ kJ/mol. We assign the relatively poor agreement of the DFT/PBE+D3 results to non-ideal gas phase behavior and inaccuracies of the harmonic approximation in determining the vibrational modes.



Figure 5.3: Reaction energy networks of CO methanation over (a) Co_{20}/Al_2O_3 , (b) $Co_{55}/Al_2O_3/NS$ site, (c) $Co_{55}/Al_2O_3/T$ site, (d) Co(0001), (e) $Co_{52}/Al_2O_3/P$ site, and (f) $Co(11\overline{2}1)$. The values are given in kJ/mol and include the ZPE correction. The arrows indicate the direction of the forward barrier for proceeding from one reaction intermediate to another. Values for Co(0001) and $Co(11\overline{2}1)$ are adapted from Zijlstra *et al.*[54] Note that for the $Co_{52}/Al_2O_3/P$ and $Co(11\overline{2}1)$ sites only direct CO dissociation is evaluated.
To accurately reproduce the overall thermodynamics of the reaction in our model, we apply the same correction method previously used by Zijlstra and coworkers.[54] Instead of using statistical thermodynamics to calculate enthalpy and entropy corrections, we base these corrections on experimental data and calculate them using the Shomate equation (as described earlier). Additionally, since the equations for microkinetic simulations are based on the standard reference conditions of T = 25 °C and p = 1 atm, we adjust the reaction energetics to ensure that the model reflects experimental values under these conditions. The reaction enthalpy at the standard reference state is $\Delta_R H_{25^\circ C} = -206 \text{ kJ/mol}$. We apply a correction of +22.72 kJ/mol to the CO adsorption energy with respect to the values shown in Figure 5.3. The motivation to apply this correction solely to CO adsorption is because PBE is known to overestimate CO adsorption on metal surfaces.[70] The reaction energy diagrams including this correction can be found in Figure C.11-C.16.

5.3.2.3 Surface reactions

After evaluating the reaction thermodynamics and adsorption energies, we will proceed to examine the reaction barriers involved in the conversion of CO to methane. We first present CO dissociation, followed by CH_x (x = 0-3) hydrogenation and finally OH and H_2O formation.

CO dissociation

Due to the absence of a step-edge configuration, direct CO dissociation is associated with relatively high barriers on the Co₂₀, Co₅₅ and Co(0001) models. On the Co₂₀ nanoparticle, CO dissociation has a barrier of 235 kJ/mol. The transition state (TS) shows C and O bonded in a fourfold and a bridge configuration, respectively. The Co atoms bonded to O are also shared with C. According to the principle of bond order conservation, the Co atoms shared between C and O stabilize each species less due to the constant total binding capability of the Co atoms.[71] This leads to a less stable TS, explaining the higher barrier. On the extended surface and on the Co₅₅ nanoparticle, only threefold sites are present. For the extended surface, direct CO dissociation has a barrier of 225 kJ/mol, where the TS consists of C bonded threefold and O bridged, with one shared Co atom. Coincidentally, the CO dissociation barriers on the Co₅₅ nanoparticle are the same on the top site and on the near support site (213 kJ/mol), despite that the geometries of these two active sites differ. For the TS on the T site, C and O are both bonded to three Co atoms, of which one is shared between C and O. On the NS site, C is also bonded threefold, but O is bridged between two Co atoms, one of which is shared with C. The Co_{52}/P site shows a substantially lower barrier (103 kJ/mol). This site exhibits a TS where no Co atoms are shared between C and O. C bonds to four Co atoms and O to two other Co atoms. Although the Co₅₂/P site is not a B₅ site as is available on Co(11 $\overline{2}$ 1), it supports the same stable TS configuration as a B₅ site, resulting in a similar barrier (100 kJ/mol on Co(11 $\overline{2}$ 1)). The high similarity in TS configuration is in line with the high similarity in site geometry according to Hammond's postulate.[77] The high similarity in site geometry is indicated by the low mHS value in Table 5.2.

With high barriers for direct CO dissociation on all sites but the Co_{52}/P site, it is likely that the preferred CO dissociation mechanism will follow an H-assisted route, either *via* COH or *via* CHO. The effective C-O bond scission barrier *via* COH is higher in energy than *via* CHO for all explored active sites. The effective barriers *via* COH are 405 kJ/mol, 280 kJ/mol, 222 kJ/mol and 247 kJ/mol for Co_{20} , Co_{55}/NS , Co_{55}/T , and Co(0001), respectively. The corresponding effective barriers *via* CHO are 335 kJ/mol, 152 kJ/mol, 176 kJ/mol and 182 kJ/mol. Notably, the most facile pathway for CO dissociation *via* CHO is on the site close to the support. On this threefold site, the TS for HC-O bond scission exhibits a more favorable geometry wherein only one Co atom is shared between C and O, in contrast to the sharing of two Co atoms on the top site and on Co(0001), which are also threefold sites.

CH_x hydrogenation

After CO bond scission, the resulting CH_x (x = 0,1) species can be hydrogenated to form methane. The effective barriers for C hydrogenation towards CH_4 are 681, 139, 106 and 119 kJ/mol for Co_{20} , Co_{55}/NS , Co_{55}/T and Co(0001), respectively. The extremely large overall activation energy for C hydrogenation to CH_4 on the Co_{20} nanoparticle is caused by the very strong metal-carbon interaction energy. Ultrastable configurations for atomic C as seen in this work have been identified earlier in the work of Nandula *et al.*[72] Due to the coordinative undersaturation of the Co_{20} nanoparticle, the hydrogenated derivatives of C also exhibit very high adsorption energies (Figure C.11 and C.15). The effective barrier for C hydrogenation to CH_4 on Co_{55}/NS is larger than on the Co_{55}/T and Co(0001) sites. This can also be linked to lower coordination of the Co_{55}/NS sites than the Co_{55}/T and Co(0001) sites (Table 5.1), which results in a higher stability of reaction intermediates at this site (shown in Figure C.16).

C hydrogenation to form CH is associated with barriers of 278, 115, 84, and 71 kJ/mol for Co_{20} , Co_{55}/NS , Co_{55}/T and Co(0001), respectively. In the TS for C hydrogenation on the Co_{20} , Co_{55}/NS , and Co_{55}/T sites, C distorts the threefold

site. Apparently, for these configurations it is favorable for the Co atoms to reconstruct to form a fourfold site, optimizing the interaction with C. As the Co(0001) site consists of Co atoms with a coordination number (*CN*) of 9, such a reconstruction would come at the expense of creating lattice defects. Nevertheless, such reconstructions have been observed for flat extended surfaces yet require higher C loadings.[73] In the TS on the Co(0001) extended surface, C resides on an FCC threefold hollow site, with H approaching over one Co atom. On Co₂₀, the TS geometry closely resembles that on the extended surface, but the Co₂₀ Co atoms have very low coordination numbers. This results in the TS being less stable compared to the extended surface, despite C and H being coordinated to only a single Co atom in the TS. On the Co₅₅ nanoparticle, at both the T and NS sites, H is bonded in a bridge configuration. In both cases, the two Co atoms that H bonds to are also shared with C.

The barriers for CH_2 formation are quite similar on the Co_{55}/NS , Co_{55}/T , and Co(0001) sites, with values of 63, 51, and 52 kJ/mol, respectively. In contrast, Co_{20} presents a significantly higher barrier of 199 kJ/mol for this reaction step, caused by its undercoordinated Co atoms. At the Co_{55}/NS site, CH is bonded in a threefold manner, unlike the fourfold bond observed in the TS for C hydrogenation. At the top site, CH still induces a fourfold coordination in the transition state. Here, H approaches CH in a bridged configuration, whereas on the Co_{55}/NS support and on the Co(0001) surface, H approaches over a single Co atom.

The barriers for CH_3 formation are also similar for the Co_{55}/NS , Co_{55}/T , and Co(0001) sites, with values of 56, 72, and 51 kJ/mol, respectively, while Co_{20} exhibits a much higher barrier of 228 kJ/mol. In all TSs, one Co atom is shared between CH_2 and H. At the top site, CH_2 bonds with its C atom to two Co atoms, while both H atoms do not bond to Co. At the NS site and Co(0001), CH_2 is bonded in a threefold configuration, with one H also bonding to Co. This difference may account for the slightly higher TS energy at the top site.

In the TS of CH₃ hydrogenation, CH₃ is bonded to a single Co atom *via* C. Along the reaction coordinate, H approaches *via* a bridge position on Co₂₀ and the Co₅₅/T site, *via* a threefold position at the Co₅₅/NS site, and is bonded to the same Co atom as CH₃ on Co(0001). Like the other CH_x hydrogenation steps, the barriers for CH₄ formation are similar for the Co₅₅/T, Co₅₅/NS and Co(0001) systems, with values of 100, 113, and 101 kJ/mol, respectively. Co₂₀ shows a much higher barrier of 254 kJ/mol. Furthermore, while CH₄ remains physisorbed on

Co(0001) with an adsorption energy of 2 kJ/mol, on the Co nanoparticles it desorbs immediately after formation.

H₂O formation

Bond scission of C-O, HC-O or C-OH results in the formation of OH_x (x = 0,1) species that need to be hydrogenated such that they can leave the surface as water. OH formation by O hydrogenation is associated with barriers of 302, 128, 109, and 121 kJ/mol for Co₂₀, Co₅₅/NS, Co₅₅/T and Co(0001), respectively. Like C hydrogenation, we assign the high barrier observed for O hydrogenation on Co₂₀ to the highly undercoordinated Co atoms present in this site. In the TSs on the Co₅₅ sites, O and H are both coordinated in a threefold manner with the Co atoms, while on the extended surface, H is bonded to a single Co atom.

Two pathways were considered for OH hydrogenation: $OH + H \rightarrow H_2O$ and OH + $OH \rightarrow H_2O + O$, here referred to as direct OH hydrogenation and OH-OH disproportionation, respectively. For all four site models. OH-OH disproportionation has a lower energy barrier than direct OH hydrogenation and O hydrogenation, and direct OH hydrogenation consistently shows higher barriers than 0 hydrogenation. This strongly suggests that, although two hydroxyl species must be formed for OH-OH disproportionation, this will likely be the dominant pathway for water formation. The energy barriers for OH-OH disproportionation are 152, 84, 86, and 47 kJ/mol for Co₂₀, Co₅₅/NS, Co₅₅/T, and Co(0001), respectively. The TS geometries at the Co_{55}/T site and Co(0001) are quite similar: one hydroxyl species is bonded in a threefold manner via O, while the other hydroxyl is bonded atop to a fourth Co atom, forming a rhombus shape when combined with the threefold site.

5.3.3 Microkinetic simulations

We computed the methanation activity and determined the preferred pathways for the discussed active sites by means of microkinetic simulations. The simulations are done for temperatures between 120 °C and 520 °C, with steps of 10 °C. The operating pressure is set to 1 bar, and the feed H₂/CO ratio is set to 3, which are typical methanation conditions.[74] To investigate the effect of a stepedge site that facilitates easy CO dissociation, additional simulations were conducted in which the forward barriers of direct CO dissociation on Co_{55}/NS and Co_{55}/T were replaced with the forward barrier of direct CO dissociation forward barrier was replaced with the forward barrier on $Co(11\overline{2}1)/B_5$ site (Figure 5.3f).

Simulations of the Co_{20} nanoparticle yielded methane production rates lower than 1.0×10^{-15} s⁻¹. Moreover, due to the vast difference in reaction rate constants for the Co₂₀ NP, microkinetic simulations for this system suffered from severe numerical precision errors, leading to poor convergence especially for low temperature conditions. Based on the reaction energy diagrams in Figure C.11 and C.15, it can be concluded that the highly undercoordinated active sites on the Co₂₀/Al₂O₃ system would exhibit negligible methane production and become poisoned by CO, its derivatives, and H species under typical CO hydrogenation conditions. For the $Co_{55}/NS(+P)$, $Co_{55}/T(+P)$, and $Co(0001)(+B_5)$ models, a sensitivity analysis was conducted where the barrier of the rate-determining step (RDS) at 230 °C was altered, which is described in Section C.2. Since a DFT error of ± 10 kJ/mol in the barrier of the RDS is likely to have a greater impact than the same error in other barriers, we chose to assess the sensitivity of the TOF to the RDS barrier. Altering the RDS barrier by up to ± 10 kJ/mol results in at most a one-order-of-magnitude change in the TOF value. However, the temperature dependence trends remain qualitatively similar, regardless of this variation in the RDS barrier (Figure C.25).

5.3.3.1 CH₄ production

Figure 5.4 shows the methane production across the six active sites as defined above. It is evident that sites lacking a pocket or B_5 site show lower methane production at FT temperature compared to those with this feature. As can be seen from Figure 5.4, at 230 °C, a typical FT temperature, the three active sites with a pocket or B_5 site for facile CO dissociation generate more methane than the three without. For all sites, methane production increases with increasing temperature, as more thermal energy is available to overcome the reaction barriers.

5.3.3.2 Excluding facile CO dissociation sites

The molar fluxes at 230 °C for the active sites without a pocket or B_5 site are visualized in Figure 5.5. The extended surface Co(0001) shows the lowest production rate, corresponding to $4.0 \times 10^{-8} \text{ s}^{-1}$. Co₅₅/T and Co₅₅/NS show turnover frequencies (TOFs) of $1.7 \times 10^{-6} \text{ s}^{-1}$ and $5.7 \times 10^{-4} \text{ s}^{-1}$. Thus, the site near the support is two orders of magnitude more active than the site on top of the Co₅₅ NP. For this particular NP, we can conclude that the edge sites are responsible for the majority of methane production, and the top sites are relatively inactive. Figure 5.5 shows that the dominant reaction pathway over the considered sites is *via* the CHO intermediate and the dominant pathway for H₂O formation is *via* OH-OH disproportionation, irrespective of the active site

configuration. In an earlier DFT and microkinetics study, CO dissociation *via* HCO was also found to be the dominant pathway on Co(0001).[27]



Figure 5.4: Intrinsic activity or turnover frequency (TOF) of CH₄ production for the near support (NS) and top (T) sites on Co_{55}/Al_2O_3 and the Co(0001) extended surface with and without inclusion of direct CO dissociation over the pocket (+P) or B₅ sites (+B₅).

The DRC analyses in Figure 5.6a,c,e indicate that CHO dissociation to CH and O is the dominant rate-limiting step for these three active sites at low temperature. Given that the surface coverages for these three models correspond to approximately half a monolayer (ML) in CO and H, it can be mathematically derived (see Section C.1) that the apparent activation energy should reflect the overall CO dissociation barrier *via* CHO from CO+H under these conditions. From Figure C.12-C.14 and C.17 it can be seen that the apparent activation energies for Co₅₅/NS, Co₅₅/T and Co(0001) correspond to 146, 177, and 184 kJ/mol which is in close agreement to the effective barriers of 152, 176, 182 kJ/mol.



Figure 5.5: Reaction pathway analysis at 230 °C for CO methanation on (a) $Co_{55}/Al_2O_3/NS$, (b) $Co_{55}/Al_2O_3/T$, and (c) Co(0001), where the TOF of each elementary reaction step is shown in s⁻¹. The nodes represent reactants, surface intermediates, and products, the lines between them the elementary reaction steps and the normalized molar rates in s⁻¹. The pathways highlighted in green indicate the dominant reaction pathway at this temperature.

However, whereas the top and Co(0001) sites are limited by CO scission over the entire computed temperature range (Figure 5.6c,e), the NS site shows a different kinetic response (Figure 5.6a). With increasing temperature, the DRC coefficient for CHO dissociation decreases while OH-OH disproportionation becomes more rate-controlling. At a temperature of approximately T = 300 °C, we observe CH₃ hydrogenation becoming increasingly rate-controlling and eventually becoming

the dominant rate-controlling step at the highest simulated temperatures. This difference between Co_{55}/NS and Co_{55}/T , Co(0001) is also reflected in how the surface coverage changes with temperature (Figure C.18). Figure C.18c,e show similar surface coverages over the temperature range, with CO and H as most abundant surface species. At lower temperatures, nearly no empty sites are present, but as temperature increases, desorption is favored and more empty sites become available. For Co_{55}/NS however, at higher temperatures CH, C and O are present at the surface. This is due to the increasing rate limitations by OH-OH disproportionation (O) and CH₃ hydrogenation (C, CH).



Figure 5.6: Degree of rate control (DRC) analyses for CO methanation on (a) $Co_{55}/Al_2O_3/NS$, (b) $Co_{55}/Al_2O_3/NS+P$, (c) $Co_{55}/Al_2O_3/T$, (d) $Co_{55}/Al_2O_3/T+P$, (e) Co(0001), and (f) $Co(0001)+B_5$.

These trends are in line with the reaction orders (Figure C.19). For Co_{55}/T and Co(0001), the reaction orders of both CO and H_2 are close to zero, irrespective of temperature. Due to CHO dissociation being the rate-limiting step, changes in the partial pressure of CO and H_2 have little effect on the surface coverage and thus provide little change in the overall reaction rate for these sites. In contrast, for the Co_{55}/NS site, the reaction order for H_2 increases with temperature, while the order for CO becomes negative. This change is attributed to the increasing rate limitations of CH_3 hydrogenation and OH-OH disproportionation as function of temperature. An increase in the H_2 partial pressure boosts the hydrogenation rates of C, O, and their hydrogenated derivatives, yielding an increased methanation rate. In contrast, an increase in the CO partial pressure leads to increased deposition of C and O species, reducing upon the available H required for methanation and thus resulting in a decreased methanation rate.

5.3.3.3 Including facile CO dissociation site

Next, we investigate the impact of the presence of an active site providing a facile CO dissociation on the kinetics. This is accomplished by substituting the energetics of the CO dissociation step in the original pathway with values found for the Co_{52}/P site or the $Co(11\overline{2}1)/B_5$ site for the $Co_{55}(NS,T)$ and Co(0001)systems, respectively. These adjustments are such that the overall thermodynamics of the reaction step remains unaffected. From Figure 5.4, it can be seen that methanation rates increase by several orders of magnitude, corresponding to TOFs of 6.3×10^{-1} s⁻¹, 7.5×10^{-3} s⁻¹, and 9.7×10^{-4} s⁻¹ for the $Co_{55}/T+P$, $Co_{55}/NS+P$, and $Co(0001)+B_5$ systems, respectively. The $Co_{55}/T+P$ is the most active at typical FT temperatures, with a TOF at least two orders of magnitude higher than the Co₅₅/NS+P and Co(0001)+B₅ system. The molar fluxes at 230 °C for the active sites including a pocket or B₅ site, the microkinetic systems are visualized in Figure 5.7. From Figure 5.7 it can be seen that in comparison to the $Co_{55}(T,NS)$ and Co(0001) systems, the preferred methanation pathway now proceeds via direct CO dissociation rather than by the hydrogenassisted route via CHO. With inclusion of the pocket sites, the effective barriers for direct CO scission are lower than for the H-assisted CO dissociation, making direct CO dissociation the preferred pathway.



Figure 5.7: Reaction pathway analysis at 230 °C for CO methanation on (a) $Co_{55}/Al_2O_3/NS+P$, (b) $Co_{55}/Al_2O_3/T+P$, and (c) $Co(0001)+B_5$, where the TOF of each elementary reaction step is shown in s⁻¹. The nodes represent reactants, surface intermediates, and products, the lines between them the elementary reaction steps and the normalized molar rates in s⁻¹. The pathways highlighted in green indicate the dominant reaction pathway at this temperature.

Zijlstra and coworkers modelled CO hydrogenation over a Co catalyst using a dual-site microkinetic model with a Co(0001) terrace to Co(11 $\overline{2}$ 1) step-edge site ratio of 10:1. They concluded that the Co(11 $\overline{2}$ 1) surface is not only necessary for efficient CO dissociation, but also for O* removal *via* H₂O formation and for CH_x (*x* = 0,1,2) hydrogenation. They found that the preferred pathway for methane formation proceeds by migration of a CH₃ moiety from a B₅ site to a terrace site,

where it is hydrogenated to form CH₄.[54] In the microkinetic model presented in this work, only CO dissociation is allowed to proceed on the Co(11 $\overline{2}$ 1) pocket site, the other elementary reaction steps occurring on Co(0001). This results in a lower methanation rate by two orders of magnitude as compared to the dualsite model of Zijlstra *et al*. It is thus important to note that although facile CO dissociation increases the activity of Co(0001) by almost five orders of magnitude, the methanation rate would increase by an additional two orders of magnitude if the Co(11 $\overline{2}$ 1)/B₅ site would also be used in C and O hydrogenation events.

Similar to the unaltered systems, i.e. without a facile CO dissociation, the methanation rates of the $Co_{55}(T,NS)+P$ systems are higher than of the $Co(0001)+B_5$ system. Despite the Co_{55}/T and Co_{55}/NS active sites being fairly similar in geometry, the methanation rates over these sites differ by two orders of magnitude, with the $Co_{55}/T+P$ system being the most active. This contrasts with the unaltered system, where the Co_{55}/NS system shows the highest TOF. The DRC analysis in Figure 5.6, again using T = 230 °C as a representative temperature, allows us to rationalize upon this. In the absence of a site allowing for a facile CO dissociation, the effective barrier for C-O bond scission (in this case occurring via CHO), determines the overall activity of the surfaces. For the Co_{55}/NS site, this effective barrier is lower than for the Co_{55}/T site. Indeed, for the latter site it is seen that with increasing temperature, the OH-OH disproportionation reaction becomes more rate-controlling. With the introduction of a site allowing for facile C-O bond scission, this previous limitation in C-O bond scission is removed and the remaining set of elementary reaction steps will control the activity. As indicated by the results in Figure 5.6a, the OH-OH disproportionation reaction on the Co₅₅/NS+P site becomes strongly rate-controlling due to its relatively high effective barrier of 149 kJ/mol. In contrast, the effective barrier for water formation on the $Co_{55}/T+P$ site is 102 kJ/mol, contributing minimally to the degree of rate control (DRC). Additionally, Figure 5.6d shows that CO hydrogenation on the $Co_{55}/T+P$ site is primarily limited by C, CH_3 , and O hydrogenation steps, which have forward barriers of 84, 100, and 109 kJ/mol, respectively — all lower than the 153 kJ/mol barrier for OH-OH disproportionation on $Co_{55}/NS+P$. This demonstrates that the $Co_{55}/T+P$ site offers a more efficient methanation pathway than $Co_{55}/NS+P$ due to more facile hydrogenation steps, leading to higher methanation rates.

5.3.4 Comparison to experiment

We compare our findings with the microkinetic model proposed by Zijlstra *et al.* and with experimental data. The microkinetic model of Zijlstra et al. $(Co(0001)+Co(11\overline{2}1))$ with Co(0001) and Co(11\overline{2}1) surface in a ratio of 10:1, results in a reaction rate of 2.0×10^{-1} s⁻¹ at 220 °C. The microkinetic models presented in this work result in rates of 1.7×10^{-8} s⁻¹ for Co(0001) and 5.7×10^{-4} s^{-1} for Co(0001)+B₅ at 220 °C, which are much lower than the methanation rates of the $Co(0001)+Co(11\overline{2}1)$ model. For $Co(0001)+Co(11\overline{2}1)$, CO bond dissociation and O hydrogenation to water occur at the step-edge sites of Co(11 $\overline{2}$ 1), whereas C hydrogenation to CH₄ happens on both Co(0001) and $Co(11\overline{2}1)$. Our Co(0001) model shows less efficient CO dissociation compared to $Co(0001)+Co(11\overline{2}1)$, because the step-edge sites on the $Co(11\overline{2}1)$ surface facilitate CO dissociation with a much lower barrier than the terrace sites of Co(0001). The Co(0001)+ B_5 does assist in easy CO dissociation, but O and C hydrogenation still occurs on Co(0001) and thus in a less efficient manner. Also, the four CH_x (x = 0.3) hydrogenation steps are more efficient on Co(1121) than on Co(0001), resulting in significantly lower reaction rates for the Co(0001) and $Co(0001)+B_5$ models compared to the $Co(0001)+Co(11\overline{2}1)$ model.

In Table C.1, a comprehensive comparison of various chemophysical and kinetic parameters between this work and experimental work in the literature is presented. The catalysts in the studies of Bezemer et al.[2] and Den Breejen et al.[33] consist of relatively small NPs of approximately 2.6 nm. Bezemer and coworkers report a TOF of 1×10^{-3} s⁻¹ at 220 °C, and Den Breejen *et al.* report a TOF of 1.5×10^{-3} s⁻¹ at 210 °C. Comparing these results with our simulations at 220 °C, we find that the TOF of the Co $_{55}/NS$ site (2.8 × 10⁻⁴ s⁻¹) is relatively similar to these values, while the TOFs for the Co_{55}/T and Co(0001) are several orders of magnitude lower: 7.4×10^{-7} s⁻¹ for Co₅₅/T and 1.7×10^{-8} s⁻¹ for Co(0001), respectively. This could suggest that for these catalysts with small particles, the main source of methane would be the sites close to the support, i.e. the edges of the small NPs. SSITKA experiments of Breejen *et al.*[33] show that small Co nanoparticles exhibit a higher coverage of irreversibly bonded CO, which blocks part of the active sites. This is ascribed to the higher abundance of lowcoordinated surface sites. Our results for Co₂₀ show that low-coordinated sites are poisoned, in line with these experiments. The work of Breejen *et al.* also shows that for small Co particles of 2.6 nm, a higher hydrogen coverage is at the origin of the higher methane selectivity of these particles. The microkinetic simulations in this work however show similar H and CO coverages for the

extended Co(0001) surface and the top and near support sites on Co₅₅. Instead, we attribute the higher methanation rate on the Co₅₅ nanoparticle compared to the Co(0001) extended surface to the lower energy barriers associated with H-assisted CO dissociation at the nanoparticle sites. Furthermore, studies by Wang *et al.*[75], Chen *et al.*[74] and Chen *et al.*[76] show that for CO hydrogenation over small Co nanoparticles (<4 nm) and over larger nanoparticles (15 nm) the reaction order in CO is negative and in H₂ is positive. This holds for methanation conditions[74] as well as for FT conditions.[75,76] This corresponds well with the reaction orders of Co₅₅/NS+P, Co₅₅/T+P and Co(0001)+B₅ simulations (Figure C.19), where methanation is limited by hydrogenation steps. For the models without a facile CO dissociation site, the reaction orders in H₂ and CO are close to zero at FT temperature. For these sites, hydrogen-assisted CO dissociation is rate-limiting.

5.3.5 Electronic structure analysis

On the active sites without a pocket or B₅ site, CO dissociation occurs via CHO (Figure 5.5). This pathway provides much lower barriers than direct dissociation (Figure 5.3). To unravel the origin of the lower barriers for CHO dissociation compared to direct CO dissociation on the non-pocket sites, we conducted a COHP analysis of the C-O bonds in adsorbed CO and CHO. The COHP analyses for both direct C-O dissociation and HC-O dissociation for all CO dissociation steps discussed in this study are shown in Figure C.20 and C.21. The C-O dissociation barriers and integrated COHP (ICOHP) values at Fermi level of the C-O bond in both CO and CHO are provided in Table 5.3. Note that these barriers are given with respect to the initial state, in contrast to Figure 5.3, where the reaction barriers are given with respect to the most stable state of the adsorbate on the active site. The initial states of CHO dissociation are visualized in Figure 5.8 and Figure C.22 and C.23. The lower barriers for C-O scission in CHO (52 – 73 kJ/mol) compared to direct C-O scission (201 – 235 kJ/mol) are evident from the less negative ICOHP values (-12.12 to -14.81) for the C-O bond in CHO, as opposed to the more negative values (-16.29 to -19.06) for the C-0 bond in CO. In an earlier study, we demonstrated that a less negative ICOHP value for the C-O bond in the initial state indicates a weaker or more activated C-O bond. This activation in the initial state facilitates a lower energy barrier for the dissociation of the C-O bond.[48] The data presented in this study shows that the ICOHP of the C-O bond correlates with the CO dissociation barrier not only for direct C-O scission, but also for C-O scission in CHO. In addition to Table 5.3, this correlation is also visible in Figure C.24. Here, we have added the CO dissociation barriers and ICOHP values for Co_{20} (direct and *via* CHO), and for Co_{55}/T , Co_{55}/NS , and Co(0001) (*via* CHO) to the data points found in our previous work, showing a strong correlation.[48] From this we conclude that the facile CHO dissociation compared to direct CO dissociation is clearly visible in the COHP analyses, since the total ICOHP value for the HC-O bonds are significantly less negative than the total ICOHP values for the C-O bonds.

Table 5.3: Energy barriers with respect to the initial state and the ICOHP of the
(H)C-O bond values for both direct C-O dissociation and HC-O dissociation.

Dissociation	Direct C-O dis	sociation	C-O dissociation in CHO	
site	Barrier	ICOHP of C-O	Barrier	ICOHP of C-O
	[kJ/mol]	bond	[kJ/mol]	bond
Co ₂₀	235	-17.01	57	-12.12
Co ₅₅ /NS	206	-16.29	52	-12.15
Co ₅₅ /T	201	-16.54	73	-13.05
Co(0001)	225	-19.06	63	-14.81

The facile CHO dissociation on the NS site as compared to the T site (52 kJ/mol and 73 kJ/mol, respectively, Table 5.3) causes a difference of 2-3 orders of magnitude in CH_4 production rate between the T and the NS sites in the T = 200-250 °C range, as shown in Figure 5.4. The geometries of the initial states of CHO dissociation at the NS and T sites are visualized in Figure 5.8. To find the origin of this key difference in CHO dissociation barrier, we analyze the COHP diagram of CHO on the T and NS sites (Figure C.21). First, the difference in CHO dissociation barrier is visible in the total ICOHP for CHO on both sites: the ICOHP of the NS site is -12.15 and for the T site it is -13.05 (Table 5.3). This indicates that the C-O bond is more activated on the NS site than on the T site. The largest difference between the COHP diagrams is clearly the lowest-lying valence orbital at approximately E = -22 eV. The ICOHP value for this orbital is -8.38 for the NS site and -9.27 for the T site, revealing that this orbital is significantly less bonding for the NS site than for the T site. The higher activation of the HC-O bond causes the CHO dissociation barrier to be lower on the NS site than on the T site. This enhanced activation stems from the higher amount of electron density donated to CHO on the NS than on the T site. Charge analysis shows that C and O possess a more negative charge at the NS site than on the T site (C+O combined -0.15 and -0.12 e on NS site and T site, respectively from DDEC6 charge analysis; and -0.91 and -0.78 e on NS site and T site, respectively from Bader charge analysis). We assign the difference in electron donation to the difference in coordination of CHO on the NS and T sites, which is fourfold on the NS site (Figure 5.8a) and threefold on the T site (Figure 5.8b). CHO adsorption at the threefold site induces a restructuring that leads to a semi-fourfold configuration, whereas no such restructuring occurs at the T site. This is supported by the displacement of Co-Co at these adsorption sites: at the NS site, a bond contraction of 4.4% is observed upon CHO adsorption, compared to a slight bond elongation of 1.0% at the T site. The favorable distortion at the NS site is further reflected in the adsorption energy of CHO relative to gaseous CO + $\frac{1}{2}$ H₂, which is -145 kJ/mol at the NS site, compared to -120 kJ/mol at the T site. This demonstrates that the enhanced adsorbate-induced restructuring results in a more stable configuration for CHO on the NS site.



Figure 5.8: Initial state geometries of CHO dissociation on (a) Co_{55}/NS , and (b) Co_{55}/T .

In conclusion, the lower CHO dissociation barrier on the NS site, compared to the T site, can be attributed to a combination of related factors: enhanced electron donation to CHO, greater activation of the C-O bond, and the favorable restructuring at the NS site that enables a semi-fourfold configuration. This concerted set of effects leads to stronger stabilization of CHO and a higher degree of C-O bond activation at the NS site, resulting in a significantly lower dissociation barrier and ultimately a 2-3 orders of magnitude higher CH_4 production rate in the temperature range of 200-250 °C.

5.4 Conclusions

Small cobalt nanoparticles (NPs), characterized by their high interface-to-bulk ratios and low metal atom coordination, play a unique role in Fischer-Tropsch synthesis (FTS). Understanding their reactivity is crucial for assessing their contribution to overall catalytic activity and for gaining insights into the behavior of interfacial sites. These insights are also relevant for larger NPs. To investigate the behavior of small Co NPs, density functional theory (DFT) calculations and microkinetic simulations were conducted for three nanoparticle models: a highly undercoordinated Co_{20} nanoparticle, a hemispherical Co_{55} nanoparticle, and a Co_{52} nanoparticle featuring a B₅-like pocket site. The results from these models are compared to the $Co(0001)+Co(11\overline{2}1)$ multi-site microkinetic model which represents a Co NP of at least 6 nm, and the Co(0001) extended surface microkinetic model, both studied by Zijlstra *et al.*[38]

We find that the CO methanation rate of the Co_{55} NP model is three orders of magnitude lower than the rate of the multi-site model representing a Co NP of at least 6 nm. Upon inclusion of the B₅-like pocket site for facile CO dissociation, for the Co_{55} NP and Co(0001) models, significantly higher turnover frequencies (TOFs) are observed. However, the TOF of the Co(0001)+B₅ model is still orders of magnitude lower than the multi-site Co(0001)+Co(1121) model. This demonstrates that step-edge sites do not merely provide the possibility for easy CO dissociation, but also for facile C and O hydrogenation, which is necessary for high conversion.

The low-coordinated Co_{20} nanoparticle is catalytically inactive due to the blockage of its active sites by strongly adsorbed H and CO species, driven by the high adsorption energies associated with its undercoordinated sites. This indicates that excessively small and highly undercoordinated Co nanoparticles on Al_2O_3 do not contribute to catalytic activity. It also implies that there is a critical nanoparticle size below which the catalytic performance of Co nanoparticles significantly diminishes due to over-stabilization of adsorbates.

Comparing the CO methanation activity of an interfacial site to that of a site on top of the Co_{55} NP reveals that the interfacial site exhibits a turnover frequency over two orders of magnitude higher than the top site. Also, given that the TOF of the interfacial site closely matches the experimental TOF for nanoparticles around 2.6 nm in size, we suggest that methane formation on small nanoparticles predominantly occurs at interfacial sites rather than top sites. Microkinetic simulations identify CHO dissociation as the rate-limiting step on both the interfacial and the top site, with a significantly lower activation barrier at the interfacial site than at the top site. This reduced barrier arises from the enhanced adsorbate-induced rearrangement of Co atoms at the interfacial site, as opposed to the threefold coordination at the top site. The higher coordination of CHO at the interface facilitates increased electron density donation to CHO, as evidenced by both DDEC6 and Bader charge analyses, which show higher electron accumulation on the C+O atoms. This enhanced electron donation at the

interfacial site weakens the C-O bond by destabilizing one of the low-lying core molecular orbitals, rendering it less bonding and promoting CHO dissociation. These findings highlight the critical role of interfacial restructuring in enhancing catalytic activity at the interfacial site.

5.5 References

- [1] S.L. Scott, C.M. Crudden, C.W. Jones, eds., Nanostructured Catalysts, Springer US, Boston, MA, 2003.
- [2] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. Van Dillen, K.P. De Jong, J. Am. Chem. Soc. 128 (2006) 3956–3964.
- [3] K. Honkala, A. Hellman, I.N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J.K. Nørskov, Science 307 (2005) 555–558.
- [4] L. Pirro, P.S.F. Mendes, S. Paret, B.D. Vandegehuchte, G.B. Marin, J.W. Thybaut, Catal. Sci. Technol. 9 (2019) 3109–3125.
- [5] S. Katare, J.M. Caruthers, W.N. Delgass, V. Venkatasubramanian, Ind. Eng. Chem. Res. 43 (2004) 3484–3512.
- [6] S. Wang, V. Petzold, V. Tripkovic, J. Kleis, J.G. Howalt, E. Skúlason, E.M. Fernández, B. Hvolbæk, G. Jones, A. Toftelund, H. Falsig, M. Björketun, F. Studt, F. Abild-Pedersen, J. Rossmeisl, J.K. Nørskov, T. Bligaard, Phys. Chem. Chem. Phys. 13 (2011) 20760.
- [7] J.K. Nørskov, T. Bligaard, J. Rossmeisl, C.H. Christensen, Nature Chem. 1 (2009) 37–46.
- [8] C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Lu, C.J. Kiely, P.H. Berben, F. Meirer, B.M. Weckhuysen, Nat. Catal. 1 (2018) 127–134.
- [9] E. Iglesia, Appl. Catal. A 161 (1997) 59–78.
- [10] G. Melaet, A.E. Lindeman, G.A. Somorjai, Top. Catal. 57 (2014) 500–507.
- [11] T.O. Eschemann, W.S. Lamme, R.L. Manchester, T.E. Parmentier, A. Cognigni, M. Rønning, K.P. De Jong, J. Catal. 328 (2015) 130–138.
- [12] J. Yang, E.Z. Tveten, D. Chen, A. Holmen, Langmuir 26 (2010) 16558–16567.
- [13] N. Fischer, E. Van Steen, M. Claeys, J. Catal. 299 (2013) 67–80.
- [14] O. Borg, P. Dietzel, A. Spjelkavik, E. Tveten, J. Walmsley, S. Diplas, S. Eri, A. Holmen, E. Rytter, J. Catal. 259 (2008) 161–164.
- [15] S. Ho, J. Catal. 135 (1992) 173–185.
- [16] S. Rane, Ø. Borg, E. Rytter, A. Holmen, Appl. Catal. A 437–438 (2012) 10–17.
- [17] H. Xiong, M.A.M. Motchelaho, M. Moyo, L.L. Jewell, N.J. Coville, J. Catal. 278 (2011) 26–40.
- [18] Q. Cheng, Y. Tian, S. Lyu, N. Zhao, K. Ma, T. Ding, Z. Jiang, L. Wang, J. Zhang, L. Zheng, F. Gao, L. Dong, N. Tsubaki, X. Li, Nat. Commun. 9 (2018) 3250.
- [19] Z. Wang, S. Skiles, F. Yang, Z. Yan, D.W. Goodman, Catal. Today 181 (2012) 75–81.
- [20] J.P. Den Breejen, J.R.A. Sietsma, H. Friedrich, J.H. Bitter, K.P. De Jong, J. Catal. 270 (2010) 146–152.

- [21] G. Prieto, A. Martínez, P. Concepción, R. Moreno-Tost, J. Catal. 266 (2009) 129–144.
- [22] T. Herranz, X. Deng, A. Cabot, J. Guo, M. Salmeron, J. Phys. Chem. B 113 (2009) 10721–10727.
- [23] A. Martinez, G. Prieto, J. Catal. 245 (2007) 470–476.
- [24] P. Van Helden, I.M. Ciobîcă, R.L.J. Coetzer, Catal. Today 261 (2016) 48–59.
- [25] R. Agrawal, P. Phatak, L. Spanu, Catal. Today 312 (2018) 174–180.
- [26] M.P.C. van Etten, B. Zijlstra, E.J.M. Hensen, I.A.W. Filot, ACS Catal. 11 (2021) 8484–8492.
- [27] S. Shetty, R.A. van Santen, Catal. Today 171 (2011) 168–173.
- [28] B. Zijlstra, R.J.P. Broos, W. Chen, H. Oosterbeek, I.A.W. Filot, E.J.M. Hensen, ACS Catal. 9 (2019) 7365–7372.
- [29] S. Shetty, A.P.J. Jansen, R.A. Van Santen, J. Phys. Chem. C 112 (2008) 14027– 14033.
- [30] M.A. Petersen, J.-A. Van Den Berg, I.M. Ciobîcă, P. Van Helden, ACS Catal. 7 (2017) 1984–1992.
- [31] R.A. Van Santen, M. Neurock, S.G. Shetty, Chem. Rev. 110 (2010) 2005– 2048.
- [32] C. Strebel, S. Murphy, R.M. Nielsen, J.H. Nielsen, I. Chorkendorff, Phys. Chem. Chem. Phys. 14 (2012) 8005.
- [33] J.P. Den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. De Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [34] S. Shetty, A.P.J. Jansen, R.A. Van Santen, J. Am. Chem. Soc. 131 (2009) 12874–12875.
- [35] I.A.W. Filot, S.G. Shetty, E.J.M. Hensen, R.A. Van Santen, J. Phys. Chem. C 115 (2011) 14204–14212.
- [36] W. Chen, B. Zijlstra, I.A.W. Filot, R. Pestman, E.J.M. Hensen, ChemCatChem 10 (2018) 136–140.
- [37] A. Tuxen, S. Carenco, M. Chintapalli, C.-H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A.P. Alivisatos, G. Thornton, W.-F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, J. Am. Chem. Soc. 135 (2013) 2273–2278.
- [38] B. Zijlstra, R.J.P. Broos, W. Chen, I.A.W. Filot, E.J.M. Hensen, Catal. Today 342 (2020) 131–141.
- [39] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251–14269.
- [40] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15–50.
- [41] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953–17979.
- [42] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758–1775.
- [43] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865-3868.
- [44] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 32 (2011) 1456–1465.
- [45] L. Goerigk, in: Non-Covalent Interactions in Quantum Chemistry and Physics, Elsevier, 2017, pp. 195–219.
- [46] G. Makov, M.C. Payne, Phys. Rev. B 51 (1995) 4014–4022.
- [47] J. Neugebauer, M. Scheffler, Phys. Rev. B 46 (1992) 16067–16080.

- [48] R.D.E. Krösschell, E.J.M. Hensen, I.A.W. Filot, J. Phys. Chem. C 128 (2024) 8947–8960.
- [49] J. Yang, H. Wang, X. Zhao, Y.L. Li, W.L. Fan, RSC Adv. 6 (2016) 40459–40473.
- [50] S. Kanungo, Y. Su, M.F. Neira d'Angelo, J.C. Schouten, E.J.M. Hensen, Catal. Sci. Technol. 7 (2017) 2252–2261.
- [51] M.-C. Silaghi, A. Comas-Vives, C. Copéret, ACS Catal. 6 (2016) 4501–4505.
- [52] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [53] M. Chase, NIST-JANAF Thermochemical Tables, 4th ed, American chemical society, Washington, D.C, 1998.
- [54] B. Zijlstra, R.J.P. Broos, W. Chen, G.L. Bezemer, I.A.W. Filot, E.J.M. Hensen, ACS Catal. 10 (2020) 9376–9400.
- [55] C.T. Campbell, ACS Catal. 7 (2017) 2770–2779.
- [56] M. Abramowitz, I.A. Stegun, Handbook of Mathematical Functions: With Formulas, Graphs, and Mathematical Tables, Dover Publications, 1965.
- [57] R. Dronskowski, P.E. Bloechl, J. Phys. Chem. 97 (1993) 8617–8624.
- [58] V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Phys. Chem. A 115 (2011) 5461–5466.
- [59] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Comput. Chem. 34 (2013) 2557–2567.
- [60] S. Maintz, V.L. Deringer, A.L. Tchougréeff, R. Dronskowski, J. Comput. Chem. 37 (2016) 1030–1035.
- [61] R. Nelson, C. Ertural, J. George, V.L. Deringer, G. Hautier, R. Dronskowski, J. Comput. Chem. 41 (2020) 1931–1940.
- [62] T. Koga, K. Kanayama, S. Watanabe, A.J. Thakkar, Int. J. Quant. Chem. 71 (1999) 491–497.
- [63] T. Koga, K. Kanayama, T. Watanabe, T. Imai, A.J. Thakkar, Theor. Chem. Acc. 104 (2000) 411–413.
- [64] R. Van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189–230.
- [65] I.A.W. Filot, M.P.C. Van Etten, D.W.J.G. Trommelen, E.J.M. Hensen, JOSS 8 (2023) 5710.
- [66] J.K. Nørskov, F. Abild-Pedersen, F. Studt, T. Bligaard, Proc. Natl. Acad. Sci. U.S.A. 108 (2011) 937–943.
- [67] T.L. Hill, An Introduction to Statistical Thermodynamics, unabridged, corr. republ. of the 2. printing of the work Reading, Mass. Addison-Wesley, 1960, Dover Publ, New York, 1998.
- [68] C.H. Shomate, J. Phys. Chem. 58 (1954) 368–372.
- [69] J. W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, 1st ed., Wiley, 2003.
- [70] P.J. Feibelman, B. Hammer, J.K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, J. Dumesic, J. Phys. Chem. B 105 (2001) 4018–4025.
- [71] Van Santen, R. A., Zonnevylle, M.C., Jansen, P.J., Phil. Trans. R. Soc. Lond. A 341 (1992) 269–282.

- [72] A. Nandula, Q.T. Trinh, M. Saeys, A.N. Alexandrova, Angew. Chem. Int. Ed. 54 (2015) 5312–5316.
- [73] I.M. Ciobîcă, R.A. Van Santen, P.J. Van Berge, J. Van De Loosdrecht, Surf. Sci. 602 (2008) 17–27.
- [74] W. Chen, R. Pestman, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen, ACS Catal. 7 (2017) 8050–8060.
- [75] W.-J. Wang, Y.-W. Chen, Appl. Catal. 77 (1991) 21–36.
- [76] W. Chen, I.A.W. Filot, R. Pestman, E.J.M. Hensen, ACS Catal. 7 (2017) 8061– 8071.
- [77] G.S. Hammond, J. Am. Chem. Soc. 77 (1955) 334-338.
- [78] P.B. Webb, I.A.W. Filot, in: Comprehensive Inorganic Chemistry III (Third Edition), Elsevier, Netherlands, 2023, pp. 354–380.

C. Appendix



Figure C.1: Co_{20}/Al_2O_3 top and side views.



Figure C.2: Co₅₅/Al₂O₃ top and side views.



Figure C.3: Co_{52}/Al_2O_3 top and side views.























Figure C.4: Stable state geometries of Co_{20}/Al_2O_3 .























Figure C.5: Transition state geometries of Co_{20}/Al_2O_3 .





















Figure C.6: Stable state geometries of $Co_{55}/Al_2O_3/NS$.























Figure C.7: Transition state geometries of $Co_{55}/Al_2O_3/NS$.





















Figure C.8: Stable state geometries of $Co_{55}/Al_2O_3/T$.























Figure C.9: Transition state geometries of $Co_{55}/Al_2O_3/T$.



Figure C.10: Initial and transition state of CO dissociation on $Co_{52}/Al_2O_3/P$.



Figure C.11: Reaction energy diagram of the dominant pathway at 230 °C for Co_{20}/Al_2O_3 .



Figure C.12: Reaction energy diagram of the dominant pathway at 230 °C for $Co_{55}/Al_2O_3/NS$.



Figure C.13: Reaction energy diagram of the dominant pathway at 230 °C for $Co_{55}/Al_2O_3/T$.



Figure C.14: Reaction energy diagram of the dominant pathway at 230 °C for Co(0001).



Figure C.15: Reaction energy diagram of the dominant pathway at 230 °C for Co_{20} , Co_{55}/NS , Co_{55}/T and Co(0001).



Figure C.16: Reaction energy diagram of the dominant pathway at 230 °C for Co_{55}/NS , Co_{55}/T and Co(0001).

Section C.1: Analytical microkinetic model

The following microkinetic model shows that the apparent activation energy for CO methanation approximately equals the effective barrier for CO dissociation *via* CHO, assuming that CHO dissociation into CH and O is the rate determining step. We assume that half of the surface is covered with CO and the other half is covered with H. Furthermore, we apply the zero-conversion approximation.

The reaction steps for CO methanation via CHO are as follows

1.
$$CO + * \leftrightarrow CO^*$$

2. $H_2 + 2 * \leftrightarrow 2H^*$
3. $CO^* + H^* \leftrightarrow CHO^* + *$
4. $CHO^* + * \leftrightarrow CH^* + O^*$
5. $CH^* + H^* \leftrightarrow CH_2^* + *$
6. $CH_2^* + H^* \leftrightarrow CH_3^* + *$
7. $CH_4 + 2 * \leftrightarrow CH_3^* + H^*$
8. $O^* + H^* \leftrightarrow OH^* + *$
9. $OH^* + H^* \leftrightarrow H_2O^* + *$
10. $H_2O + * \leftrightarrow H_2O^*$

We assume step (4) is the rate determining step and all other steps are in quasiequilibrium. We use the nine reaction steps that are in equilibrium to express the surface coverages of the intermediates in terms of the partial pressures of the reactants and products, the equilibrium constants of the reaction steps and the fraction of the surface that is empty.

$$\theta_{\rm CO} = K_1 \, p_{\rm CO} \, \theta_*$$

$$\theta_{\rm H} = \sqrt{K_2 \, p_{\rm H_2}} \, \theta_*$$

$$\theta_{\rm H_2O} = K_{10} \, p_{\rm H_2O} \, \theta_*$$

$$\theta_{\rm OH} = \frac{K_9 \, K_{10} \, p_{\rm H_2O} \, \theta_*}{\sqrt{K_2 \, p_{\rm H_2}}}$$

$$\theta_{0} = \frac{K_{8} K_{9} K_{10} p_{H_{2}0} \theta_{*}}{K_{2} p_{H_{2}}}$$

$$\theta_{CH_{3}} = \frac{K_{7} p_{CH_{4}} \theta_{*}}{\sqrt{K_{2} p_{H_{2}}}}$$

$$\theta_{CH_{2}} = \frac{K_{6} K_{7} p_{CH_{4}} \theta_{*}}{K_{2} p_{H_{2}}}$$

$$\theta_{CH} = \frac{K_{5} K_{6} K_{7} p_{CH_{4}} \theta_{*}}{(K_{2} p_{H_{2}})^{3/2}}$$

$$\theta_{CH0} = K_{1} K_{3} p_{C0} \theta_{*} \sqrt{K_{2} p_{H_{2}}}$$

We assume that CO and H are the most abundant reaction intermediates (MARI), so that the site balance is defined as

$$1 = \theta_* + \theta_{\rm CO} + \theta_{\rm H}$$

The site balance can be used to express the fraction of empty sites as

$$\theta_* = \left(1 + K_1 \, p_{\rm CO} + \sqrt{K_2 \, p_{\rm H_2}}\right)^{-1}$$

We assume the forward reaction rate for step (4) is dominant, so that the overall reaction rate becomes

$$r^{+} = k_{4}^{+} \theta_{\text{CHO}} \theta_{*}$$
$$r^{+} = k_{4}^{+} K_{1} K_{3} p_{\text{CO}} \sqrt{K_{2} p_{\text{H}_{2}}} \left(1 + K_{1} p_{\text{CO}} + \sqrt{K_{2} p_{\text{H}_{2}}}\right)^{-2}$$

The apparent activation energy can now be computed using the following equation

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T}$$

$$\Delta E_{act}^{app} = RT^2 \left(\frac{\partial \ln(k_4^+)}{\partial T} + \frac{\partial \ln(K_1)}{\partial T} + \frac{\partial \ln(K_3)}{\partial T} + \frac{1}{2} \frac{\partial \ln(K_2 p_{H_2})}{\partial T} - 2 \frac{\partial \ln(1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}})}{\partial T} \right)$$

$$\Delta E_{\rm act}^{\rm app} = (1 - 2 \,\theta_{\rm CO}) \,\Delta H_{\rm R}^{(1)} + \left(\frac{1}{2} - \theta_{\rm H}\right) \Delta H_{\rm R}^{(2)} + \Delta H_{\rm R}^{(3)} + \Delta E_{\rm act}^{(4)}$$

Assuming $\theta_{CO} = \frac{1}{2}$ and $\theta_{H} = \frac{1}{2}$, the apparent activation energy simplifies to the effective barrier for CO dissociation *via* CHO

 $\Delta E_{\rm act}^{\rm app} = \Delta H_{\rm R}^{(3)} + \Delta E_{\rm act}^{(4)}$



Figure C.17: Apparent activation energies.



Figure C.18: Surface coverages.



Figure C.19: Reaction orders.

Source	Catalyst	Т	р	H ₂ / CO	Est. partic le size	TOF or reaction rate	$ heta_{CO}; E_{act}^{app};$ CH ₄ selectivity; Reaction order
Wang et al. (1991) [75]	Co/γ-Al ₂ O ₃	260 °C	1 bar	2	< 4 nm	$8 \times 10^{-2} \mu\text{m} \cdot$ g ⁻¹ · s ⁻¹	E ^{app} _{act} = 97-112 kJ/mol; Negative order in CO and positive in H ₂
Bezemer <i>et al.</i> (2006) [2]	Co/carbon nanofiber	220 °C	1 bar	2	2.6 nm	1 × 10 ⁻³ s ⁻¹	CH ₄ selectivity = 53%
Den Breejen <i>et al.</i> (2009) [33]	Co/carbon nanofiber	210 °C	1.9 bar	10	2.6 nm	1.5 × 10 ⁻³ s ⁻¹	$\theta_{\rm CO} = 0.18$
Herranz <i>et al.</i> (2009) [22]	Co/SiO2	240 °C	1 bar	3.3	3 nm	$6.0 \times 10^2 \text{s}^{-1} \cdot$ (exposed Co) ⁻¹	$E_{\rm act}^{\rm app} = 105$ kJ/mol
Chen <i>et</i> <i>al.</i> (2017) [74]	Co/SiO2 Pt promoted	260 °C	1.5 bar	3	15 nm	1 × 10 ⁻² s ⁻¹	Order in CO = - 0.72 and in H ₂ = 1.20
Chen <i>et</i> <i>al.</i> (2017) [76]	Co/SiO2 Pt promoted	240 °C	3 bar	5	15 nm	7 × 10 ⁻³ s ⁻¹	$E_{act}^{app} = 127$ kJ/mol; Order in CO = -1.0
This work	Co/γ- Al ₂ O ₃ (110)	220 °C	1 bar	3	1 nm	$2.8 \times 10^{-4} \text{ s}^{-1}$ (Co ₅₅ /NS) $7.4 \times 10^{-7} \text{ s}^{-1}$ (Co ₅₅ /T) $1.7 \times 10^{-8} \text{ s}^{-1}$ (Co(0001))	$E_{act}^{app} = 177$ kJ/mol (Co ₅₅ /T) $E_{act}^{app} = 148$ kJ/mol (Co ₅₅ /NS)
This work	Co/γ- Al ₂ O ₃ (110)	230 °C	1 bar	3	1 nm	$\begin{array}{c} 5.7 \times 10^{-4} {\rm s}^{-1} \\ ({\rm Co}_{55}/{\rm NS}) \\ 1.7 \times 10^{-6} {\rm s}^{-1} \\ ({\rm Co}_{55}/{\rm T}) \\ 4.0 \times 10^{-8} {\rm s}^{-1} \\ ({\rm Co}(0001)) \end{array}$	$E_{act}^{app} = 177$ kJ/mol (Co ₅₅ /T) $E_{act}^{app} = 146$ kJ/mol (Co ₅₅ /NS)

Table C.1: Comparison to experiment.


Figure C.20: COHP of C-O bond in CO.



Figure C.21: COHP of C-O bond in CHO.



Figure C.22: Initial state of CHO dissociation on Co₂₀.



Figure C.23: Initial state of CHO dissociation on Co(0001).



Figure C.24: CO dissociation versus integrated COHP.

Section C.2: Sensitivity of the production rate on the barrier of the ratedetermining step

To assess the sensitivity of the production rate in the six kinetic models presented in this chapter to the barrier of the rate-determining step (RDS), we varied the RDS barrier at 230 °C by multiplying it by factors of 0.90, 0.95, 1.00, 1.05, and 1.10. These modifications correspond to deviations of \pm 6 – 10 kJ/mol, aligning with the assumed DFT error margin of \pm 10 kJ/mol. The resulting production rates are shown in Figure C.25.

For the three models without a pocket or B_5 site (Figure C.25a,c,e), the RDS is CHO dissociation into CH + O. For $Co_{55}/Al_2O_3/NS+P$, the RDS is OH–OH disproportionation, for $Co_{55}/Al_2O_3/T+P$ and $Co(0001)+B_5$, it is CH₃ hydrogenation toward methane. As shown in Figure C.25, methane production increases when the barrier is reduced (factors of 0.90 or 0.95) and decreases when the barrier is raised (factors of 1.05 or 1.10), as expected.

Despite these changes, the altered barriers follow a temperature dependence trend similar to the unaltered model, suggesting that the results remain qualitatively consistent. The TOF varies by at most one order of magnitude for the 0.90 and 1.10 modifications. From this analysis, we conclude that the microkinetic models are accurate within an order of magnitude.



Figure C.25: Sensitivity of the turnover frequency of CH_4 production to the barrier height of the rate-determining step for (a) $Co_{55}/Al_2O_3/NS$, (b) $Co_{55}/Al_2O_3/NS+P$, (c) $Co_{55}/Al_2O_3/T$, (d) $Co_{55}/Al_2O_3/T+P$, (e) Co(0001), and (f) $Co(0001)+B_5$.

6. Understanding Structure Sensitivity of CO₂ Hydrogenation over Partially Reduced Co Catalysts: A DFT Study of Co_{1,4,8}/CoO

Abstract

To investigate the structure sensitivity of partially reduced Co catalysts that exhibit high activity in CO₂ hydrogenation, we utilized density functional theory (DFT) and microkinetic modeling to study the CO_2 methanation pathway over a single Co atom (Co_1), a four-atom cluster (Co_4), and an eight-atom cluster (Co_8) on a CoO(100) surface. Genetic algorithms were used to identify the most stable configuration of the Co₄ cluster. High computational costs prevented the identification of the most stable configuration for Co₈. Our findings show that oxygen vacancies are not formed due to the high barriers for hydrogenating lattice oxygen. C-O bond scission in CO_2 occurs in a direct manner on CO_1 , CO_4 and Co₈, and this step is associated with low energy barriers. In contrast, C-O cleavage is associated with high barriers across Co₁, Co₄ and Co₈, which lack B₅-like sites. The high CO dissociation barriers prevent methane formation on the clusters. The Co single atom site is spatially too constrained for effective hydrogenation of CO and O species when these are both adsorbed, leading to site poisoning by atomic oxygen. On the Co_4 and Co_8 clusters, CO is the primary product, with oxygen removal as water being rate limiting for higher conversion. These results reveal the reaction mechanisms of CO_2 hydrogenation over few-atom Co clusters, providing valuable insights to guide future research on the structure sensitivity of partially reduced cobalt catalysts.

6.1 Introduction

To prevent further global temperature rise, reducing CO_2 emissions is essential. As a result, CO_2 methanation has gained renewed interest in recent years. Utilizing methane as an energy carrier offers the advantage that it be directly integrated into existing infrastructure to replace natural gas. The development of an efficient process to transform CO_2 and renewable hydrogen into methane would be a pivotal step in the transition towards a circular carbon economy. Supported metal nanoparticle catalysts are commonly used for methanation processes due to their high surface area and tunable properties. CO_2 methanation is catalyzed by the pure metals Ni, Fe, Co, and Ru.[1] Supported catalysts based on these metals are known to be structure sensitive for CO and CO_2 hydrogenation. Structure sensitivity refers to the phenomenon where the activity and selectivity depend on the structure of the catalyst, i.e. the size or morphology of the nanoparticles. A well-known example of structure sensitivity is observed in Co-catalyzed Fischer-Tropsch synthesis, where only nanoparticles larger than 6-8 nm can sustain the step-edge sites required for facile CO dissociation.[2,3] A similar relationship has been reported by Simons *et al.*, who found that step-edge sites are crucial for CO dissociation and CH_x hydrogenation in CO_2 hydrogenation over Ni.[4] Structure sensitivity trends for CO_2 hydrogenation are still under debate, since these trends depend on multiple factors such as the nature of the support,[5–8] the preparation method,[9] the operating pressure,[10] or operating temperature.[11,12]

Typically, the metal nanoparticles are fully reduced before the catalyst is used, leading to conventional structure sensitivity trends such as described above. However, several studies report that partially reduced catalysts, i.e. catalysts reduced at a lower temperature, exhibit higher activity compared to their fully reduced counterparts. This phenomenon is observed with specific metal-support combinations. Partially reduced cobalt supported on TiO₂ (titania) or CeO₂-ZrO₂ (ceria-zirconia) shows greater activity in CO₂ hydrogenation compared to its fully reduced counterparts or those supported on SiO₂, Al₂O₃ or CeO₂. In these cases, conventional structure sensitivity trends do not apply, leaving the relationship between catalyst structure and reaction mechanism unclear. Several experimental studies have explored these catalysts in detail.

Melaet *et al.*[13] reported that a partially reduced Co/TiO₂ catalyst exhibited ten times the activity of a fully reduced Co/TiO_2 catalyst for CO_2 conversion. In contrast, for SiO₂-supported Co, the fully reduced catalysts demonstrated the highest activity. The authors hypothesized that the superior performance of the partially reduced sample is due to the highly active $CoO-TiO_2$ interface. Meanwhile, the lower activity of fully reduced Co/TiO₂ is attributed to partial encapsulation of metallic Co by TiO_{2-x} (strong metal-support interactions), which reduces the number of accessible active sites. Zhao and coworkers[14] synthesized a series of Co_x/CoO_{1-x} catalysts with compositions of x = 0.2, 0.5, 0.8, 0.8along with Co_3O_4 as a reference. Among these, $Co_{0.2}/CoO_{0.8}$ was the most active. The high activity of this catalyst is explained by ample CO₂ adsorption being a rate-limiting step on metallic Co. Metallic Co remains necessary for the hydrogenation steps, as established in earlier studies and demonstrated by the low activity of Co₃O₄. Ten Have et al.[15] also compared Co/TiO₂ catalysts reduced at 250 and 450 °C, observing similar activity differences to those reported by Melaet *et al.* Additionally, they found that for Co supported on SiO₂, Al₂O₃ and CeO₂, the fully reduced catalysts were more active than those reduced at 250 °C. Parastaev et al.[16] investigated partially reduced Co/CZ catalysts for CO₂ hydrogenation. Their study revealed that a 1% Co sample reduced at 300 °C showed higher CO_2 conversion per Co atom compared to samples reduced at higher or lower temperatures (225 °C – 500 °C) or those with higher Co loadings (ranging from 1% to 20%). The partially reduced samples demonstrated optimal CO_2 conversion at the lowest Co loading (1% Co reduced at 300 °C). The hypothesis is posed that for the low loading samples, CO_2 conversion is limited by hydrogen activation. This limitation is overcome in partially reduced samples, where the Co-CoO interface enhances hydrogen activation, a critical step for Hassisted CO dissociation.[17]

To unravel the structure sensitivity of partially reduced Co catalysts, we employed density functional theory (DFT) to simulate CO₂ hydrogenation over Co clusters supported on a CoO surface. As criterion for these models, we have used the observation from Parastaev et al. that the partially reduced catalysts consist of significant amounts of both Co²⁺ and Co⁰.[16] With a genetic algorithm Co_4 and Co_8 clusters on a CoO(100) support were generated. We found that due to its high computational costs, the GA for Co₈ did not converge within reasonable time frames, while for the Co₄ the GA did converge within reasonable time frames. The most stable position for a single Co atom on a CoO(100) surface (Co₁) was found heuristically. On the most stable configurations of the Co₁, Co₄, and Co₈ systems, we simulated the reaction pathways leading from CO₂ to methane, including pathways involving oxygen vacancies. Microkinetic models are used to reveal the reaction mechanisms over the modelled catalysts. These simulations allow us to correlate catalyst morphology with performance. The results reveal that CO_2 dissociation is facile across all systems, with no further decrease in the dissociation barrier of CO_2 when CO_2 splits at an oxygen vacancy. However, oxygen vacancy formation is difficult due to high barriers for hydrogenation of lattice oxygen. The Co_1 system appeared to be inactive for CO_2 conversion because the limited space restricts the hydrogenation of the respective CO and O fragments after CO₂ cleavage when the other fragment is co-adsorbed. Both Co₄ and Co_8 clusters show 100% selectivity for the reverse water-gas shift (RWGS) reaction and no methane formation. This selectivity pattern arises from high barriers associated with CO dissociation and water formation. A difference between the Co_4 and Co_8 cluster is that the CO_2 methanation pathway over Co_8 involves several highly stable intermediate states. This is attributed to adsorbate induced reconstruction of the cluster, and this reveals that more stable configurations of Co₈ exist that are geometrically close to the original configuration. These results provide more insight into the structure sensitivity of partially reduced catalysts.

6.2 Methods

6.2.1 DFT

Plane-wave density functional theory calculations were performed using the Vienna ab initio simulation package (VASP)[18,19], that employs the projectoraugmented wave (PAW) method to describe the core electrons.[20,21] The Perdew-Burke-Ernzerhof (PBE) functional is used to describe electron exchange and correlation.[22] The long-range dispersion interactions were described by the semi-empirical method of Grimme (DFT-D3).[23] To increase the on-site electron-electron repulsion that is underestimated for CoO by standard DFT settings, we employed a Hubbard correction term using the DFT+U method.[24] The Dudarev approach implementation in VASP was used with $U_{\text{eff}} = U - I = 3.0$ eV for Co atoms.[25] This value for U was chosen based on an earlier study showing this value describes both Co and CoO phases with sufficiently accuracy.[26] Solutions to the Kohn-Sham equations were calculated using a plane wave basis set with a cut-off of 400 eV. For all calculations, spin polarization was included. We used Gaussian smearing with a smearing width of 0.05 eV. The CoO rock-salt bulk structure (space group Fm $\overline{3}$ m) was k-point converged with a mesh of 7 × 7 × 7 for a bulk cell with 4 Co and 4 O atoms of 3.02 × 6.00 × 5.19 Å³. A lattice constant of 4.25 Å was obtained, in good agreement with experiments (4.26 Å).[27,28] A rhombohedral unit cell was used to correctly simulate the antiferromagnetic type II (AF-II) ordering that exists in CoO, in line with previous studies. [26,29,30] In the AF-II ordering, the Co atoms in one (111) plane possess a positive magnetic moment or positive spin, while the metal atoms on the two adjacent planes possess a negative magnetic moment or negative spin.[31,32] The initial magnetic moments were set to 1.0 and -1.0 $\mu_{\rm B}$. After optimization, the Co atoms in the CoO bulk arranged into 2.637 and -2.637 $\mu_{\rm B}$, corresponding to the (111) planes. The Co_{1.4.8} nanoclusters were given an initial magnetic moment of zero. After optimization, the spins of these Co atoms aligned with the planes of positive and negative magnetic moments of the CoO phase. The $Co_{1,4,8}$ nanoclusters are supported by a CoO(100) surface in a supercell of $12.1 \times 12.1 \times 21.4$ Å³. The vacuum slab in all models is at least 11 Å. A Γ -centered *k*-point mesh of 3 × 3 × 1 was used to sample the Brillouin zone of these supercells. For the gas phase molecules, only the Γ -point was used. The CoO(100) surface consists of four layers of which the bottom two are frozen. The CoO(100) surface was chosen because with a surface energy of 1.19 J/m² it was found to be more stable than CoO(110) and CoO(111), which surface energies are 1.77 and 1.38 J/m², respectively. In earlier work, CoO(100) was also found to be the most stable termination.[30,33] Experiments show that nanoparticles smaller than 10 nm exhibit both CoO(100) and CoO(111) terminations.[34] We optimized the stable states and the transition states using an ionic convergence criterion of 5×10^{-5} eV and an electronic convergence criterion of 1×10^{-5} eV. It was verified that for the adsorbate atoms the absolute force is less than 0.1 eV/Å. All energies are corrected for the vibrational zero-point energy. We searched for transition states with the climbing image nudged elastic band (CI-NEB) method[35] as implemented in VASP. We verified that the optimized transition states show one imaginary frequency in the direction of the reaction coordinate.

6.2.2 Genetic algorithm

To find the most stable structures of $Co_4/CoO(100)$ and $Co_8/CoO(100)$ clusters, a DFT-based genetic algorithm was employed. This genetic algorithm (GA) is written by Chang et al.[36] and based on the procedure by Vilhelmsen and Hammer.[37] The algorithm is designed to generate a large population of structures with a high degree of configurational diversity. When no new unique structures can be created, it indicates that all possible configurations have been explored, and the most stable structures can then be identified and collected. For both the Co_4 and Co_8 GA runs, the initial population consisted of fifteen randomly generated structures. These structures were placed 2.0 Å above the center of the CoO(100) surface. The clusters were optimized using VASP until the norms of the forces of all atoms were reduced to less than 0.05 eV/Å. A minimum of twelve structures is collected per generation, after which duplicate structures are systematically removed. New generations, each generation consisting of fifteen structures, are created through the application of crossover, mutation, and natural selection processes, ensuring the diversification of the population over the generations.

6.2.3 Microkinetic simulations

Microkinetic simulations were conducted using MKMCXX.[38] This software solves a set of ordinary differential equations describing adsorption, reaction and desorption events by performing time integration. The absolute and relative tolerances were set to 1×10^{-9} . It was verified that the simulations were time-converged at all temperatures.

The net adsorption rate of gas phase species *i* is modelled as

$$r_i = k_{i, \text{ ads}} \theta_* p_i - k_{i, \text{ des}} \theta_i \tag{1}$$

The adsorption rate of gas molecules, that in their transition state for adsorption lose one translational degree of freedom, is described by

$$k_{i, \text{ ads}} = S \frac{A}{\sqrt{2\pi m_i k_{\text{B}} T}}$$
(2)

where *S* is the sticking coefficient that is set to unity, *A* the area of the adsorption site, m_i the mass of the adsorbate *i*, k_B the Boltzmann constant and *T* the temperature. The desorption rate of adsorbates is calculated from $k_{i, ads}$ and the equilibrium constant for adsorption, which yields

$$k_{i, \text{des}} = S \frac{A}{\sqrt{2\pi m k_{\text{B}} T}} \exp\left(\frac{\Delta H_{\text{ads}}}{RT}\right) \exp\left(\frac{S_{\text{gas}}}{R}\right) \frac{1}{Q_{\text{ads}, \text{v}}}$$
(3)

where $Q_{ads,v}$ is the product of the vibrational partition functions of the adsorbate in the adsorbed state, S_{gas} the entropy in the gas phase as calculated using the Shomate equation (*vide infra*), *R* the gas phase constant, and ΔH_{ads} is the adsorption enthalpy as given by

$$\Delta H_{\rm ads} = \Delta E_{\rm elec} + \Delta E_{\rm zpe} + \frac{NRT}{2} \tag{4}$$

with ΔE_{elec} the electronic adsorption energy, ΔE_{zpe} the difference in the ZPE between the adsorbed and gas phase state, and *N* the total number of rotational and translational degrees of freedom in the gas phase. To incorporate the entropic contribution in the adsorption and desorption rate, the gas phase entropy is calculated using the Shomate equation for CO, H₂, H₂O and CH₄.[39]

The reaction rate for surface reactions is given by

$$k_{\text{react}} = \frac{k_{\text{B}}T}{h} \frac{Q^{\ddagger}}{Q} \exp\left(\frac{-\Delta E_{\text{act}}}{k_{\text{B}}T}\right)$$
(5)

where Q^{\ddagger} and Q are the partition functions of the activated complex and the corresponding initial state, respectively, and ΔE_{act} is the energy needed to activate the reaction.

For elementary reaction steps with very low barriers, the application of the zeropoint energy correction sometimes results in negative barriers. Cleary, such barriers are in disagreement with transition state theory as the rates associated with such barriers will decrease with increasing temperature. On top of that, negative and very low barriers cause numeric instabilities in the ordinary differential equation solver of MKMCXX. To correct this undesirable behavior, any barriers found that are lower than 5 kJ/mol are adjusted. This adjustment involves increasing both the forward and backward barrier by the same value such that the lowest of the two barriers corresponds to 5 kJ/mol. The systematic adjustment of both the forward and the backward barrier ensures that the equilibrium constant for the elementary reaction step is not affected by the correction, ensuring invariance of overall reaction thermodynamics. Sensitivity analysis towards pressure, temperature and barriers is conducted in MKMCXX by evaluating the reaction order, the apparent activation energy and the degree of rate control, respectively. The reaction orders are calculated according to

$$n_i = p_i \frac{\partial \ln r^+}{\partial p_i} \tag{6}$$

where n_i is the reaction order of species *i*, p_i is the partial pressure of species *i* and r^+ is the forward rate of the product of interest. The apparent activation energy is evaluated *via*

$$\Delta E_{\rm act}^{\rm app} = RT^2 \frac{\partial \ln r^+}{\partial T} \tag{7}$$

where r^+ is the forward rate of the product of interest. The degree of rate control X of elementary reaction step *i* is defined as:[40]

$$X_{i} = \left(\frac{\partial \ln r}{\partial \ln k_{i}}\right)_{k_{j\neq i},K_{j}}$$
(8)

where r is the net rate of the product of interest, and where all the equilibrium constants K_j and the rate constants k of all other reaction steps except i are held constant. All of the above quantities are evaluated numerically by means of a five-point centered finite difference stencil.[41]

6.3 Results and discussion

We considered three models corresponding to $Co_1/CoO(100)$, $Co_4/CoO(100)$, and $Co_8/CoO(100)$ to investigate the reactivity of a partially reduced Co catalyst. These models are inspired by the catalyst structure proposed by Parastaev *et al.*[16] Multiple possible CO_2 hydrogenation pathways are simulated over these model structures to assess their reactivity and establish structure-sensitivity relationships for these model catalysts.

6.3.1 Models

The $Co_1/CoO(100)$ model visualized in Figure 6.1a was obtained by heuristically finding the most stable position for a Co atom on the CoO(100) surface. The Co atom is placed on top of an oxygen atom, as shown in Figure 6.1a. Another potentially stable position is to place the Co atom between two oxygen atoms, yet this state is higher in energy by 2.23 eV (Figure D.2).



Figure 6.1: Top view of the models for $Co_1/CoO(100)$ (a), $Co_4/CoO(100)$ (b), and $Co_8/CoO(100)$ (c) that are used for reaction pathway calculations. The Co atoms of the clusters are shown in darker blue to distinguish them from the Co atoms of the CoO, which are shown in lighter blue.

We used an in-house genetic algorithm [36,37] (GA) to explore the geometry and adsorption site for Co₄ and Co₈ nanoclusters on a CoO(100) support. The procedure and settings are described in the Methods section. For the Co₄/CoO(100) model, the GA generated over 200 structures across eighteen generations, among which 135 were identified as geometrically distinct. In the last generation, no new unique structures were found. This indicates that the GA run has reached a high level of convergence. The nine most stable structures from this GA run were further optimized according to a more stringent criterion, i.e. that the total energy between two ionic steps is smaller than 1×10^{-5} eV. These structures are shown in Figure D.1, including the corresponding energy with respect to the most stable cluster. The second most stable structure (+0.06 eV) was chosen for further calculations (Figure 6.1b) because the most stable cluster underwent reconstruction when adsorbates were introduced. This inherent instability rendered it challenging, if not impossible, to reliably identify adsorbed states and transition states on the most stable cluster.

For the $Co_8/CoO(100)$ model, two genetic algorithm (GA) explorations were performed, generating twelve and fifteen generations, respectively. These explorations produced 115 and 417 unique structures. Due to the high computational cost associated with the GA for an eight-atom cluster, neither of the two explorations was extended to full convergence. Instead, the ten most stable structures from each simulation were refined with higher accuracy, resulting in a total of twenty optimized structures, which were subsequently categorized into five archetype groups. The most stable structure of each archetype group is shown in Figure D.3. The corresponding energy is the energy relative to the most stable structure. The most stable structure was used in further calculations and is shown in Figure 6.1c.

6.3.2 Reaction energetics

We assessed the most stable adsorption sites of reactants and products on Co_1 , Co_4 , Co_8 , and the bare CoO(100) surface. We compare these values to the most stable adsorption sites on the extended surfaces Co(0001) and $Co(11\overline{2}1)$ as reported by Zijlstra *et al.*[42]

6.3.2.1 Reactant adsorption

The most stable adsorption sites of reactants CO_2 and H_2 are shown in Figure 6.2 for CO_2 and in Figure 6.3 for H_2 . Both figures display the zero-point energy corrected energies of the most stable adsorption configurations relative to the gas-phase energies, along with the corresponding atomic configurations (excluding those for the extended surfaces). On CoO(100), Co_1 , and Co_4 , CO_2 adsorbs with an adsorption enthalpy comparable to that on $Co(11\overline{2}1)$, with values ranging from -84 to -97 kJ/mol. In contrast, CO_2 exhibits weak adsorption on Co(0001), with an adsorption enthalpy of only -4 kJ/mol. Conversely, Co_8 provides an extremely stable adsorption site for CO_2 , with an adsorption energy of -200 kJ/mol.

 H_2 adsorbs in a dissociative manner, since the transition of H_2 to H+H was found to be barrierless. On CoO(100), hydrogen adsorption will not occur, because the most stable adsorption is endothermic (Figure 6.3). The adsorption enthalpy for H_2 on Co₁, Co₄, Co(0001), and Co(11 $\overline{2}$ 1) ranges from -99 to -63 kJ/mol. Again, Co₈ is the outlier with an extremely stable adsorption for H_2 of -228 kJ/mol.



Figure 6.2: (left) Adsorption energy of the most stable adsorption of CO_2 on CoO(100), $Co_1/CoO(100)$, $Co_4/CoO(100)$, $Co_8/CoO(100)$, Co(0001), and $Co(11\overline{2}1)[42]$ with (right) the corresponding geometries for the first four models (a-d).



Figure 6.3: (left) Adsorption energy of the most stable adsorption of H_2 on CoO(100), Co₁/CoO(100), Co₄/CoO(100), Co₈/CoO(100), Co(0001), and Co(11 $\overline{2}$ 1)[42] with (right) the corresponding geometries for the first four models (a-d).

Since CO_2 can adsorb on CoO(100) while H_2 cannot, the necessity of metallic centers for sufficient hydrogen supply becomes evident. The adsorption energies of CO_2 and H_2 on CO_1 and CO_4 are comparable to those of extended Co surfaces. This contrasts with findings from Chapter 4 and Chapter 5, which showed that CO and H_2 adsorption on Co nanorods and small Co nanoparticles is in general stronger than on extended surfaces, in these cases leading to reduced CO methanation activity. In contrast, Co₈ displays highly exothermic adsorption energies for both CO_2 and H_2 . We attribute this to adsorbate-induced rearrangements within the Co_8 cluster. When H_2 or CO_2 adsorbs, significant displacement of Co atoms occurs, driving the cluster into a lower-energy configuration. This effect is particularly pronounced for the three topmost Co atoms, which exhibit high mobility due to their lack of bonding to the CoO(100)surface and the absence of constraints from surrounding lattice atoms, as illustrated in Figure 6.1. The mobility of these top atoms promotes a wide range of rearrangements within the cluster-adsorbate system, allowing access to multiple stable configurations that occupy closely related positions in the configurational space. In comparison, this behavior is less evident for the single Co atom and the Co_4 cluster, as these systems appear to already reside in their most stable configurations.

6.3.2.2 Effect of co-adsorption

In addition to the adsorption of CO_2 and H_2 on the empty Co_1 , Co_4 , and Co_8 , we also explored the adsorption energies of these intermediates in the presence of

co-adsorbates. Due to the variety of reaction trajectories possible in the chemokinetic network relevant to CO₂ methanation, this study is rather extensive. An overview is presented in Table D.1-3, and the corresponding geometries are shown in Figure D.4, D.6, and D.8. We highlight the most significant findings of this investigation. The co-adsorption of H₂ in the presence of both HCO and OH on Co₄ is associated with an adsorption energy of -230 kJ/mol, which is extremely low for H₂. In comparison, for the empty cluster an adsorption energy of only -63 kJ/mol was found. We attribute this enhanced stability to adsorbate induced reconstruction of Co₄. This can be seen in Figure D.6, where the geometry of HCO + OH + 2H on Co_4 shows that the four cluster atoms are at different positions than in the empty cluster. We also observe situations where adsorbates exhibit decreased stability due to the presence of another adsorbate. These interactions arise primarily from steric hindrance, where the proximity of H_2 and H_2CO creates spatial constraints, or from the conservation of bond order, which limits the availability of surface bonding electrons. Consequently, the presence of H_2CO weakens the bond between H and the Co atoms, leading to reduced adsorption stability.

6.3.2.3 Product desorption

The desorption energies of the products H_2O , CH_4 , CO, and CH_3OH can be found in Table 6.1. CH_3OH adsorbed on Co_1 , Co(0001) and $Co(11\overline{2}1)$ have not been calculated since the pathways towards CH_3OH are not possible (Co_1) or expected (extended surfaces) on these systems.[42] For all products, Co_8 exhibits significantly higher desorption energies compared to Co_1 , Co_4 , and the extended surfaces, whereas the desorption energies of H_2O , CH_4 , and CO on Co_1 and Co_4 are similar to those observed on the extended surfaces. Similar to adsorption of CO_2 and H_2 , we attribute the higher desorption energies on Co_8 to the low coordination of the three top Co atoms of Co_8 and adsorbate induced reconstruction.

Table 6.1: Desorption energies in kJ/mol of H₂O, CH₄, CO, and CH₃OH on Co₁, Co₄, and Co₈. For comparison the desorption energies on Co(0001) and Co($11\overline{2}1$) are included, obtained from Zijlstra *et al.*[42]

	H ₂ O	CH ₄	СО	CH ₃ OH
Co1	30	20	175	-
Co ₄	22	18	160	19
Co ₈	107	124	219	184
Co(0001)	24	2	165	-
$Co(11\overline{2}1)$	53	6	171	-

6.3.2.4 Thermodynamic assessment

We compare the reaction enthalpies for CO_2 methanation, CO methanation, rWGS reaction, CO_2 to methanol and CO to methanol obtained with DFT calculations to the reaction enthalpies obtained from the NIST database using the Shomate equation.[39,43] At T = 25 °C and p = 1 atm the experimental reaction enthalpy is as follows:

$$CO_2 + 4 H_2 \rightleftharpoons CH_4 + 2 H_2 O \qquad [\Delta H_R^{\Theta} = -165 \text{ kJ/mol}]$$
 (1)

$$CO + 3 H_2 \rightleftharpoons CH_4 + H_2 O \qquad [\Delta H_R^{\Theta} = -206 \text{ kJ/mol}]$$
(2)

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad [\Delta H_R^{\Theta} = 41 \text{ kJ/mol}]$$
 (3)

$$CO_2 + 3 H_2 \rightleftharpoons CH_3 OH + H_2 O \qquad [\Delta H_R^{\Theta} = -49 \text{ kJ/mol}]$$
(4)

$$CO + 2 H_2 \rightleftharpoons CH_3 OH \qquad [\Delta H_R^{\Theta} = -91 \text{ kJ/mol}]$$
(5)

From the DFT calculations we found that the vibrational zero-point energy corrected electronic energy of reaction at 0 K for reactions (1), (2), (4) and (5) is $\Delta H_R^0 = -146$, -227, -56 and -97 kJ/mol, respectively. This deviates by 19, -21, -6 and -6 kJ/mol from the experimental values. To ensure thermodynamically correct microkinetic models, we corrected the adsorption energies of CO, CO₂ and CH₃OH by +21.0 kJ/mol for CO, -18.7 kJ/mol for CO₂, and -6.1 kJ/mol for CH₃OH. The same correction for CO and CO₂ was done by Zijlstra and coworkers.[42] These adapted values were used as reference for the microkinetic model.

6.3.2.5 Surface reactions

For Co₁, Co₄, and Co₈, the forward and backward activation energies of the reaction steps possible in CO₂ hydrogenation, and the initial, transition and final state geometries of these reaction steps can be found in Table D.1-3 and Figure D.5,7,9. Different activation energies are found depending on which species are co-adsorbed on the site. These differences are explained by the same reasoning that holds for adsorption events when spectator species are already present. Spectator species can modify the arrangement of cluster atoms, resulting in the creation of distinct active sites and variations in transition state stabilization. Furthermore, electron withdrawal from Co atoms may diminish their ability to donate electrons to the reacting adsorbate(s), while the close proximity of co-adsorbates induces Pauli repulsion. All these effects can potentially influence the reaction network.

In catalysts containing reducible metal oxides, oxygen vacancies may contribute to the reaction mechanism. For CO_2 hydrogenation over Co, Parastaev *et al.* suggest that oxygen vacancies can be healed by CO_2 dissociation and regenerated

by H_2O formation.[16] For the water-gas shift (WGS) reaction over Co, Saini *et al.* point toward enhancement of CO activation by oxygen vacancies.[44] For Co₁, Co₄, and Co₈, we simulated both CO₂ and CO dissociation into an oxygen vacancy to see whether this proceeds more easily than direct dissociation without oxygen vacancy. The results are found in Table 6.2 and Table D.1-3. The corresponding stable and transition state geometries can be found in Figure D.4-9.

-					
	$CO_2 + V_0 \rightleftharpoons CO$		$CO + V_0 \rightleftharpoons C$		
	E _{act} forward [kJ/mol]	E _{act} backward [kJ/mol]	E _{act} forward [kJ/mol]	E _{act} backward [kJ/mol]	
Co ₁	211	327	No TS found	No TS found	
Co ₄	58	178	98	46	
Co ₈	79	158	191	233	

Table 6.2: Energy barriers of CO_2 and CO dissociation into an oxygen vacancy for Co_1 , Co_4 , and Co_8 .

Table 6.2 shows that CO₂ dissociation over Co₁ is highly unlikely as the forward energy barrier is 211 kJ/mol. The high backward barrier reveals that an oxygen vacancy may be relatively unstable for this system. For CO dissociation into an oxygen vacancy, no transition state could be found. We hypothesize this transition state (TS) does either not exist or it is very unstable. As a highly unstable TS yields a very high activation barrier, we assume either way that this reaction step is not relevant to the reaction mechanism of CO_2 hydrogenation. Near Co_4 and Co_8 , CO_2 dissociation into an oxygen vacancy is associated with low energy barriers. The energy barrier for CO dissociation into an oxygen vacancy near Co₄ can be overcome at a reaction temperature of 250 °C, but for Co₈ this barrier is too high to be overcome at this reaction temperature. In Figure 6.4, the initial, transition, and final state geometries of CO_2 dissociation over CO_8 are depicted: the top row showing direct CO_2 dissociation over the cluster, the bottom row direct CO_2 dissociation where the leaving O heals an oxygen vacancy. The activation energy of direct CO_2 dissociation over CO_8 (top row) is 81 kJ/mol, the activation energy of CO_2 dissociation healing the oxygen vacancy (bottom row) is 79 kJ/mol. These transition states are geometrically very different from each other in terms of the number of Co atoms to which CO and O bond, and the number of Co atoms that are shared between CO and O in TS. However, they result in practically the same energy barrier. This observation supports the hypothesis from the study of Parastaev et al. that CO₂ activation is not structure sensitive and that the first part of the reaction mechanism does not depend on the extent of Co reduction.[16] For CO dissociation we observe significantly lower barriers for dissociation into the vacancy for Co_4 and Co_8 than without vacancy. Direct CO dissociation without an oxygen vacancy present is associated with activation energies of 422, 321, and 224 kJ/mol for Co₁, Co₄, and Co₈, respectively. These are prohibitively high barriers, as would be expected for direct CO dissociation over sites other than B₅-like sites, and these results are consistent with other studies.[45,46] For Co₈, the barrier for CO dissociation into the oxygen vacancy is lower (191 kJ/mol) than without oxygen vacancy (224 kJ/mol), but still too high to be overcome at 250 °C. For Co₄ however, direct CO dissociation becomes accessible if an oxygen vacancy is present (98 kJ/mol), while without oxygen vacancy this step would not occur (321 kJ/mol).



Figure 6.4: The initial (a,d), transition (b,e), and final (c,f) states of CO_2 dissociation on Co_8 without (a-c) and with (d-f) oxygen vacancy.

Oxygen vacancy formation

An oxygen vacancy in the CoO surface can be formed by adsorption of H_2 and subsequent desorption of H_2O . To assess whether oxygen vacancies will be formed under reaction conditions, we computed the stability of an oxygen vacancy compared to the stoichiometric surface. The results are shown in Figure 6.5. The oxygen vacancy formation energy is calculated as the difference between the stoichiometric surface and H_2 in the gas phase versus the surface with an oxygen vacancy and gaseous H_2O . The energy and corresponding geometry of the most stable oxygen vacancy close to Co₁, Co₄, and Co₈ are shown. We observed that oxygen vacancies farther from Co₁, Co₄, or Co₈ are less stable than those in closer proximity to the single atom or the clusters. This stabilization effect diminishes with increasing distance, and when the separation becomes larger than the range of electrostatic effects of the atom or cluster, the oxygen vacancy formation energy converges to the value characteristic of the bare CoO(100) surface, i.e. 280 kJ/mol. The range of electrostatic effects is typically a distance of a few atoms.[47] This indicates that the presence of a single atom or a small cluster stabilizes oxygen vacancies in their vicinity.



Figure 6.5: (left) Formation energy of the most stable oxygen vacancy for CoO(100), Co₁/CoO(100), Co₄/CoO(100), and Co₈/CoO(100) with (right) the corresponding geometries (a-d). For clarity, the vacancy is indicated with a colored circle.

In Table 6.3, the energy barriers for oxygen vacancy formation are listed. The corresponding transition states are visualized in Figure D.5, D.7, and D.9. The first step is the hydrogenation of an oxygen atom directly near Co₁, Co₄, or Co₈. For Co₁ and Co₄, the H atom approaches the oxygen while being bonded in a bridged manner in TS. For Co₈, the H is bonded to only one Co atom, and this is associated with a lower barrier than for Co₁ and Co₄. At reaction temperature, the first hydrogenation step is energetically only accessible for Co₈. The high barriers for this step on Co₁ and Co₄ could indicate that H spillover is not likely for these systems. In all models, the oxygen remains positioned within the lattice in the final state, while the hydrogen atom bends toward the Co atom or cluster. The second hydrogenation of the lattice O is associated with very high barriers on Co₁ and Co_8 (266 and 301 kJ/mol for Co_1 and Co_8 , respectively), and a low barrier on Co_4 (87 kJ/mol). In all three TSs, the oxygen has vacated its position in the lattice. The difference in the second hydrogenation barrier is explained by the coordination of O in TS. On Co₁ and Co₈, the oxygen is bonded to one Co atom in TS. On Co₄ the oxygen is bonded to two Co atoms, significantly enhancing the

stabilization of this TS. The final state of this reaction step looks similar for Co₁, Co₄ and Co₈, with H₂O bonded *via* O to a lattice Co atom adjacent to the newly created oxygen vacancy. Desorption of H₂O is endothermic on Co₄ and Co₈, as expected, but exothermic on Co₁, suggesting that H₂O would leave Co₁ as soon as it is formed in one concerted reaction step. Calculating the effective barriers, i.e. the largest difference between a stable state and a transition state following that stable state, reveals that oxygen vacancy formation is most likely on Co₄. However, considering the first O hydrogenation barrier of 182 kJ/mol, it is expected that also on Co₄ there will be very little oxygen vacancies formed at typical reaction temperatures of T = 250 °C.

Table 6.3: Energy barriers of hydrogenation of an oxygen from the support (twice) and subsequent H_2O desorption for Co_1 , Co_4 , and Co_8 in kJ/mol. The last column shows the effective barrier for oxygen vacancy formation.

	$2H \rightleftharpoons O_{sup}H + H$		$O_{sup}H + H \rightleftharpoons H_2O_{sup}$		H ₂ O _{sup}	O _{vac} formation
	E _{act} forward [kJ/mol]	E _{act} backward [kJ/mol]	E _{act} forward [kJ/mol]	E _{act} backward [kJ/mol]	E _{des} [kJ/mol]	E _{effective} [kJ/mol]
Co_1	225	122	266	93	-14	369
Co ₄	182	39	87	15	48	231
Co ₈	115	38	301	134	10	378

CO₂ dissociation

The energy barriers and the stable and transition states for direct and H-assisted CO_2 dissociation can be found in Table D.1-3 and Figure D.4-9. In Table 6.4, we summarize the effective barriers for the various CO_2 dissociation routes on the single atom and the clusters, and we compare these values with the barriers for direct CO₂ scission over the extended surfaces Co(0001) and Co($11\overline{2}1$) from Zijlstra *et al.*[42] This study investigates CO hydrogenation and therefore does not report H-assisted CO_2 scission. Direct CO_2 dissociation is associated with relatively low barriers: 115, 57, and 81 kJ/mol for Co₁, Co₄, and Co₈, respectively. These barriers are similar to those on the Co extended surfaces in the sense that direct CO₂ scission is expected not to be rate-limiting across all sites. In the three transition states on the single atom and the clusters, the dissociating oxygen has a bridged configuration and CO in an on-top position. On Co_1 and Co_4 , two Co atoms are involved in the TS, on Co₈ three Co atoms are involved. The presence of two hydrogen atoms as spectator species significantly reduces the energy barrier for Co₁ and Co₄, while notably increasing it for Co₈, despite the otherwise similar TS geometries. The effective barriers for four different pathways for breaking the first C-O bond in CO_2 are tabulated in Table 6.4. Direct CO_2 dissociation exhibits the lowest effective barrier across all three models, indicating that CO_2 dissociation over Co_1 , Co_4 , and Co_8 proceeds through this reaction step.

Table 6.4: Effective barriers for various pathways for CO_2 dissociation in kJ/mol. The data for the extended surfaces was obtained from Zijlstra *et al.*[42]

	$CO_2 \rightarrow$	$CO_2 \rightarrow COOH$	$CO_2 \rightarrow COOH$	$CO_2 \rightarrow HCOO \rightarrow$
	CO+0	\rightarrow CO+OH	\rightarrow COH+O	HCO+O
Co ₁	115	132	232	259
Co ₄	57	140	196	83
Co ₈	81	226	226	228
Co(0001)	30	-	-	-
$Co(11\overline{2}1)$	84	-	-	-

CO dissociation

We comprehensively explored CO dissociation considering direct and hydrogenassisted mechanisms, the latter *via* HCO, COH, HCOH, H₂CO, H₂COH, H₃CO, and H₃COH. The energy barriers and corresponding stable and transition states for direct and H-assisted CO dissociation can be found in Table D.1-3 and Figure D.4-9. To summarize the data, Table 6.5 presents the effective barriers for the various pathways under consideration. For Co₁, alternative reaction steps beyond direct CO dissociation could not be simulated. This limitation arises from the confined space on Co₁, which prevents the hydrogenation of CO in the presence of an O atom. These constraints were evidenced by the inability to locate viable transition states for these steps, or by the extremely high energy barriers associated with them. As a result, no data for these reaction steps are reported for Co₁.

The effective barriers for CO dissociation on Co₄ and Co₈ are significantly higher than those for CO₂ dissociation, indicating that the subsequent C–O bond scission is considerably more challenging than the first. Only for CO dissociation *via* HCO over Co₄ we found an effective barrier of 166 kJ/mol, all other effective barriers being larger than 200 kJ/mol. For Co₈, the pathways with the lowest effective barriers are direct CO dissociation (224 kJ/mol) and dissociation *via* H₂CO (≥228 kJ/mol). To determine the dominant reaction pathways, microkinetic simulations (*vide infra*) will be performed for both Co₄ and Co₈.

	CO	CO →	CO →	CO →	CO →	$CO \rightarrow$	Other	Other
	\rightarrow	$COH \rightarrow$	НСО	HCO \rightarrow	COH \rightarrow	HCO \rightarrow	via	via
	C+0	C+OH	\rightarrow	$H_2CO \rightarrow$	НСОН	$\rm HCOH \rightarrow$	НСОН	H ₂ CO
			CH+O	CH ₂ +0	\rightarrow	СН+ОН		
					СН+ОН			
Co ₁	422	-	-	-	-	-	-	-
Co ₄	321	408	166	253	408	365	≥286	≥ 253
Co ₈	224	327	247	322	350	350	≥270	≥ 228

Table 6.5: Effective barriers for various pathways for CO dissociation in kJ/mol.

We compare the activation energy of direct CO dissociation on the three clusters with those on Co(0001) and Co(11 $\overline{2}$ 1) from Zijlstra *et al.*, as shown in Table 6.6. A trend is observed between the stabilization of C and O in the transition state (TS), which is quantified by their metal coordination numbers, and the activation energy for CO dissociation. The activation energies on Co₁, Co₄, Co₈, and on Co(0001) are high, as expected for active sites without a step-edge, B₅ or pocket site present. On the Co(11 $\overline{2}$ 1) surface, which can be regarded as a continuous array of B₅ sites, CO dissociation is very efficient. On Co₁, where only a few Co atoms are close together, direct CO dissociation is extremely difficult, with an energy barrier of 422 kJ/mol. Co₄ exhibits a significantly lower barrier (~100 kJ/mol less) due to the presence of a larger active site composed of four Co atoms. The energy barrier for the TS on top of the Co₈ cluster, which displays two threefold sites, approaches the one found for the Co(0001) surface, which can be regarded as a continuous array of threefold sites.

Table 6.6: Metal coordination number of C and O in the transition state (TS) of direct CO dissociation, the total number of Co atoms involved in the transition state, and the activation energy with respect to the most stable adsorbed CO state on the respective active sites. The data for the extended surfaces was obtained from Zijlstra *et al.*[42]

	Metal	Metal	Total	Activation
	coordination	coordination	number of	energy
	number of C in	number of 0 in	Co atoms	[kJ/mol]
	TS	TS	involved in	
			TS	
Co ₁	2	1	2	422
Co ₄	3	2	4	321
Co ₈	3	3	4	224
Co(0001)	3	2	4	225
Co(1121)	4	2	6	100

CH_x hydrogenation

After (H-assisted) CO dissociation, CH_x (x = 0-3) can be hydrogenated further to form methane. The barriers associated with CH_x hydrogenation, and the corresponding geometries can be found in Table D.2 and D.3 and Figure D.6-9 for Co_4 and Co_8 . For Co_1 , these reaction steps have not been simulated because a CH_x species cannot be formed on Co_1 due to the prohibitively high barriers for C-O bond scission. On Co₄, the hydrogenation forward barriers are 175, 86, 138, and 118 kJ/mol for CH, CH₂, CH₃, and CH₄ formation, respectively. On Co₈, these values are 187, 160, 105, and 151 kJ/mol, respectively. These hydrogenation steps have significantly higher barriers than those on Co(0001) or Co($11\overline{2}1$), which lie between 41 and 101 k[/mol.[42] On both clusters, C hydrogenation to CH appears to be the most difficult CH_x hydrogenation step, with barriers of 175 and 187 kJ/mol on Co₄ and Co₈, respectively. The barriers for CH_x (x = 1-3) hydrogenation on Co₄ range from 86 to 138 kJ/mol, and can be overcome at 250 °C. On Co₈, the barriers for CH_x (x = 1-3) hydrogenation lie between 105 and 160 kJ/mol, which is relatively high. These results indicate that carbon hydrogenation on these small clusters is significantly more difficult than on larger Co nanoparticles.

H₂O formation

 CO_2 hydrogenation produces water as a side product, where the number of H_2O species produced corresponds to the number of C-O bonds broken. The energies and geometries of the O and OH hydrogenation steps can be found in Table D.1-3 and Figure D.4-9. On Co₁, in the absence of any spectator species, O hydrogenation is facile with a barrier of only 19 kJ/mol. The subsequent OH hydrogenation has a high barrier of 177 kJ/mol. When CO is present, the formation of OH faces an even higher energy barrier of 200 kJ/mol, making this process highly unlikely to occur. On Co₄, O hydrogenation on the empty cluster has an energy barrier of 110 kJ/mol, relatively low compared to 0 hydrogenation on Co extended surfaces, which is 121 and 139 kJ/mol for Co(0001) and Co(11 $\overline{2}$ 1), respectively.[42] In the presence of CH and CH₃, the barrier for O hydrogenation is even lower. For the other co-adsorbates that were considered, the barrier for OH formation is higher. H_2O formation on Co₄ is associated with an activation energy of 81 kJ/mol, lower than on the Co extended surfaces (89 and 123 k[/mol for Co(0001) and Co(11 $\overline{2}$ 1), respectively).[42] The presence of spectator species, with seven candidates considered, consistently increases the energy barriers, with the lowest observed value being 136 kJ/mol. On Co₈, the barrier for 0 hydrogenation is 128 kJ/mol, comparable to those on the previously discussed Co extended surfaces. Except for one case, this barrier increases when spectator species are present. For OH hydrogenation on Co₈, the lowest barrier of 56 kJ/mol is observed on the empty cluster, while the presence of other species raises it to between 85 and 262 kJ/mol. Thus, we observe a high dependence of the activation energies for 0 and OH hydrogenation on the presence of coadsorbates. While for pathway simulations on extended surfaces, co-adsorbates are typically not considered due to their minor influence on the reaction energetics, [42] for these single atom and few-atom cluster systems, we find coadsorbates play a significant role. For all three models, we observe one or multiple low barriers for 0 and OH hydrogenation, indicating that water formation is possible at reaction temperature at these sites. However, *via* which pathways H_2O formation occurs (which co-adsorbates are present) cannot be derived from the pure DFT data. To elucidate the reaction mechanism of water formation on Co_1 , Co_4 , and Co_8 , we employ microkinetic modelling.

6.3.3 Microkinetic simulations

Microkinetic models are used to compute the CO_2 hydrogenation rate on Co_1 , Co_4 and Co_8 , using the reaction energetics obtained with DFT. Since these single atom and small cluster models are spatially limited, we cannot assume a barrierless and swift migration of co-adsorbates, an assumption which is typically done for microkinetic models of extended surfaces.[45,48–50] Hence, the co-adsorbates are modelled explicitly for all stable and transition states. Thus, we do not take migration of intermediates between different active sites into account. Co-adsorbed species are modelled as distinct variations of a single active site.



Figure 6.6: CO_2 consumption rate on Co_1 , Co_4 , and Co_8 in s⁻¹ as function of temperature.

In Figure 6.6, the CO_2 consumption rate of the three models is presented. For Co_1 , the pathways to CH_4 and CH_3OH were not considered since this site is too small to hydrogenate CO or O in the presence of the other. Therefore, the only product

possible on Co₁ is CO, which would desorb prior to O hydrogenation to H₂O. However, simulations revealed that the rate of CO production is negligibly low, on the order of 10^{-16} s⁻¹ for Co₁. In contrast, Co₄ and Co₈ exhibited appreciable CO production with very high selectivity, while CH₄ and CH₃OH were formed only in trace amounts. CO formation on Co₄ and Co₈ follows the same temperature dependence. At the representative reaction temperature of *T* = 250 °C, as also used in the experiment of Parastaev *et al.*[16], CO formation on Co₄ is one order of magnitude higher than on Co₈.

6.3.3.1 Co₁

We find that CO_2 conversion over Co_1 is negligible, as can be seen in Figure 6.6. At all simulated temperatures, Co_1 is poisoned by atomic oxygen. H_2 does not adsorb on the Co_1 site if O is already present; this adsorption is endothermic by 23 kJ/mol and will therefore not occur. Co_1 with atomic oxygen is more stable than with two additional H atoms. If H_2 would adsorb prior to CO desorption, OH formation is associated with a very high barrier, and this does not occur. Therefore, there is no accessible possibility for H_2O formation on Co_1 and thus no CO_2 conversion. We ascribe the fact that this Co_1 is not active in CO_2 hydrogenation to the limited space, which makes it impossible to hydrogenate CO or O species when co-adsorbates are present.

6.3.3.2 Co₄

Reaction pathway

On the Co₄ cluster, no methane is formed but merely CO. At 250 °C, on the Co₄ cluster a turnover frequency towards CO of 2.2×10^{-4} s⁻¹ was found. The rate of methane production at this temperature is negligible with a value of 1.8×10^{-23} s⁻¹, with the rate for methanol formation being even lower. CO formation proceeds via the pathway that is depicted in Figure 6.7, which shows the dominant reaction pathways for Co₄ and Co₈ at 250 °C. The net fluxes of all elementary reaction steps considered for both Co₄ and Co₈ are listed in Table D.4. On Co₄, first CO₂ adsorbs, then H_2 . CO₂ dissociates to CO + O in the presence of 2H, after which CO desorbs. The remaining oxygen atom is hydrogenated twice, after which H₂O desorbs. On Co₄ and CO₈, CO₂ dissociation occurs in a direct manner, without prior hydrogenation of CO₂. For both clusters, this is as predicted from the effective barriers for CO₂ dissociation in Table 6.4, since on both clusters direct CO₂ dissociation is associated with lower effective barriers than the pathways *via* COOH or HCOO. We observe that oxygen vacancies do not play a role in CO formation on Co₄ and Co₈. Although CO₂ dissociation that results in healing an oxygen vacancy is associated with a low barrier, oxygen vacancy formation was found to be very difficult.



Figure 6.7: Reaction energy diagram of the dominant pathways at 250 °C for CO formation over Co_4 and Co_8 .

Sensitivity analysis

The rate limiting step for CO_2 hydrogenation is OH hydrogenation, as shown in Figure 6.8a. This step is rate limiting for the entire simulated temperature range with a DRC coefficient of (nearly) unity. This indicates that 0 removal is more difficult than CO_2 dissociation, which is visible in that both hydrogenation barriers (110 and 73 kJ/mol for 0 and 0H hydrogenation, respectively) are higher than the direct CO₂ dissociation barrier (57 kJ/mol). Furthermore, the O and OH hydrogenation steps are relatively endothermic with reaction energies of 82 and 76 kJ/mol, indicating that atomic 0 is very stable on Co₄. In Figure D.10 and D.11, the corresponding reaction orders and apparent activation energies are presented. The reaction orders are 0.00 in CO and 0.37 in H₂ at 250 °C, which is in line with 0 hydrogenation being rate limiting. Figure 6.8b shows that at reaction temperature, the Co_4 cluster has a 0.37 probability of being occupied by an oxygen atom, and 0.63 probability of being occupied by one oxygen and two hydrogen atoms. This is in line with the facile CO_2 dissociation and facile CO desorption, and relatively difficult O and OH hydrogenation. The apparent activation energy for CO formation at 250 °C is 138 kJ/mol. Based on the reaction orders, coverage, and apparent activation energy trends, we can identify two distinct temperature regimes and a transition regime between those two. The H₂ adsorption rate is high at temperatures below 200 °C, but the energy barriers are difficult to overcome at these temperatures, limiting CO formation. At lower temperatures, the reaction order in H_2 is zero, and one O and two H are adsorbed on the cluster. The apparent activation energy is at its maximum. In the transition regime between 200 and 350 °C, more reaction steps become accessible, but H_2 adsorption becomes increasingly less favorable because the pseudo-equilibrium of H_2 adsorption is shifting towards gas phase H_2 . At temperatures above 350 °C, the H₂ adsorption rate is low. The energy barriers are easily overcome, but there is little supply of H_2 . The adsorption of H_2 is limiting the CO_2 conversion towards CO by limiting O hydrogenation. One oxygen atom is present on the Co_4 cluster, and the reaction order is unity in H_2 .



Figure 6.8: (a) The degree of rate control (DRC) coefficients for the reactions that have nonzero DRC coefficients as function of temperature, and (b) the occupation of the Co₄ cluster as function of temperature.

Alternative microkinetic models

After CO₂ dissociation, CO desorbs rather than reacting further. CO binds quite strongly to Co₄ with adsorption energies of -139, -111 and -199 kJ/mol for CO adsorption on an empty cluster and with co-adsorbates one O and two H. respectively. These values are comparable with earlier results of extended surfaces, where CO adsorbs with an energy of -148 and -142 kJ/mol for Co($11\overline{2}1$) and Co(0001), respectively. [42] Since the microkinetic model is operated under the zero-conversion limit, we explored whether methane formation is possible on Co₄ when CO desorption is less favorable. A first scenario is that we operate at 50% conversion instead of zero conversion, and a second that CO desorption is disabled completely. The results of these simulations can be found in Figure D.12-15. Under 50% conversion conditions, less CO and more methane is formed than under zero conversion conditions (Figure D.12). Still at 250 °C, CO formation is orders of magnitude higher than methane formation: 2.0×10^{-6} CO s^{-1} , 3.5×10^{-12} CH₄ s^{-1} and 1.1×10^{-19} CH₃OH s^{-1} . If CO adsorption and desorption are disabled, at 250 °C, 3.8×10^{-12} CH₄ s⁻¹ and 1.1×10^{-15} CH₃OH s⁻¹ are formed (Figure D.16-19). In both scenarios, methane formation proceeds via the pathway shown in Figure D.20. In this pathway, CO_2 dissociation proceeds in a direct manner, after which the dissociated O is removed as H₂O. CO dissociation proceeds via HCO, which is in line with the observation that CO dissociation via HCO has the lowest effective barrier. After O dissociation from HCO, the second O is also removed as H_2O . CH is then hydrogenated three times to form CH₄. In both the 50% conversion and the disabled CO desorption scenarios, at 250 °C, OH hydrogenation is the rate limiting step with a DRC coefficient of (nearly) unity (as can be seen in Figure D.13 and D.17). For the scenario where CO desorption is disabled, OH hydrogenation in the presence of CH is rate-limiting. The reaction order in CO_2 is zero and the reaction order in H_2 is between 0.7 and 2.1 at all temperatures. For the 50% conversion scenario, the reaction order in CO_2 is positive at temperatures below 350 °C, because CO_2 adsorption would enhance CO formation. At higher temperatures, the order becomes unity for H_2 and zero for CO_2 . The CO_4 cluster is at 250 °C primarily covered with one CO and two H in both scenarios. This is the dominant state since the subsequent step, CO hydrogenation to HCO, is associated with a relatively high barrier of 166 kJ/mol. We observe that when we lower the barriers for (H-assisted) CO dissociation, methane production increases.

To explore the influence of the height of the energy barriers of O and OH hydrogenation to form H₂O, a microkinetic simulation is conducted where CO adsorption and desorption are disabled, and the O and OH hydrogenation barriers are lowered. For these reaction steps, the energy of the transition state is lowered in such a way that the lowest of the forward and backward barrier is 5 kI/mol. Methane production as function of temperature, the DRC, and the reaction energy diagram of the dominant pathway for methane formation can be found in Figure D.21-23. Methane is formed at a rate of 1.5×10^{-4} s⁻¹, while methanol is not produced in a significant quantity. The fact that with these adaptations, methane production is as high as the CO production rate in the original model, shows that these two factors are responsible for the absence of methane production over Co₄. If CO desorption is not disabled, CO desorption is easier than CO dissociation and no methane is produced. Also, water formation is associated with high barriers, and the TOF of water formation must be twice as high for methane formation than for CO formation. These two factors steer the selectivity of CO₂ conversion over this Co₄ cluster towards 100% CO and 0% methane.

Thus, at 250 °C, on the Co₄ cluster a turnover frequency towards CO of 2.2×10^{-4} s⁻¹ was found, a relatively low production rate. CO₂ dissociation is associated with low barriers, but O removal as H₂O is difficult due to the high barriers for the O and OH hydrogenation steps. The difficult water formation on Co₄ explains the relatively low activity of this cluster. The 100% selectivity towards CO and 0% towards CH₄ is ascribed to CO dissociation being difficult on Co₄, i.e. CO dissociation is associated with high energy barriers. Also, two H₂O molecules must be formed for a CH₄ molecule instead of one for CO, which further complicates CH₄ formation.

6.3.3.3 Co₈

Reaction pathway

On Co₈, the RWGS reaction occurs with a rate of 1.3×10^{-5} s⁻¹ at 250 °C, as shown in Figure 6.6. Methane and methanol are formed at a rate of 5.2×10^{-24} s⁻¹ (methane) or even less (methanol) at 250 °C, which are negligible quantities. The reaction pathway of CO formation in Figure 6.7 shows that CO₂ is dissociated into CO + 0 on the otherwise empty cluster. In contrast to Co₄, where direct CO₂ dissociation has a lower barrier in the presence of two hydrogen atoms, on Co₈ CO₂ dissociation is much easier when there are no spectator species present. After CO desorption, H₂ adsorbs, and 0 is removed as H₂O. The H₂O formation pathways are similar for both clusters. The lower RWGS activity of Co₈ compared to Co₄ can be explained by the difference in stability of the most stable reaction intermediate. On Co₄, the most stable intermediate state is with CO + 0 + 2H adsorbed, which has a relative energy of -235 kJ/mol, on Co₈ the most stable state is CO + 0 with a relative energy of -279 kJ/mol.

Sensitivity analysis

The degree of rate control (DRC) coefficients of CO₂ conversion over Co₈ and the occupation of Co_8 as function of temperature are visualized in Figure 6.9. Both the DRC analysis and the coverage as function of temperature reveal that over the entire simulated temperature range, O removal is rate-limiting for CO formation. At low temperatures, CO formation is limited by H₂O desorption and the cluster is covered with 0 + 2H or atomic oxygen. At higher temperatures, desorption processes become easier due to larger entropic contributions, and Co_8 is covered by a single O. The hydrogenation of OH is then the rate determining step. Whereas for Co₄ at 900 °C, a fraction of the clusters becomes empty, this does not hold for Co_8 clusters. This shows that reactant adsorption on Co_8 is very strong. stronger than on Co₄. At 250 °C, the coverage is 95% 0 and 5% 0 + 2H. The DRC coefficients are 0.82 for water desorption and 0.18 for OH hydrogenation. The reaction order at this temperature is 0.94 in H₂ and zero in CO₂ (Figure D.24). The positive order in H₂ reveals that the rate of CO formation would increase with adsorption and hydrogenation of oxygen. The apparent activation energy at 250 °C is 148 kJ/mol and decreases with increasing temperature (Figure D.25). This value is quite close to the effective barrier of H₂O formation on the empty Co₈ cluster, which is the energy difference between 0 + 2H and the transition state of OH hydrogenation to H_2O and equals 158 kJ/mol (Figure 6.7). These results show that at 250 °C, CO production is limited by water formation and removal.



Figure 6.9: (a) The degree of rate control (DRC) coefficients for the reactions that have nonzero DRC coefficients as function of temperature and (b) the occupation of the Co_8 cluster as function of temperature.

Alternative microkinetic models

To explore why only CO is formed and no methane, similar additional microkinetic simulations as conducted for Co4 are performed, where CO adsorption and desorption is disabled, and the barriers for O and OH hydrogenation are lowered. The CH₄ and CH₃OH production and the corresponding DRC analysis can be found in Figure D.26 and D.27. In contrast to Co_4 , where these adaptations resulted in methane formation at approximately the same rate as CO formation in the original models $(1.5 \times 10^{-4} \text{ s}^{-1})$, on Co₈ still no methane can be formed. At 250 °C, methane formation is 4.2×10^{-12} s⁻¹, which is practically nonexistent. Similar to Co₄, methanol production is even lower. The DRC analysis shows that methane formation is limited by HCO dissociation into CH and O at this temperature. This is in line with the effective barriers for various manners of CO dissociation listed in Table 6.5. Whereas for Co_4 , one relatively low effective barrier is present, i.e. *via* HCO with a barrier of 166 kJ/mol, for Co₈ the lowest barrier is still too high to be overcome at 250 °C. Direct CO dissociation and via H_2CO show the lowest effective barriers of 224 and 228 kJ/mol, respectively. However, Figure D.28 reveals that the dominant pathway for methane formation is via HCO, thus via the same mechanism as CO dissociation on Co₄. This is due to the high barriers associated with water formation in the presence of atomic carbon and CH₂. O hydrogenation in the presence of these species has energy barriers of 235 kJ/mol with C and 307 kJ/mol with CH_2 . In the presence of CH, this barrier is only 162 kJ/mol.

The main reason that methane is not formed on Co_8 is the high stability of the reaction intermediates on the cluster. For Co_8 , the most stable states are much more stable than for Co_4 , as can be seen in Figure D.29. For Co_4 the most stable state is -301 kJ/mol relative to the empty cluster and the reactants in gas phase, for Co_8 the most stable intermediate state is CO + OH + H with an energy of -375

kJ/mol. In fact, when we decrease all barriers for methane and water formation on Co_8 , the cluster still does not produce any methane. We attribute the existence of these stable intermediate states to adsorbate induced reconstruction of the cluster, as discussed previously. Since for Co_4 , we expect to have found the most stable configuration of four Co atoms on a CoO(100) surface, for Co_8 we are certain that this is not the case. This makes that the Co_8 cluster can rearrange to a more stable cluster configuration when reaction intermediates are present, a phenomenon that does not occur for Co_4 .

Conclusively, on the Co₈ cluster, CO is formed at a rate of 1.3×10^{-5} s⁻¹ at 250 °C, an order of magnitude lower than on the Co₄ cluster. We attribute this difference to the higher stability of intermediate states on the Co₈ cluster in the dominant CO formation pathway. This higher stability stems from reconstruction of the Co₈ cluster that occurs during DFT optimizations that include adsorbates. More stable configurations of the Co₈ cluster were found upon the placement of adsorbates on the cluster, indicating that this Co₈ cluster does not possess the most stable configuration possible. Similar to Co₄, CO formation is limited by water formation on the Co₈ cluster. In contrast to Co₄, the absence of methane formation on Co₈ is not only attributed to the high barriers for CO formation, but also to the high stability of some intermediate states in the methane formation pathway.

6.4 Conclusions

The experimental observation of unconventional structure sensitivity trends in CO_2 hydrogenation over cobalt reveals a higher-than-expected activity, whose origin remains unclear. Understanding this phenomenon could provide crucial insights into the behavior of partially reduced catalysts. Therefore, we modelled active sites consisting of both Co and CoO phases to explore the reaction mechanisms on these catalysts. Density functional theory (DFT) was employed to study a Co single atom and two small Co clusters (Co₄ and Co₈) supported on a CoO surface. A comprehensive set of reaction steps within the CO_2 hydrogenation chemokinetic network, including a high variety of co-adsorbates, was simulated. The calculated reaction energetics and subsequent microkinetic simulations shed light on the behavior of these Co/CoO systems. The results indicate that the single-atom Co/CoO site is inactive in CO₂ conversion. The site is too constrained for effective hydrogenation of CO and O species when both are present, leading to site poisoning by atomic oxygen. In contrast, the Co₄ and Co₈ clusters are active in the reverse water-gas shift (RWGS) reaction, producing CO. Methane cannot be formed on these clusters due to high barriers for CO scission. Additionally, water formation is found to be rate-limiting on these clusters.

The adsorption behavior of reactants on the Co single atom and the Co₄ cluster resembles that on extended Co surfaces, while Co₈ shows exceptionally stable adsorption of CO_2 and hydrogen. This is attributed to the fact that, unlike Co_1 and Co_4 , the used configuration for the Co_8 cluster appeared to be not the most stable configuration possible. Hydrogen atoms are unstable on the CoO(100) surface. ruling out the possibility of hydrogen spillover effects. Oxygen vacancies are unstable on the bare CoO(100) surface but become increasingly stable with larger cluster sizes when the vacancy is formed in proximity of the cluster. However, the barriers for sequential hydrogenation of lattice oxygen remain prohibitively high, excluding the possibility of oxygen vacancy formation in these systems. CO₂ dissociation is associated with low activation barriers across all systems and is not rate-limiting. At all sites, direct CO₂ dissociation is favored over any H-assisted pathway. The dissociation of CO_2 into an oxygen vacancy, healing the vacancy with the dissociating oxygen, does not further reduce the CO_2 dissociation barrier for Co₈. In contrast to CO₂ dissociation, direct and H-assisted CO dissociation is difficult on all studied systems. The Co₁ and Co₄ sites are too small to adequately stabilize carbon and oxygen in the transition state of direct CO scission, resulting in very high barriers. On Co₈, direct CO dissociation exhibits an energy barrier comparable to a threefold site on an extended Co(0001)surface, but this barrier is still high, as step-edge or pocket-like sites are absent on these systems. On both the Co_4 and Co_8 cluster, the HCO pathway emerges as the most favorable route. The difficult CO dissociation steers the reactivity over the clusters toward CO, resulting in no methane being formed. Water formation limits the CO formation rate on Co₄ and Co₈. The Co₄ cluster exhibits a tenfold higher activity compared to Co₈. The lowered activity on Co₈ is attributed to the presence of highly stable intermediate states, which appeared during optimization of the cluster with adsorbates on top. This resulted in more stable configurations of the Co_8 cluster, revealing that the used configuration of the Co_8 cluster is not the most stable configuration possible. These results provide mechanistic insights into Co/CoO active sites, revealing that for small Co clusters on a CoO(100) surface, oxygen vacancies do not take part in the reaction mechanism, because the hydrogenation of lattice oxygen is too difficult. Also, hydrogen spillover to the CoO phase does not occur on the Co/CoO active sites considered in this study.

6.5 References

- R. Mutschler, E. Moioli, W. Luo, N. Gallandat, A. Züttel, J. Catal. 366 (2018) 139–149.
- [2] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. Van Dillen, K.P. De Jong, J. Am. Chem. Soc. 128 (2006) 3956– 3964.

- [3] J.P. Den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. De Jong, J. Am. Chem. Soc. 131 (2009) 7197–7203.
- [4] J.F.M. Simons, T.J. De Heer, R.C.J. Van De Poll, V. Muravev, N. Kosinov, E.J.M. Hensen, J. Am. Chem. Soc. 145 (2023) 20289–20301.
- [5] R.C. Reuel, C.H. Bartholomew, J. Catal. 85 (1984) 78–88.
- [6] A. Guerrero-Ruiz, I. Rodríguez-Ramos, React. Kinet. Catal. Lett. 29 (1985) 93–99.
- [7] D. Beierlein, D. Häussermann, M. Pfeifer, T. Schwarz, K. Stöwe, Y. Traa, E. Klemm, Appl. Catal. B 247 (2019) 200–219.
- [8] A. Parastaev, V. Muravev, E. Huertas Osta, A.J.F. Van Hoof, T.F. Kimpel, N. Kosinov, E.J.M. Hensen, Nat. Catal. 3 (2020) 526–533.
- [9] V. Iablokov, S.K. Beaumont, S. Alayoglu, V.V. Pushkarev, C. Specht, J. Gao, A.P. Alivisatos, N. Kruse, G.A. Somorjai, Nano Lett. 12 (2012) 3091–3096.
- [10] N.L. Visser, O. Daoura, P.N. Plessow, L.C.J. Smulders, J.W. De Rijk, J.A. Stewart, B.D. Vandegehuchte, F. Studt, J.E.S. Van Der Hoeven, P.E. De Jongh, ChemCatChem 14 (2022) e202200665.
- [11] J. Tu, H. Wu, Q. Qian, S. Han, M. Chu, S. Jia, R. Feng, J. Zhai, M. He, B. Han, Chem. Sci. 12 (2021) 3937–3943.
- [12] J.J.C. Struijs, V. Muravev, M.A. Verheijen, E.J.M. Hensen, N. Kosinov, Angew. Chem. Int. Ed. 62 (2023).
- [13] G. Melaet, A.E. Lindeman, G.A. Somorjai, Top. Catal. 57 (2014) 500–507.
- [14] K. Zhao, M. Calizzi, E. Moioli, M. Li, A. Borsay, L. Lombardo, R. Mutschler, W. Luo, A. Züttel, J. Energy Chem. 53 (2021) 241–250.
- [15] I.C.T. Have, J.J.G. Kromwijk, M. Monai, D. Ferri, E.B. Sterk, F. Meirer, B.M. Weckhuysen, Nat. Commun. 13 (2022) 324.
- [16] A. Parastaev, V. Muravev, E.H. Osta, T.F. Kimpel, J.F.M. Simons, A.J.F. Van Hoof, E. Uslamin, L. Zhang, J.J.C. Struijs, D.B. Burueva, E.V. Pokochueva, K.V. Kovtunov, I.V. Koptyug, I.J. Villar-Garcia, C. Escudero, T. Altantzis, P. Liu, A. Béché, S. Bals, N. Kosinov, E.J.M. Hensen, Nat. Catal. 5 (2022) 1051–1060.
- [17] A. Tuxen, S. Carenco, M. Chintapalli, C.-H. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A.P. Alivisatos, G. Thornton, W.-F. Pong, J. Guo, R. Perez, F. Besenbacher, M. Salmeron, J. Am. Chem. Soc. 135 (2013) 2273–2278.
- [18] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251–14269.
- [19] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15–50.
- [20] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953-17979.
- [21] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758–1775.
- [22] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.
- [23] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132 (2010) 154104.
- [24] V.I. Anisimov, M.A. Korotin, J. Zaanen, O.K. Andersen, Phys. Rev. Lett. 68 (1992) 345–348.
- [25] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Phys. Rev. B 57 (1998) 1505–1509.

- [26] A. Cadi-Essadek, A. Roldan, D. Santos-Carballal, P.E. Ngoepe, M. Claeys, N.H. De Leeuw, S. Afr. J. Chem. 74 (2021).
- [27] J. Van Elp, J.L. Wieland, H. Eskes, P. Kuiper, G.A. Sawatzky, F.M.F. De Groot, T.S. Turner, Phys. Rev. B 44 (1991) 6090–6103.
- [28] W. Jauch, M. Reehuis, H.J. Bleif, F. Kubanek, P. Pattison, Phys. Rev. B 64 (2001) 052102.
- [29] M. Forti, P. Alonso, P. Gargano, G. Rubiolo, Proc. Mater. Sci. 1 (2012) 230– 234.
- [30] B.S. Youmbi, F. Calvayrac, Surf. Sci. 621 (2014) 1–6.
- [31] W.L. Roth, Phys. Rev. 110 (1958) 1333–1341.
- [32] U.D. Wdowik, K. Parlinski, Phys. Rev. B 75 (2007) 104306.
- [33] K.-W. Park, A.M. Kolpak, J. Catal. 365 (2018) 115–124.
- [34] A. Lu, Y. Chen, J. Jin, G.-H. Yue, D.-L. Peng, J. Power Sources 220 (2012) 391– 398.
- [35] G. Henkelman, B.P. Uberuaga, H. Jónsson, J. Chem. Phys. 113 (2000) 9901– 9904.
- [36] M.-W. Chang, L. Zhang, M. Davids, I.A.W. Filot, E.J.M. Hensen, J. Catal. 392 (2020) 39–47.
- [37] L.B. Vilhelmsen, B. Hammer, J. Chem. Phys. 141 (2014) 044711.
- [38] I.A.W. Filot, R.A. van Santen, E.J.M. Hensen, Angew. Chem. Int. Ed. 53 (2014) 12746–12750.
- [39] M. Chase, NIST-JANAF Thermochemical Tables, 4th ed, American chemical society, Washington, D.C, 1998.
- [40] C.T. Campbell, ACS Catal. 7 (2017) 2770–2779.
- [41] M. Abramowitz, I.A. Stegun, Handbook of Mathematical Functions: With Formulas, Graphs, and Mathematical Tables, Dover Publications, 1965.
- [42] B. Zijlstra, R.J.P. Broos, W. Chen, I.A.W. Filot, E.J.M. Hensen, Catal. Today 342 (2020) 131–141.
- [43] C.H. Shomate, J. Phys. Chem. 58 (1954) 368–372.
- [44] P. Saini, P. Koley, D. Damma, D. Jampaiah, S.K. Bhargava, Chem. Asian J. 19 (2024) e202400752.
- [45] B. Zijlstra, R.J.P. Broos, W. Chen, G.L. Bezemer, I.A.W. Filot, E.J.M. Hensen, ACS Catal. 10 (2020) 9376–9400.
- [46] R.D.E. Krösschell, E.J.M. Hensen, I.A.W. Filot, J. Phys. Chem. C 128 (2024) 8947–8960.
- [47] T.W. van Deelen, C. Hernández Mejía, K.P. de Jong, Nat. Catal. 2 (2019) 955– 970.
- [48] I.A.W. Filot, B. Zijlstra, R.J.P. Broos, W. Chen, R. Pestman, E.J.M. Hensen, Faraday Discuss. 197 (2017) 153–164.
- [49] E.B. Sterk, A.-E. Nieuwelink, M. Monai, J.N. Louwen, E.T.C. Vogt, I.A.W. Filot, B.M. Weckhuysen, JACS Au 2 (2022) 2714–2730.
- [50] R.J.P. Broos, B. Klumpers, B. Zijlstra, I.A.W. Filot, E.J.M. Hensen, Catal. Today 342 (2020) 152–160.
D. Appendix



Figure D.1: Top view of the nine most stable models for $Co_4/CoO(100)$. The Co atoms of the clusters are shown in darker blue to distinguish them from the Co atoms of the CoO, which are shown in lighter blue.



Figure D.2: Top view of the other stable model for $Co_1/CoO(100)$. The Co atom of Co_1 is shown in darker blue to distinguish it from the Co atoms of the CoO, which are shown in lighter blue.



Figure D.3: Top view of the five most stable archetypes for $Co_8/CoO(100)$. The Co atoms of the clusters are shown in darker blue to distinguish them from the Co atoms of the CoO, which are shown in lighter blue.

Eact forward Eact backward **CO₂ adsorption** $\{CO2\} + \{*\} => \{CO2^*\}$ 0.0 102.8 $\{CO2\} + \{2H^*\} => \{CO2_2H^*\}$ 0.0 -14.7 H₂ adsorption $\{*\} + \{H2\} => \{2H^*\}$ 0.0 91.4 $\{H2\} + \{CO2^*\} => \{CO2_2H^*\}$ 0.0 -26.2 $\{H2\} + \{CO_0^*\} => \{CO_0^2H^*\}$ 0.0 -1.6 $\{CO^*\} + \{H2\} => \{CO_2H^*\}$ 0.0 56.9 $\{C_0^*\} + \{H2\} => \{C_0_2H^*\}$ 0.0 -35.3 $\{C^*\} + \{H2\} => \{C_2H^*\}$ 0.0 209.9 0.0 $\{0^*\} + \{H2\} => \{0_2H^*\}$ -23.0 H₂O adsorption $\{H20\} + \{*\} => \{H20^*\}$ 0.0 30.0 $\{CO^*\} + \{H2O\} => \overline{\{CO_H2O^*\}}$ 0.0 51.3 $\{C^*\} + \{H20\} => \{C_H20^*\}$ 0.0 10.4 **CO** adsorption $\{0_2H^*\} + \{CO\} => \{CO_0_2H^*\}$ 0.0 131.7 $\{CO\} + \{*\} => \{CO^*\}$ 0.0 153.6 0.0 $\{2H^*\} + \{CO\} => \{CO_2H^*\}$ 119.1 $\{0^*\} + \{C0\} => \{C0_0^*\}$ 0.0 110.2 **CO₂ dissociation** $\{CO2^*\} => \{CO \ O^*\}$ 115.1 57.8 $\{CO2_2H^*\} => \{CO_0_2H^*\}$ 89.6 56.9 $\{CO2_2H^*\} => \{COOH_H^*\}$ 131.6 138.3 $\{COOH_H^*\} => \{CO_OH_H^*\}$ 34.1 74.1 $\{COOH_H^*\} => \{COH_O_H^*\}$ 232.3 70.2 $\{CO2_2H^*\} => \{HCOO_H^*\}$ 151.4 207.0 $\{HCOO_H^*\} => \{HCO_O_H^*\}$ 258.6 130.4 **CO** dissociation $\{CO^*\} => \{C O^*\}$ 421.7 47.1 $\{CO_2H^*\} => \{C_0_2H^*\}$ 549.8 83.0 **O** hydrogenation $\{0_2H^*\} => \{OH_H^*\}$ 19.4 209.2 $\{C_0_2H^*\} => \{C_0H_H^*\}$ 34.4 89.9 $\{CO_0_2H^*\} => \{CO_0H_H^*\}$ 200.3 279.8

Table D.1: Elementary reaction step barriers for CO_2 methanation over $Co_1/CoO(100)$. The values are given in kJ/mol and include the zero-point energy (ZPE) correction.

OH hydrogenation		
{0H_H*} => {H20*}	176.8	63.5
{C_OH_H*} => {C_H2O*}	5.0	14.6
Ovac formation		
{2H*} => {OH_H_Ov*}	225.1	122.3
$\{OH_H_Ov^*\} => \{H2O_Ov^*\}$	265.7	93.0
$\{0v^*\} + \{H20\} => \{H20_0v^*\}$	0.0	-13.5
Ovac healing		
$\{0v^*\} + \{C0\} => \{C0_0v^*\}$	0.0	184.2
$\{CO2\} + \{Ov^*\} \Longrightarrow \{CO2_Ov^*\}$	0.0	166.8
$\{CO2_Ov^*\} \Longrightarrow \{CO^*\}$	210.9	327.1

Table D.2: Elementary reaction step barriers for CO_2 methanation over $Co_4/CoO(100)$. The values are given in kJ/mol and include the zero-point energy (ZPE) correction.

Eact forward	Eact backward
0.0	115.7
0.0	112.1
0.0	62.9
0.0	59.3
0.0	54.0
0.0	122.6
0.0	32.2
0.0	77.5
0.0	68.5
0.0	22.6
0.0	18.5
0.0	58.5
0.0	89.2
0.0	58.4
0.0	229.8
0.0	157.3
0.0	28.8
0.0	21.6
0.0	135.9
0.0	5.8
0.0	28.8
	Eact forward 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0

(C*) + (U2O) = (C U2O*)	0.0	20.7	
$\frac{\{0\} + \{120\} - 2\{0, 120\}}{(21, 120, 120)} = (21, 120, 120)$	0.0	-20.7	
$\frac{\{(\Pi_{\Pi}^{+}) + \{\Pi_{2}0\} => \{(\Pi_{\Pi}^{+}, \Pi_{2}^{-}) => (\Pi_{2}^{+}, \Pi_{2}^{-}) => (\Pi_{2}^{+}, \Pi_{2}^{-}) = (\Pi_{2}^{+}, $	0.0	02.3	
$\frac{\{(H2^{+})\} + \{H20\} => \{(H2_{H2}^{+})\} + (H20) => ((H2_{H2}^{+})) + (H20) => ((H2_{H2}^{+})) + (H20) => ((H2_{H2}^{+})) + ((H20_{H2}^{+})) + (($	0.0	-38.8	
$\{CH3_H^{+}\} + \{H20\} => \{CH3_H20_H^{+}\}$	0.0	74.3	
		10.0	
{LH4} + {*} => {LH4*}	0.0	18.0	
		400.4	
$\frac{\{(0)\} + \{^*\} => \{(0)^*\}}{(0)^*}$	0.0	139.4	
$\frac{\{2H^*\} + \{CO\} => \{CO_2H^*\}}{\{CO_2H^*\}}$	0.0	199.1	
$\{0^*\} + \{C0\} => \{C0_0^*\}$	0.0	111.5	
$\{0_2H^*\} + \{CO\} => \{CO_0_2H^*\}$	0.0	97.0	
H ₃ COH adsorption			
{H3COH} + {*} => {H3COH*}	0.0	-12.6	
CO ₂ dissociation			
$\{CO2^*\} \Rightarrow \{CO_0^*\}$	57.3	122.3	
$\{CO2_2H^*\} => \{CO_0_2H^*\}$	19.4	79.1	
$\{CO2_2H^*\} => \{COOH_H^*\}$	140.4	144.0	
$\{COOH_H^*\} => \{CO_OH_H^*\}$	23.8	146.4	
{COOH_H*} => {COH_O_H*}	195.8	287.8	
{CO2_2H*} => {HCOO_H*}	66.0	83.5	
{HCOO_H*} => {HCO_O_H*}	83.5	86.1	
CO dissociation			
$\{CO^*\} => \{C_O^*\}$	321.0	226.5	
$\{CO_2H^*\} => \{C_0_2H^*\}$	219.6	34.8	
{CO_2H*} => {COH_H*}	408.0	298.3	
{COH_H*} => {C_OH_H*}	140.8	59.2	
{CO_2H*} => {HCO_H*}	166.1	80.7	
{HCO_H*} => {CH_O_H*}	71.0	55.2	
{HCO_H*} => {H2CO*}	168.0	177.8	
{H2CO*} => {CH2_O*}	77.7	115.5	
{COH_H*} => {HCOH*}	203.8	135.0	
{HCO_H*} => {HCOH*}	200.3	107.3	
{HCOH*} => {CH_OH*}	186.3	277.1	
{HCOH_2H*} => {H2COH_H*}	130.2	217.6	
{H2COH_H*} => {CH2_OH_H*}	121.5	271.6	
{H2COH_H*} => {H3COH*}	234.6	119.1	
{H3COH*} => {CH3_OH*}	71.3	346.6	
{H2C0 2H*} => {H3C0 H*}	18.9	5.0	
{H3C0 H*} => {CH3 0 H*}	106.4	174.8	
{H3COH*} => {H3CO H*}	5.0	118.0	
{H2CO_2H*} => {H2COH H*}	69.8	58.5	

CH _x hydrogenation		
$\{C_2H^*\} => \{CH_H^*\}$	175.5	219.8
{CH_H*} => {CH2*}	86.1	84.9
{CH2_2H*} => {CH3_H*}	138.0	200.8
{CH3_H*} => {CH4*}	117.6	61.4
O hydrogenation		
$\{0_2H^*\} \Rightarrow \{OH_H^*\}$	109.8	28.1
$\{C_0_2H^*\} => \{C_0H_H^*\}$	269.2	205.1
_{CO_0_2H*} => {CO_0H_H*}	200.9	267.4
{COH_0_H*} => {COH_OH*}	330.3	178.0
{HCO_O_H*} => {HCO_OH*}	169.5	72.5
{CH_O_H*} => {CH_OH*}	72.6	86.2
{CH2_0_2H*} => {CH2_0H_H*}	234.8	265
{CH3_0_H*} => {CH3_0H*}	58.1	151.9
OH hydrogenation		
{OH_H*} => {H2O*}	80.5	5.0
{C_OH_H*} => {C_H2O*}	173.6	57.1
{C0_0H_H*} => {C0_H20*}	157.4	90.4
{COH_OH_2H*} => {COH_H2O_H*}	286.5	150.8
{HCO_OH_2H*} => {HCO_H2O_H*}	282.2	95.6
{CH_OH_2H*} => {CH_H2O_H*}	146.7	136.6
{CH2_OH_H*} => {CH2_H2O*}	229.8	6.4
{CH3_OH_2H*} => {CH3_H2O_H*}	135.9	108.4
Ovac formation		
{2H*} => {OH_H_Ov*}	182.2	38.6
$\{0H_H_0v^*\} \Rightarrow \{H20_0v^*\}$	87.0	15.3
$\{0v^*\} + \{H20\} => \{H20_0v^*\}$	0.0	48.3
O _{vac} healing		
$\{CO2\} + \{Ov^*\} \Longrightarrow \{CO2_Ov^*\}$	0.0	178.8
$\{CO2_Ov^*\} => \{CO^*\}$	58.0	178.2
$\{0v^*\} + \{CO\} => \{CO_Ov^*\}$	0.0	97.9
$\{CO_Ov^*\} => \{C^*\}$	98.0	45.8

Table D.3: Elementary reaction step barriers for CO_2 methanation over $Co_8/CoO(100)$. The values are given in kJ/mol and include the zero-point energy (ZPE) correction.

	Eact forward	Eact backward
CO ₂ adsorption		
{CO2} + {*} => {CO2*}	0.0	218.8
$\{CO2\} + \{2H^*\} => \{CO2_2H^*\}$	0.0	42.0

H ₂ adsorption			
{*} + {H2} => {2H*}	0.0	228.2	
${H2} + {CO2^*} => {CO2_2H^*}$	0.0	51.4	
$\{H2\} + \{C0_0^*\} => \{C0_0^2H^*\}$	0.0	95.5	
$\{CO^*\} + \{H2\} => \{CO_2H^*\}$	0.0	198.1	
$\{C_0^*\} + \{H2\} => \{C_0_2H^*\}$	0.0	187.1	
$\{C^*\} + \{H2\} => \{C_2H^*\}$	0.0	147.5	
$\{0^*\} + \{H2\} => \{0_2H^*\}$	0.0	56.8	
{HCOH*} + {H2} => {HCOH_2H*}	0.0	115.3	
{H2CO*} + {H2} => {H2CO_2H*}	0.0	169.8	
{CH2*} + {H2} => {CH2_2H*}	0.0	81.1	
{CH2_0*} + {H2} => {CH2_0_2H*}	0.0	249.2	
{CH_OH*} + {H2} => {CH_OH_2H*}	0.0	158.3	
{HCO_OH*} + {H2} => {HCO_OH_2H*}	0.0	170.9	
{COH_OH*} + {H2} => {COH_OH_2H*}	0.0	21.2	
{CH3_OH*} + {H2} => {CH3_OH_2H*}	0.0	103.0	
H ₂ O adsorption			
{H20} + {*} => {H20*}	0.0	107.1	
{CO*} + {H2O} => {CO_H2O*}	0.0	144.3	
{HCO_H*} + {H2O} => {HCO_H2O_H*}	0.0	49.3	
{COH_H*} + {H2O} => {COH_H2O_H*}	0.0	101.7	
$\{C^*\} + \{H20\} => \{C_H20^*\}$	0.0	123.2	
{CH_H*} + {H2O} => {CH_H2O_H*}	0.0	61.5	
{CH2*} + {H2O} => {CH2_H2O*}	0.0	148.5	
{CH3_H*} + {H2O} => {CH3_H2O_H*}	0.0	143.2	
CH4 adsorption			
{CH4} + {*} => {CH4*}	0.0	124.1	
_CO adsorption			
$\{CO\} + \{*\} \Longrightarrow \{CO^*\}$	0.0	198.2	
${2H*} + {CO} => {CO_2H*}$	0.0	168.1	
$\{0^*\} + \{C0\} => \{C0_0^*\}$	0.0	164.1	
$\{0_2H^*\} + \{CO\} => \{CO_0_2H^*\}$	0.0	202.8	
CH ₃ OH adsorption			
{H3COH} + {*} => {H3COH*}	0.0	189.8	
CO ₂ dissociation			
{CO2*} => {CO_O*}	81.5	141.7	
{CO2_2H*} => {CO_0_2H*}	175.3	279.6	
{CO2_2H*} => {COOH_H*}	225.8	205.6	
{COOH_H*} => {CO_OH_H*}	124.8	149.0	
{COOH H*} => {COH O H*}	204.7	180.7	

{CO2_2H*} => {HCOO_H*}	93.9	200.8	
{HCOO_H*} => {HCO_O_H*}	228.1	10.5	
CO dissociation			
{CO*} => {C_O*}	223.9	197.3	
$\{CO_2H^*\} => \{C_0_2H^*\}$	262.5	224.9	
{CO_2H*} => {COH_H*}	327.1	126.3	
{COH_H*} => {C_OH_H*}	57.8	125.9	
{CO_2H*} => {HCO_H*}	110.4	5.0	
{HCO_H*} => {CH_O_H*}	141.1	194.1	
{HCO_H*} => {H2CO*}	122.6	39.0	
{H2CO*} => {CH2_O*}	133.4	240.3	
{COH_H*} => {HCOH*}	69.5	12.2	
{HCO_H*} => {HCOH*}	269.0	116.3	
{HCOH*} => {CH_OH*}	91.4	170.7	
{HCOH_2H*} => {H2COH_H*}	111.1	132.4	
{H2COH_H*} => {CH2_OH_H*}	216.3	332.9	
{H2COH_H*} => {H3COH*}	102.5	108.2	
{H2CO_2H*} => {H3CO_H*}	87.4	64.5	
{H3CO_H*} => {CH3_O_H*}	282.2	359.2	
{H3COH*} => {H3CO_H*}	98.0	171.8	
{H2CO_2H*} => {H2COH_H*}	233.3	131.0	
{H3COH*} => {CH3_OH*}	137.4	278.1	
CH _x hydrogenation			
{C_2H*} => {CH_H*}	186.9	215.6	
{CH_H*} => {CH2*}	159.5	133.4	
{CH2_2H*} => {CH3_H*}	104.9	138.5	
{CH3_H*} => {CH4*}	150.9	158.2	
0 hydrogenation			
{0_2H*} => {0H_H*}	128.4	28.4	
{C_0_2H*} => {C_0H_H*}	235.4	154.5	
{CO_O_2H*} => {CO_OH_H*}	186.8	86.5	
{COH_O_H*} => {COH_OH*}	185.7	194.5	
{HCO_O_H*} => {HCO_OH*}	50.4	109.5	
{CH_0_H*} => {CH_0H*}	162.3	35.9	
{CH2_0_2H*} => {CH2_0H_H*}	306.9	135.0	
{CH3_0_H*} => {CH3_0H*}	178.7	168.6	
OH hydrogenation			
{OH_H*} => {H2O*}	56.2	50.5	
{C_OH_H*} => {C_H2O*}	166.0	83.9	
{CO_OH_H*} => {CO_H2O*}	93.5	120.5	
{COH_OH_2H*} => {COH_H2O_H*}	149.1	149.0	
{HCO_OH_2H*} => {HCO_H2O_H*}	190.9	100.4	

{CH_OH_2H*} => {CH_H2O_H*}	84.9	5.0
{CH2_OH_H*} => {CH2_H2O*}	262.0	227.2
{CH3_OH_2H*} => {CH3_H20_H*}	256.8	198.9
O _{vac} formation		
{2H*} => {OH_H_Ov*}	115.1	37.5
$\{0H_H_0v^*\} => \{H20_0v^*\}$	300.6	133.9
$\{0v^*\} + \{H20\} => \{H20_0v^*\}$	0.0	10.4
O _{vac} healing		
$\{CO2\} + \{Ov^*\} => \{CO2_Ov^*\}$	0.0	104.5
{CO2_Ov*} => {CO*}	78.9	157.9
$\{0v^*\} + \{CO\} \Longrightarrow \{CO_Ov^*\}$	0.0	51.3
$\{CO_Ov^*\} => \{C^*\}$	190.8	233.4

Figure D.4: Stable state geometries of Co₁.



2H



C+2H



C+0



CO



 CO_2



CO₂+2H



 $CO_2 + O_{vac}$







CO+2H



CO+H₂O



COH+O+H





CO+O+2H



 H_2O



СО+ОН+Н

 $C+H_2O$



COOH+H



 H_2O_{sup}



CO+O_{vac}



HCO+0+H



HCOO+H







OH+H

C+OH+H



O_{sup}H+H

Figure D.5: Transition state geometries of Co₁



CO₂+2H≓CO+O+2H





C0**≓**C+0



СООН+Н≓СО+ОН+Н



COOH+H≓CO₂+2H



H₂O+C≓OH+H+C



 $CO_2+O_{vac} \rightleftharpoons CO$



СООН+Н≓СОН+О+Н



H₂0≓0H+H



СО+2Н≓С+О+2Н



С0+0Н+Н≓С0+0+2Н



 $H_2O_{sup} \rightleftarrows O_{sup}H+H$









HCOO+H≓CO₂+2H

НСОО+Н≓НСО+О+Н

0H+H+C**≓**0+2H+C

0H+H**≓**0+2H



O_{sup}H+H≓O_{sup}+2H

Figure D.6: Stable state geometries of Co₄







С







 CH_2



CH3+H



CH3+OH+2H



CH₂+2H



CH₃+H₂O+H



CH₂+O

CH₃+O+H



CH2+0+2H



CH3+OH



CH₄



CH+H





CH+O+H





C+0



 CO_2





C+O+2H



CO+2H



CO₂+O_{vac}



СО



CO+H₂O



C+OH+H



СОН+Н



COH+H₂O+H



C0+0



COH+O+H



CO+O+2H



СОН+ОН



СОН+ОН+2Н





CO+OH+H



COOH+H





CO+O_{vac}





H₂CO+2H



H₂COH+H







H₂O+CH₂



H₂O+H+CH



H₂O+H+HCO



 H_2O_{sup}



H₃CO+H



H₃COH



HCO+H



нсон



HCOH+2H



HCO+O+H



НСО+ОН



HCOO+H



HCO+OH+2H



0



0+2H



0+2H+C



OH+2H+CH

OH+H

OH+H+C



OH+H+CH₂



O_{sup}H+H

Figure D.7: Transition state geometries of Co₄



CH₂≓CH+H



CO₂+2H⊂CO+O+2H



CH₃+H≓CH₂+2H



CO₂ *⊂*CO+0





CH₄ **∠**CH₃+H



 $CO_2 + O_{vac} \rightleftharpoons CO$

СН+Н≓С+2Н



CO+2H≓C+O+2H



C0≓C+0



 $CO+O_{vac} \rightleftharpoons C$





СОН+Н≓СО+2Н

СОН+Н≓С+ОН+Н



СООН+Н≓СО₂+2Н



СООН+Н≓СОН+О+Н



СООН+Н≓СО+ОН+Н



H₂CO≓CH₂+O



H₂CO≓HCO+H

 $H_2O+CH_2 \rightleftharpoons OH+H+CH_2$



H₂COH+H≓CH₂+OH+H



 $H_2O+C \rightleftharpoons OH+H+C$







 $H_2O+H+CH_3 \rightleftharpoons OH+2H+CH_3$

 $H_2O+H+CH \rightleftharpoons OH+2H+CH$ $H_2O+H+COH \rightleftharpoons OH+2H+COH$ $H_2O+H+HCO \rightleftharpoons OH+2H+HCO$





H₂O+CO≓OH+H+CO





H₂COH+H≓H₂CO+2H

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 $H_2Osup \rightleftharpoons O_{sup}H+H$



H₃CO+H≓H₂CO+2H





H₃CO+H≓H₃C+O+H



H₃COH≓H₃C+OH



HCO+H≓CO+2H



H₃COH≓H₃CO+H



H₃COH≓H₂COH+H

НСО+Н≓СН+О+Н



НСОН≓СН+ОН



НСОН≓СОН+Н



НСОН≓НСО+Н



HCOO+H≓CO₂+2H



НСОО+Н≓НСО+О+Н



 $OH+CH_3 \rightleftharpoons O+H+CH_3$

OH+H+C≓O+2H+C



ОН+СН≓О+Н+СН



0H+H+C0≓0+2H+C0



ОН+СОН≓О+Н+СОН



0H+HCO≓O+H+HCO



OH+H+CH₂ ≥O+2H+CH₂





0H+H**≓**0+2H

O_{sup}H+H≓O_{sup}+2H

Figure D.8: Stable state geometries of Co₈



2H



CH₂+2H

CH₃+H₂O+H

 CH_4



С



CH₂+O



CH3+O+H



CH+H







CH2+0+2H



CH3+OH



CH+O+H



 CH_2



CH₃+H



CH₃+OH+2H



CH+OH



C+0



CO



CO₂+2H

 CO_2





C+O+2H



CO+2H







C+OH+H



СОН+Н





COH+O+H

COH+H₂O+H



СОН+ОН



CO+OH+H



СОН+ОН+2Н



СООН+Н



C0+0



CO+O_{vac}



CO+O+2H



H₂CO



H₂CO+2H



H₂COH+H



H₂O+C



 H_2O+CH_2



H₂O+H+CH





 H_2O_{sup}



H₃CO+H



H₃COH



HCO+H



нсон



HCOH+2H



НСО+ОН+2Н



HCO+O+H

0



НСО+ОН



0+2H



HCOO+H



0+2H+C



OH+2H+CH







OH+H+C

OH+H+CH₂



O_{sup}H+H

Figure D.9: Transition state geometries of Co₈



 $CH_2 \rightleftharpoons CH + H$



СН₃+Н≓СН₂+2Н



CO₂ **≈**CO+O



CH₄ **∠**CH₃+H



СО+2Н≓С+О+2Н



СОН+Н≓С+ОН+Н



СН+Н≓С+2Н



 $CO_2+O_{vac} \rightleftharpoons CO$



СООН+Н≓СО₂+2Н



C0≓C+0







СООН+Н≓СОН+О+Н



СООН+Н≓СО+ОН+Н



H₂CO≓CH₂+O



H₂CO≓HCO+H



 $H_2O+CH_2 \rightleftharpoons OH+H+CH_2$



H₂COH+H≓CH₂+OH+H



H₂O+C≓OH+H+C



H₂COH+H≓H₂CO+2H



H₂0+C0≓0H+H+C0



 $H_2O+H+CH_3 \rightleftharpoons OH+2H+CH_3$





 $H_2O+H+CH\rightleftarrows OH+2H+CH \quad H_2O+H+COH\rightleftarrows OH+2H+COH \quad H_2O+H+HCO\rightleftarrows OH+2H+HCO$



H₂O≓OH+H



 $H_2Osup \rightleftharpoons O_{sup}H+H$



H₃CO+H≓H₂CO+2H



H₃COH≓H₂COH+H



H₃CO+H≓H₃C+O+H











H₃COH≓H₃C+OH



H₃COH≓H₃CO+H



НСО+Н≓СН+О+Н



НСОН≓СН+ОН



НСО+Н≓СО+2Н



НСОО+Н≓НСО+О+Н



НСОН≓СОН+Н



OH+CH₃ ≓O+H+CH₃







ОН+СОН≓О+Н+СОН



 $OH+H+CH_2 \rightleftharpoons O+2H+CH_2$

0H+H**≓**0+2H



0H+H+C**≓**0+2H+C



O_{sup}H+H≓O_{sup}+2H



ОН+Н+СО≓О+2Н+СО



ОН+НСО≓О+Н+НСО



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Reaction step	Net flux Co ₄ [s ⁻¹]	Net flux Co ₈ [s ⁻¹]
H2 + C0_0* -> C0_0_2H*	-7.7E-05	6.4E-07
H2 + CO2* -> CO2_2H*	1.7E-04	-1.2E-05
CO* + H2 -> CO_2H*	3.1E-17	1.9E-11
* + H2 -> 2H*	4.2E-05	1.2E-05
C_0* + H2 -> C_0_2H*	0.0E+00	5.3E-29
C* + H2 -> C_2H*	-5.8E-34	1.2E-27
CH2* + H2 -> CH2_2H*	0.0E+00	5.0E-24
HCO_OH* + H2 -> HCO_OH_2H*	6.6E-17	1.2E-16
0* + H2 -> 0_2H*	2.2E-04	1.3E-05
CH_OH* + H2 -> CH_OH_2H*	0.0E+00	5.0E-24
CH2_O* + H2 -> CH2_O_2H*	0.0E+00	7.2E-32
HCOH* + H2 -> HCOH_2H*	0.0E+00	6.2E-30
H2CO* + H2 -> H2CO_2H*	0.0E+00	-1.2E-29
CH3_OH* + H2 -> CH3_OH_2H*	0.0E+00	1.0E-31
COH_OH* + H2 -> COH_OH_2H*	4.2E-46	0.0E+00
CH4 + * -> CH4*	-7.0E-27	-5.0E-24
0v* + H20 -> H20_0v*	-1.1E-21	-1.0E-29
C* + H2O -> C_H2O*	-6.6E-40	-1.2E-27
CO* + H2O -> CO_H2O*	-1.6E-16	-1.9E-11
CH_H* + H2O -> CH_H2O_H*	-7.5E-27	-5.0E-24
H20 + * -> H20*	-2.2E-04	-1.3E-05
CH2* + H2O -> CH2_H2O*	1.9E-32	-2.7E-53
CH3_H* + H2O -> CH3_H2O_H*	5.1E-28	-1.3E-39
HCO_H* + H2O -> HCO_H2O_H*	-1.3E-26	-1.4E-17
COH_H* + H2O -> COH_H2O_H*	4.1E-51	-2.2E-26
2H* + CO -> CO_2H*	-3.1E-17	-1.9E-11
CO + * -> CO*	-1.3E-16	-1.2E-21
0v* + C0 -> C0_0v*	-5.8E-34	-2.5E-40
0* + CO -> CO_O*	-8.0E-05	-1.2E-05
0_2H* + CO -> CO_0_2H*	-1.4E-04	-6.4E-07
H3COH + * -> H3COH*	4.3E-30	-7.2E-33
CO2 + * -> CO2*	1.8E-04	6.5E-07
CO2 + 0v* -> CO2_0v*	1.1E-21	1.0E-29
CO2 + 2H* -> CO2_2H*	4.2E-05	1.2E-05
CO2_2H* -> CO_0_2H*	2.1E-04	1.1E-16
C02_0v* -> C0*	1.1E-21	1.0E-29
CO2* -> CO_O*	3.1E-06	1.3E-05
HCOO_H* -> HCO_O_H*	6.6E-17	1.2E-16
COOH_H* -> CO_OH_H*	1.6E-16	6.1E-22
COOH_H* -> COH_O_H*	3.4E-32	1.2E-25
CO_2H* -> C_O_2H*	0.0E+00	1.4E-25
CO* -> C_O*	-1.2E-41	5.3E-29
CO Ov* -> C*	-5.8E-34	-2.5E-40

Table D.4: Net flux of all elementary reaction steps on Co_4 and Co_8 .

COH_H* -> C_OH_H*	0.0E+00	2.2E-26
HCO_H* -> CH_O_H*	7.5E-27	5.0E-24
H2CO* -> CH2_O*	1.2E-27	7.2E-32
H2COH_H* -> CH2_OH_H*	-2.0E-29	2.0E-40
H3CO_H* -> CH3_O_H*	-5.1E-28	4.5E-39
H3COH* -> CH3_OH*	1.4E-42	4.9E-32
HCOH* -> CH_OH*	-2.6E-41	1.3E-32
CO2_2H* -> COOH_H*	1.6E-16	6.1E-22
CO2_2H* -> HCOO_H*	6.6E-17	2.4E-09
CO_2H* -> HCO_H*	-5.3E-27	-1.4E-17
COH_H* -> HCOH*	-7.7E-34	6.2E-30
HCO_H* -> H2CO*	6.7E-28	-1.2E-29
H2COH_H* -> H3COH*	-6.2E-41	6.2E-30
H3COH* -> H3CO_H*	4.3E-30	6.1E-30
H2CO_2H* -> H3CO_H*	-5.0E-28	0.0E+00
HCO_H* -> HCOH*	7.7E-34	-2.9E-35
HCOH_2H* -> H2COH_H*	5.9E-38	6.2E-30
H2CO_2H* -> H2COH_H*	-2.0E-29	-1.4E-32
CO_2H* -> COH_H*	1.5E-43	-2.6E-30
C_2H* -> CH_H*	-5.8E-34	7.4E-28
CH_H* -> CH2*	7.5E-27	5.0E-24
CH2_2H* -> CH3_H*	7.5E-27	5.0E-24
CH3_H* -> CH4*	7.0E-27	5.0E-24
0_2H* -> OH_H*	2.2E-04	1.3E-05
2H* -> OH_H_Ov*	1.1E-21	0.0E+00
HC0_0_H* -> HC0_0H*	6.6E-17	1.2E-16
C_0_2H* -> C_0H_H*	-1.0E-42	-2.1E-26
CO_O_2H* -> CO_OH_H*	5.6E-20	1.9E-11
COH_O_H* -> COH_OH*	4.2E-46	1.2E-25
CH_O_H* -> CH_OH*	7.5E-27	5.0E-24
CH2_0_2H* -> CH2_OH_H*	-4.8E-28	-2.0E-40
_CH3_O_H* -> CH3_OH*	-5.1E-28	-5.6E-35
OH_H* -> H2O*	2.2E-04	1.3E-05
_OH_H_Ov* -> H2O_Ov*	1.1E-21	1.0E-29
_HCO_OH_2H* -> HCO_H2O_H*	1.3E-26	1.4E-17
CH3_OH_2H* -> CH3_H2O_H*	-5.1E-28	1.3E-39
CH2_OH_H* -> CH2_H2O*	-1.9E-32	2.7E-53
CH_OH_2H* -> CH_H2O_H*	7.5E-27	5.0E-24
COH_OH_2H* -> COH_H2O_H*	1.3E-56	2.2E-26
CO_OH_H* -> CO_H2O*	1.6E-16	1.9E-11
C_OH_H* -> C_H2O*	6.6E-40	1.2E-27



Figure D.10: Reaction orders of Co₄.



Figure D.11: Apparent activation energy of Co₄.



Figure D.12: Production rate of Co₄ at 50% conversion to CO.



Figure D.13: DRC of Co_4 at 50% conversion to CO.



Figure D.14: Reaction orders of Co_4 at 50% conversion to CO.



Figure D.15: Surface coverage of Co₄ at 50% conversion to CO.



Figure D.16: Production rate of Co₄ with CO adsorption and desorption disabled.



Figure D.17: DRC of Co₄ with CO adsorption and desorption disabled.



Figure D.18: Reaction orders of Co₄ with CO adsorption and desorption disabled.



Figure D.19: Surface coverage of Co₄ with CO adsorption and desorption disabled.



Figure D.20: Reaction energy diagram of the dominant pathway for CH_4 formation on Co_4 with CO adsorption and desorption disabled.



Figure D.21: Production rate of Co_4 with CO adsorption and desorption disabled and lowered O and OH hydrogenation barriers.







Figure D.23: Reaction energy diagram of the dominant pathway for CH_4 formation on Co_4 with CO adsorption and desorption disabled and lowered O and OH hydrogenation barriers.



Figure D.24: Reaction orders of Co₈.



Figure D.25: Apparent activation energy of Co₈.



Figure D.26: Production rate of Co_8 with CO adsorption and desorption disabled and lowered O and OH hydrogenation barriers.



Figure D.27: DRC of Co_8 with CO adsorption and desorption disabled and lowered O and OH hydrogenation barriers.



Figure D.28: Reaction energy diagram of the dominant pathway for CH_4 formation on Co_8 with CO adsorption and desorption disabled and lowered O and OH hydrogenation barriers.



Figure D.29: Reaction energy diagram of the dominant pathways for CH_4 formation on Co_4 and Co_8 with CO adsorption and desorption disabled and lowered O and OH hydrogenation barriers.

7. Summary and Outlook

7.1 Summary

In this thesis, we explore the relationship between the structure of various cobalt (Co) catalysts and their reactivity in CO and CO₂ methanation at the molecular level. To achieve this, we modelled a wide range of active sites, including various environments of the active sites, and correlated the site geometry with the reactivity of the site. Using density functional theory (DFT), we simulated the reaction pathways for CO+H₂ and CO₂+H₂ conversions, analyzing stable states through density of states (DOS), crystal orbital Hamilton population (COHP), and charge analyses. Microkinetic modeling was employed to simulate the activity and selectivity of these active sites. By correlating the electronic structure of the site-adsorbate complex and its influence on the stabilization of intermediate and transition states, we gained deeper insights into catalytic behavior at the molecular level.

Breaking the strong C–O bond is often the rate-limiting step in Fischer–Tropsch synthesis and CO₂ methanation. In **Chapter 3**, we investigate this process using DOS and COHP analyses to understand how the electron density redistributes between the active site and the CO molecule upon adsorption, and how this redistribution influences the stabilization of the transition state (TS) of CO scission. Twelve active sites are examined, including configurations where CO coordinates to cobalt in three-, four-, five-, and sixfold manners. These models include extended surface models as well as Al₂O₃- and TiO₂-supported nanoparticles and -rods. We find that the distance between the C, O atoms and the Co atoms in the active site is a good descriptor for the CO dissociation barrier. Consistent with established models for linear CO adsorption, we identify key descriptors for C–O bond activation: a decrease in electron density in the 1π orbital of CO, occupation of 2π anti-bonding orbitals, and redistribution of electrons in the 3σ orbital. These three effects are more pronounced for more activated bonds. We attribute the low CO dissociation barrier observed at sites where CO adsorbs in a five- or sixfold manner to a greater weakening of the CO 1π molecular orbital. To minimize electron-electron repulsion with the Co dband, which emerges from the alignment of the C–O bond parallel to the surface, the 1π orbital shifts away from the Co site, weakening the C–O bond.

In **Chapter 4**, we investigate the reactivity of the interfacial regions of Co nanoparticles (NPs) of at least a few nanometers in size. This is achieved by

simulating CO+H₂ conversion over Co nanorods supported on γ -Al₂O₃(110) and rutile-TiO₂(110), using DFT and microkinetic modeling. The nanorods are continuous in one direction and act as proxy for the interface of larger nanoparticles. Our findings reveal that interfacial sites exhibit significantly lower activity compared to the extended Co $(11\overline{2}1)$ surface, primarily due to the higher stability of intermediates at the interface. This increased stability originates from the lower coordination of Co atoms at the interface relative to the extended surface. We positioned B₅-like pocket sites at the interface and as a consequence, CO dissociation was found to be rate inhibiting at the interface as it results in extremely stable C and O species which block the active site. Although charge transfer occurs between the Co nanorods and the supports, it predominantly affects Co atoms directly bonded to the support. These Co atoms exhibit positive or negative charges depending on whether they are near oxygen or aluminum/titanium atoms of the support, respectively. However, most interfacial sites remain unaffected by charge transfer, resulting in a negligible overall influence on the reactivity.

Building on the results of Chapter 4, in **Chapter 5**, we study the same reaction and use a similar methodology to investigate the role of small (~ 1 nm) Co nanoparticles supported on Al₂O₃. From experiment, such particles are considered sub-optimal in CO methanation and Fischer-Tropsch synthesis, as they lack a high abundance of important B₅ step sites. Our studies reveal however that this is not the only important characteristic of small nanoparticles. The coordination of the Co atoms in the NP appears to be of large influence, since highly under-coordinated Co atoms bind reactants too strongly, hindering CO conversion. On small nanoparticles with higher-coordinated Co atoms, the binding of reactants resembles that observed on extended Co surfaces. However, the top sites of these nanoparticles are inactive due to high barriers for CO scission, due to the absence of pocket sites and because the TS of CHO dissociation is not stabilized as well as at the interface. At the interface, the Co atoms appear to be more mobile, allowing for C-O bond scission via CHO, albeit at a relatively low rate. Based on this result, we infer that in the absence of B_5 sites, the locus of the catalytic activity for small NP lies at the nanoparticlesupport interfacial perimeter.

In contrast to fully reduced nanoparticles, **Chapter 6** focuses on CO_2 methanation over partially reduced cobalt systems, i.e. those reduced at lower temperatures. These systems are modeled by placing a single Co atom (Co₁), a four-atom cluster (Co₄), and an eight-atom cluster (Co₈) on a CoO(100) surface.

The four- and eight-atom clusters were generated using a genetic algorithm (GA), which generates a large population of cluster structures in order to identify the most stable cluster configuration. The results reveal that the single Co atom is inactive due to spatial constraints that hinder the hydrogenation of both CO and O in the presence of the other. The Co_4 and Co_8 clusters are active in the reverse water-gas shift (RWGS) reaction, producing CO. Methane formation is not observed on these clusters, which is attributed to the absence of pocket sites at the Co_8 cluster, and the insufficient number of Co atoms at Co_1 and Co_4 to effectively stabilize C and O in the transition state. Additionally, water formation is found to be challenging on these clusters when C derivative species are coadsorbed, which favors CO desorption. Oxygen vacancies are not formed in proximity of Co_{14.8} due to high barriers associated with the hydrogenation of lattice oxygen. CO₂ dissociation occurs via a direct pathway and is associated with low barriers for all systems considered. The Co₈ cluster exhibits greater susceptibility to adsorbate-induced restructuring, resulting in highly stable reaction intermediate states and lower CO production rates compared to Co₄. We propose that the enhanced adsorbate-induced restructuring of Co₈ arises from the incomplete convergence of the Co_8 genetic algorithm, which hinders the identification of the most stable cluster configuration.

7.2 Comprehensive insights and synthesis of findings

The observed structure sensitivity in CO and CO_2 methanation over various supported cobalt catalysts directly correlates with the structural factors governing Fischer-Tropsch synthesis. The analysis of CO dissociation pathways highlights the critical role of specific adsorption sites, particularly those facilitating the shift in the 1π orbital during five- or sixfold CO adsorption, which is essential for efficient bond scission. Such sites are prevalent on larger cobalt particles but absent on smaller nanoparticles, resulting in higher activation barriers for direct CO scission.

In Fischer-Tropsch synthesis, where chain growth and hydrocarbon formation depend on the efficiency of CO dissociation and subsequent hydrogenation steps, these structural disparities between different nanoparticle sizes become crucial. The interfacial perimeter sites on smaller nanoparticles, which support CHO intermediate anchoring and activation through the mobility of Co atoms, may provide alternative pathways for C–O bond scission and catalytic activity. However, the absence of B_5 sites and reduced availability of optimal adsorption

sites on small nanoparticles inherently limit their catalytic efficiency for producing longer hydrocarbon chains. The low methane formation at the metalsupport interface of larger NPs is due to these effects as well. Smaller nanoparticles and the NP interface predominantly promote the formation of unwanted methane, as the imbalance between the slow rate of CO dissociation and the rapid rate of hydrogenation favors methane over longer hydrocarbon chains. If the NPs are too small, they easily deactivate due to undercoordination of Co atoms. These particles show no appreciable catalytic activity at all. This interplay between particle size, adsorption site availability, and CO activation underscores the structural dependencies critical to catalytic performance in Fischer-Tropsch synthesis, with smaller nanoparticles and the metal-support interface exhibiting a bias toward methane over higher hydrocarbons.

Within the conventional structure sensitivity trends as discussed above, the assumption is that fully metallic sites dominate catalytic activity. However, a broader perspective that includes partially reduced species, rather than only purely metallic, can offer a more nuanced understanding of catalytic behavior and break from traditional structure sensitivity paradigms. Experiments show that partially reduced cobalt supported on ceria-zirconia, titania, or cobalt oxide is highly active in CO_2 hydrogenation, yielding mostly methane and to a lesser extent CO. We observe a low CO_2 conversion activity on single atom and few-atom clusters of Co/CoO, with 100% selectivity towards CO. This suggests that the experimentally observed CO originates from single atom and few-atom clusters, and methane is formed on larger NPs. The computed reaction energetics show that the mechanism of CO formation on single atom and few-atom clusters on a CoO(100) surface does not include hydrogen spillover nor oxygen vacancy formation.

7.3 Outlook

Further investigations could be undertaken to explore the structure sensitivity of CO_2 hydrogenation over partially reduced cobalt. In this study, we modeled the CoO phase by applying a Hubbard *U* correction term to the Co atoms, to account for the strong electron-electron correlations in CoO. This approach prevents CoO from being incorrectly simulated as a metallic conductor with high electron delocalization. The accuracy of this method significantly depends on the choice of the Hubbard *U* value for each Co atom. We used a *U* value that has been reported to optimize the simulation of both the CoO and Co phases using a single parameter. However, to achieve greater accuracy in our simulations, it would be beneficial to assign different *U* values to different Co atoms depending on their
chemical environment, such as Co in the clusters, surface Co (in the CoO surface), and bulk Co (in bulk CoO). For different Co atoms in the system, the U correction term can be determined using precise adsorption energy calculations for surface atoms, and bulk energy calculations for subsurface Co, derived from higher-level theoretical methods such as hybrid functionals. Another way to achieve a higher level of accuracy for simulating Co/CoO structures, is to use a meta-GGA functional instead of GGA+U, which we have used in the Co/CoO study reported in this thesis. A meta-GGA is computationally less expensive than employing hybrid functionals such as HSE06 or PBE0, which incorporate exact exchange calculated using Hartree-Fock theory. We found that the use of hybrid functionals is unfeasible for the kind of studies reported in this thesis due to very high computational costs for the few-hundred-atom systems that we consider. Where GGA functionals depend only on the electron density and its gradient or first derivative, meta-GGA functionals additionally depend on either the kinetic energy density (e.g. the functional M06-L), or the Laplacian or second derivative of the electron density (e.g. the functional SCAN-L). Due to these additional dependencies, meta-GGA functionals show lower self-interaction errors than GGA functionals, yielding better results for highly correlated systems such as CoO than GGA's.

Furthermore, the Co₈ cluster used in our study on partially reduced Co catalysts did not represent the most stable configuration. More stable configurations, geometrically similar to the initial structure, were observed upon introducing adsorbates. To address this, the genetic algorithm (GA) used to generate the cluster configurations should be run to convergence. However, this process is computationally demanding. To accelerate the GA procedure and reduce its computational costs, instead of randomly initializing the first generation of clusters, as done in this study, previously computed clusters can be used to obtain a first generation of clusters that is already known to be relatively stable. The already computed clusters can be obtained from living a dataset such as described in [*J. Chem. Theory Comput.*, 2024, 20 (15), 6801-6812]. This dataset can be used for this purpose because there appears to be high geometrical similarity between clusters of different transition metals. Making use of these similarities can significantly reduce the computational costs of a GA run.

In studies involving Co nanoparticles and nanoclusters supported on Al_2O_3 and TiO_2 , the potential role of oxygen vacancy formation was initially not considered, potentially overlooking a critical aspect of the interaction between Co species and the oxide supports. On the $TiO_2(110)$ surface the formation of oxygen

vacancies near Co sites is exothermic, indicating that it is energetically favorable and may significantly influence the local electronic structure and catalytic properties of the Co active sites. These vacancies might facilitate unique reaction pathways, such as the activation of CO or H_2 , or alter the binding energies of key intermediates, thereby impacting the overall reaction mechanism. To further understand the role of oxygen vacancy formation in CO methanation, it is essential to calculate the energy barriers for vacancy formation in TiO₂supported systems. Such calculations would help determine whether the formation of vacancies is kinetically feasible under operating conditions and if these vacancies contribute to catalytic turnover.

In contrast, on an $Al_2O_3(110)$ surface, oxygen vacancy formation is highly endothermic, suggesting that it is unlikely to occur under typical reaction conditions. Despite this, the support may play a mechanistic role through its ability to stabilize reaction intermediates, such as formate or methoxy species, which could significantly influence the reaction pathway. This distinction between the two supports highlights the importance of support effects in determining the activity and selectivity of Co-based catalysts for CO methanation.

Our study on CO_2 hydrogenation over CoO-supported Co clusters revealed that the barriers for oxygen vacancy formation are too high to be overcome at typical reaction temperatures, and that hydrogen spillover does not occur in these systems. These results are based on the CoO(100) surface, yet experimental evidence indicates the coexistence of both CoO(100) and CoO(111) facets in cobalt oxide nanoparticles. Thus, the role of CoO(111) surfaces in modifying the behavior of supported Co clusters remains underexplored. The CoO(100) and CoO(111) facets are known to exhibit distinct electronic and structural properties, which could influence their interaction with Co clusters and their ability to facilitate catalytic processes such as oxygen vacancy formation or hydrogen spillover.

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List of Publications

Publications within the scope of this thesis

<u>Rozemarijn D.E. Krösschell</u>, Emiel J.M. Hensen and Ivo A.W. Filot. Unravelling CO Activation on Flat and Stepped Co Surfaces: A Molecular Orbital Analysis, *J. Phys. Chem. C* **2024**, 128 (22), 8947–8960.

Lulu Chen, Ying-Ying Ye, <u>Rozemarijn D.E. Krösschell</u>, Emiel J.M. Hensen and Ivo A.W. Filot. Multiscale Modelling of CO₂ Hydrogenation of TiO₂-Supported Ni₈ Clusters: On the Influence of Anatase and Rutile Polymorphs, *Catal. Sci. Technol.* **2024**, *14* (21), 6393–6410.

Zhaochun Liu, <u>Rozemarijn D.E. Krösschell</u>, Ivo A.W. Filot and Emiel J.M. Hensen. A Combined Density Functional Theory and Microkinetics Simulations Study of Electrochemical CO_2 Reduction on $Cu_8/SnO_2(110)$: The Crucial Role of Hydrogen Coverage, *Electrochim. Acta* **2024**, *493*, 144409.

Xianxuan Ren, <u>Rozemarijn D.E. Krösschell</u>, Zhuowu Men, Peng Wang, Ivo A.W. Filot and Emiel J.M. Hensen. A Theoretical Study of the Role of K on the Reverse Water-Gas Shift Reaction on Hägg Carbide, **submitted**.

Publications outside the scope of this thesis

Pia Müller, <u>Rozemarijn D.E. Krösschell</u>, Wyatt Winkenwerder and John van der Schaaf. The Butoxylation of Dodecylamine: Reaction Mechanism and Kinetics, *J. Chem. Eng.* **2020**, *382*, 122939.

Curriculum Vitae

Rozemarijn Dorothea Elisabeth Krösschell was born on the 27th of February 1996 in Nijmegen. After finishing high school in 2014 at Stedelijk Gymnasium Nijmegen *cum laude*, she studied Chemical Engineering and Chemistry at Eindhoven University of Technology. In 2020 she graduated within the Inorganic Materials and Catalysis group with the MSc thesis 'Modelling porous catalyst particles in C++'. In the same year she started a PhD project at Eindhoven University of Technology of which the results are presented in this dissertation.



