

Unraveling the Mechanistic Role of Promoters in Fe-Carbide-Catalyzed Fischer-Tropsch Synthesis

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Unraveling the Mechanistic Role of Promoters in Fe-Carbide-Catalyzed Fischer-Tropsch Synthesis

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 maandag 3 April 2025
om 11:00 uur

door

Xianxuan Ren

Geboren te Hebei, China

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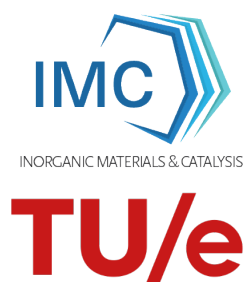
Xianxuan Ren

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Chapter 1. Introduction

1.1 The Energy Transition

Global energy consumption is continuously increasing and is expected to double in the coming decades compared to recent levels. The growing demand for energy is driven by population growth, urbanization, industrialization, and rising energy demands from emerging economies. Energy consumption still relies on fossil fuels including coal, oil and natural gas, with a limited contribution of nuclear and renewable energy like solar, wind and hydropower.¹ The greenhouse gas emissions from using these conventional energy sources lead to serious climate problems. To address these problems, significant efforts are being directed toward technologies that reduce our dependence on fossil feedstocks for energy and chemicals, which should include the use of alternative renewable carbon sources. CO₂ and biomass have emerged as promising feedstocks in this transition as they are renewable and can significantly contribute to a circular carbon economy.

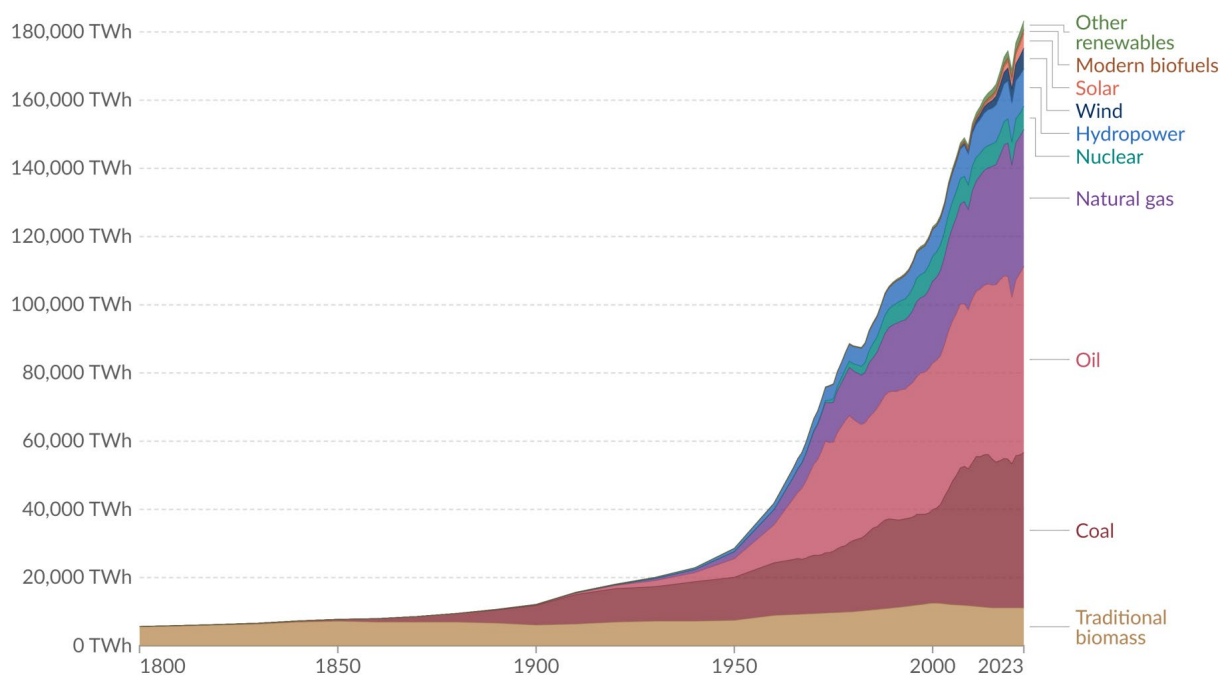


Figure 1.1. Global primary energy consumption by source (from reference¹).

Fischer–Tropsch synthesis (FTS) is a critical process for converting syngas, a mixture of CO and H₂, into valuable liquid hydrocarbons such as synthetic diesel, gasoline, and waxes. Currently, syngas is primarily derived from coal and natural gas using gasification and reforming. Gasification decomposes coal at high temperatures, while reforming employs steam or oxygen to process natural gas. While efficient, these methods are not inherently carbon-neutral due to the significant CO₂ emissions associated with the conversion of fossil feedstocks.

To address these limitations, alternative approaches are being explored. Renewable feedstocks, such as captured CO₂ and biomass, present promising pathways for syngas production with reduced carbon, enabling FTS applications that align with climate goals. Carbon Capture, Utilization, and Storage (CCUS) expands on CCS by incorporating the conversion of captured CO₂ into valuable products, such as fuels, chemicals, and materials, enabling a circular carbon economy. A key example is CO₂-Fischer–Tropsch (CO₂-FT) synthesis, which uses captured CO₂ to produce syngas through reverse water-gas shift (rWGS) and converts it into liquid hydrocarbons via Fischer–Tropsch synthesis. CCUS not only mitigates greenhouse gas emissions but also offers an innovative way to align climate action with industrial and economic growth. Biomass-to-Liquids (BTL) utilizes renewable biomass to generate syngas via gasification, subsequently producing liquid fuels through Fischer–Tropsch synthesis. Although BTL offers a cleaner alternative, challenges such as high costs, feedstock variability, and scalability hinder its feasibility. These processes, being more energy-intensive and complex than conventional refining, require significant advancements in catalyst design and process optimization to achieve cost-effective and scalable solutions.

1.2 Catalysis

Catalysis plays a crucial role in numerous industrial and everyday processes due to its ability to enhance reaction rates, improve efficiency, and reduce energy consumption by a substance known as a catalyst. The difference between catalytic and non-catalytic reactions is highlighted in Figure 1.2. Unlike in non-catalytic reactions, where reactants must overcome a high energy barrier to form products, catalysts provide an alternative pathway with a much lower energy requirement. This allows the reaction to proceed more quickly and under milder conditions, which is especially valuable in industrial processes where efficiency and time are crucial. Additionally, catalysts can be designed to favor the formation of specific products, improving selectivity and reducing unwanted by-products. This makes catalytic processes more energy-efficient, cost-effective, and environmentally friendly compared to non-catalytic reactions. Beyond industrial applications, catalysis is also deeply integrated into daily life, playing a key role in processes such as water purification, fermentation, the action of enzymes in our bodies, and the operation of three-way catalysts (TWC) in vehicle exhaust systems to reduce harmful emissions.²

A catalyst is introduced into a chemical reaction to accelerate the process by facilitating the dissociation or formation of chemical bonds in a lower energy barrier pathway. In the catalytic process, the catalyst is formally described as both reactant and product in a reaction, implying that

itself is not consumed during the process. In practice, a catalyst typically undergoes changes over time, resulting in its deactivation via various mechanisms, such as material loss, structural change and poison deposition on the surfaces. This deactivation requires the catalysts to be regenerated or removed from the chemical process.³ The interaction between catalysts and reactants in terms of catalytic activity obeys the Goldilocks's principle: If the bond between catalysts and reactants is too weak, the reactant is insufficiently activated and there will be no conversion. If such interaction is too strong, the product will not desorb from the surface of the catalyst, leading to the poison on the surface. This requirement for an optimal catalyst is known as Sabatier's principle.^{4, 5}

In catalysis, catalysts are usually classified into two main categories, homogeneous and heterogeneous catalysts, based on their phase relative to the reactants. Homogeneous catalysts are in the same phase as the reactant following uniform distribution and interaction with the reactants. The disadvantage is the separation and the recovery of these catalysts. Heterogeneous catalysts exist in a different phase with the reactant, usually as a solid interaction with liquid or gaseous reactants. With the advantages of easy separation from the reaction mixture, heterogeneous catalysts are widely used in most chemical processes,⁶ such as ammonia synthesis, petroleum refining, methane steam reforming, electronic catalysis, and polymerization like Fischer-Tropsch synthesis.

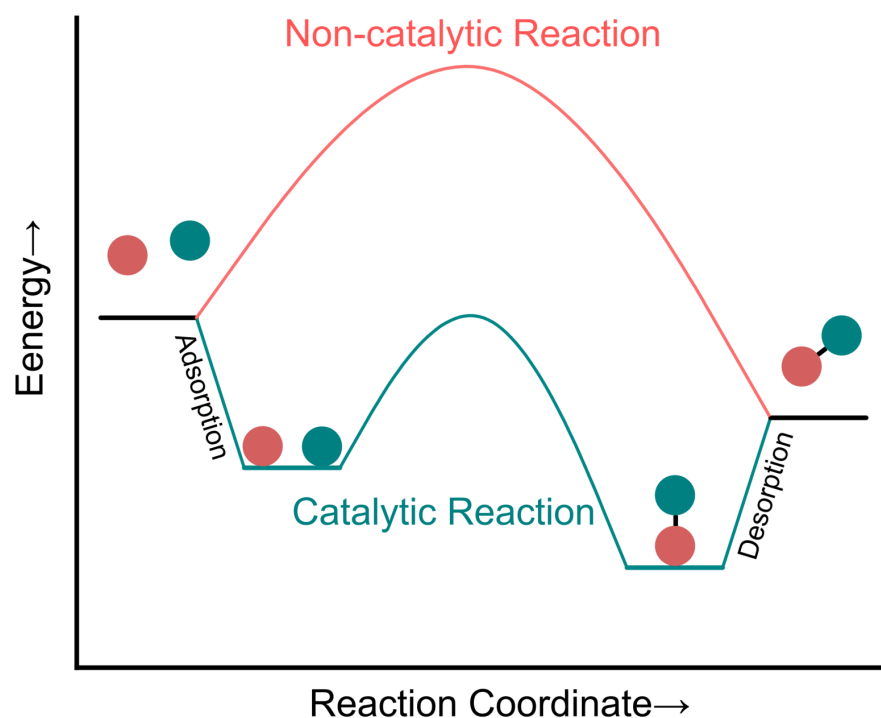


Figure 1.2. Schematic diagram illustrates the reaction energy for the association of two arbitrary compounds in both non-catalytic and catalytic reactions. The top line represents a non-catalytic pathway, the bottom line depicts a catalytic pathway for the association reaction.

1.3 Fischer-Tropsch Synthesis

1.3.1 A Brief History of Fischer-Tropsch Synthesis

Fischer-Tropsch (FT) synthesis provides an attractive route to produce clean fuels and value-added chemical building blocks from synthesis gas, a mixture of CO and H₂. Syngas can be obtained from non-petroleum feedstocks, including coal, shale gas, natural gas and biomass.⁷⁻⁹ The overall process is typically referred to as GTL, CTL or BTL, depending on the starting feedstock used as carbon sources to generate syngas.¹⁰ Furthermore, CO₂ can also be used as a source of carbon to generate syngas, offering a means to mitigate the emissions CO₂ of greenhouse, which cause serious changes in the climate. FT synthesis presents an alternative for converting CO₂ directly into fuels and chemicals, providing a sustainable alternative to traditional processes and addressing environmental concerns.

FT synthesis was developed in the 1920s by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute for Coal Research in Mülheim. Initially, the process was used to convert coal-derived syngas (a mixture of carbon monoxide and hydrogen) into liquid hydrocarbons.¹¹ During World War II, FT synthesis was used to generate synthetic fuels due to limited access to crude oil.¹² After the war, interest in FT synthesis diminished, as crude oil became the primary source of fuel, offering an abundant and more easily refined alternative. This shift led to a decline in the focus on synthetic fuel production.¹³ However, FT synthesis resurged during the 1970s due to the oil crisis, driving further research and development.¹⁴ In the late 20th and early 21st centuries, companies like Sasol, Shell and Chevron began constructing large-scale commercial plants, particularly in regions with abundant natural gas and coal reserves. Around the same time, China also emerged as a major player in FT synthesis development, investing heavily in coal-to-liquid (CTL) technology to capitalize on China's vast coal reserves.¹⁵ The largest CTL project in China is the 2016 Shenhua Ningmei project, which has a capacity of 100,000 barrels per day. Other significant CTL projects under construction include the Shenhua Xinjiang, Lu'an CTL, and Yitai CTL projects.¹⁶⁻¹⁸

1.3.2 Mechanisms of Fischer-Tropsch Synthesis

FT synthesis is a polymerization reaction with *in situ* generation of monomers from CO reactant.¹⁹ This process involves the catalytic conversion of CO and H₂ into liquid hydrocarbons and other products through a series of chain-growth mechanisms. Among the various proposed mechanisms, the most prominent two are the carbide mechanism and CO-insertion mechanism.^{11, 20-23} Figure 1.3 depicts a schematic representation of both the carbide and CO-insertion mechanism. The critical distinguishing feature between these two mechanisms is the manner of CO dissociation. In

the carbide mechanism, CO dissociation occurs prior to C-C coupling, whereas in the CO-insertion mechanism, C-O bond scission occurs after C-C bond formation. In the carbide mechanism, the C_1 monomers formed after CO dissociation undergo polymerization to form long-chain hydrocarbons through carbon-carbon coupling and hydrogenation steps. Growing hydrocarbon chains on the catalyst surface can desorb, resulting in the formation of linear olefins. These linear olefins can then be reabsorbed and further hydrogenated to produce alkanes. Surface oxygen is primarily removed through the formation of H_2O with CO_2 formation occurring at higher conversion. The carbide mechanism is favored on iron-based catalysts,²⁴ where CO dissociation is a key step in generating the C_1 monomers for the formation of long-chain hydrocarbons. For the CO-insertion mechanism, it involves the direct insertion of CO into the growing hydrocarbon chain without prior dissociation. Following the insertion, the O atom is dissociated and removed via H_2O .

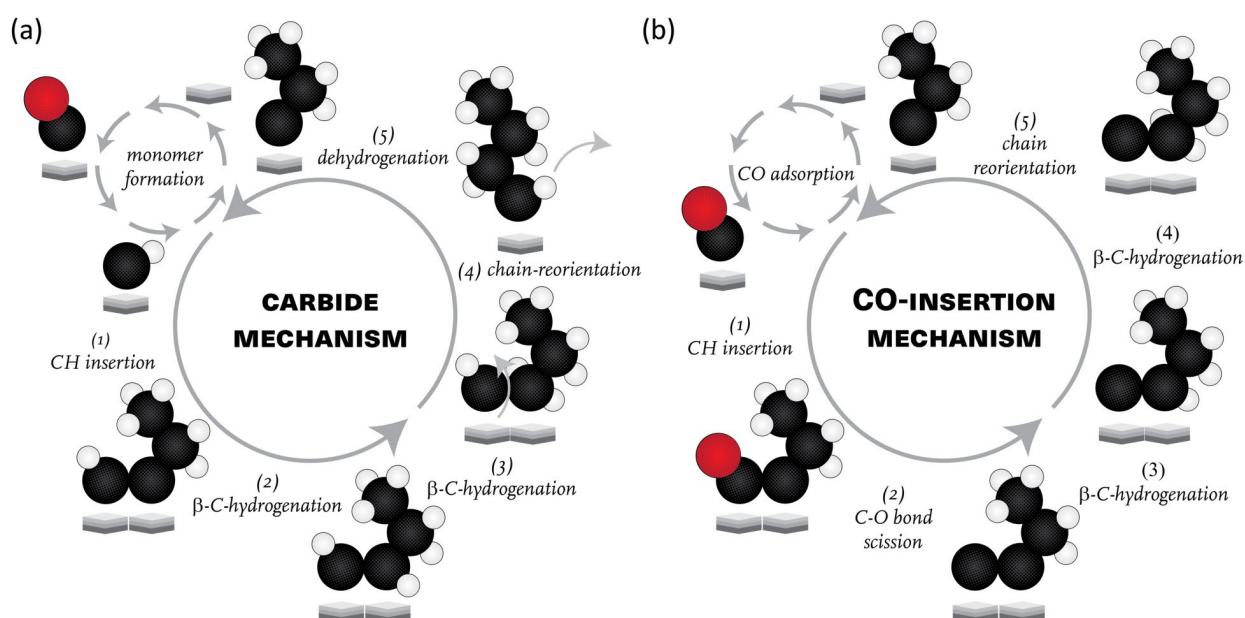


Figure 1.3. Chain-growth mechanism in Fischer-Tropsch mechanism: (a) Carbide mechanism and (b) CO insertion mechanism (from reference²⁵).

1.3.3 Catalysts for Fischer-Tropsch Synthesis

Transition metals often exhibit high performance in catalytic reactions due to their partially filled d-band, which allows for effective interaction with reactant molecules. This d-band structure facilitates the adsorption and activation of reactants, improving the catalyst overall activity and selectivity in various chemical processes like Fischer-Tropsch (FT) synthesis. Catalysts used in FT synthesis reactions should efficiently facilitate CO dissociation to provide sufficient C_1 monomers, maintaining a high rate of chain propagation. Pd, Os, Ir, and Pt are not suitable for catalyzing FT synthesis reactions due to their limited ability for efficient CO dissociation. For the

formation of long-chain hydrocarbons, an essential precondition is that the termination rate must be slower than the rate of the carbon chain propagation, allowing for the growth of longer chains before the reaction completes. Additionally, the hydrogenation rate should be relatively slower compared to CO dissociation and chain propagation to further support the formation of long chains. Ni precludes its industrial application in FT synthesis, as it predominantly produces methane. This is caused by its excessive hydrogenation activity compared to CO dissociation and carbon-carbon coupling, preventing the formation of long-chain hydrocarbons.²⁶ Ru, Co and Fe are effective in FT synthesis due to their high activity in CO dissociation and C₁ monomer insertion. However, the scarcity of Ru excludes its utilization in commercial FT synthesis.²⁷ Co and Fe are the primary industrial catalysts in FT synthesis due to their cost-effectiveness.²⁸⁻³⁰ Co is typically used in low-temperature FT synthesis, and its low rate of water-gas-shift (WGS) reaction restricts its application mainly to converting syngas from natural gas. The benefits of Fe are its very low price, high selectivity to lower olefins, and adaptability to various operating conditions.³¹ This flexibility is particularly crucial in practical operation conditions, accommodating a wide range of temperature, pressure and H₂/CO ratios.^{32, 33} This latter aspect is relevant to the high activity in the water-gas shift (WGS) reaction, making it highly suitable for processing synthesis gas with low H₂/CO ratios, such as those derived from coal and biomass.^{24, 34-37} Furthermore, this property also provides an alternative for CO₂ direct conversion to high-value added chemical such as olefins, which is known as CO₂-FT synthesis.

1.4 Fe-based Catalyst

Fe-based catalysts are used in large-scale Fischer-Tropsch synthesis due to the abundance of Fe and the high selectivity to olefins. Under practical conditions, unsupported Fe catalysts are not stable, leading to plugging of the catalyst bed or fouling of downstream equipment in fluidized bed operation. In contrast, supported Fe catalysts exhibit higher active phase dispersion and tolerance to mechanical degradation.³⁸ Under reaction conditions, the Fe-oxide precursor inevitably transforms into a mixture of metallic, oxidized, and carbide phases.³⁷ The composition of such phases highly depends on parameters, such as the precursor and the pretreatment and reaction conditions. Considerable efforts were put into investigating the dominant active phase of Fe-based catalysts.^{37, 39} X-ray diffraction (XRD) and Mössbauer spectroscopy have been instrumental in linking the FT activity to the Fe-carbide phases.^{8, 40-43} There is a broad range of distinct crystalline carbide phases, including ϵ -Fe₂C, ϵ' -Fe_{2.2}C, χ -Fe₅C₂, θ -Fe₃C, and Fe₇C₃.^{39, 44, 45} These carbide phases show different stability concerning various FT synthesis reaction

conditions,³⁷ as shown in Figure 1.4. At high temperatures and low carbon chemical potential (μ_C), θ -Fe₃C is most stable. Fe₇C₃ is reported as an active phase at high temperatures.^{46, 47} At moderate temperatures and high μ_C , low H₂/CO, χ -Fe₅C₂ is the most thermodynamically stable phase.⁴⁶ ϵ -Fe₂C, ϵ' -Fe_{2.2}C were found to be only stable at low temperature. Table 1.1 summarizes the crystal parameters and thermodynamic conditions of the most significant iron-carbide phases. Among them, Hägg iron carbide (χ -Fe₅C₂) is typically reported as one of the primary active phases for CO activation and chain growth in FT synthesis.^{37, 43, 48}

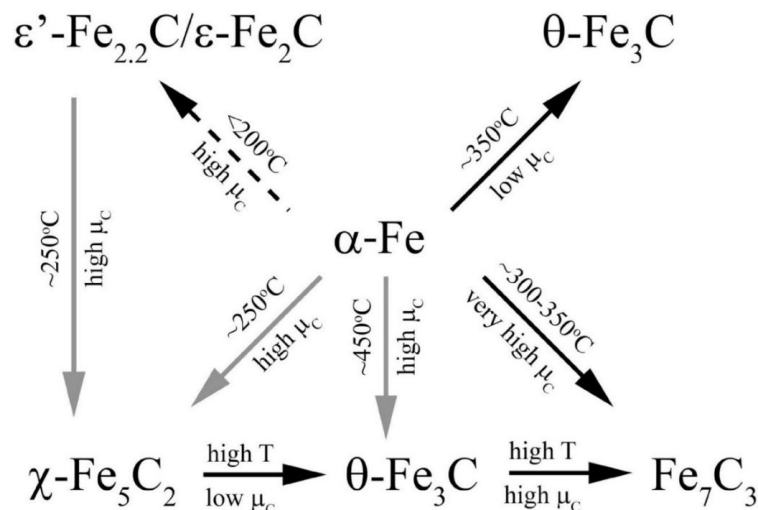
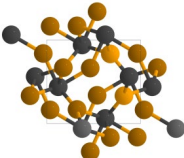
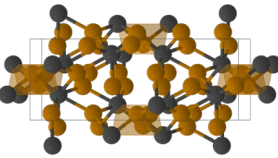
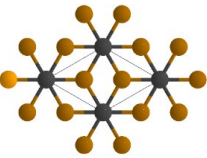


Figure 1.4. Qualitative interpretation of the ab initio atomistic thermodynamics study of iron carbide structures (from reference³⁷).

Table 1.1. Three most representative phases θ -Fe₃C, χ -Fe₅C₂ and $\epsilon(\epsilon')$ -Fe₂C of Fe-carbide phases with their corresponding parameters.

Carbide phase	θ -Fe ₃ C	χ -Fe ₅ C ₂	$\epsilon(\epsilon')$ -Fe ₂ C
Space group	Pnma (orthorhombic)	C2/c (monoclinic)	P6 ₃ /mmc (hexagonal)
Unit cell parameters	a = 5.092 Å, b = 6.741 Å, c = 4.527 Å, $\alpha = \beta = \gamma = 90^\circ$	a = 11.588 Å, b = 4.579 Å, c = 5.059 Å, $\alpha = \gamma = 90^\circ, \beta = 97.75^\circ$	a = 2.794 Å, b = 2.794 Å, c = 4.340 Å, $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Fe/C ration	0.33	0.4	0.45-0.5
Stable condition	Low (high T, low H ₂ /CO)	Low (moderate T, low H ₂ /CO)	High (low T, high H ₂ /CO)
Reference	49	50	51
Geometries			

The geometries refer to the database of The Material Project.⁵²

Fe is a common choice for the active metal for high-temperature Fischer-Tropsch synthesis in slurry bubble column reactors. However, these catalysts experience deactivation due to sintering, particle agglomeration, and attrition.⁵³ Catalyst deactivation due to oxidation is also recognized, as it obstructs the active sites of metallic iron or iron carbide phases.⁵⁴ This oxidation also promotes CO₂ selectivity, attributed to the WGS reaction occurring in the oxidized phase.⁸ Excessive carbon deposition can lead to coke formation, further contributing to the deactivation of Fe catalysts.⁵⁵ Graphite-like carbonaceous species will accumulate on the catalyst surface, blocking active sites and facilitating undesired side reactions.³⁷

Effort to stabilize the active phase of the Fe-based catalyst have focused on structural modifications and compositional enhancements. One common approach involves the use of supports to stabilize the active phase, improve dispersion, and reduce physical degradation, such as sintering and attrition.⁵⁶ The stabilization effect is primarily attributed to the strong interaction between the support and the active phase.⁵⁷ In addition to supports, promoters play a crucial role in optimizing the performance of Fe-catalysts. Promoters function works through two major mechanisms: structural promotion, which stabilizes the active phase;⁵⁸ and electronic promotion, which tunes the electronic properties of the catalyst.^{59, 60} For instance, structural promoters like S and B enhance the catalyst resistance to carbon deposition,^{61, 62} while electronic promoters improve resistance to oxidation and carburization.^{63, 64} Promoter also influence the product distribution and catalytic efficiency. They can increase the CO conversion, adjust the product profile, enhance selectivity toward long-chain hydrocarbons, and suppress methane formation, the latter being highly undesirable in FT synthesis.⁶⁵ Specific promoters such as Zn, Cu and alkali metals were found to be effective in boosting CO conversion and improving selectivity of lower olefins.⁶⁶⁻⁷⁰

1.5 Alkali Promoter

Alkali promoter is a substance used to enhance the performance of catalysts in various chemical reactions. Typically, these promoters include alkali metals such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs). They are often employed in small quantities to modify the electronic and structural properties of catalytic materials, thereby improving their activity, selectivity, and stability. Alkali metals are extensively used as promoters or active phases in various important chemical processes, including ammonia synthesis,⁷¹ methanethiol formation,^{72, 73} higher alcohol ⁷⁴ and FT synthesis.⁷⁵

Incorporating alkali promoters can significantly tune the catalyst performance for Fe-based catalysts, by enhancing the CO/CO₂ conversion, altering the product distribution and increasing

selectivity to long-chain hydrocarbons while suppressing undesirable selectivity of methane.^{65, 67-69} For instance, Li, Na and K were found to increase the catalytic activity and the selectivity to lower olefins.⁷⁶ Among these, K is usually reported to be the most effective promoter for increasing the rates of the FT reaction and WGS and reverse WGS (rWGS) reactions. Regarding the product distribution, K lowers the methane selectivity, presumably by increasing the chain-growth probability.^{63, 77-79} Considerable investigations were conducted to study the mechanistic role of K promoter.⁸⁰ Experimentally, the main role of the K promoter is thought to stabilize the active phase by enhancing O resistance and increasing carburization.^{63, 81, 82} Theoretical investigations mainly focused on the K effect on adsorption energies, with a few studies discussed a positive effect on CO and CO₂ dissociation.^{81, 83-86} Despite these insights, the nature of K species under FT conditions and their mechanistic role in promoting the FT and (r)WGS reactions remains unclear.

1.6 Research Scope

This thesis focuses on the mechanistic role of alkali promoters, specifically potassium (K), in Fe-catalyzed CO/CO₂-Fischer-Tropsch (FT) synthesis using density functional theory in conjunction with microkinetic modelling. The study systematically explores the nature of potassium and its mechanistic impact on key processes within FT synthesis, such as CO/CO₂ dissociation, CH₄ formation, O removal as well as the carbon chain growth on the most active Hägg carbide phase. This dual quantum-level and kinetic perspective offers insights into the significant promotional effects of potassium on iron catalysts in FT synthesis. The thesis expands the investigation about alkali promotion, exploring the intrinsic activity of cesium (Cs) as an active phase in H₂S-containing syngas conversion as suggested by experimental observation.⁶⁰

Chapter 2 provides an overview of the computational methods employed in this thesis, including Density Functional Theory (DFT) calculations for determining the electronic structure. From the computed electronic structure, key parameters such as adsorption energies, activation barriers, and pre-exponential factors for each elementary reaction step are derived. These parameters serve as the foundation for constructing a microkinetic model to describe the reaction mechanisms.

Chapter 3 offers a quantum-level understanding of K promotion on CO dissociation across 5 representative facets of χ -Fe₅C₂ using DFT calculations. The study investigates both direct and hydrogen-assisted CO dissociation on these surfaces, providing a comprehensive understanding of how K influences this crucial reaction step in Fischer-Tropsch synthesis. By employing a combination of Crystal Orbital Hamilton Population (COHP) and Density of States (DOS) analyses, alongside charge density analysis, the chapter offers mechanistic insights into the nature

Chapter 1. Introduction

of K promotion for CO dissociation. Furthermore, it reveals the potential deactivation of the catalyst resulting from excessive promoter loading.

In **Chapter 4**, the mechanistic role of the K promoter in the chemokinetic network of CO hydrogenation to methane and longer hydrocarbons is investigated using density functional theory (DFT) combined with microkinetics modeling. This chapter begins by identifying the most stable state of potassium promoter on the (010) surface of χ -Fe₅C₂. Utilizing the unpromoted and K₂O-promoted models, electronic analyses were employed to explore how K₂O promotes the electron density of the surface from a quantum perspective. DFT calculations were performed to compare the energetic differences in key processes, including species adsorption, CO activation, methane formation and chain growth, between unpromoted and promoted systems. With these energetics, comprehensive microkinetics simulations were built to provide a detailed analysis of how potassium influences the surface activity, reaction pathways and intermediates involved in the conversion of CO and hydrogen to methane and longer-chain hydrocarbons.

Chapter 5 examines the role of potassium (K) as a promoter in CO₂ Fischer-Tropsch synthesis on two representative surfaces, (510) and (010), using a combination of density functional theory (DFT) and microkinetic simulations. The enhancement of CO₂ activation by K is explored through detailed electronic analysis, integrating bond analysis with charge density evaluation. Microkinetic simulations further reveal the influence of K promotion on reaction kinetics across low and high-temperature regimes, providing critical insights that bridge theoretical studies with experimental observations.

In **Chapter 6**, we extend the study of alkali metals by examining their role as intrinsic active phases in H₂S-containing syngas conversion. This chapter reveals the intrinsic active sites across six low-index Miller planes of Cs₂S and provides insights into the adsorption effects on Cs₂S using density functional theory (DFT) and thermodynamic analysis. Combining DFT with microkinetic modeling, we compare the Langmuir-Hinshelwood (LH) and Mars-van Krevelen (MvK) mechanisms to identify the dominant pathway for COS formation. Additionally, we evaluate the normalized facet contributions based on a hypothetical Wulff particle to evaluate the intrinsic activity of different surfaces. This highlights the importance of investigating the intrinsic activity of supported alkali metals, as understanding their role could lead to significant advancements in syngas conversion processes.

The thesis is concluded with **Chapter 7**, which summarizes the main results and provides an outlook on remaining challenges.

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Chapter 2. Computational Methods

2.1 Introduction

Over the past few decades, the rapid evolution of semiconductor technology and material science has led to exponential growth in computing power, driving significant advancements in computational chemistry. This progress has enabled the investigation for more complex chemical systems with higher accuracy, facilitating breakthroughs in molecular modeling, reaction mechanisms, and material design. With the capacity to handle intricate systems—such as catalysts, surfaces, and large molecular structures—these advancements support sophisticated electronic structure calculations. In the following sections, we provide a concise introduction to the computational methods used in this thesis, specifically Density Functional Theory (DFT) and Microkinetic modelling.

2.2 Quantum-Chemical Methods

2.2.1 The Electronic Structure Problem

Quantum mechanical methods, like density functional theory (DFT), can be applied to investigate the electronic structure of chemical systems. These approaches for electronic structure calculations focus on solving the non-relativistic time-independent Schrödinger equation:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian operator, Ψ the wavefunction and E the energy. For a system containing N electrons and M nuclei, the Hamiltonian operator $\hat{H}$ in atomic units is given by¹

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{j=1}^M \frac{1}{M_j} \nabla_j^2 - \sum_{i=1}^N \sum_{j=1}^M \frac{Z_j}{r_{i,j}} + \sum_{i=1}^N \sum_{k>1}^N \frac{1}{r_{i,k}} + \sum_{j=1}^M \sum_{l=1}^M \frac{Z_j Z_l}{R_{j,l}} \quad (2.2)$$

where i and k correspond to the electrons and j and l iterate over the nuclei. M_j is the ratio of the mass of nucleus j , $r_{i,k}$ the distance between electrons i and j , $r_{i,k}$ the distance between electron i and nucleus k , $R_{j,l}$ the distance between nuclei j and l , and Z_j the charge of nucleus j . The five terms in the above equation refer, in order, to the kinetic energy of the electrons, the kinetic energy of the nuclei, the coulombic attraction between the electrons and the nuclei, the repulsion between the electrons and finally the repulsion between the nuclei.

Due to the significantly larger mass of the nuclei compared to the electrons (over 3 orders of magnitude), it can be assumed that changes in the position of the nuclei cause a near-instantaneous

redistribution of the electrons. Furthermore, the repulsion between the nuclei is considered constant. Therefore, the motion of electrons and nuclei can be treated separately. This assumption is known as the Born-Oppenheimer approximation. With this approximation, the electronic structure problem only depends on the position of fixed nuclei. The electron motion then can be described by its motion in an electrostatic field produced by these nuclei. This approximation allows us to simplify Equation (2.2) to the so-called electronic Hamiltonian ($\hat{H}_{\text{elec}}$), describing the motion of electrons in the field of M point charges, as given by equation (2.3).

$$\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{j=1}^M \frac{Z_j}{r_{i,j}} + \sum_{i=1}^N \sum_{k>1}^N \frac{1}{r_{i,k}} \quad (2.3)$$

This electronic Hamiltonian operates on the many-electron wavefunction Ψ to generate the energy E . Due to the separation of nuclear and electronic degrees of freedom, the nuclear repulsion energy (the fifth term in Equation (2.2)) becomes a constant that is added to electronic energy to compute the total energy of the electronic problem. The solution to the Schrödinger equation, which involves this electronic Hamiltonian, provides the electronic wavefunction. Finding this solution is the central objective of electronic structure calculations.

To completely describe the quantum statistics of the electrons, the wavefunction of a multi-electron system is expressed as a linear combination of all possible Hartree products. This ensures the wavefunction adheres to the Pauli exclusion principle and the antisymmetric requirement for fermions. The object used to encapsulate these properties is known as a Slater determinant as provided by Equation (2.4).

$$\Psi(x_1, x_2, \dots, x_N) = (N!)^{-\frac{1}{2}} \begin{bmatrix} \chi_1(x_1) & \cdots & \chi_N(x_1) \\ \vdots & \ddots & \vdots \\ \chi_1(x_N) & \cdots & \chi_N(x_N) \end{bmatrix} \quad (2.4)$$

In the above equation, $\chi(x)$ corresponds to the spin-orbitals, which are a combination of a spatial wave-function and spin component. These spin-orbitals can be assumed, without any limitation, to form an orthonormal set, meaning that each spin-orbital is orthogonal with respect to others and individually normalized. The factor $(N!)^{-\frac{1}{2}}$ serves as a normalization factor for the Slater determinant. This formulation provides a fundamental framework for electronic structure methods, ensuring that the wavefunction accurately reflects the indistinguishable and antisymmetric nature of electrons.

By constructing the wavefunction in this manner, a many-electron system can be systematically described, which is the basis for further methods in quantum chemistry, such as the Hartree-Fock (HF) approximation. Hartree-Fock theory simplifies the many-electron problem by assuming that

electrons move independently in an averaged field created by all other electrons. However, this method neglects electron-correlation effects, which are crucial for accurate energy calculations. To further improve the electron-electron description, various post-Hartree-Fock methods have been developed that include electron correlation effects. These methods, such as Møller-Plesset perturbation theory (MPPT),² Coupled-Cluster theory (CC)³ and Configure interaction (CI)⁴ provide a more accurate treatment of electron correlation. Nevertheless, these methods are still computationally demanding, especially for larger systems, which limits their practical use in modeling systems with more than 50 atoms. This constraint makes it unsuitable for modelling typical heterogeneous catalysts, which generally contain many more atoms. For such systems, more computationally efficient approaches are essential.

2.2.2 Density Functional Theory

Density Functional Theory (DFT) provides an alternative approach to find an approximate solution to the Schrödinger equation by focusing on electron density. By using the electron density as the central quantity, DFT allows for the derivation of approximate solutions with significantly reduced computational complexity. DFT scales according to N^3 where N represents the number of basis functions, which typically scale linearly with the number of atoms when they are from the same element. The N^3 scaling relates to the most complex step in the algorithm, corresponding to (partial) matrix diagonalization. In contrast, wavefunction-based methods exhibit a computational scaling of at least N^4 , largely stemming from the evaluation of two-electron integrals. This difference in scaling makes DFT particularly advantageous for studying larger systems, enabling efficient exploration of complex electronic structures and interactions.⁵

2.2.2.1 Hohenberg-Kohn Theorems

To simplify the complexity associated with many-body wave function problems, Hohenberg and Kohn postulated two fundamental theorems.⁶ These theorems establish a theoretical framework for understanding and calculating the properties of many-body quantum systems.

The first Hohenberg-Kohn theorem states that the ground-state energy of a many-electron system is a functional of the electron density. In other words, there exists a one-to-one correspondence between the electron density and the external potential, known as the electron density being v -representable, such that provided an external potential and a fixed number of electrons, there is only a single electron density that yields the ground state energy. Under these conditions, the energy can be expressed as a functional of the electron density, as represented by the equation:

$$E[\rho] = T[\rho] + V[\rho] + U[\rho], \quad (2.5)$$

where $T[\rho]$, $V[\rho]$ and $U[\rho]$ refer to the kinetic energy, the external potential of the nuclei acting upon the electrons and inter-electron interaction energy, respectively. Though the theory states that the kinetic energy can be assessed based on electron density, its functional dependency remains unknown. In practice, it is typically approximated using wave functions of independent particles. Herein, the electron density in Equation (2.5) is defined as:

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\Psi_i(\mathbf{r})|^2. \quad (2.6)$$

Although the first Hohenberg-Kohn theorem establishes the possibility of using a functional of the electron density to address the electronic problem, it does not elucidate upon the specific form of this functional. To tackle this, the second Hohenberg-Kohn theorem invokes using the variational principle to determine the ground state energy, stating that the density yielding the lowest energy is the exact ground state density. As a result, the second theorem provides a detailed approach for evaluating both the wave function and the electron density in the ground state, offering a practical method for solving electronic structure problems. With a given external potential $v(\mathbf{r})$, the energy functional can be rewritten to explicitly depend on this potential, as given by

$$E[\rho(\mathbf{r})] = \int v(\mathbf{r})_{xc} \rho(\mathbf{r}) d\mathbf{r} + F[\rho(\mathbf{r})]. \quad (2.7)$$

Herein, $F[\rho(\mathbf{r})]$ represents the universal functional of electron density, which includes the kinetic energy and electron-electron interaction terms, as given by

$$F[\rho(\mathbf{r})] = T_s[\rho] + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho]. \quad (2.8)$$

Substituting the above equation into the energy expression in equation (2.5), yields:

$$E[\rho] = T_s[\rho] + \int v_{xc}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho]. \quad (2.9)$$

Herein, the four terms correspond to the kinetic energy of non-interacting electrons, the potential energy, the (classical) electron-electron repulsion energy and the exchange-correlation energy. The kinetic energy $T_s[\rho]$ can be calculated exactly, but not directly from the electron density ρ . Instead, it must be derived from the underlying wave function of the system. Equation (2.9) merely reshuffles the energy terms, but does not solve upon the problem that an exact expression for the exchange-correlation functional $E_{xc}[\rho]$, remains unknown. Instead, this term encapsulates all non-classical aspects of electron-electron interactions, as well as the part of the kinetic energy that arises from the real, interacting system as opposed to the idealized, non-interacting reference system. In this way, the exchange-correlation functional is a critical parameter dictating the accuracy of the quantum chemical calculation and responsible for accounting for the quantum

effects of the electron system that are not captured by the other, more straightforwardly calculable terms.

2.2.2.2 Kohn-Sham Theorems

The Hohenberg-Kohn theorems provide a theoretical framework for determining the ground-state energy of a system using a functional of the electron density. However, the challenge lies in finding the ground-state energy solution from this total energy functional, primarily because the exact exchange-correlation functional $E_{XC}[\rho]$ remains undefined.

To address this issue, Kohn and Sham proposed a practical approach by demonstrating that the electron density can be described by solving a set of single-electron equations. Under the independent electron approximation, the kinetic energy for the many-electron system is given by

$$T_S[\chi_i] = \sum_i^N \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle. \quad (2.10)$$

This leads to a modified version of the total energy equation, where $E_{XC}[\rho]$ now represents the combined effects of both the exchange and the residual correlation contributions from the interacting electron system. The total energy functional can thus be expressed as:

$$E[\rho] = T_S[\rho] + \int v_{XC}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{XC}[\rho]. \quad (2.11)$$

By recognizing the independent electron approximation, this expression can be reformulated into a set of single-electron Kohn-Sham equations ε_i , which are equivalent to:

$$E[\rho] = \sum_i^N \varepsilon_i + \int v_{XC}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{XC}[\rho] \quad (2.12)$$

by means of introducing the following one-electron eigenfunction equations

$$\left\{ -\frac{\nabla^2}{2} + V_{KS}[\rho(\mathbf{r})] \right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2.13)$$

wherein the one-electron Kohn-Sham potential V_{KS} is defined as

$$V_{KS}[\rho(\mathbf{r})] = V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})}, \quad (2.14)$$

where $V(\mathbf{r})$ refers to the interaction between an electron and the collection of atomic nuclei. The second term corresponds to Hartree potential describing the Coulombic repulsion between the electrons. The third term is the potential for the exchange and correlation contributions to the single-electron equations.

The Kohn-Sham equations are a set of integro-differential equations used to describe a system of non-interacting electrons within an effective potential. The solution process is iterative, starting with an initial guess for the electron density, used to compute the effective potential. This potential allows solving the Kohn-Sham equations to obtain new orbitals, which are then used to update the electron density. The cycle repeats until the input and output densities converge, yielding a self-consistent solution that accurately represents the ground state of the system. A brief schematic representation of the self-consistent loop for solving the Kohn-Sham equations is presented in Figure 2.1.

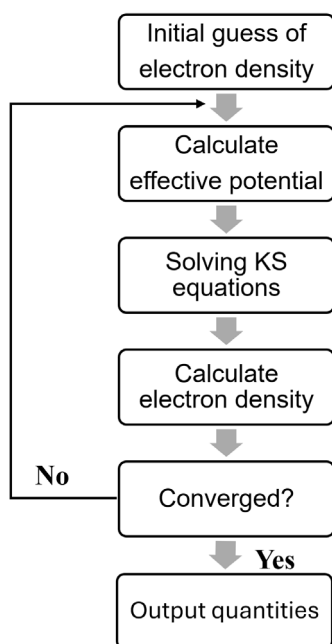


Figure 2.1. Schematic representation of the self-consistent loop for solving the Kohn-Sham equations.

2.2.2.3 Exchange and Correlation Functionals

Local density approximation (LDA)

The Kohn-Sham equations provide a useful approximation to the full Schrödinger equation, however, an explicit expression for the exchange-correlation function as a function of electron density remains unknown. To tackle this, some approximations have been derived, with the earliest one being generated from the homogeneous electron gas. Based on the quantum Monte-Carlo approach from Ceperly and Alder,⁷ Vosko, Wilk and produce a correlation functional for the correlation interaction by means of a Padé approximation interpolation.⁸ Hohenberg and Kohn also provide an expression for the exchange part based on homogeneous electron gas. The combination of the exchange and correlation interactions forms the so-called Local Density Approximation (LDA).

In LDA, the exchange-correlation energy is determined based on the idealized situation of homogeneous electron gas. In this approach, the total exchange-correlation energy is calculated by using the integral as given by

$$E_{XC}^{LDA}(n) = \int \rho(\mathbf{r}) \varepsilon_{XC}[\rho(\mathbf{r})] d\mathbf{r}, \quad (2.15)$$

where $\varepsilon_{XC}[\rho(\mathbf{r})]$ represents a functional corresponding to the exchange-correlation energy per particle, i.e. the potential, of the homogeneous electron gas with a density $\rho(\mathbf{r})$.

Although the local density approximation provides a reasonable solution for some systems, it oversimplifies the true nature of the electron density distribution and tends to overestimate bond energies. It assumes that the electron density changes slowly, making it effective for systems like metals and semiconductors. However, this assumption breaks down for chemically complex systems where rapid density variations occur.

Generalized gradient approximation (GGA)

To address the limitations of LDA, a relatively natural extension known as Generalized Gradient Approximation (GGA) was introduced. GGA improves upon LDA by incorporating not only the electron density but also its gradient, allowing for a more accurate description of the system with rapidly changing densities. The general expression for the exchange-correlation energy in GGA is given by Equation (2.16).

$$E_{XC}^{GGA}[\rho] = \int f[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})] d\mathbf{r}. \quad (2.16)$$

Many GGA-type functionals have been developed, utilizing different methods for incorporating gradient information of the electron density into the exchange-correlation term. This diversity has led to the creation of various GGA functionals, each tailored to improve accuracy for specific types of systems or properties, thereby enhancing the predictability of density functional theory in quantum chemistry. Throughout this thesis, the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁹ is applied, as it efficiently balances the exchange and correlation effects, which is critical for accurately describing the electronic properties of both metallic systems and metal-carbides.¹⁰

The GGA functionals are part of a hierarchical framework known as Jacob's ladder, which categorizes functionals based on their complexity and accuracy. A schematic representation of Jacob's ladder is provided in Figure 2.2. Each rung of the ladder represents a different level of accuracy and computational time in the approximation methods. Quantum chemical calculations therefore always act on a balance between model accuracy and system size.¹¹ At higher rungs on

the ladder, meta-GGA functionals include the second derivative of electron density or the Laplacian, therefore enhancing the description of a wide spectrum of chemical and physical properties. The next rung involves hybrid functionals, which integrate GGA with exact exchange derived from the Hartree-Fock method. This combination enhances the accuracy of computational predictions by offering a more refined treatment of electron correlation, partially mitigating upon the self-interaction error inherent in DFT.^{12, 13} The top rung is double hybrid functionals, such as meta-GGA + HF + [PT2, RPA], which represent an advanced class of DFT methods that combine the strengths of various, but which are associated with vastly increased computational cost as compared to the GGA level of theory.

Given the scope and size of the systems studied in this thesis, the GGA-PBE exchange-correlation functional is adopted throughout. A notable limitation of this exchange-correlation functional is that it struggles to accurately represent long-range electron correlation effects, especially dispersion forces.¹⁴⁻¹⁶ To address this limitation, several approaches, including semiclassical treatments for dispersion interactions,¹⁷⁻¹⁹ van der Waals density functionals^{20, 21} and the effective one-electron potentials,^{22, 23} have been introduced. In this work, we applied D3 correction, developed by Grimme et al., which includes Becke-Johnson damping^{17, 18} to improve the reliability of our calculations, particularly in systems where dispersion forces are essential.

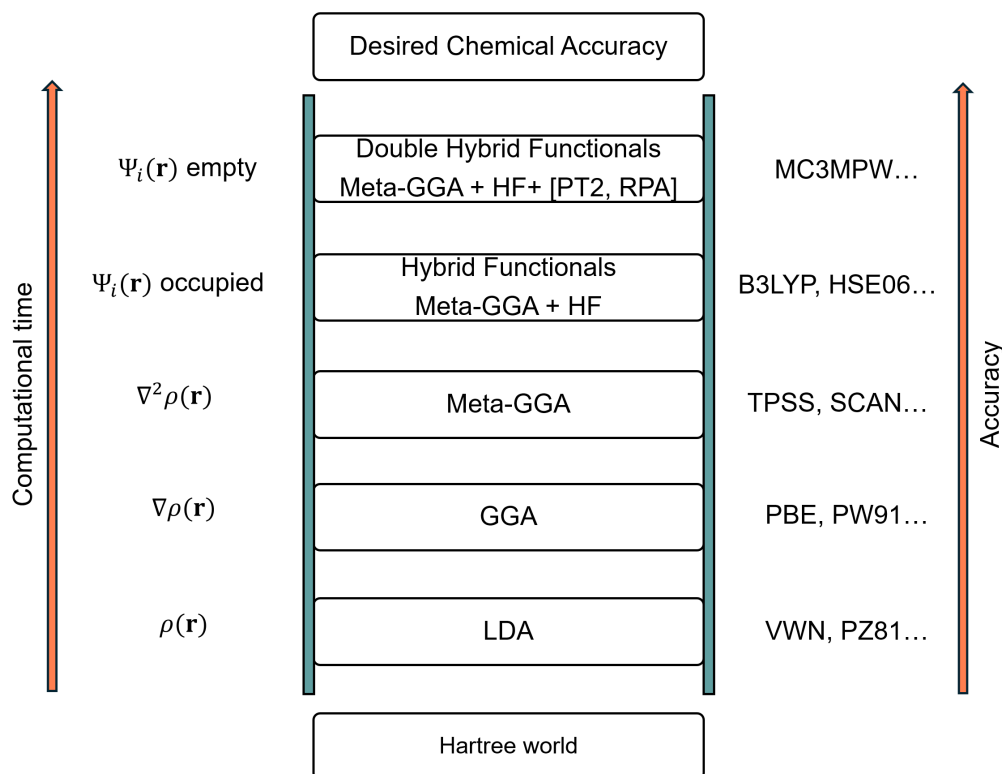


Figure 2.2. Schematic representation of the self-consistent loop for solving the Kohn-Sham equations.

2.2.3 Electron Density Analysis

In addition to the electronic total energy, the underlying electronic structure, particularly the electron density distribution and its partitioning in the canonical orbitals, is essential for understanding the properties of systems ranging from atoms and molecules to complex materials. By analyzing the electronic structure, one is able to identify key quantifiable descriptors rationalizing how the interaction between reactants and the catalyst system tend to facilitate the chemical transformation.

The electronic structure of molecules is described through molecular orbital (MO) theory, which associates energy levels of electrons based on molecular orbitals. In smaller molecules, these orbitals exhibit distinct energy levels. Electron density analysis offers a deeper insight into how electron redistribution influences the stability and reactivity of the molecular system, enhancing the understanding of adsorption, activation and promoter effect at a quantum level. A notable example is the well-known π -bond donation in both theory and experiment for CO adsorption, which highlights how electrons redistribute during interactions, particularly the filling of anti-bonding 2π orbital, destabilizing the C-O bond.^{24,25} Furthermore, electron density analysis can be employed to investigate the surface properties of catalysts, which is crucial for understanding the common interactions such as support effect,²⁶ doping²⁷ and promoter promotion.²⁸ In this thesis, we used an open-source EDP package²⁹ to investigate the electron redistribution by projecting the three-dimensional charge density scalar field onto a plane. The net charges are calculated by DDEC6 charge analysis implemented in the Chargemol software.^{30,31}

Density of states (DOS) analysis can be used to evaluate the electronic states (electrons) with respect to different energy levels in a system. A detailed DOS analysis reveals critical features like band gaps, the density of energy levels around the Fermi energy, and the population of electrons in these states. This analysis is crucial for understanding chemical processes, as it provides information on how energy levels change during reactions, bonding, and charge transfer.

Investigation into the electron distribution cannot directly be used to understand interatomic bonding features. Instead, one can use Crystal Orbital Hamilton Population (COHP) analysis to provide a quantitative assessment which orbitals as function of their position in the energy spectrum contribute to bond formation or destabilize the interaction between any two atoms. In the COHP procedure, the many-electron wave function is projected onto a new basis set, effectively performing a basis transformation from delocalized plane waves to localized atomic orbitals. Using the resulting (partial) Hamiltonian matrix in the localized basis, its off-diagonal terms corresponding to specific pairs of atoms can be utilized to assess whether specific Kohn-

Sham states in the original basis are bonding, anti-bonding or non-bonding, as shown by Equation (2.18).

$$\text{COHP}_{ij}(E) = H_{ij} \sum_i c_i^k c_j^k \delta(E - E_k) \quad (2.18)$$

Herein, H_{ij} is the Hamiltonian matrix element between atomic orbitals ϕ_i and ϕ_j . c_i^k and c_j^k refer to the linear coefficients of ϕ_i and ϕ_j in the energy state of k . By integrating COHP values over energy, one can quantify the total bonding energy or antibonding orbitals, providing insights into the strength and nature of chemical bonds.

Combining DOS and COHP analyses then allow for a comprehensive understanding of both the electronic structure and the bonding characteristics of a system, offering a powerful toolset for interpreting material properties and chemical processes. Throughout this thesis, the Lobster software (version 4.1.0).^{32, 33} has been used to perform the projection and to produce the DOS and COHP analyses.

2.2.4 Spin Effects in Fe-Based FT Synthesis

Transition metals, with their diverse d-electron configurations and intrinsic magnetic properties, play a significant role in catalytic processes.³⁴ Their spin and magnetic characteristics influence the electronic structure, which in turn can affect reaction pathways, rates, and selectivity.^{35, 36} Iron-based catalysts, in particular, exhibit strong magnetic properties, which may impact adsorption behavior and phase stability. However, in the context of Fischer-Tropsch (FT) synthesis, these effects remain secondary to dominant factors such as adsorption energetics and reaction kinetics. While magnetic ordering can subtly alter adsorption energies and intermediate stability, its overall influence on catalytic activity is typically small compared to reaction barriers and thermodynamic driving forces. Here, we briefly assess the relevance of spin polarization in Fe-based FT synthesis, which aspects are explicitly taken into account, the assumptions taken, and their impact on the accuracy with respect to the conclusions drawn in this work.

1. Electronic Structure and Reactivity

Within the framework of the ligand field model, the electronic structure of iron is governed by crystal field splitting, which determines the distribution of d-electrons and, consequently, the spin state. In a high-spin configuration, reduced crystal field splitting results in a greater number of available electronic states near the Fermi level, increasing the density of states (DOS) and facilitating electron transfer processes. This enhanced electronic accessibility promotes more efficient adsorption and activation of reactants such as CO and CO₂, potentially improving catalytic performance. However, it is important to recognize that the spin state itself is a consequence of the underlying electronic structure

rather than an independent driving force. Since both the observed reactivity and the spin state arise from the same electron density distribution, establishing direct causality between spin state and catalytic behavior is not straightforward. Instead, these properties should be understood as correlated outcomes of the broader electronic environment. Furthermore, while the ligand field model provides valuable insights into spin-dependent reactivity, its applicability to bulk iron catalysts may be limited, as additional factors such as metallic bonding and extended electronic interactions play a significant role in defining catalytic properties.

2. Spin-Polarized Adsorption

Spin-polarized adsorption arises from the spin-dependent electronic structure of magnetic surfaces, where differences in the density of states (DOS) for spin-up and spin-down electrons influence adsorption behavior. While spin-polarized DFT captures exchange splitting and adsorption trends, it employs a non-relativistic Hamiltonian and assumes collinear magnetism, as implemented in VASP by default. This means effects such as spin-orbit coupling (SOC), non-collinear magnetism, and dynamic spin fluctuations are not explicitly accounted for. However, the impact of SOC in 3d transition metals like Fe is typically on the order of 10–50 meV (1–5 kJ/mol), and non-collinear effects contribute around 10–100 meV (1–10 kJ/mol), both of which are small compared to typical adsorption energies in catalysis (~100–200 kJ/mol). Given these energy scales, we assume that such deviations introduce only minor corrections to adsorption energies and reaction pathways, and that a collinear, non-relativistic spin treatment provides a sufficiently accurate description for the adsorption processes considered in this thesis.

3. Reaction Pathways and Kinetics

The spin state of iron influences activation energies and reaction barriers in catalytic processes such as Fischer-Tropsch synthesis and CO₂ reduction by altering the stability of reaction intermediates and adsorption energies.³⁷ Magnetic ordering can stabilize specific intermediates, affecting reaction selectivity, while spin-dependent interactions may modify charge transfer and reaction kinetics.³⁸ In a standard DFT + Microkinetic Modeling (MKM) framework, spin effects are typically considered secondary corrections, as they usually contribute 10–100 meV (1–10 kJ/mol), whereas reaction barriers are often on the order of 100 kJ/mol or higher. Perhaps more important, given the relatively high temperature ($T > 200^{\circ}\text{C}$) at which FTS is conducted, thermal excitations and spin fluctuations become significantly more prevalent, vastly reducing the impact that spin has on reaction events. As such, while spin polarization can subtly influence catalytic trends, it is not expected to be a dominant factor in reaction kinetics.

In contrast, radical-based reactions and spin-crossover systems at low temperature exhibit significantly stronger spin effects, as their reactivity is directly governed by spin state transitions and exchange

interactions. In such systems, spin-state changes can modify activation energies by tens to hundreds of kJ/mol, making an explicit treatment of spin a necessity rather than a minor correction. Therefore, while the collinear spin-polarized DFT approach used in this thesis provides a reasonable approximation for bulk iron-carbide catalysts, it is less applicable to systems where spin transitions drive reactivity, such as molecular catalysts or transition-metal complexes involved in radical reactions.

4. Magnetically Driven Phase Stability

Iron-carbide catalysts can undergo phase transitions under reaction conditions,³⁹ with these transitions often being strongly influenced by their magnetic properties. While magnetic interactions can play a role in stabilizing specific phases,⁴⁰ thereby impacting catalyst lifetime and resistance to deactivation, our microkinetic modeling (MKM) approach employs a static surface approximation, where surface composition and structure remain fixed throughout the reaction. As a result, we do not explicitly model phase transitions or their magnetic effects within the kinetic framework. However, to ensure that our models remain representative of realistic catalytic conditions, we carefully align our computational model systems with experimental insights on stable and active catalyst phases. By doing so, we capture the dominant trends in catalytic behavior while acknowledging the limitations of a static surface assumption in modeling dynamic phase changes.

2.3 Microkinetics Modelling

Microkinetic modelling is employed to simulate complex chemo-kinetic networks, such as those involved in Fischer-Tropsch (FT) synthesis, by representing them as a set of elementary reaction steps. Parameters for constructing microkinetic simulations can be derived from DFT calculations or experimental data. Using these parameters, for each compound in the system an ordinary differential equation (ODE) is constructed involving all the elementary reaction steps that this compound is involved in. The time-independent behavior of a chemical reaction system is then analyzed by time-integration of the system of ODEs until steady-state is observed. This section first outlines the process of deriving microkinetic parameters from DFT-calculated data. It then demonstrates how a sequence of elementary reaction steps can be formulated into a corresponding system of ODEs. Finally, the process of solving ODE is discussed, highlighting the advantages of sensitivity analysis in microkinetic modeling for gaining deeper insights into reaction dynamics.

2.3.1 Key Parameters for Microkinetics Modeling

Establishing a microkinetic model requires the reaction rate constants, both forward and backward, of each elementary reaction step. Using DFT calculations of the initial, transition and final state of

every elementary reaction step, electronic activation energies can be determined. By performing subsequent frequency analysis for all states, zero-point energy corrections can be applied, which are crucial in accurately modeling catalytic reactions. The reaction rate constant is then calculated by means of the Eyring equation as shown in Equation (2.19).

$$k = \frac{k_B T}{h} \frac{Q_{TS}^*}{Q_{IS}} \exp\left(\frac{-\Delta E}{k_B T}\right), \quad (2.19)$$

In this equation, k represents the reaction rate of a single elementary reaction step, k_B and h are the Boltzmann and Planck constants, respectively. T is the temperature in Kelvin. Q_{TS}^* and Q_{IS} correspond to the total molecular partition functions for the transition and initial states, respectively. Importantly, Q_{TS}^* excludes the partition function corresponding to the imaginary frequency associated with the transition state, a mode which is used in transition state theory to construct the crossing frequency term $\frac{k_B T}{h}$. Finally, ΔE refers to the zero-point energy corrected electronic activation energy. The Eyring equation is based on *harmonic* transition state theory, which relies on the following underlying assumptions:

1. The transition state is in thermal equilibrium with the initial state as described by a thermal equilibrium constant.
2. The process of proceeding from the transition state to the final state is considered irreversible.
3. The crossing of the transition state occurs with a specific velocity or frequency over the hyperdimensional potential energy surface.
4. The transmission coefficient is assumed to be unity and no other crossing trajectories are being sampled.

In theoretical modeling of chemical reactions occurring on surfaces, we distinguish between three types of elementary reaction steps, which are adsorption, surface reaction and desorption. In this classification, adsorbate diffusion would correspond to a unimolecular surface reaction.

For a surface reaction, the initial state and transition state are described by partition functions corresponding to $3N$ and $3N-1$ vibrational degrees of freedom, respectively, where $3N$ is the number of atoms in the reactant. The initial state includes all $3N$ vibrational modes, accounting for the complete set of atomic motions assuming a strongly bound state. In contrast, the transition state has $3N-1$ vibrational modes, as the vibrational mode associated with the reaction coordinate, represented by an imaginary frequency, is excluded (see Equation (2.19)). Furthermore, it is assumed that the catalytic surface has a negligible contribution to the vibrational partition function, as the mass of the metal atoms is much larger than that of the adsorbates. The values of the partition

function are determined using a frequency analysis, which is calculated by means of Equation (2.20).

$$q_{\text{vib}} = \frac{1}{1 - \exp\left(\frac{-h\nu}{k_B T}\right)}, \quad (2.20)$$

where ν is the vibrational frequency. The vibrational frequencies are calculated considering the forces as a function of $6N$ perturbed states (two per cartesian direction and per atom). From the forces evaluated, a Hessian matrix can be constructed with its elements given by Equation (2.21).

$$H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}, \quad (2.21)$$

In this equation, E is the electronic energy, and x_i and x_j are the atomic positions along the Cartesian coordinates. The Hessian matrix is a square matrix that contains the second derivatives of the electronic energy with respect to atomic positions, reflecting the local curvature of the hyperdimensional potential energy surface. The element values of the Hessian matrix are approximated using the following four-point finite difference stencil

$$H_{ij} = \frac{1}{2} \left(\frac{\left(\frac{\partial E}{\partial x_i}\right)_{+\frac{1}{2}\Delta x_j} - \left(\frac{\partial E}{\partial x_i}\right)_{-\frac{1}{2}\Delta x_j}}{\Delta x_j} + \frac{\left(\frac{\partial E}{\partial x_j}\right)_{+\frac{1}{2}\Delta x_i} - \left(\frac{\partial E}{\partial x_j}\right)_{-\frac{1}{2}\Delta x_i}}{\Delta x_i} \right). \quad (2.22)$$

The Hessian matrix is then converted to a root-mass-weighted Hessian matrix by

$$H_{ij,mw} = \frac{H_{ij}}{\sqrt{m_i m_j}}. \quad (2.23)$$

Diagonalization of the mass-weighted Hessian Matrix gives $3N$ eigenvector/-value pairs. The eigenvectors refer to the normal modes of the vibrations and the eigenvalues corresponding to the vibrational energies, which can be used in equation (2.20). For the eigenmode corresponding to the single imaginary frequency for transition states, it is explicitly assessed that they correspond to the direction of the reaction coordinate.

For surface reactions, the entropy does not change significantly and as a result, the pre-exponential factor under typical catalytic conditions is in order of 10^{13}s^{-1} . In contrast, for adsorption or desorption steps, the entropy changes significantly due to the transition between the gaseous phase and the adsorbed state on a surface. It is typically assumed that a gaseous compound has 3 translational degrees of freedom and 0, 2, or 3 rotational degrees of freedom, depending on whether the adsorbate is a single atom, a linear molecule or a non-linear molecule. The translational and rotational degrees of freedom give rise to the complex having a higher entropy, which will decrease

upon the adsorption of the reactants due to the loss of these degrees of freedom. From the degrees of freedom, the entropy can be directly calculated by means of known statistical thermodynamics equations. These equations however assume idealized conditions. Alternatively, the Shomate equation⁴¹ as given by

$$S^0 = A \cdot \ln(T) + B \cdot T \frac{C \cdot T^2}{2} + \frac{D \cdot T^3}{3} - \frac{E}{2 \cdot T^2} + G \quad (2.24)$$

can be used which takes non-ideal contributions using a more empirical approach into account. In Equation (2.24), S^0 is the standard molar entropy and A-G refer to the parameters obtained from the NIST Chemistry Webbook.⁴²

For the description of adsorption steps, each adsorbate is assumed to lose one translational degree of freedom (perpendicular to the direction of the surface), which is converted to a vibrational degree of freedom, in the transition state with respect to the initial gas-phase state. If the magnitude of the corresponding vibrational partition function can be considered negligible compared to the other partition functions, we can directly derive the following reaction rate constant for the adsorption step as given by Equation (2.25).

$$k_{\text{ads}} = \frac{k_B T}{h} \frac{q_{\text{vib,gas}} q_{\text{rot,gas}} q_{\text{trans2D,gas}}}{q_{\text{vib,ads}}} = \frac{k_B T}{h} \frac{p A_{\text{st}}}{\sqrt{2\pi m k_B T}}, \quad (2.25)$$

In Equation (2.25), A_{st} and m are the effective area for adsorption and the molar mass of the gas species, respectively and p is the corresponding partial pressure of the gas species.

On the basis of microscopic reversibility, the assumptions used describing the transition state of the adsorption process are identical to those in the desorption process. This allows us to derive the rate constant for desorption from the adsorption equilibrium constant as given by

$$K_{\text{ads}} = \frac{k_{\text{ads}}}{k_{\text{des}}} = \exp \left(-\frac{\Delta H_{\text{ads}}}{RT} + \frac{S_{\text{ads}}}{R} \right), \quad (2.26)$$

from which by insertion of Equation (2.25), the desorption constant can be expressed as

$$k_{\text{des}} = \frac{k_B T}{h} \frac{p A_{\text{st}}}{\sqrt{2\pi m k_B T}} \exp \left(\frac{\Delta H_{\text{ads}}}{RT} - \frac{S_{\text{ads}}}{R} \right). \quad (2.27)$$

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

$$\Delta S_{\text{ads}} = R \ln Q_{\text{ads}} - S^0, \quad (2.28)$$

where S^0 can either be calculated using Shomate equation (2.24) or determined by fundamental thermodynamic principles. Insertion of equation (2.28) in (2.27) and yields

$$k_{\text{des}} = \frac{k_B T}{h} \frac{p A_{\text{st}}}{\sqrt{2\pi m k_B T}} \exp \left(-\frac{\Delta H_{\text{ads}}}{RT} \right) \frac{\exp \left(\frac{S^0}{R} \right)}{Q_{\text{ads}}}. \quad (2.29)$$

Assuming that the adsorbed complex has only vibrational degrees of freedom, and under the harmonic approximation, Q_{ads} can be calculated from the vibrational frequencies using the following equation

$$Q_{\text{ads}} = \prod_i \frac{1}{1 - \exp\left(\frac{-hv_i}{k_B T}\right)}, \quad (2.30)$$

where the zero-point energy contribution of the vibrational frequencies has been omitted, as it has already been accounted for in the definition of the activation energy in equation (2.19). Finally, we can construct the set of ordinary differential equations for all surface reaction intermediates. The rate expression for an elementary reaction step j is given in equation (2.31).

$$r_j = k_j \prod_i c_i^{v_i^j}. \quad (2.31)$$

In this expression, k_j represents the reaction rate constant calculated using the Eyring equation, c_i is the concentration of reactant i in the elementary reaction step j on the surface, and v_i^j refers to the stoichiometric coefficient of reactant i in the elementary reaction step j . It should be noted that in equation (2.31), we only consider the elementary reaction step in one direction. As a result, for each elementary reaction step, two rate expressions for the forward and backward reaction are obtained as shown in equation (2.31).

2.3.2 Solving ODEs

The equations described in (2.32) represent a set of ordinary differential equations (ODEs) with respect to time. To build such a set of ODEs, a series of elementary reaction steps and their associated rate constants are established. This results in a total of $2R$ elementary reaction equations involving N compounds. For each surface compound, the rate of change over time can be described by

$$\frac{\partial \theta_i}{\partial t} = \sum_j \left(v_{j,k} k_j \prod_q^{N_i} \theta_{q,j}^{v_{q,j}} \right), \quad (2.32)$$

where θ_i is the concentration of species i on the surface. $v_{j,k}$ refers to the stoichiometric coefficient of compound j . R represents the total number of elementary reaction steps. k_j corresponds to the rate constant of reaction j , $\theta_{q,j}^{v_{q,j}}$ and $v_{q,j}$ are the concentration and the stoichiometric coefficient, respectively, of compound q in reaction j . By integrating these equations over time, we can calculate the kinetic properties of the reaction including the overall reaction rate and steady-state coverage. The set of ODEs is solved until a steady-state solution is reached for all surface species i .

The equations involved in chemical systems are often classified as stiff equations. Stiffness is a phenomenon in which extremely small-time steps are required to time-integrate the system of differential equations. Herein, we use a multiple-step backward differentiation formula (BDF) method, as implemented in the Sundials library⁴³⁻⁴⁸ to perform the time integration of equation (2.32). This method dynamically adjusts the order of the differentiation between 1 and 5. Higher discretization orders are used when the hyperdimensional surface is steep, requiring greater numerical accuracy. In contrast, lower orders are used when the surface is relatively flat, optimizing computational efficiency by reducing the computational load. In this method, the steepness of the system is determined by evaluating the Jacobian matrix, which is approximated using a finite difference method encapsulated in the Sundials library. This adaptive approach allows for a balance between accuracy and computational efficiency when solving stiff chemical kinetic systems.

2.3.3 Kinetic Sensitivity Analysis

Reaction orders

The reaction order can be used to describe how the reaction rate responds to the changes in the partial pressure of the gaseous reactants or products. It offers insight into the influence of the reactants and products on the overall reaction rate.

Considering a generic bimolecular reaction $A + B = C$, the reaction rate can be expressed by

$$r = k \cdot [A]^{n_A} \cdot [B]^{n_B} \cdot [C]^{n_C} \quad (2.33)$$

or

$$r = k \cdot p^{n_A} \cdot p^{n_B} \cdot p^{n_C}, \quad (2.34)$$

where n_A, n_B, n_C are the reaction order of compounds A, B and C, respectively. The reaction order can then be calculated by the formula:

$$n_i = \frac{\partial \ln r^+}{\partial \ln p_i} = p_i \frac{\partial \ln r^+}{\partial p_i}. \quad (2.35)$$

Herein n_i refers to the reaction order of component i , r^+ corresponds to the reaction rate in the forward direction. Finally, p_i is the partial pressure of gaseous compounds i . The reaction order can be examined in experiments by evaluating how the reaction rate changes with respect to the change in partial pressure of gaseous reactants.

Apparent activation energy

The apparent activation energy provides insight into how temperature affects the reaction rate, essentially representing the sensitivity of the reaction kinetics to temperature variations. The mathematical expression for the apparent activation energy is given by

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r^+}{\partial T}, \quad (2.36)$$

where $\Delta E_{\text{act}}^{\text{app}}$ is the apparent activation energy, R is the gas constant. A positive $\Delta E_{\text{act}}^{\text{app}}$ value indicates that the overall reaction rate increases as temperature rises, while a negative value represents that the overall reaction rate decreases with increasing temperature. This $\Delta E_{\text{act}}^{\text{app}}$ value can be determined through experimental kinetics by fitting the temperature dependence of the reaction rate or rate constant to the Arrhenius law.

Degree of rate and selectivity control

The analysis of the rate-determining step has proven crucial in the analytical modelling of chemical kinetics. Under this assumption, it is considered that a single elementary reaction step is so slow that it completely determines the overall reaction rate. In practice, multiple elementary reaction steps can potentially control the overall reaction rate. To further evaluate the contribution of each reaction step to the overall rate and product distribution, we used the concepts of the degree of rate control (DRC) developed by Kozuch and Shaik^{49, 50} and popularized by Campbell.⁵¹ Here, we conduct a sensitivity analysis on the activation energy for all elementary steps. For each elementary reaction step, a DRC coefficient is assigned as given by

$$\chi_{\text{DRC},i} = \frac{k_i}{r} \left(\frac{\partial r}{\partial k_i} \right)_{k_{j \neq i}, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i}, \quad (2.37)$$

where $\chi_{\text{DRC},i}$ corresponds to the DRC coefficient, K_i is the equilibrium constant, k_i is the reaction rate constant and r corresponds to the overall reaction rate. The differential in the above equation evaluates the relative influence of the reaction rate by changing the activation energy (barrier) by an infinitesimal amount while keeping the rate constants of all other elementary reactions fixed as well as the overall thermodynamics of the reaction.

A positive $\chi_{\text{DRC},i}$ value indicates that a decrease in the barrier of elementary reaction step i facilitates the overall reaction rate, i.e. the elementary reaction step is rate-limiting. In contrast, a negative value implies that lowering the barrier of the elementary reaction step i , the overall reaction rate would decrease, i.e. the elementary step corresponds to the rate-inhibiting step. In the case that only a single elementary reaction step has a DRC coefficient of 1, that step is termed the rate-determining step from the perspective of Langmuir-Hinshelwood-Hougen-Watson kinetics.

Assuming that the reaction is evaluated at zero conversion, i.e., under kinetic conditions and infinitely far from equilibrium, the DRC coefficients obey the following sum rule

$$\sum \chi_{RC,i} = 1. \quad (2.38)$$

Analogous to the degree of rate control, the degree of selectivity control (DSC) coefficient is defined to evaluate the influence of a particular elementary step on the selectivity of the overall reaction. The DSC value is determined by

$$\chi_{DSC,i,c/r} = \left(\frac{\partial \eta_{c/r}}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} = \eta_c (\chi_{RC,i,c} - \chi_{RCi,r}), \quad (2.39)$$

Herein $\eta_{c/r}$ refers to the selectivity of compound c with respect to some reference compound r , $\chi_{RC,i,c}$ is the DRC coefficient to compound c , $\chi_{RCi,r}$ is the DRC coefficient for the rate of a reactant r . The corresponding sum rule for the DSC is given by

$$\sum_i \chi_{DSC,i,c} = 0, \quad (2.40)$$

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

Degree of chain growth control

In Fischer-Tropsch synthesis, the product distribution can be predicted by the Anderson-Schulz-Flory (ASF) distribution, which depends on the chain-growth probability. To evaluate the chain-growth probability (α), which is defined as the ratio between the rates of chain propagation (r_p) over the sum of the rate of chain propagation and termination (r_t), the chain-growth probability (α) is determined by the slope of Anderson-Schulz-Flory (ASF) distribution for carbon numbers C_n , where $F_{C_n}^{out}$ is the molar flow rate.

The chain-growth probability (α) is determined assuming an ASF distribution using a linear fit via Equation (2.41).⁵²

$$\alpha = \frac{r_p}{r_p + r_t} \cong \exp \left(\frac{\partial \ln F_{C_n}^{out}}{\partial n} \right), \quad (2.41)$$

In this equation, r_p and r_t are the rates for chain propagation and termination, n is the number of monomers in the hydrocarbon chain and F_n is the molar rate of production of a chain with length n .

To evaluate the impact of individual elementary reaction steps on the chain-growth probability, we also used the concept of the degree of chain-growth control (DCGC),⁵³ which is calculated via

$$\text{DCGC}^i = \left(\frac{\partial \alpha}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i}. \quad (2.42)$$

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Chapter 2. Computational Methods

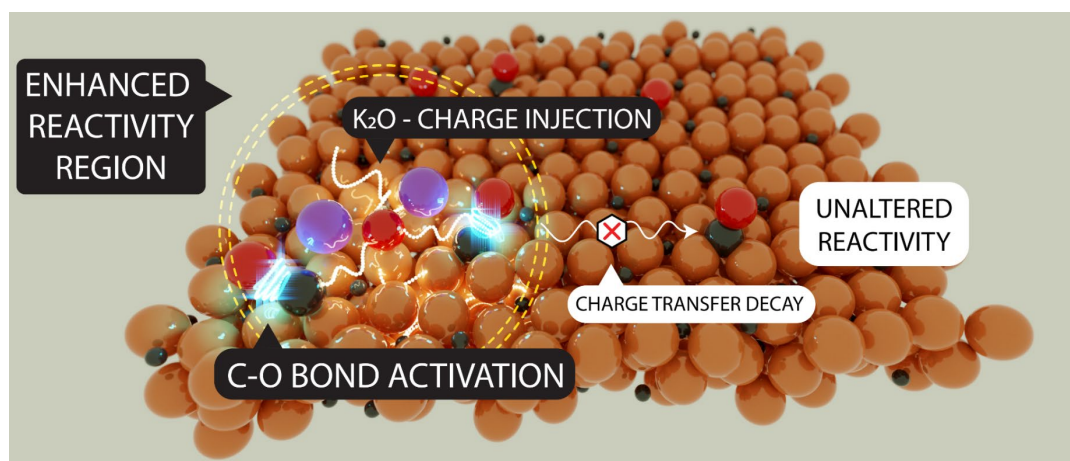
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Chapter 3. A Computational Study of K Promotion of CO Dissociation on Hägg Carbide

Abstract

The dissociation of CO is a critical step in producing long-chain hydrocarbons in the Fischer-Tropsch (FT) synthesis reaction. Although potassium (K) is known to enhance CO conversion and the selectivity to olefins of Fe-carbide FT catalysts, its precise mechanistic role remains unclear. In this work, we used density functional theory to show that K_2O facilitates C-O bond dissociation in CO, HCO, and COH by increasing the electron density of the Fe surface atoms of Hägg carbide (χ -Fe₅C₂) that bind these surface intermediates. This leads to a higher electron density in anti-bonding orbitals and enhanced electron-electron repulsion between the bonding orbitals of the CO, COH, and HCO intermediates and the Fe atoms. Effective promotion of C-O bond dissociation requires K to be adjacent to the active site on the χ -Fe₅C₂ surface.

Keywords: Fischer-Tropsch synthesis, CO dissociation, Hägg carbide, promoter, potassium



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3.1 Introduction

Fischer–Tropsch synthesis is a chemical process for the production of clean fuels and valuable chemical building blocks from synthesis gas, a mixture of CO and H₂, which can be derived from non-petroleum feedstocks, such as coal, shale gas, natural gas and biomass.¹⁻⁴ The Fischer-Tropsch (FT) reaction is a polymerization reaction with *in situ* generation of monomers from CO reactant.⁵ One of the most critical steps in the FT reaction is the activation of the CO bond, which leads to the CH_x intermediates acting as the monomers. Without a low barrier for C-O bond scission, the rate of monomer formation is too low for effective chain growth, leading to unwanted light hydrocarbon products such as methane. Co, Fe and Ru are the transition metals that display high activity in the FT reaction.⁶⁻⁹ Despite its high activity, the scarcity of Ru precludes its use in practical FT catalysts. Co is typically employed in low-temperature FT synthesis using synthesis gas mixtures obtained from natural gas. The benefits of Fe are its very low price, high selectivity to lower olefins and activity in the water-gas shift (WGS) reaction. This latter aspect is relevant when utilizing synthesis gas with low H₂/CO ratios, such as those derived from coal and biomass.¹⁰⁻¹⁵ Under typical FT synthesis conditions, the Fe-based catalysts will typically convert into Fe-carbides, such as ϵ -Fe₂C, ϵ' -Fe_{2.2}C, χ -Fe₅C₂, θ -Fe₃C, and Fe₇C₃.¹⁵⁻¹⁷ X-ray diffraction (XRD) and Mössbauer spectroscopy have been instrumental in linking the FT activity to these Fe-carbide phases.^{3, 18-21} Among them, Hägg carbide (χ -Fe₅C₂) is usually reported as the dominant and most active phase for CO activation and chain growth.^{13, 21, 22}

The performance of Fe-based catalysts can be tuned by incorporating promoters.²³ Promoters can increase the CO conversion or change the product distribution, increase the selectivity to long-chain hydrocarbons and suppress the methane selectivity.²⁴ Promoters such as Zn, Cu, S and alkali metals are known to increase the CO conversion and the selectivity to lower olefins.²⁵⁻³⁰ Li, Na and K were found to increase the catalytic activity and the selectivity to lower olefins.³¹ K is usually the most effective promoter for increasing the FT reaction among these. K also promotes the WGS reaction and inhibits the methane selectivity, presumably by increasing the chain-growth probability.³²⁻³⁵

The precise role of the K promoter in the mechanism of the FT reaction on Fe-carbide has not been established yet. Amoyal et al. found that K promoter makes Fe-carbide more resistant against oxidation, enhancing CO conversion.³⁴ Huo et al. suggested based on transmission electron microscopy (TEM) and XRD in conjunction with density functional theory (DFT) calculations that the main function of K is to stabilize the active Fe-carbide phases.³⁶ Zhao et al. show that K

increases the Fe carburization rate by facilitating CO dissociation at the catalyst surface while suppressing methane formation.³⁷ An increased rate of Fe carburization by K was also concluded in the work of Cheng et al..³⁸ They identified a linear relationship between the surface basicity and the Hägg carbide concentration. Using DFT calculations, Petersen et al. reported that K increased CO and O adsorption energies on Hägg carbide.³⁹ Despite these insights, the nature of K species under FT conditions and their mechanistic role in promoting the FT reaction remains unclear.

As it has been challenging to resolve the role of K by experiments, we here adopt a theoretical approach to study the impact of K on the dissociation of the C-O bond, which leads to the surface monomers required for the FT reaction. DFT calculations are carried out for four representative active site configurations on χ -Fe₅C₂. It is found that the K enhances the CO dissociation by injecting additional electrons into the surface, leading to increased occupation of anti-bonding orbitals and increased electron-electron repulsion in bonding orbitals of C-O, weakening the C-O bond in CO, HCO and COH intermediates. Moreover, the effective promotion of C-O bond dissociation requires K to be adjacent to the active site on the χ -Fe₅C₂ surface. If K is placed directly at the active site or a greater distance under higher loading conditions, it has little effect or can even inhibit the reaction. This finding differs from the experimental explanation, where a high loading of the K promoter increases the particle size and C deposition, decreasing the CO conversion.³⁸

3.2 Computational Methods

3.2.1 Density Functional Theory Calculations

All quantum-chemical simulations were performed using spin-polarized density functional theory (DFT), wherein effective ion cores are described by projector-augmented wave (PAW) potentials, as implemented in the Vienna Ab Initio Simulation Package (VASP 5.4.4).⁴⁰⁻⁴² The exchange and correlation energies were computed using the Perdew-Burke-Ernzerhof (PBE) functional.⁴³ The PBE+D3 method was used to include dispersion corrections in our calculations.⁴⁴ The plane-wave basis set cut-off energy was 400 eV. Geometry optimization was conducted using the conjugate gradient method with a force-based stopping criterion of 0.05 eV/Å for each cartesian direction and for each atom. The climbing-image nudged elastic band method (CI-NEB) was used to explore the transition states for all reaction pathways.^{45, 46} A frequency analysis was performed for all states, where stable states were verified to have no imaginary frequencies, while all transition states were verified by the presence of a single imaginary frequency in the direction of the reaction coordinate. The Hessian matrix for frequency analysis was determined using the finite difference

approach in which individual atoms were displaced in each Cartesian direction. The corresponding normal mode vibrations were used to calculate the zero-point energy (ZPE). The Brillouin zone was sampled using a $1 \times 1 \times 1$ Monkhorst-Pack grid (Γ -point only).

We used four representative active site configurations to describe the reactivity of χ -Fe₅C₂, namely (i) the planar five-fold site (P5) on Fe₅C₂(510), (ii) a distorted five-fold site (D5) on Fe₅C₂(111), (iii) a quasi-fourfold rectangle (FR) and (iv) a C-defect five-fold site (C*5), the latter two on Fe₅C₂(010). The first two layers of the solid, including the adsorbed molecules, were allowed to relax while keeping the atoms in the bottom layers frozen during geometry optimization. A vacuum layer of 15 Å was added perpendicular to the surface to mitigate spurious interactions between neighbouring slabs.

To analyze the electronic structure, crystal orbital Hamilton population (COHP) and density of states (DOS) analyses are conducted using the Lobster software (version 4.1.0).^{47, 48} The DDEC6 charge analysis method was applied to calculate net charges on atoms using the Chargemol software (version 3.5).^{49, 50} Electronic density differences between slab, adsorbate and adsorbate-on-slab configurations were constructed by the VTST electronic tools (version 5.4).⁵⁰ Electronic structure analysis using electron density differences was performed by projecting the three-dimensional scalar fields onto two-dimensional planes. Analysis and visualization of the electron density were conducted using the EDP program (version 2.0.3).⁵¹

3.3 Results and Discussion

3.3.1 Surface Models

Before constructing the surface terminations hosting the four active site configurations, the monoclinic unit cell (space group C2/c) corresponding to bulk χ -Fe₅C₂ was optimized using DFT. The computed lattice parameters of 11.53 Å $\times$ 4.50 Å $\times$ 4.95 Å and angles $\beta = 97.75^\circ$ ($\alpha = \gamma = 90^\circ$) are in good agreement with the experimental values for Hägg carbide ($a = 11.588$ Å, $b = 4.579$ Å, $c = 5.059$ Å, and $\beta = 97.75^\circ$).⁵² The optimized unit cell is shown in Appendix A (Figure A1). Based on the optimized bulk unit cell, four slab models were created, corresponding to the (510), (111), (010) and (010*) surface terminations. Figure 3.1 shows these surface terminations exhibit four distinct active site configurations, corresponding to P5, D5, QF and C* sites. It should be mentioned that the latter surface is created by removing a lattice C atom, residing in a fourfold site in the pristine surface. These active configurations were selected as they are sufficiently distinct and stable and are expected to exhibit different reactivity patterns under CO hydrogenation

conditions.⁵³⁻⁵⁶ Among these models, the P5 site has recently been identified as a highly reactive site, where direct CO dissociation is the dominant pathway.⁵⁷ The D5 site is one of the most active sites on the (111) surface, although the CO dissociation has a significantly higher barrier than sites on other χ -Fe₅C₂ surfaces.⁵⁵ The QF site represents the most active site on the (010) surface, where hydrogen-assisted CO dissociation is the most feasible pathway.⁵⁶ CO dissociation on a C vacancy site is studied on the C* site. By employing these representative models, we can reasonably capture the promotional effect of potassium (K) on Hägg carbide (χ -Fe₅C₂).

To understand K promotion of χ -Fe₅C₂ in the FT reaction, we first established the most likely state of K on the surface by exploring the stability of K, KO, K₂O, KOH and K₂CO₃ as candidates on all the surfaces during CO hydrogenation. The potential energy diagrams of these reactions are shown in Figure A2. Therefore, it can be said that K is likely to present as K₂O, in good agreement with other studies.^{31, 33, 58}

Next, we considered K₂O adsorption modes on the (510), (111), (010), and (010*) surfaces. Figure A3-A6 shows the adsorption configurations and corresponding adsorption energies. It was found that K₂O is most stable on a bridge site of the (510) surface (-588 kJ/mol), a top site of the (111) surface (-546 kJ/mol), a semi-fourfold site of the (010) surface (-613 kJ/mol), and a 3-fold site of the (010*) surface (-586 kJ/mol). The geometries of the corresponding K₂O-containing surfaces are given in Figure 3.1.

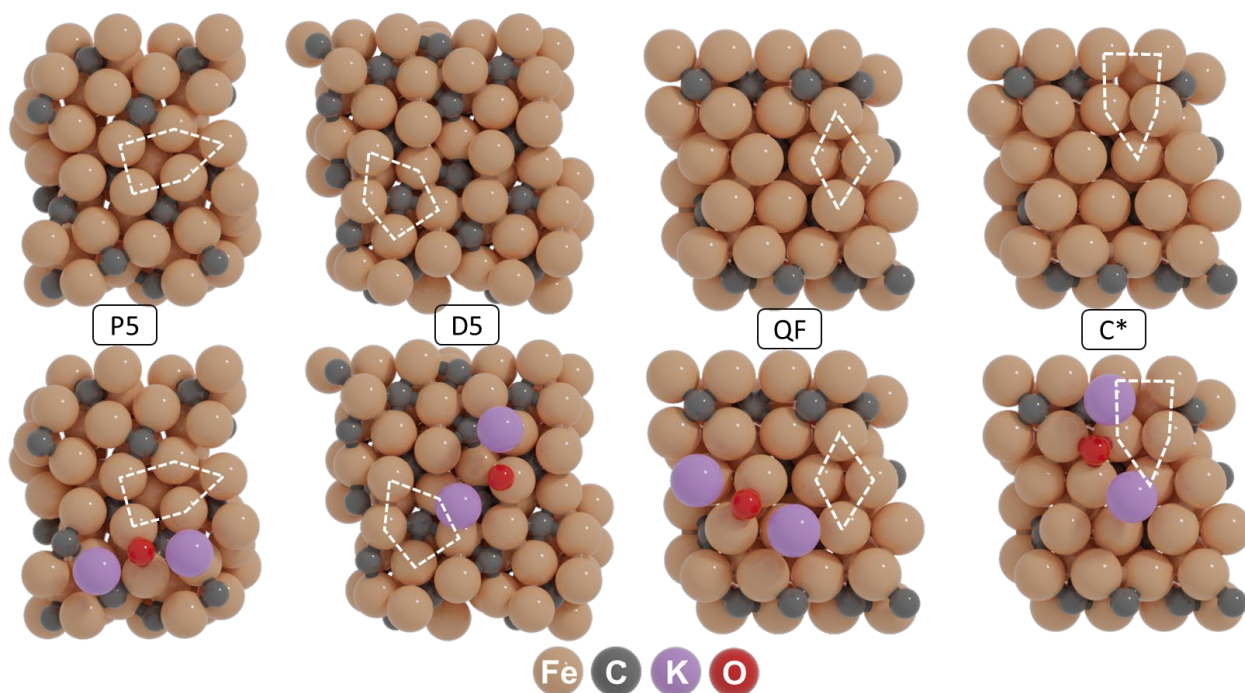


Figure 3.1. (top row) Active site configurations of the P5, D5, QF and C* sites as exposed on the (510), (111), (010) and (010*) surface terminations of χ -Fe₅C₂. (bottom row) Most stable adsorption sites for the K₂O species.

3.3.2 CO Activation

3.3.2.1 Adsorption of CO and H

The adsorption energy of the reactants and the stability of the reaction intermediates critically determine the surface composition under reaction conditions and the reaction rate. Therefore, we investigated the influence of K₂O on the adsorption of CO and H on the four surface models. Top, bridge, three-fold, four-fold and five-fold adsorption modes were considered for CO and H. The most stable adsorption geometries and their corresponding adsorption energies of CO and H on the four adsorption sites, with and without the K₂O promoter, are provided in Figure 3.2 and Figure 3.3, respectively.

On the (510) surface, the most stable CO adsorption position corresponds to a four-fold site within the P5 site. A relatively low adsorption energy of -203 kJ/mol was found, in agreement with the results found by Pham et al..⁵⁹ In the presence of K₂O, CO binds stronger at -211 kJ/mol. On the (111) surface, the highest adsorption energy of CO, corresponding to -233 kJ/mol, is obtained for a top configuration on one of the Fe atoms of the D5 site. In the presence of K₂O, the adsorption is almost the same. On the (010) surface, CO preferentially adsorbs on a quasi-fourfold site, where its C atoms bind to four Fe atoms. An adsorption energy of -204 kJ/mol was found for this configuration. In the presence of K₂O, the CO adsorption energy becomes more exothermic by 52 kJ/mol. Finally, on the C-vacancy site C* of the (010*) surface, CO adsorbs with an adsorption energy of -207 kJ/mol, which is further enhanced to -231 kJ/mol in the presence of K₂O. It can be observed that the promoter can be near the adsorbate, with a shorter distance (2.58 Å) compared to the intrinsic bond distance of the K-O bond (2.68 Å). Irrespective of the surface, we observe an enhanced CO adsorption strength in the presence of K₂O, in line with the earlier findings of Petersen et al..³⁹

Due to the strong Fe-H bond, molecular H₂ readily dissociates upon adsorption over both the pristine and K₂O-promoted surfaces. On the (510) surface, H* preferentially adsorbs on a threefold site within the P5 site with an adsorption energy of -82 kJ/mol referenced against gaseous H₂. In the presence of K₂O, this adsorption becomes slightly more exothermic with an adsorption energy of -83 kJ/mol. On the (111) surface, the most stable adsorption geometry is obtained at a three-fold site adjacent to the D5 site, with an adsorption energy of -73 kJ/mol. In the presence of K₂O, H adsorption becomes more exothermic by 13 kJ/mol. For the (010) surface, the H adsorption energy is -72 kJ/mol which only becomes marginally more exothermic (1 kJ/mol) in the presence of K₂O. In contrast to the other surfaces, it was found for the (010*) surface that the presence of

K₂O lowers the H* adsorption strength. Whereas for the unpromoted surface, the adsorption energy is -83 kJ/mol, it is marginally lower for the K₂O-promoted surface (-76 kJ/mol).

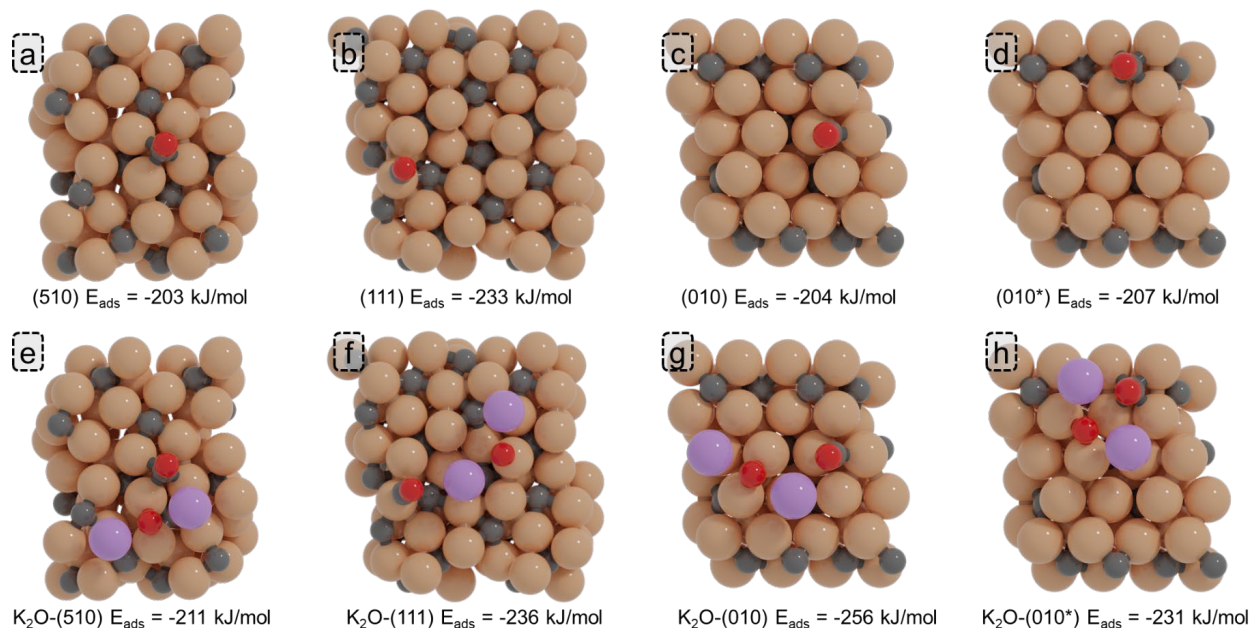


Figure 3.2. The most stable adsorption structures and energy values of CO in (top row) pristine and (bottom row) K₂O-promoted (510), (111), (010) and (010*) surface of χ -Fe₅C₂.

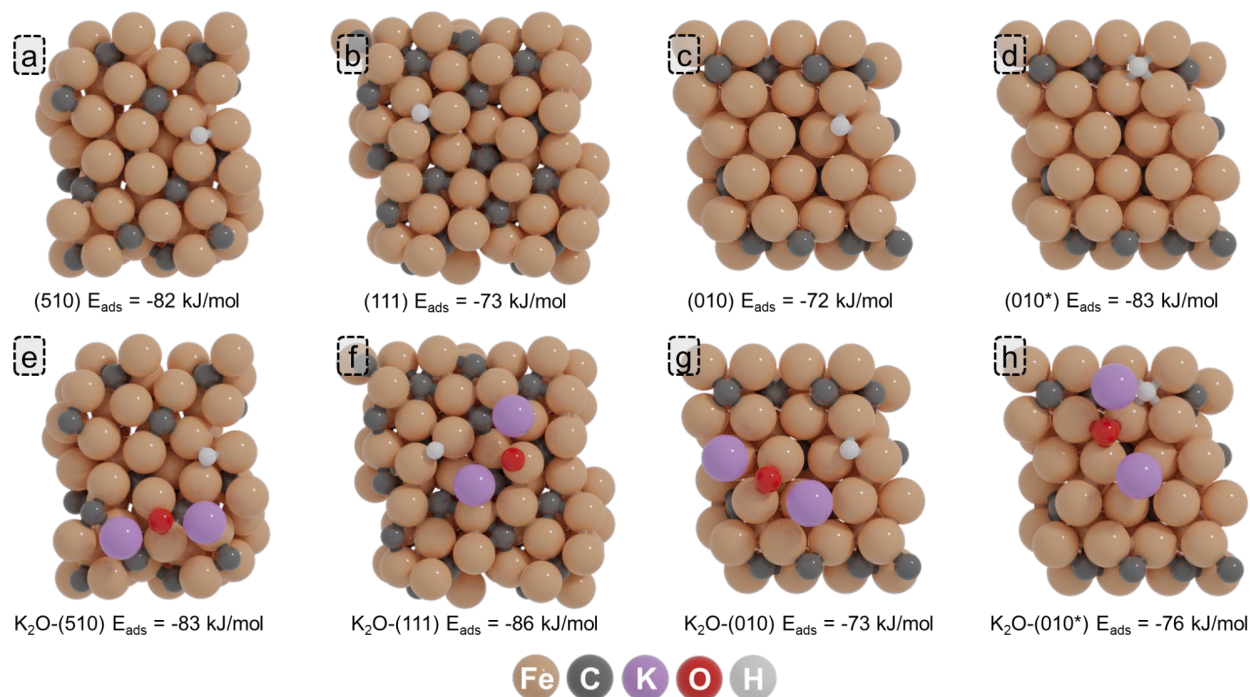


Figure 3.3. The most stable adsorption structures and energy values of H* in (top row) pristine and K₂O-(bottom row) promoted (510), (111), (010) and (010*) surface of χ -Fe₅C₂.

3.3.2.2 CO Activation

The activation of adsorbed CO is known to be a crucial step in FT synthesis, producing the monomers for hydrogenation and chain growth.^{59, 60} CO dissociation can proceed either in a direct

Chapter 3. A Computational Study of K Promotion of CO Dissociation on Hägg Carbide

fashion by which the C-O bond is broken directly after CO adsorption or in a hydrogen-assisted fashion wherein first the C or O atom is hydrogenated before C-O bond scission.⁶¹ We investigate how K₂O promotion influences the adsorption energy and dissociation of the CO reactant on the pristine and promoted surfaces. The barriers of CO dissociation via the direct and H-assisted pathways are listed in Table 3.1. The corresponding geometries of the initial state (IS), transition state (TS) and final state (FS) involved in these pathways on the four considered surfaces are provided in Figure A7-A14.

From Table 3.1, it can be seen that K₂O induces a decrease in the barrier for direct CO dissociation for all four surfaces under consideration. The barriers decrease by 10 kJ/mol on the (510), 25 kJ/mol on the (111) surfaces, 26 kJ/mol on the (010) surface and 21 kJ/mol on the (010*) surface. Comparing the FS geometries of CO dissociation on the pristine and promoted surfaces, it is found that the O moiety formed upon C-O bond scission moves closer to the K₂O promoter, the latter effectively stabilizing O*.

Table 3.1. Forward reaction barriers (E_f), backward reaction barriers (E_b) and reaction energies (E_{rxn}) of CO dissociation *via* direct and H-assisted pathways on the four considered surfaces of χ -Fe₅C₂.

Surface	Active Site	Elementary steps	Pristine Surface			Promoted Surface		
			E_f (kJ/mol)	E_b (kJ/mol)	E_{rxn} (kJ/mol)	E_f (kJ/mol)	E_b (kJ/mol)	E_{rxn} (kJ/mol)
(510)	P5	CO* + * $\rightarrow$ C* + O*	116	231	-115	106	195	-89
(510)	P5	CO* + H* $\rightarrow$ HCO* + *	143	10	133	126	2	124
(510)	P5	CO* + H* $\rightarrow$ COH* + *	180	104	76	150	50	100
(510)	P5	HCO* + * $\rightarrow$ CH*+O*	69	261	-195	51	201	-150
(510)	P5	COH* + * $\rightarrow$ C*+OH*	195	298	-97	95	171	-76
(111)	D5	CO* + * $\rightarrow$ C* + O*	178	94	84	153	51	101
(111)	D5	CO* + H* $\rightarrow$ HCO* + *	156	12	144	147	2	145
(111)	D5	CO* + H* $\rightarrow$ COH* + *	210	39	171	238	36	202
(111)	D5	HCO* + * $\rightarrow$ CH*+O*	139	215	-76	88	47	41
(111)	D5	COH* + * $\rightarrow$ C*+OH*	136	176	-40	101	252	-151
(010)	QF	CO* + * $\rightarrow$ C* + O*	163	200	-27	137	113	24
(010)	QF	CO* + H* $\rightarrow$ HCO* + *	119	61	58	108	22	86
(010)	QF	CO* + H* $\rightarrow$ COH* + *	160	67	93	170	44	126
(010)	QF	HCO* + * $\rightarrow$ CH*+O*	66	173	-107	45	110	-65
(010)	QF	COH* + * $\rightarrow$ C*+OH*	100	148	-48	77	124	-47
(010)	QF	HCO*+H* $\rightarrow$ CH ₂ O* + *	127	49	78	99	15	84
(010)	QF	CH ₂ O* + * $\rightarrow$ CH ₂ *+O*	73	188	-115	56	127	-71
(010*)	C*	CO* + * $\rightarrow$ C* + O*	127	241	-114	106	184	-78
(010*)	C*	CO* + H* $\rightarrow$ HCO* + *	158	26	132	139	17	122
(010*)	C*	CO* + H* $\rightarrow$ COH* + *	200	108	92	181	82	99
(010*)	C*	HCO* + * $\rightarrow$ CH*+O*	131	326	27	88	251	-163
(010*)	C*	COH* + * $\rightarrow$ C*+OH*	93	213	-120	40	162	-122

Barriers for CO hydrogenation to form HCO show little effect due to the presence of K₂O. For C-O bond scission in HCO, the presence of K₂O results in a decrease in the dissociation barriers

($\Delta E_{\text{act,forward}}^{\text{promoted-pristine}} = -18, -51, -21, \text{ and } -43 \text{ kJ/mol}$ for the (510), (111), (010) and (010*) surfaces, respectively), similar to the result observed for direct CO dissociation. For the (510) surface, we observe a decrease in the barrier for CO hydrogenation to HCO from 143 to 126 kJ/mol. For the (111), (010) and (010*) surfaces, the barriers decrease by -9, -11 and -19 kJ/mol values, respectively.

The same trend for K₂O promotion is observed for C-O bond scission via COH. Whereas a systematic decrease in the C-O bond scission in COH is found in the presence of K₂O, no trend can be established for initial CO hydrogenation to COH. Moreover, we did not find a trend in whether K₂O acts as a promoting or inhibiting agent for CO hydrogenation, either to HCO or to COH, for the same surface. K₂O acts as a promoter for HCO formation on (111), (010) and (010*). In contrast, for COH formation, K₂O acts as a promoter for the (510) and (010*) surfaces by decreasing the hydrogenation barrier by -30 and -19 kJ/mol, respectively. For the (111) and (010) surfaces, the barrier increases by 28 and 10 kJ/mol, respectively. In contrast, C-O bond scission barriers in COH are substantially decreased due to K₂O by ($\Delta E_{\text{act,forward}}^{\text{promoted-pristine}} = -100, -35, -23, \text{ and } -53 \text{ kJ/mol}$ for the (510), (111), (010) and (010*) surfaces, respectively).

Based on the above results, it is evident that the K₂O promoter reduces the C-O bond strength in CO, HCO, and COH. To fully understand how K₂O facilitates the dissociation of these species, electronic analysis, which will be discussed in the next section.

To evaluate the most facile CO activation pathway and assess how K₂O affects this, we calculated the overall C-O bond scission barrier with respect to co-adsorbed CO* and H*. The results are listed in Table 3.2. The corresponding energy diagram that compares these pathways is provided in Figure A15-A18. Table 3.2 shows that CO preferentially dissociates via the direct dissociation pathway on the (510), (111) and (010*) surfaces with overall barriers of 116 kJ/mol, 178 kJ/mol and 127 kJ/mol, respectively. In the presence of K₂O, these barriers decrease by 10 kJ/mol (510), 25 kJ/mol (111), and 21 kJ/mol (010*). The direct CO dissociation pathway remains the dominant pathway on the (510), (111) and (010*) surfaces in the presence of K₂O. In contrast, for the (010) surface, where K₂O promotion changes the preferred pathway from direct CO dissociation to the HCO pathway. The latter offers a more facile pathway in the presence of K₂O, with an overall barrier of 131 kJ/mol compared to 137 kJ/mol for the direct CO dissociation pathway.

Table 3.2. Overall barriers of CO dissociation in CO direct dissociation and H-assisted pathways on considered four surfaces of χ -Fe₅C₂.

Overall barrier (kJ/mol)	CO direct dissociation	HCO pathway	COH pathway
(510)	116	202	271
K ₂ O-(510)	106	176	195
(111)	178	283	307
K ₂ O-(111)	153	233	303
(010)	163	124	193
K ₂ O-(010)	137	131	203
(010*)	127	263	185
K ₂ O-(010*)	106	210	139

It should be emphasized that the overall barriers for the direct and HCO pathways over (010) are very similar. This also holds for the overall barriers for the direct and COH pathways over (010*). As such, these pathways are envisioned to be competitive, and it is likely that under CO hydrogenation conditions, both pathways participate in the overall reaction.

3.3.2.3 Electronic Structure Analysis

Table 3.1 shows that C-O bond scission barriers in CO, COH and HCO decrease in the presence of K. To understand the way K₂O impacts C-O bond activation, the density of states (DOS) and the crystal orbital Hamilton population (COHP) analyses^{47, 48} were conducted on the C-O bonds of CO, COH and HCO.

The analysis for the CO molecule in Figure 3.4 compares the electronic structure of CO in the gas phase with CO adsorbed on the (510) surface, both in the presence and absence of K₂O. Based on the canonical molecular orbital solutions of CO in the gas phase⁶² (see also Figure A19 in Appendix A), the Kohn-Sham states are categorized into distinct energy ranges, as indicated by the dashed horizontal lines in the DOS and COHP analyses in Figure 3.4. From the lowest to highest energy, these energy ranges are labeled as 3 σ , 4 σ , 1 π and 5 σ for gaseous CO (Figure 3.4a and 3.4d). The energy ranges corresponding to 1 π and 5 σ will overlap upon adsorption (Figures 3.4b and 3.4c). By projecting the Kohn-Sham states onto localized atomic orbitals, we could deconvolute these interactions and distinguish between σ and π contributions, based on the procedure of CO dissociation on Co by Krösschell et al..⁶³ By orienting the atomic basis functions for the projection such that the p_z orbitals are aligned with the C-O bonding axis, the s-s, s-p_z and p_z-p_z interactions corresponding to σ contributions were identified, whereas p_x-p_x, p_x-p_y, p_y-p_x and p_y-p_y interactions correspond to π contributions. In this way, we could distinguish between 1 π and 5 σ contributions. Figure 3.4 shows that, upon CO adsorption, the 3 σ and 4 σ molecular orbitals

shift with respect to the Fermi level. Yet, their DOS features remain sharp, indicative that these orbitals do not readily mix with the d -states on the metal. This result is to be expected as these orbitals are compact in size (Figure A19 in Appendix A). In contrast, the 1π and 5σ MOs broaden. As these molecular orbitals are more diffuse, they will mix with the d -states of the metal. Above the energy range assigned to the 1π and 5σ MOs, a new set of occupied states can be observed following CO adsorption. These states are labeled as 2π as they predominantly correspond to the unoccupied $2\pi^*$ orbitals mixing with the d -states, resulting in their shift from above to below the Fermi level, thus becoming occupied upon adsorption of CO to the surface.

Figure 3.4d-3.4f shows how this redistribution of the Kohn-Sham state results affects the bond stability by observing the COHP features per energy range. The COHP features were integrated for the corresponding energy ranges to quantify the changes in bonding characteristics. The dashed curves show the integrated COHP as a function of the state energy. The integrated COHP (iCOHP) and the integrated DOS (iDOS) per energy range for gaseous and adsorbed CO for the (510) surface are depicted in Figure 5a. Similarly, the iDOS and iCOHP values for the other surfaces are shown in Figure 3.5b-3.5d. The original DOS and COHP diagrams used to construct Figure 5 can be found in the supporting information in Figure A20-A22.

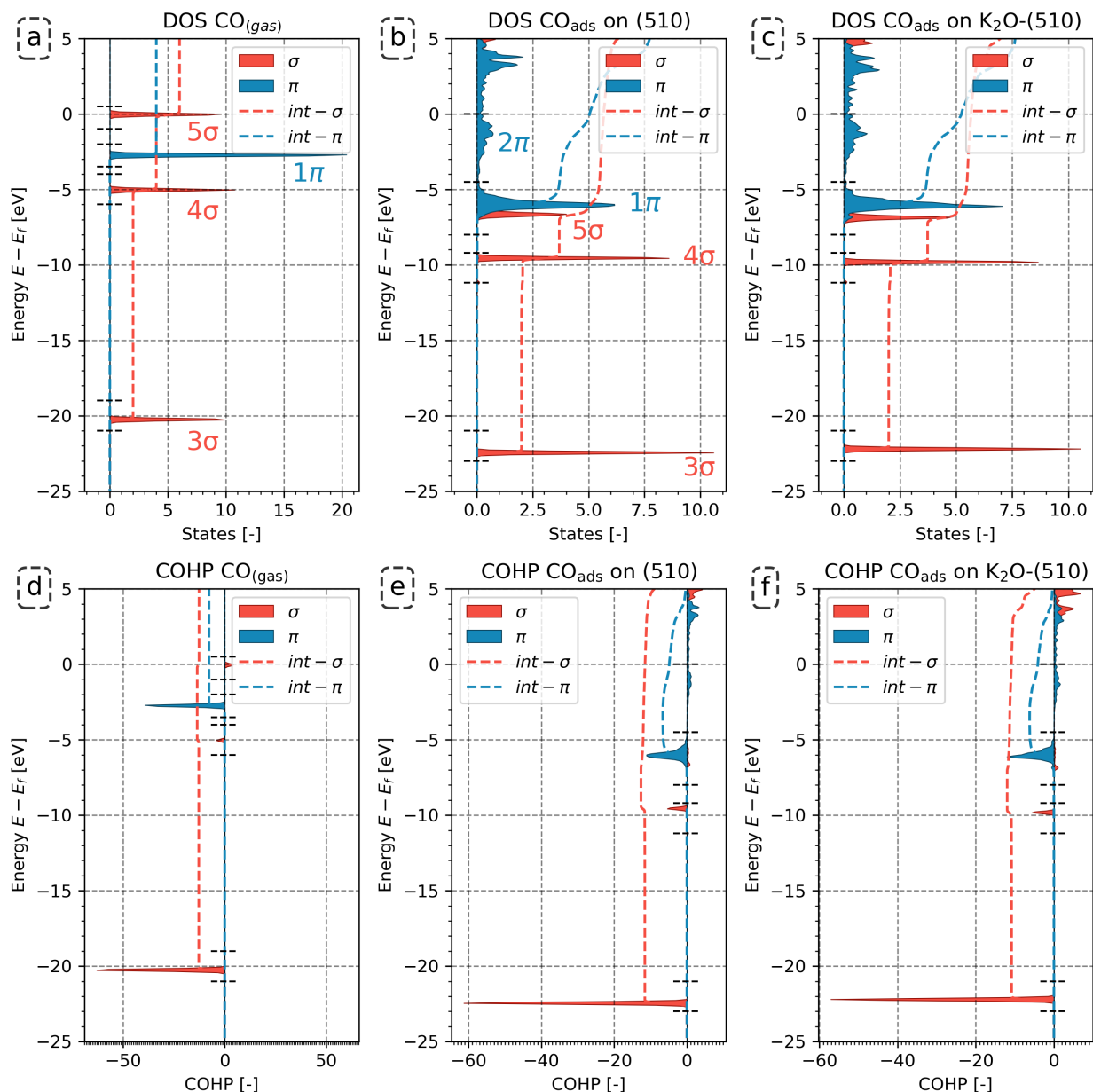


Figure 3.4. DOS of C-O bond of CO (a) in gas phase; (b) on (510) surface; (c) on K₂O promoted (510) surface; COHP of C-O bond of CO (d) in gas phase; (e) on (510) surface; (f) on K₂O promoted (510) surface.

From Figures 3.5a-3.5d, it can be seen that CO adsorption leads to additional electron density on the CO molecule. Whereas gaseous CO has 10 valence electrons (core electrons are part of the pseudopotential and are not shown in the DOS/COHP analyses), the total number of occupied states of CO increases by 0.69 on (510), 0.40 on (111), 0.85 on (010), and 0.87 on (010*). In the presence of K₂O, a further 0.15, 0.11, 0.23 and 0.21 states for the (510), (111), (010) and (010*) are occupied upon adsorption. Considering the states, we observe that the number of states corresponding to the 3 σ molecular orbital (MO) on CO remains constant upon adsorption. In contrast, fewer states are assigned to the 4 σ , 5 σ and 1 π molecular orbitals. The 2 π orbital,

unoccupied in gaseous CO, gains electron density upon adsorption. The number of states (electrons) gained by the 2π MO is larger than the number of states lost by the other orbitals. This electron accumulation in the 2π MO is further enhanced in the presence of K_2O . For example, it is observed for the (510) surface that with respect to the combined number of states lost in the 4σ , 5σ and 1π molecular orbitals, the 2π orbital gains 0.85 and 0.89 more electrons for the pristine and promoted surfaces, respectively.

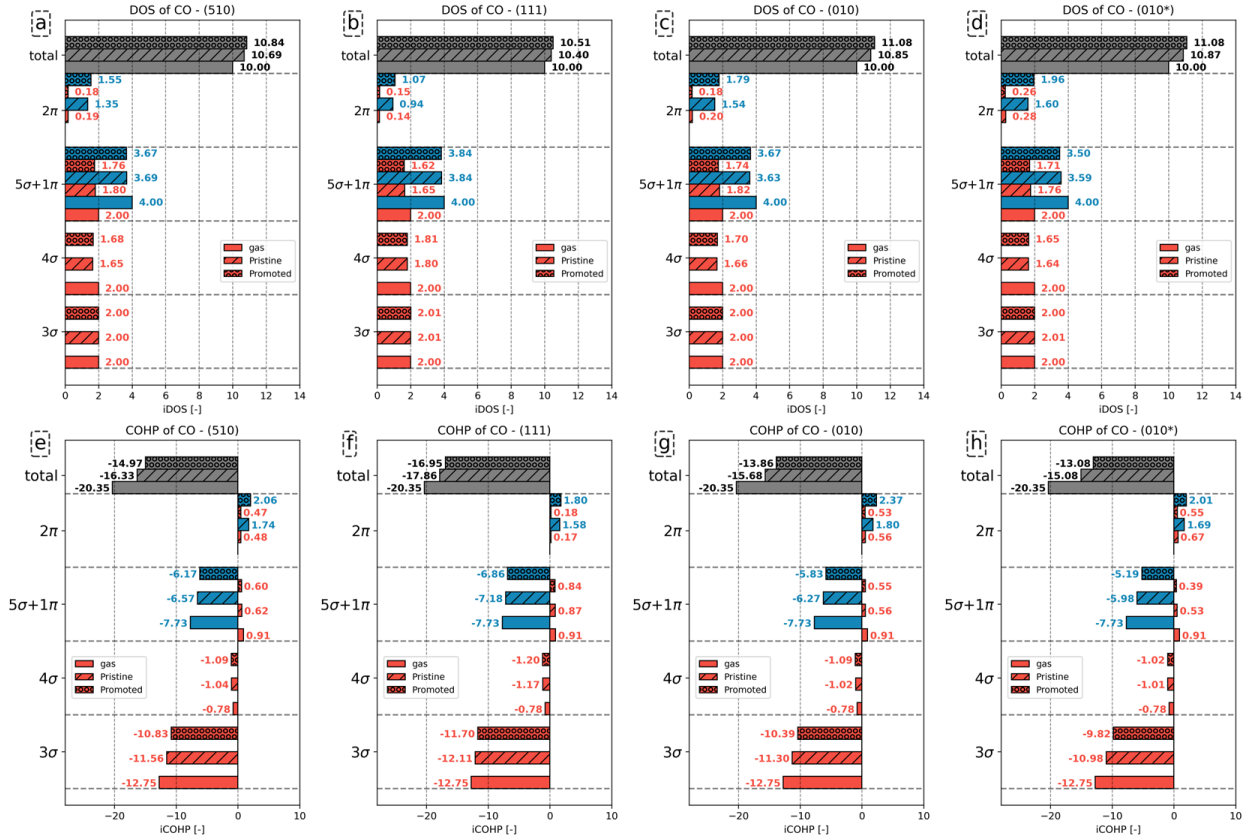


Figure 3.5. (a) - (d) iDOS and (e) - (h) iCOHP of C-O bond of CO in gas phase, CO adsorbate on pristine surfaces and K_2O promoted surfaces. The red bars correspond to σ -interactions whereas the blue bars refer to π -interactions. The results for the pristine and K_2O -promoted surfaces are indicated by hashed and dotted bars, respectively.

To understand how the redistribution of the Kohn-Sham states affects the bond stability and how the presence of K_2O affects this, we consider Figure 3.5e-3.5h. In this analysis, we primarily focus on the 3σ , 1π and 2π as these orbitals were most important in describing CO bond activation.⁶³ For gaseous CO, the 3σ and 1π orbitals are strongly bonding with iCOHP values of -12.75 and -7.73, respectively, whereas the 4σ and 5σ show minor (anti-)bonding contributions of -0.78 and 0.91, respectively. Upon adsorption of CO, the bonding contributions become less bonding, while the anti-bonding features become more anti-bonding. For instance, for the pristine surfaces, it is observed that the iCOHP value of 3σ orbital increases by 1.19, 0.64, 1.45 and 1.77 for (510), (111),

(010) and (010*) surfaces, respectively. In the presence of K₂O, a further increase of 0.73, 0.41, 0.91 and 1.16 for (510), (111), (010) and (010*) surfaces are found, respectively. As the 3σ peak in the DOS does not show any significant broadening upon CO adsorption, mixing of the 3σ orbital with the surface states is considered negligible. In lieu of any mixing effects, the decrease in bonding character can only be assigned to the increased electron-electron repulsion due to the increased proximity of this orbital with the surface electron density. Similarly, the 1π orbitals also become less bonding upon adsorption, yet in contrast to the 3σ orbital, here the loss of bonding character is assigned to the mixing of this orbital with surface states, as can be readily assessed from the peak broadening observed in Figure 3.4 and Figures A20-A22. Akin to the 3σ orbital, the loss in bonding character is also observed to be more pronounced in the presence of K₂O. Besides losing overall bonding character, the additional occupation of the anti-bonding 2π states further destabilizes the C-O bond. For the 2π states, iCOHP values of 2.22, 1.75, 2.36 and 2.36 are found for the pristine (510), (111), (010) and (010*) surfaces, respectively. For the promoted surfaces, the iCOHP values increase to 2.53, 1.98, 2.90 and 2.56, respectively.

Based on these results, we infer that the role of K₂O is to inject additional electron density into the surface, as shown in Figure A23. The Blyholder concept of σ-donation and π-backdonation also leads to charge accumulation on the CO adsorbate, as shown in Figure A24. Compared to the situation where K₂O is absent, this charge injection into the surface, and indirectly into CO, has a twofold effect. For CO, it results in the occupation of additional 2π anti-bonding states. For the surface, the increased electron density enhances electron-electron repulsion in the 3σ and 1π orbitals. Since K₂O injects additional electron density into the surface, which is redirected to the CO adsorbate, both these effects contribute to enhanced activation of the C-O bond in the presence of K₂O.

Besides CO, we also conducted the same analysis for the HCO and COH adsorbates as shown in Figures 3.6 and 3.7, respectively. This analysis is performed in a similar manner as for CO, with the notable difference that for these molecules, a further distinction between σ and π contributions is not possible due to these complexes being non-linear upon adsorption. To categorize the Kohn-Sham states in terms of energy for adsorbed CO, we compared the adsorbed state with its fictitious gaseous counterpart (COH⁻ and HCO⁻). This yields the set of energy ranges shown in Figures A25-A32 in Appendix A.

Figures 3.6a-3.6d show that the total number of electrons assigned to the C-O bond in HCO corresponds to 10.96. Including the number of electrons assigned to H in HCO⁻, a total of 12 electrons is found. Upon adsorption, we observe that the number of states assigned to the S1 and

S2 orbitals remains largely the same, irrespective of the presence of K₂O. The number of electrons assigned to orbitals S3-S5, for convenience purposes taken together in this analysis, decreases upon adsorption and even more so in the presence of K₂O. The converse is valid for the anti-bonding S6 states, which gain electrons upon adsorption and more so upon K₂O promotion. From the total iCOHP value, it is found that HCO⁻ has a weaker C-O bond in the gas phase (-12.67) than in the adsorbed state on the pristine (111) surface (-13.90) and the pristine (010) surface (-12.84). This is mainly caused by the fact that HCO⁻ in lieu of an octet configuration is coordinately unsaturated and thus unstable in the gas phase. In a sense, the coordinative unsaturation is repaired upon adsorption to these surfaces, leading to enhanced stability. The effect of electron density rearrangement in the C-O bond can be found in Figure 3.6e-3.6h. In the presence of K₂O, the C-O bond is readily activated, as seen from the increase in the iCOHP values by 1.51 (510), 0.84 (111), 2.93 (010), and 0.67 (010*). Comparing the iCOHP values for the various orbitals between pristine and promoted surfaces, we observe a large decrease in bonding character for the S1 orbital in the presence of K₂O. Also, the S3-S5 orbitals become slightly less bonding, and the S6 orbitals become slightly more anti-bonding. For HCO, the role of K₂O in activating the C-O bond is mainly due to a destabilization of the S1 states by enhanced electron-electron repulsion between this state and the enhanced electron density on the Fe atoms as well as an additional occupation of anti-bonding S6* orbitals. These results are similar to how K₂O affects C-O bond activation in CO.

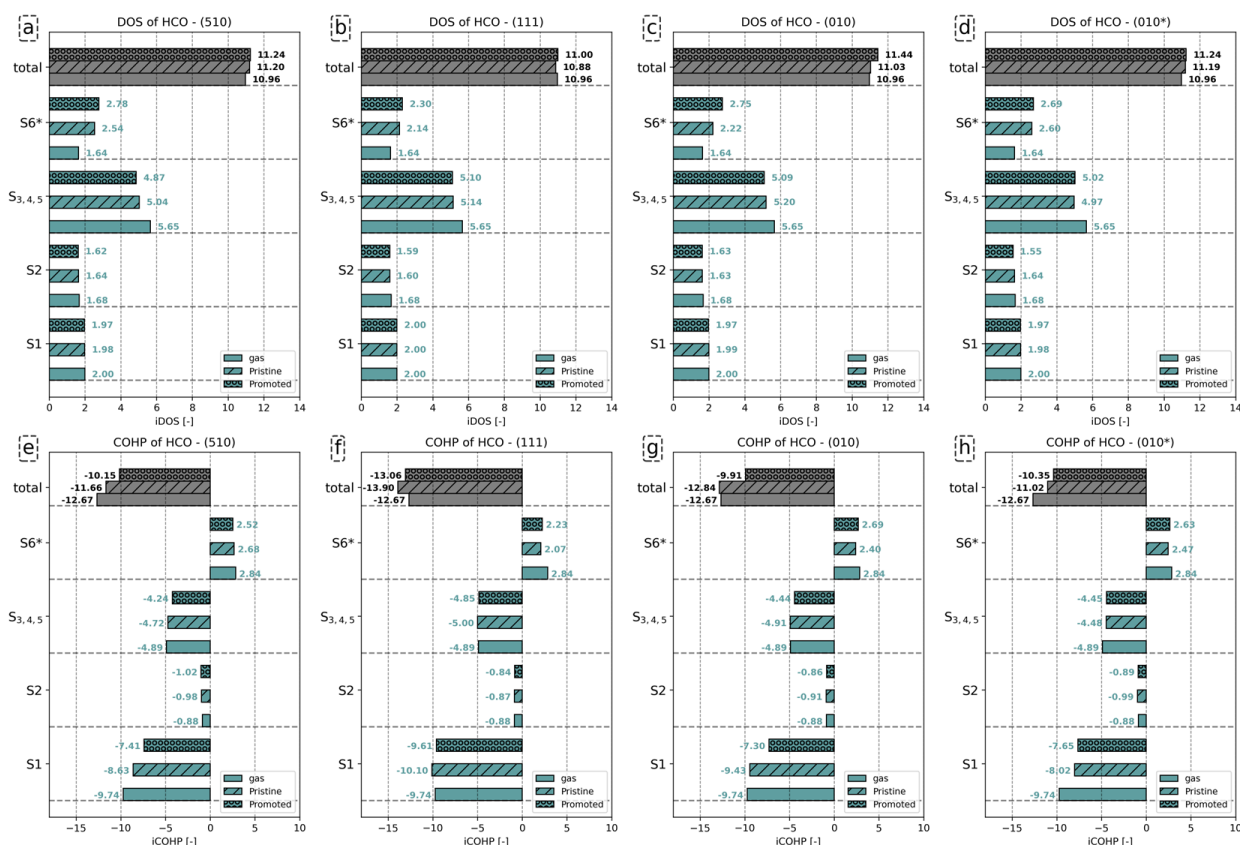


Figure 3.6. (a) - (d) iDOS and (e) - (h) iCOHP of C-O bond of HCO^- in gas phase, HCO adsorbate on pristine surfaces; and K_2O promoted surfaces. The result for the pristine and K_2O -promoted surfaces are indicated by hashed and dotted bars, respectively.

Figure 3.7a-d shows that the total charge on the C-O bond is comparable between gaseous and adsorbed COH^- , with little effect on whether K_2O promotes the surface. Analysis of the individual orbitals reveals that the number of electrons assigned to the S1 and S2 orbitals differs little between the three configurations. Compared to the number of states for the S3 orbitals of gaseous COH^- (1.93), a decrease by 0.45 (510), 0.38 (111), 0.46 (010) and 0.47 (010*), is found upon adsorption. Only minimal differences in the number of occupied states for the S3 orbital between the pristine and promoted surface are found. For the S4 and S5 orbitals, a similar decrease in the number of states is observed upon COH adsorption. Whereas gaseous COH^- hosts (3.94) states for the S4 and S5 orbitals, 3.61, 3.62, 3.66 and 3.61 are observed for these orbitals for the pristine (510), (111), (010) and (010*) surfaces, respectively. Upon K_2O promotion, these values decrease to 3.50, 3.72, 3.67, and 3.64, respectively. Finally, for the S6 orbital the number of states corresponds to 2.44 on (510), 2.01 on (111), 2.50 on (010), and 2.72 (010*) for the pristine surface. K_2O promotion results in a further increase in states by 0.38 on (510), 0.08 on (111), 0.12 on (010), and 0.08 (010*).

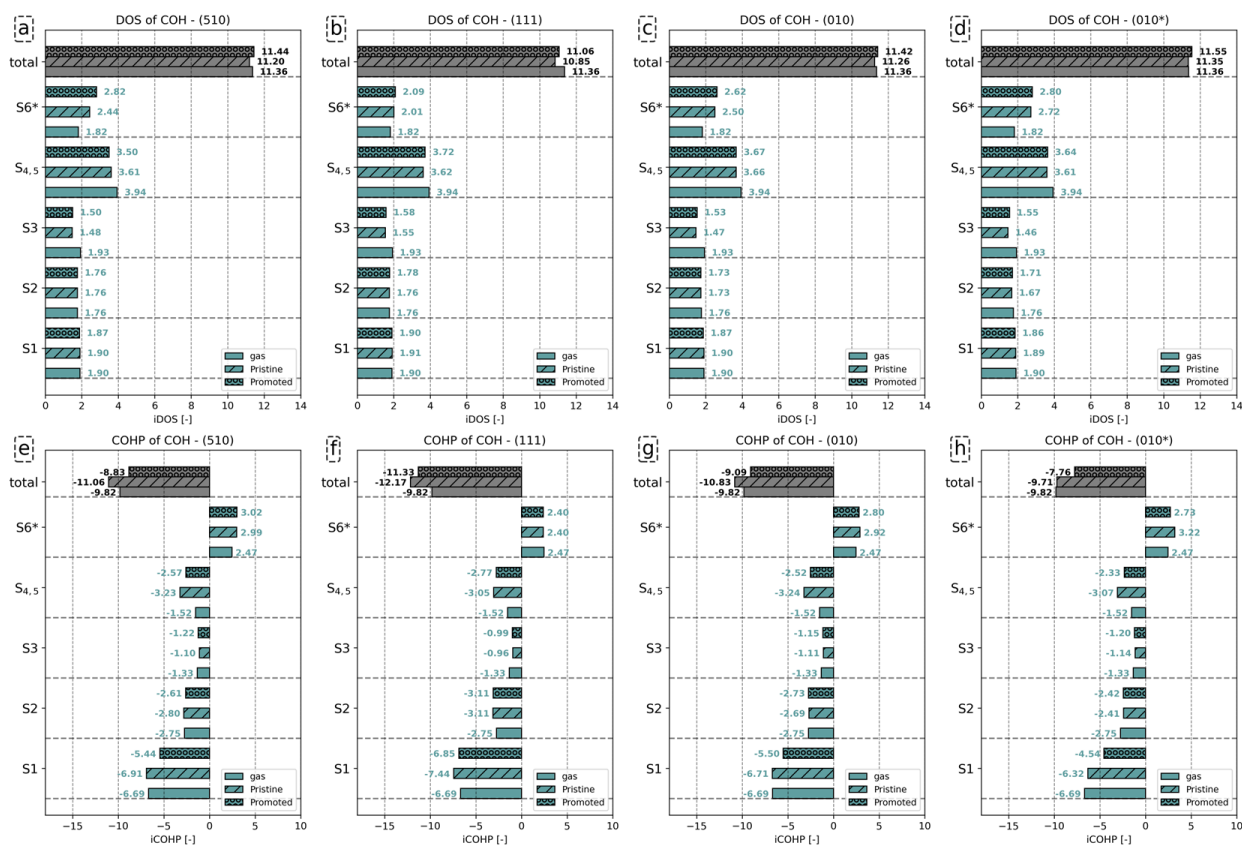


Figure 3.7. (a) - (d) iDOS and (e) - (h) iCOHP of C-O bond of COH⁻ in gas phase, COH adsorbate on pristine surfaces; and K₂O promoted surfaces. The results for the pristine and K₂O-promoted surfaces are indicated by hashed and dotted bars, respectively.

Similar to HCO, the C-O bond in the gas phase is less stable as compared to the C-O bond for adsorbed COH⁻ due to the COH⁻ not having an octet configuration in the gas phase. Also similar to HCO, surface promotion by K₂O results in a further activation of this C-O bond. Indeed, the iCOHP value for the C-O bond in COH adsorbed on the K₂O-promoted surface is lower than its counterpart found for the pristine surface. This difference in total iCOHP value between the pristine and promoted surfaces originates predominantly from a decreased bonding character for the S1, S4 and S5 orbitals. The other orbitals show little difference in their iCOHP values between the pristine and promoted surfaces. Conclusively, the mechanism of C-O bond activation by K₂O is, akin to its role for HCO, due to enhanced electron-electron repulsion between the increased surface charge and the S1, S4 and S5 orbitals and the enhanced occupation of S6 states.

3.3.3 Effect of K₂O Location

In a previous experimental study conducted by Chen et al., the effect of K promotion in Fe-based FT synthesis was studied.³⁸ These authors observed that K promotion results in an increase of the size of the Hägg carbide nanoparticles, which the authors assigned as the origin of the lower CO conversion. Furthermore, an increased thickness of the carbon layer as a function of increasing K

content was observed, hinting at the ability of K to enhance C deposition, which can result in the poisoning of active sites, facilitating CO dissociation as observed in other experimental studies.^{35,}

⁶⁴ As an alternative to decreasing the active site by enhanced carbide size and C deposition, we consider the possibility of K₂O inhibiting CO bond scission by directly poisoning the active site responsible for CO dissociation.

Compared to the most stable adsorption energy of K₂O (-588 kJ/mol), where K₂O adsorbs in the vicinity of the P5 active site (K₂O-(510)_a; Figure 3.8b), we explored two alternative K₂O adsorption sites (K₂O-(510)_b and K₂O-(510)_c; Figures 3.8c and 3.8d) that portray similar K₂O adsorption energies (-581 and -578 kJ/mol). We calculated the CO direct dissociation barriers for these surface sites and compared the result with the pristine surface. The CO direct dissociation barrier is found to be decreased by 10 kJ/mol when K₂O is in the vicinity of the P5 site. However, when K₂O resides at the P5 site, with one K atom occupying the center of the P5 site, direct CO dissociation is significantly inhibited, resulting in an increase of the CO direct dissociation barrier by 74 kJ/mol and by 124 kJ/mol for the two configurations shown in Figures 3.8c and 3.8d, respectively. These results suggest that K₂O can also exhibit an inhibiting role towards CO dissociation, which becomes more prevalent upon high loadings of K.

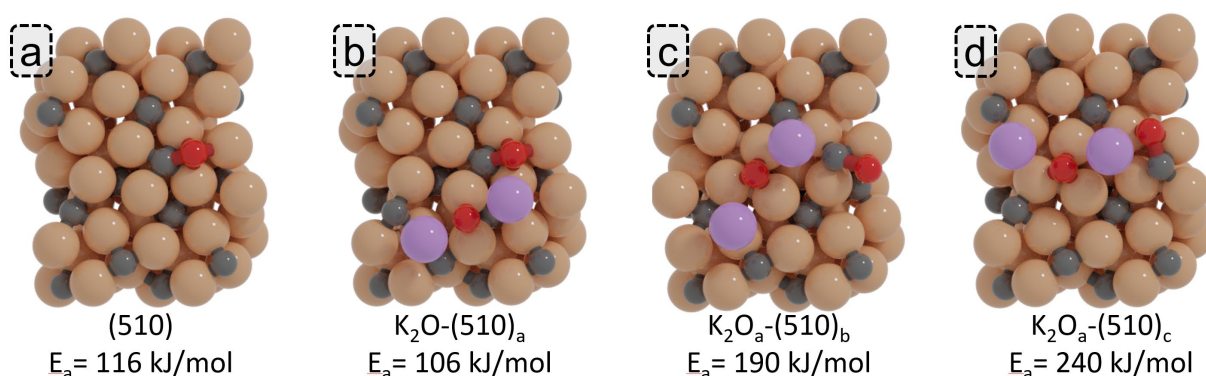


Figure 3.8. ZPE corrected reaction barriers and Transition states geometries of CO direct dissociation on (a) pristine (510) surface and (b) - (d) K₂O promoted surfaces.

We also explored the impact of the position of K₂O on the (010*) surface. We considered one alternative configuration of K₂O near the active site for CO dissociation, as shown in Figure 3.9c. Compared to the most stable adsorption configuration of K₂O (K₂O-(010*)_a; Figure 3.9b) for the (010*) surface (-586 kJ/mol), this alternative configuration yields a similar adsorption energy of -583 kJ/mol. Whereas the K₂O-(010*)_a gives a CO dissociation barrier of 106 kJ/mol, the K₂O-(010*)_b configuration shows a CO dissociation barrier of 131 kJ/mol, only 4 kJ/mol higher than the barrier found for the unpromoted surface. We assign this minor difference to K₂O being more distanced with respect to the active site.

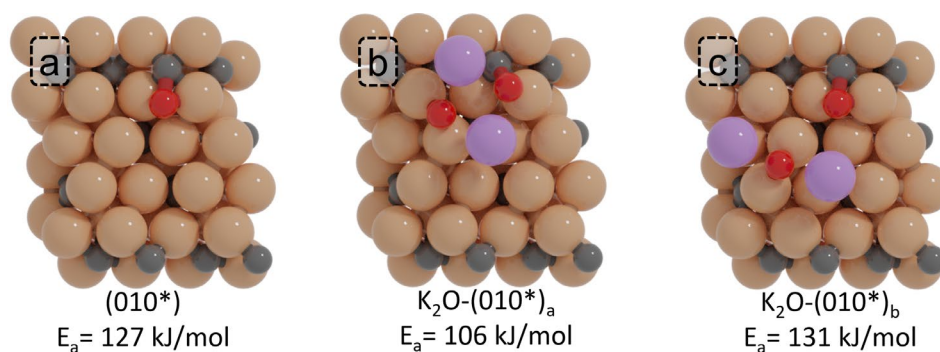


Figure 3.9. ZPE corrected reaction barriers and Transition states geometries of CO direct dissociation on the (a) pristine (010*) and (b) - (d) K_2O -promoted surfaces.

These results show that the location of K_2O with respect to the active site is important. When K_2O resides at the active site, it will inhibit the reaction due to steric effects. When K_2O is not at the active site yet near it, C-O bond scission is promoted via charge injection into the catalyst surface and the CO moiety. Finally, when K_2O is at a greater distance from the reacting surface intermediate, its beneficial effects become negligible due to the charge injection being very localized in nature, only affecting the first coordination shell of K_2O .

3.4 Conclusions

To investigate the mechanistic role of K_2O on C-O bond scission, we calculated dissociation barriers for direct and hydrogen-assisted CO dissociation for several active site configurations in the presence and absence of K_2O . The results show that the K_2O promoter can strengthen the adsorption of CO while decreasing the C-O bond strength when the K_2O promoter adsorbs in the vicinity of the active site. Enhanced CO bond activation due to the presence of K_2O , leading to lower dissociation barriers, is assigned to its ability to inject additional electrons into the catalytic surface, which also results in an enhanced charge on the CO, HCO, or COH adsorbates. The effect of this charge injection is twofold; it destabilizes low-lying bonding orbitals due to increased electron-electron repulsion and increased occupation of high-lying anti-bonding orbitals. For CO, this predominantly entails decreased bonding of the 3σ and 1π orbitals and enhanced antibonding of the 2π orbitals. For HCO and COH, the same pattern is observed for the analogous orbitals. The propensity of K_2O to effectively promote C-O bond scission depends on its proximity to the active site for (hydrogen-assisted) CO dissociation. When K_2O resides at the active site, it will act as an inhibitor due to vastly increased steric repulsion. If K_2O is adjacent to the active site such that K and C share one or more Fe atoms, it can act as a promoting agent via a charge injection mechanism. The nature of this effect is, however, very localized. As soon as K_2O is at a greater

distance with respect to the active site such that none of the Fe atoms can be shared between K and the adsorbate, its promoting effect becomes negligible and similar barriers as found for the unpromoted situation are observed.

3.5 References

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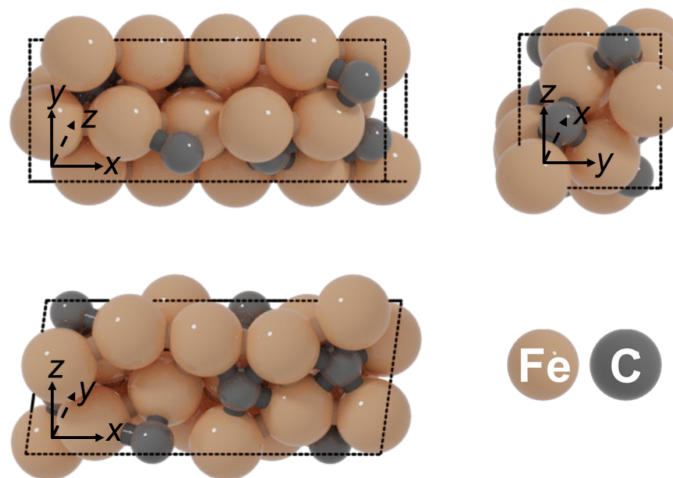
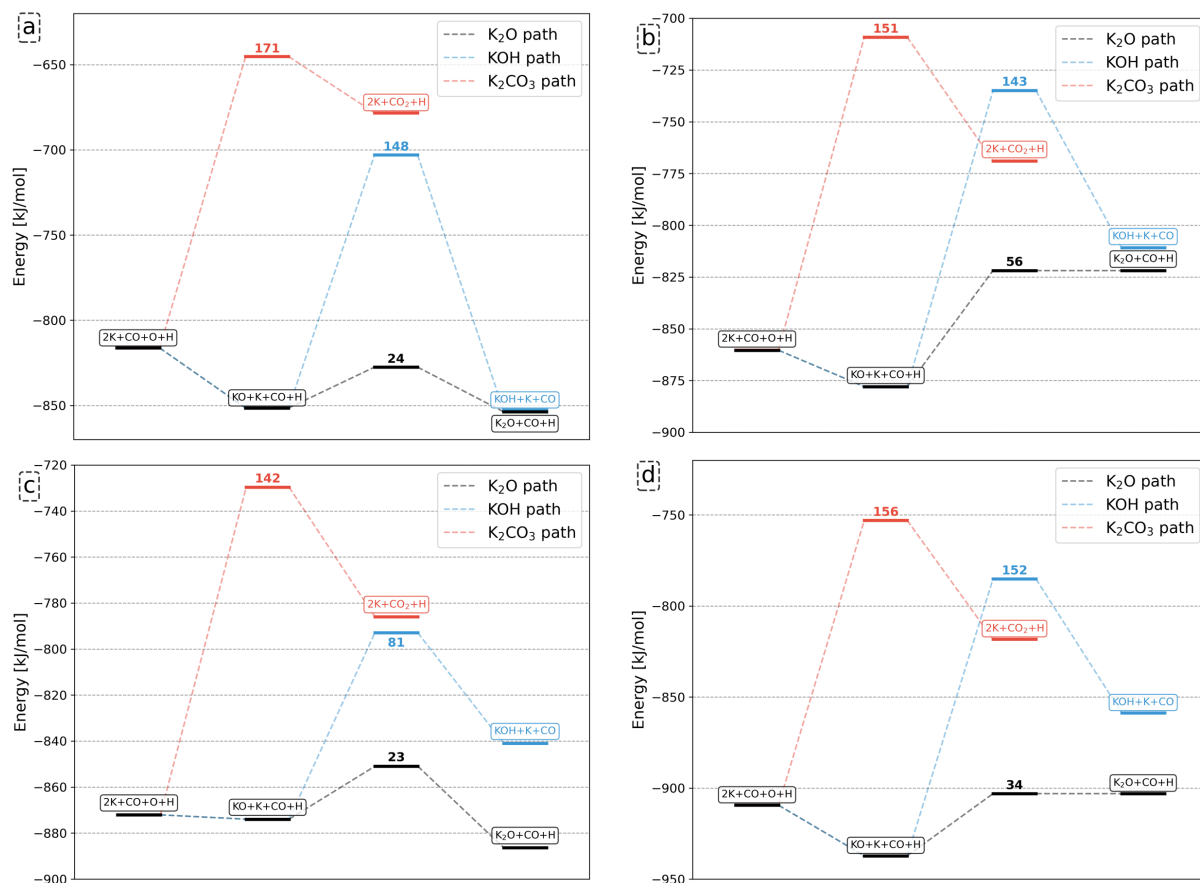
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Chapter 3. A Computational Study of K Promotion of CO Dissociation on Hägg Carbide

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Appendix A


 Figure A1. The configurations of optimized bulk of Fe_5C_2 .

 Figure A2. Reaction energy diagrams of the formation of K_2O , KOH , and K_2CO_3 on the (a) (510), (b) (111), (c) (010) and (d) (010*) surfaces of $\chi\text{-Fe}_5\text{C}_2$. In practice, the high oxygen content makes K_2O the most stable form of the K promoter, with the lowest overall barrier on these surfaces, while the significantly difficult CO_2 formation results in the formation of K_2CO_3 unfavored on all surfaces.

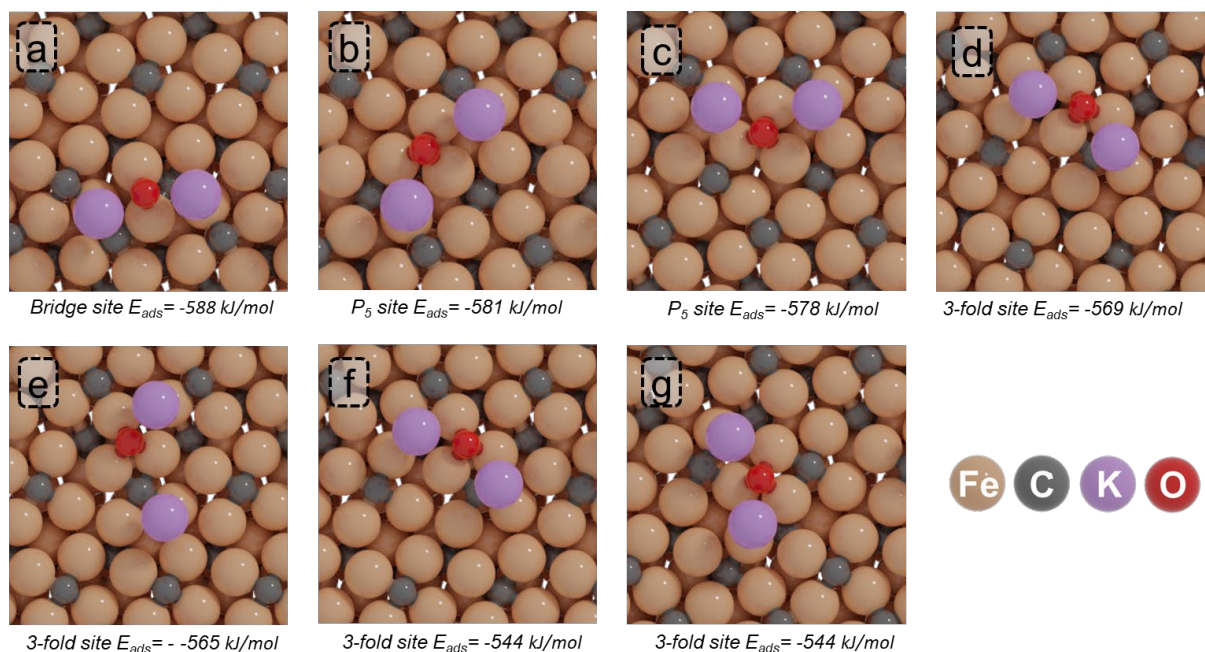


Figure A3. The adsorption structures and energy values of K_2O promoter in the possible sites on the (510) surface of $\chi\text{-Fe}_5\text{C}_2$.

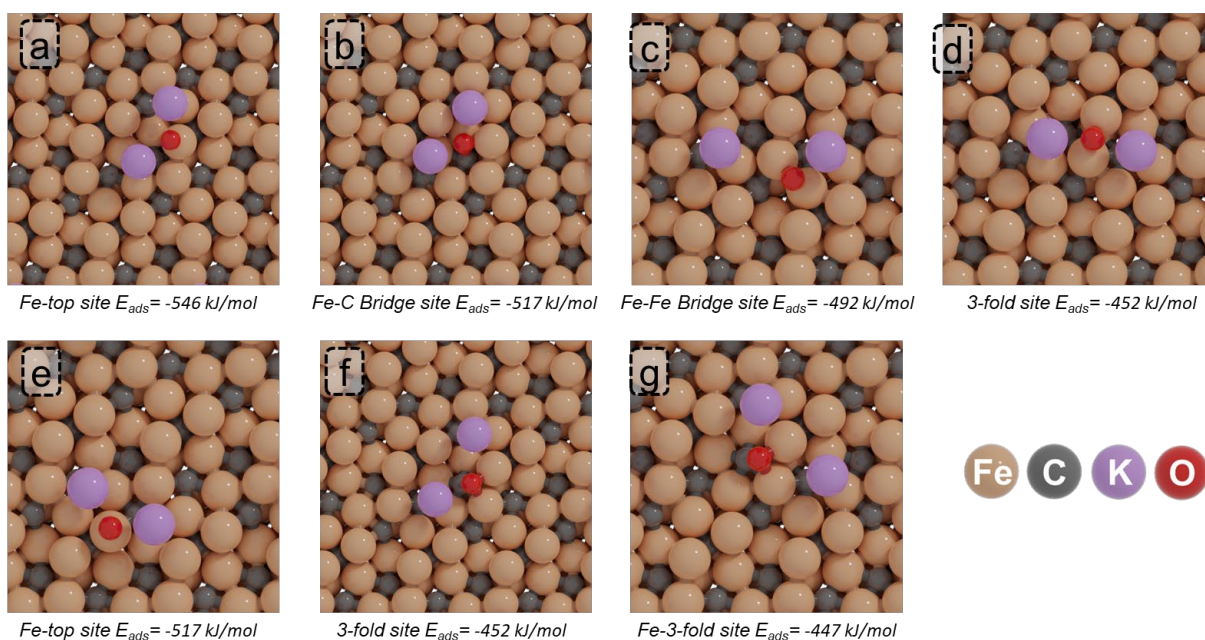


Figure A4. The adsorption structures and energy values of K_2O promoter in the possible sites on the (111) surface of $\chi\text{-Fe}_5\text{C}_2$.

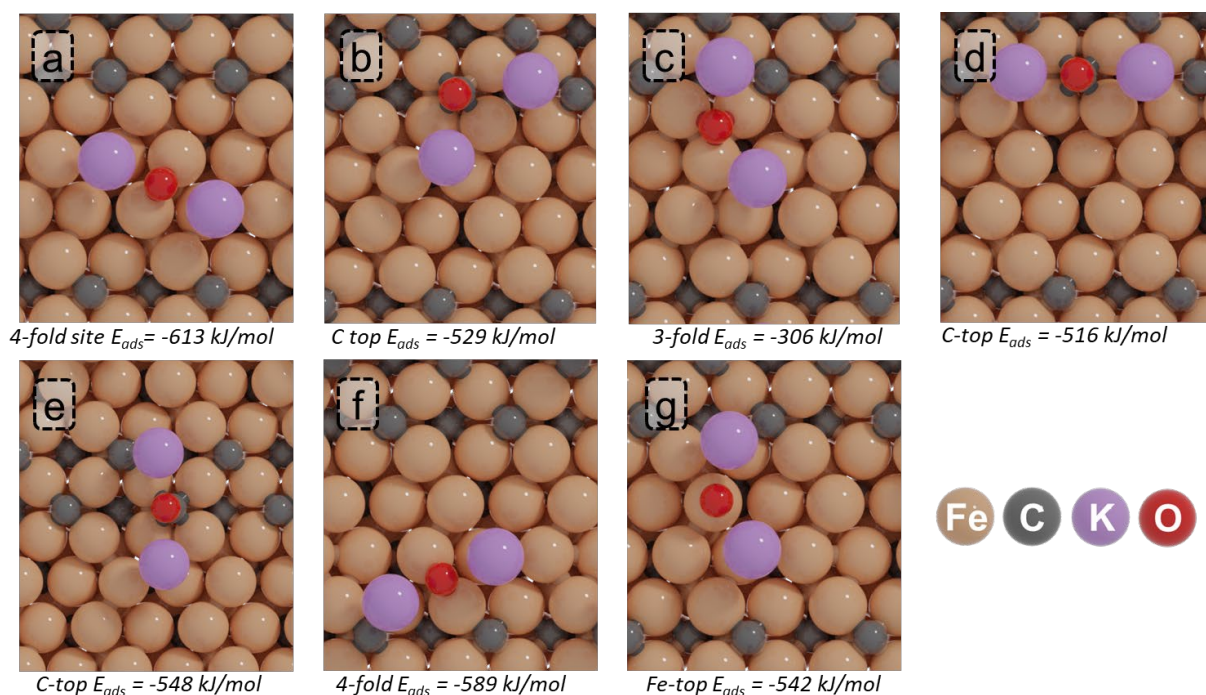


Figure A5. The adsorption structures and energy values of K_2O promoter in the possible sites on the (010) surface of χ - Fe_5C_2 .

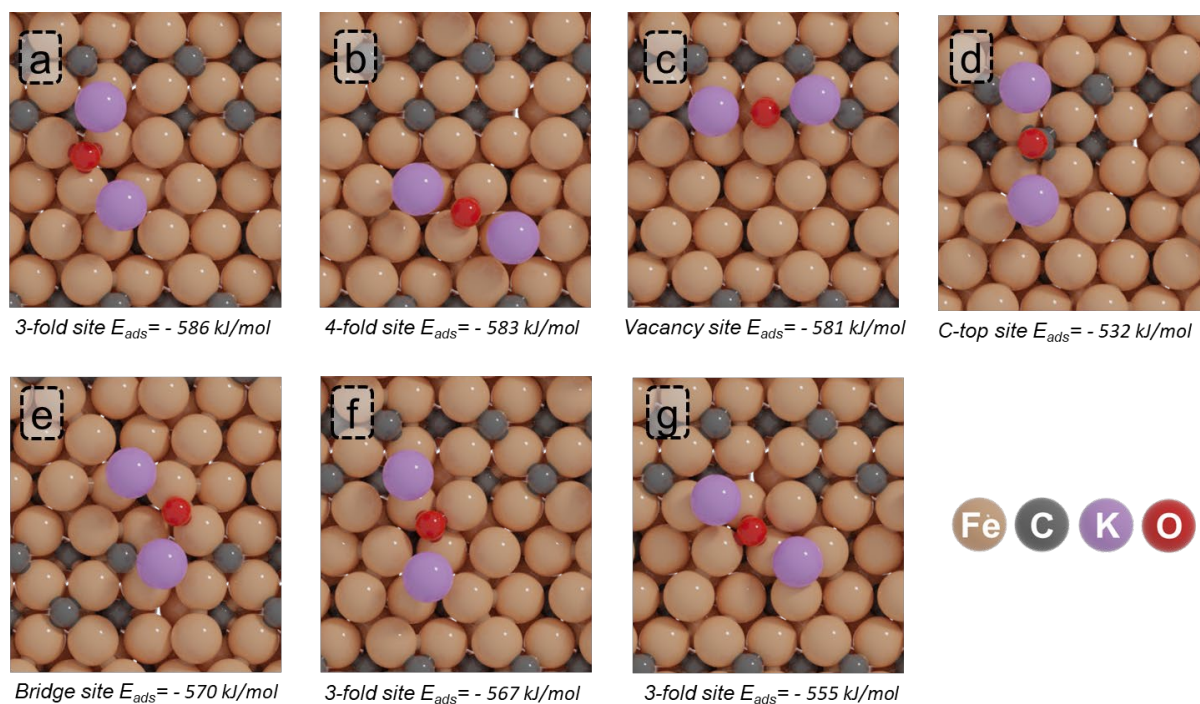


Figure A6. The adsorption structures and energy values of K_2O promoter in the possible sites on the (010*) surface of χ - Fe_5C_2 .

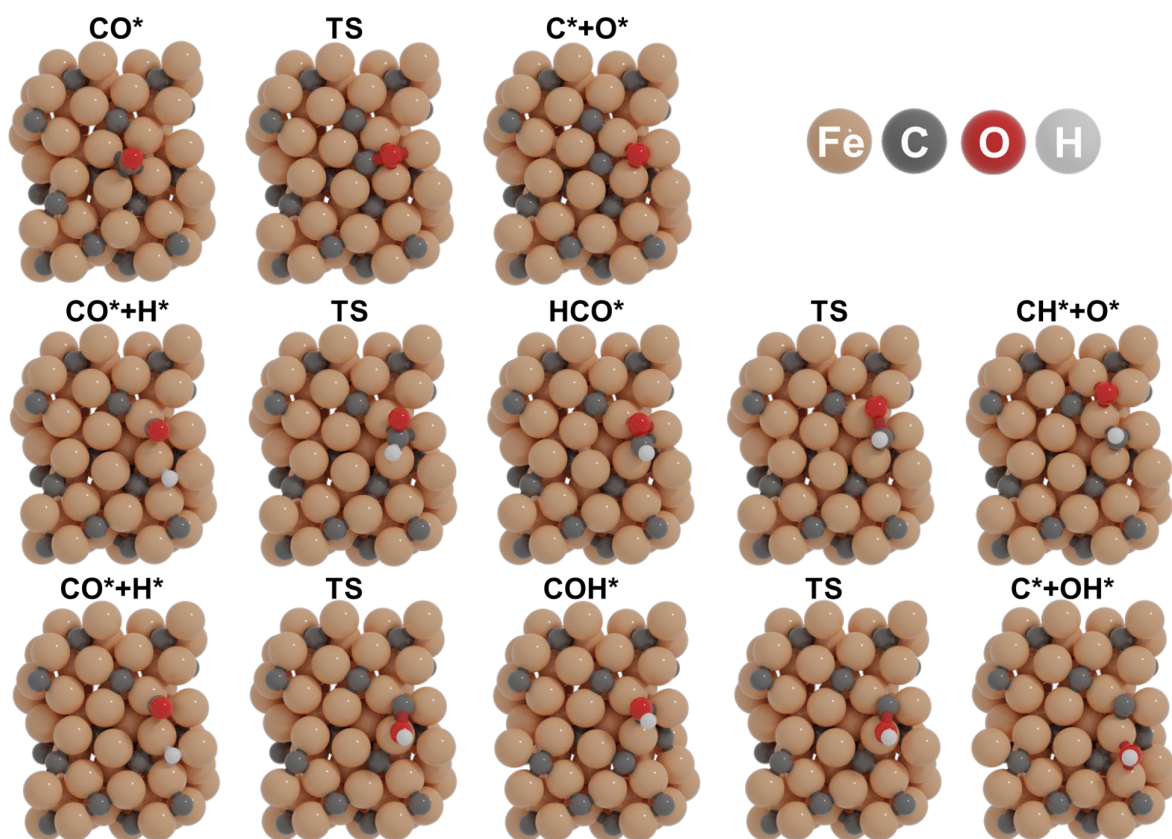


Figure A7. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (510) surface of χ -Fe₅C₂.

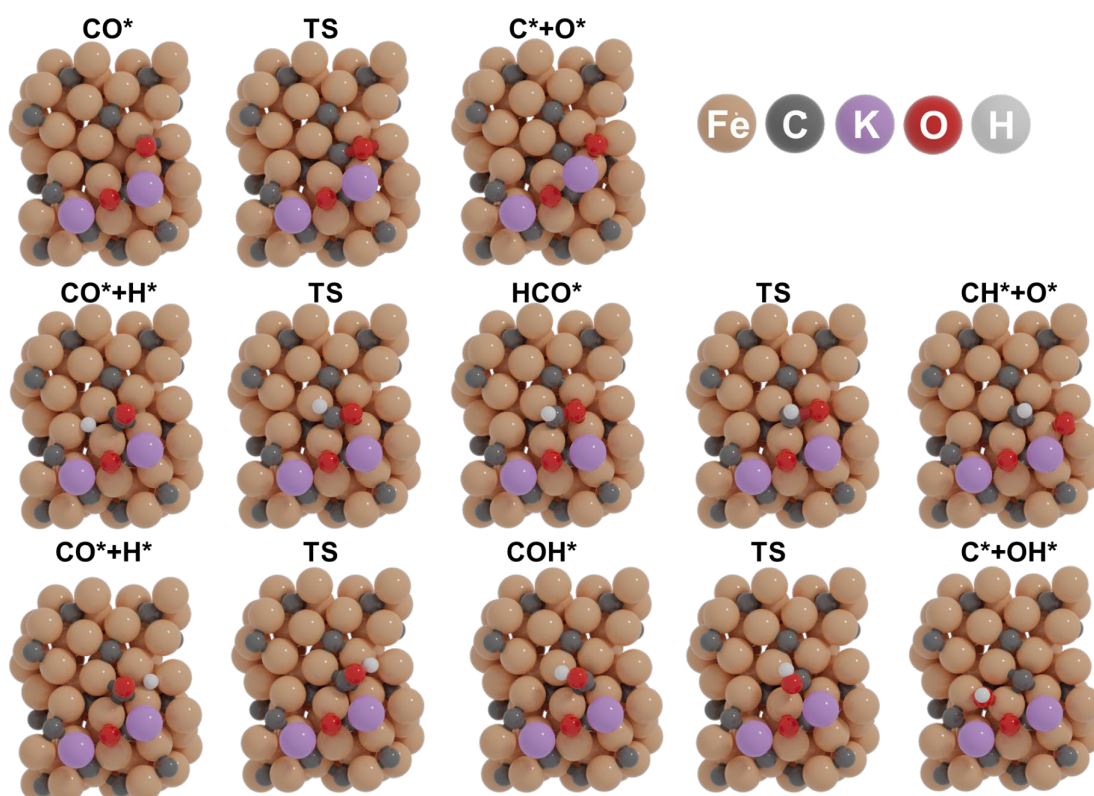


Figure A8. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K₂O-promoted (510) surface of χ -Fe₅C₂.

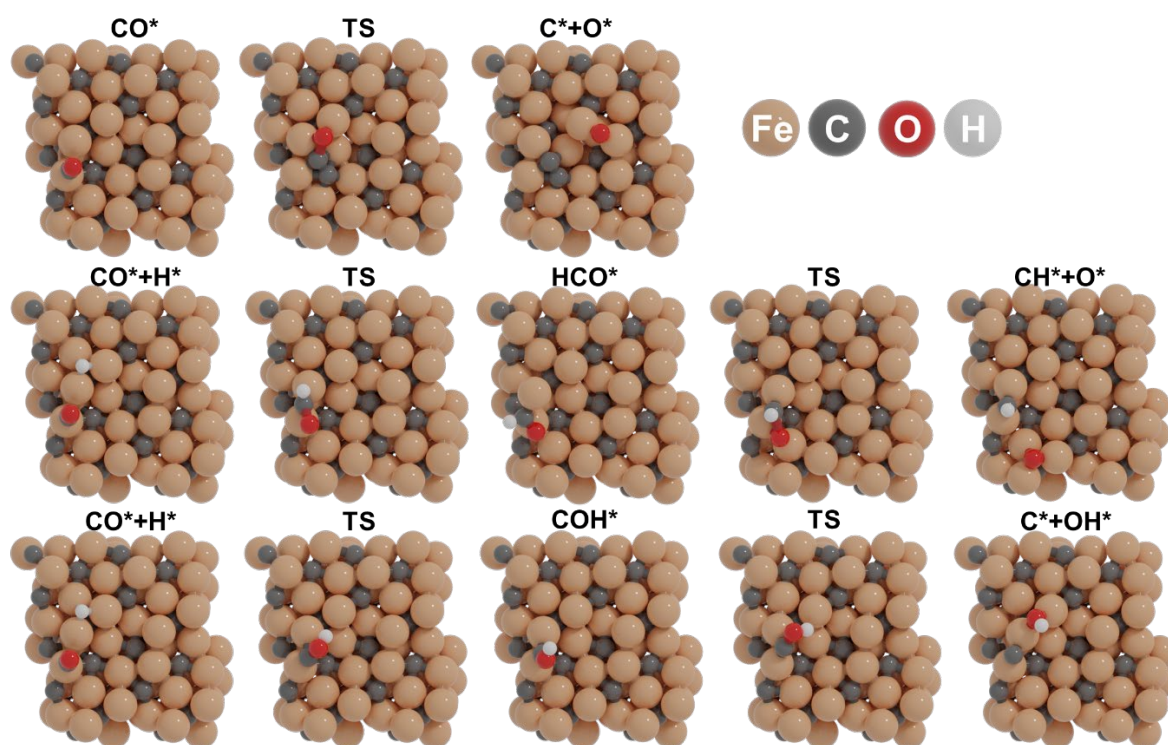


Figure A9. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (111) surface of χ -Fe₅C₂.

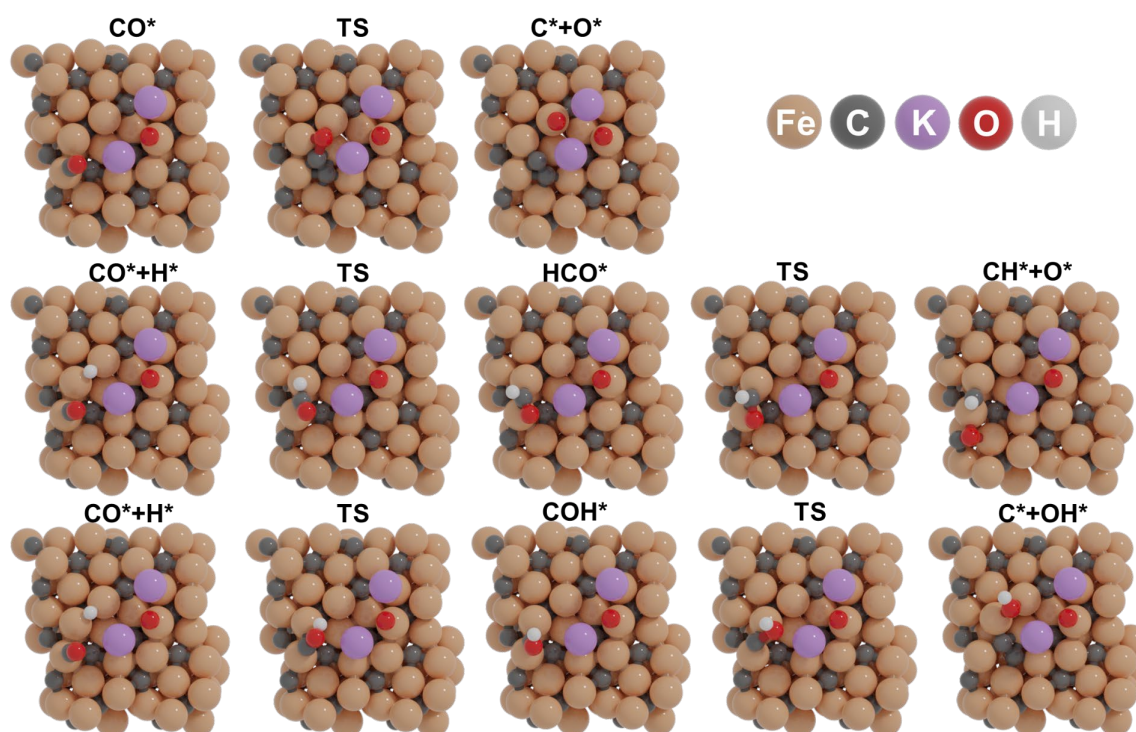


Figure A10 Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K₂O-promoted (111) surface of χ -Fe₅C₂.

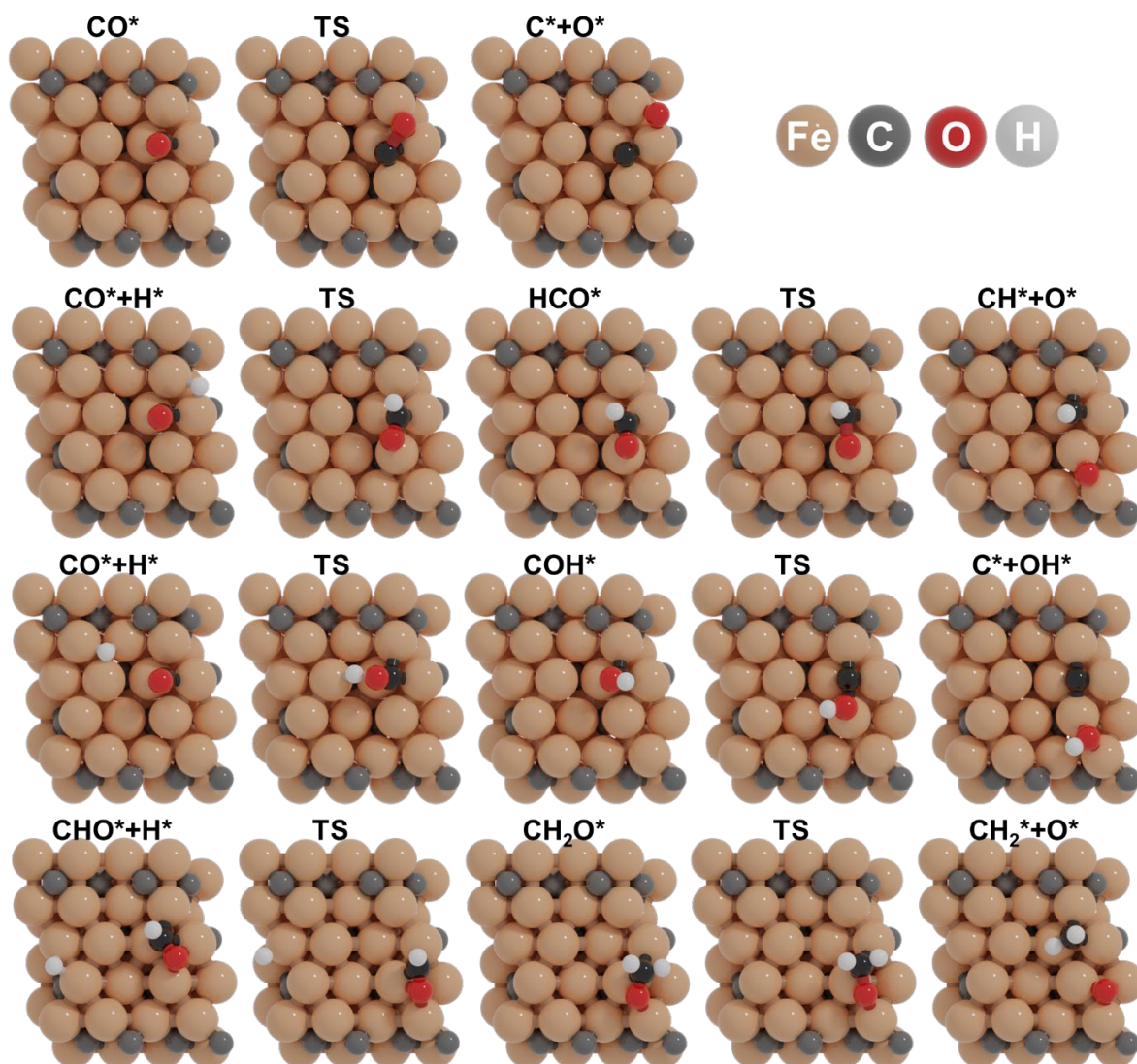


Figure A11. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (010) surface of χ -Fe₅C₂.

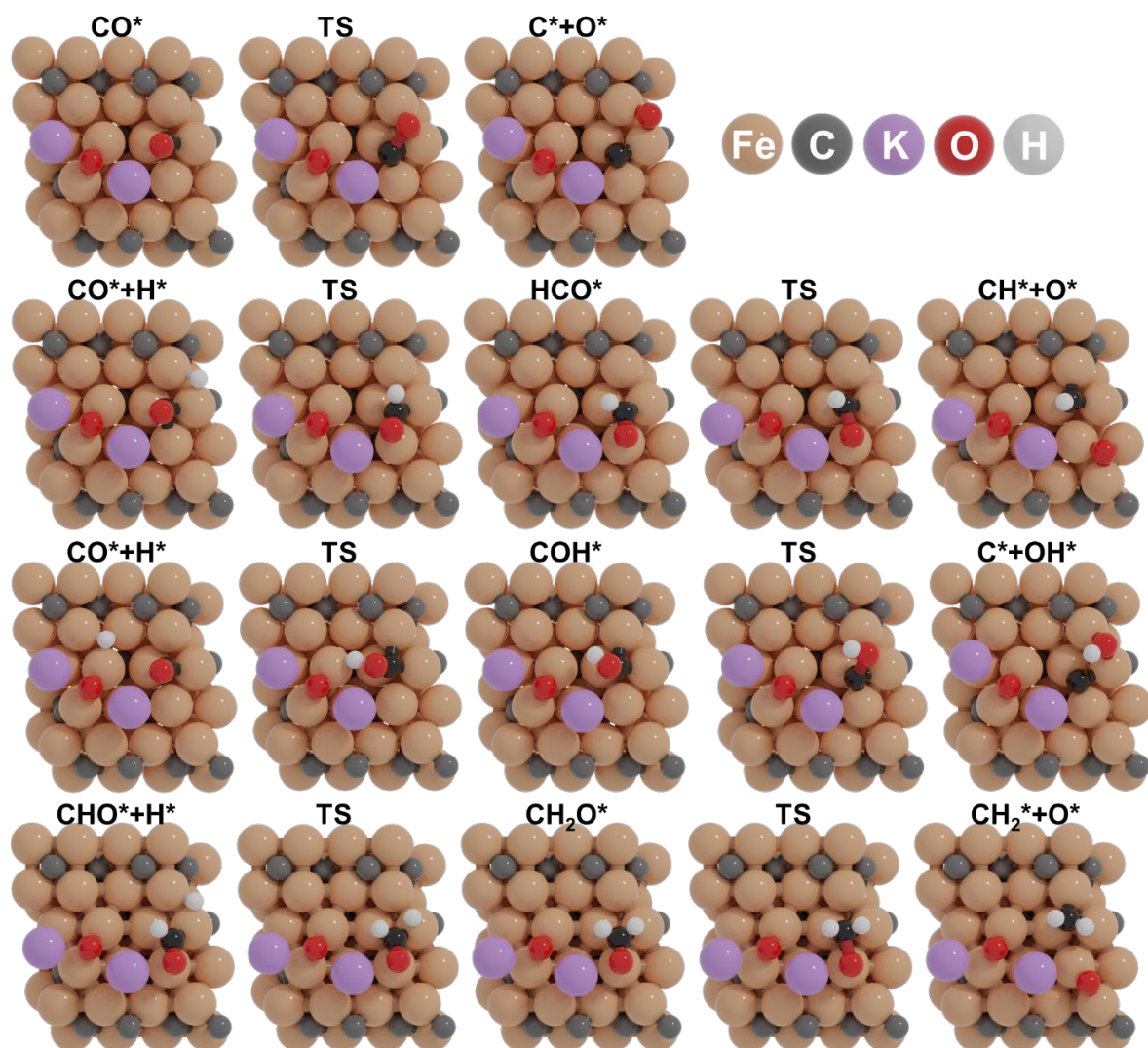


Figure A12. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K₂O-promoted (010) surface of χ -Fe₅C₂.

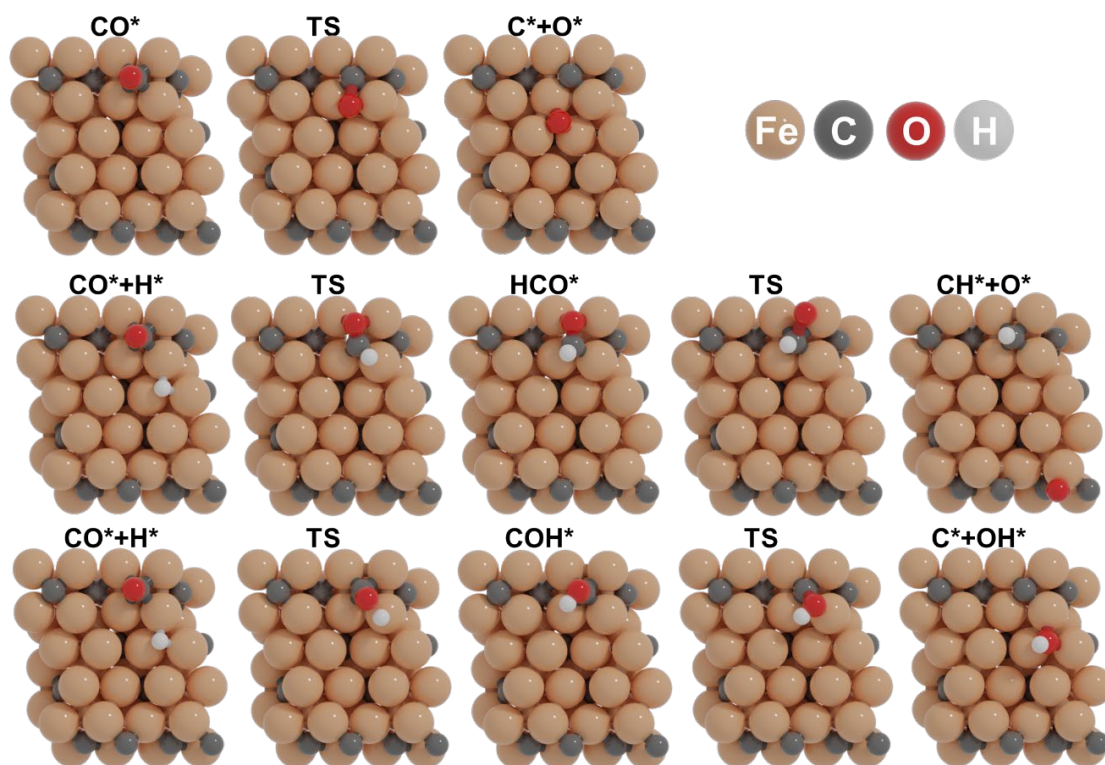


Figure A13. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (010*) surface of χ -Fe₅C₂.

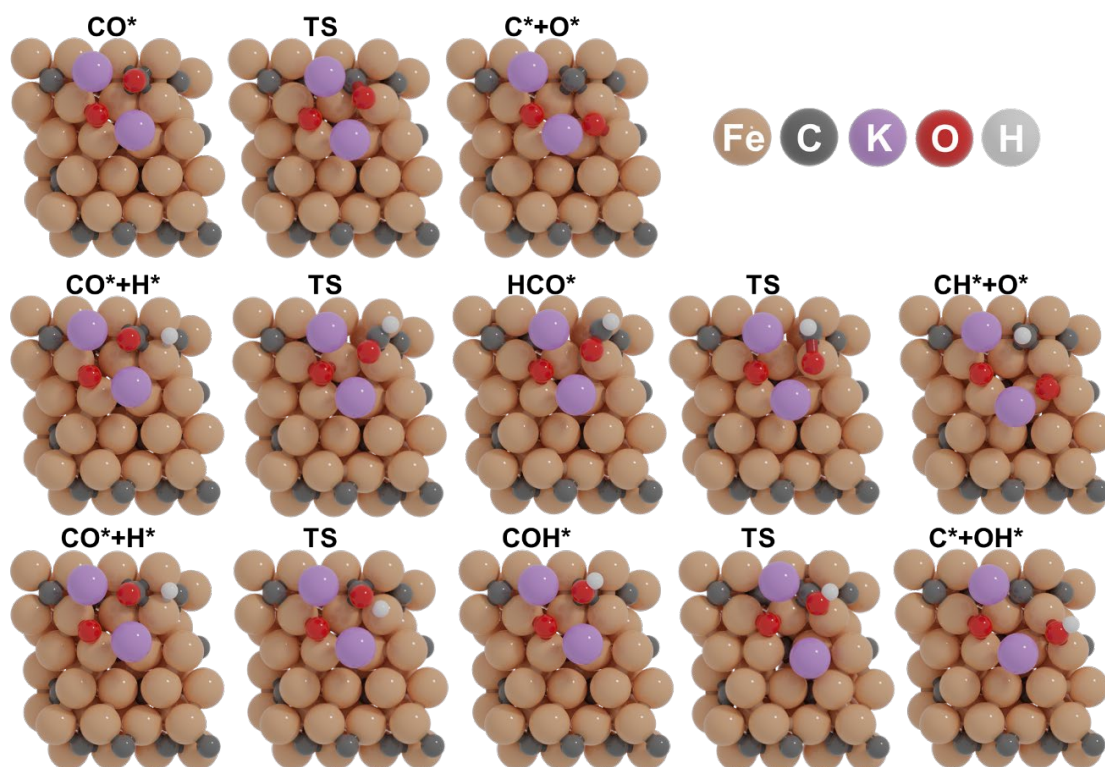


Figure A14. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K₂O-promoted (010*) surface of χ -Fe₅C₂.

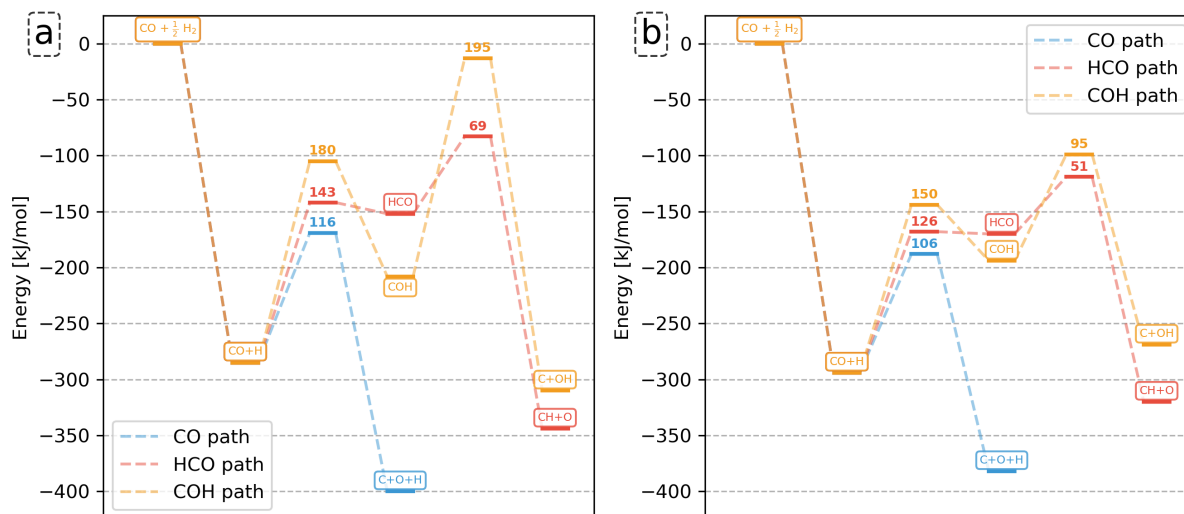


Figure A15. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (510) and (b) K₂O-promoted (510) surfaces of χ -Fe₅C₂. The value upon the TS corresponds to the activation barrier of each elementary step.

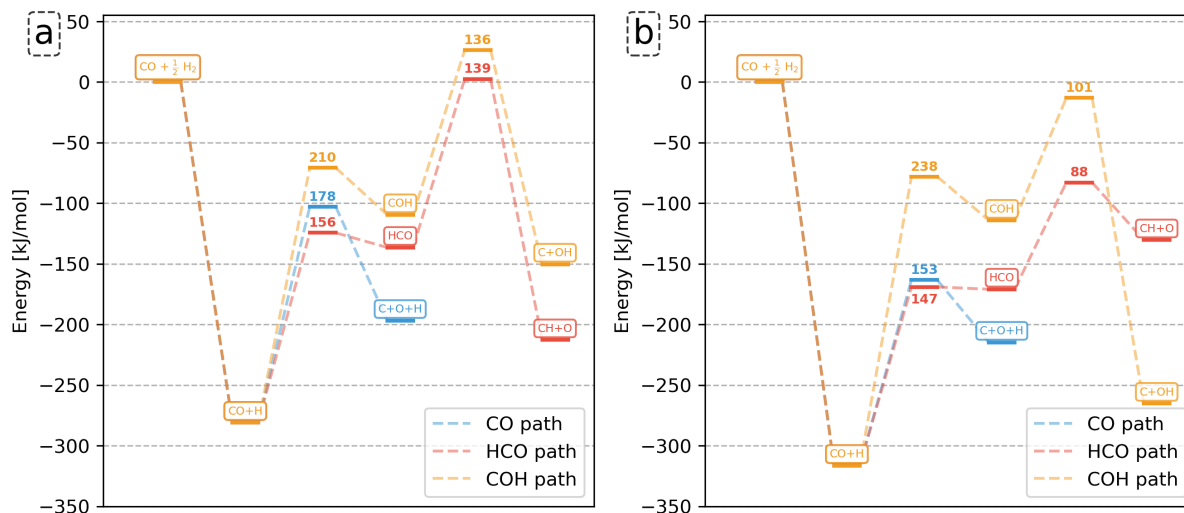


Figure A16. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (111) and (b) K₂O-promoted (111) surfaces of χ -Fe₅C₂.

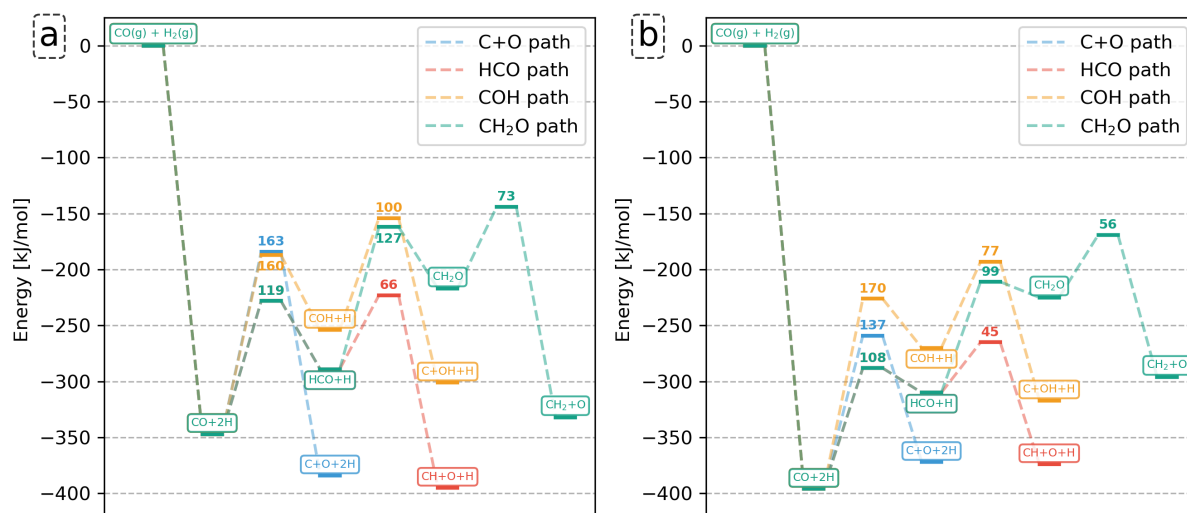


Figure A17. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (010) and (b) K₂O-promoted (010) surfaces of χ -Fe₅C₂.

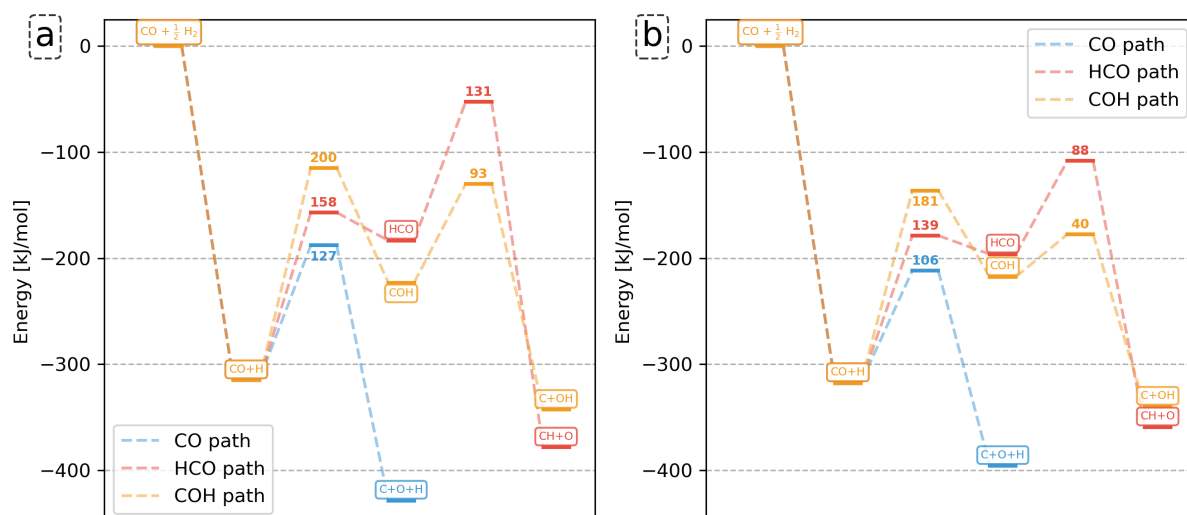


Figure A18. Energy profiles for the direct or H-assisted dissociation of CO from co-adsorbed H and CO on the (a) (010*) and (b) K₂O-promoted (010*) surfaces of χ -Fe₅C₂.

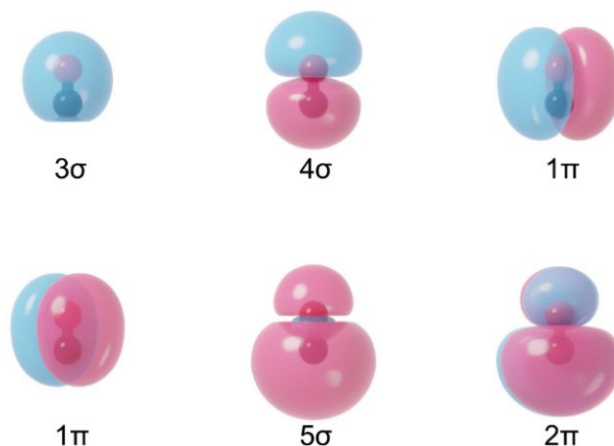


Figure A19. The canonical molecular orbital solutions of CO in the gas phase. This figure is generated by Quantumsculpt suite.

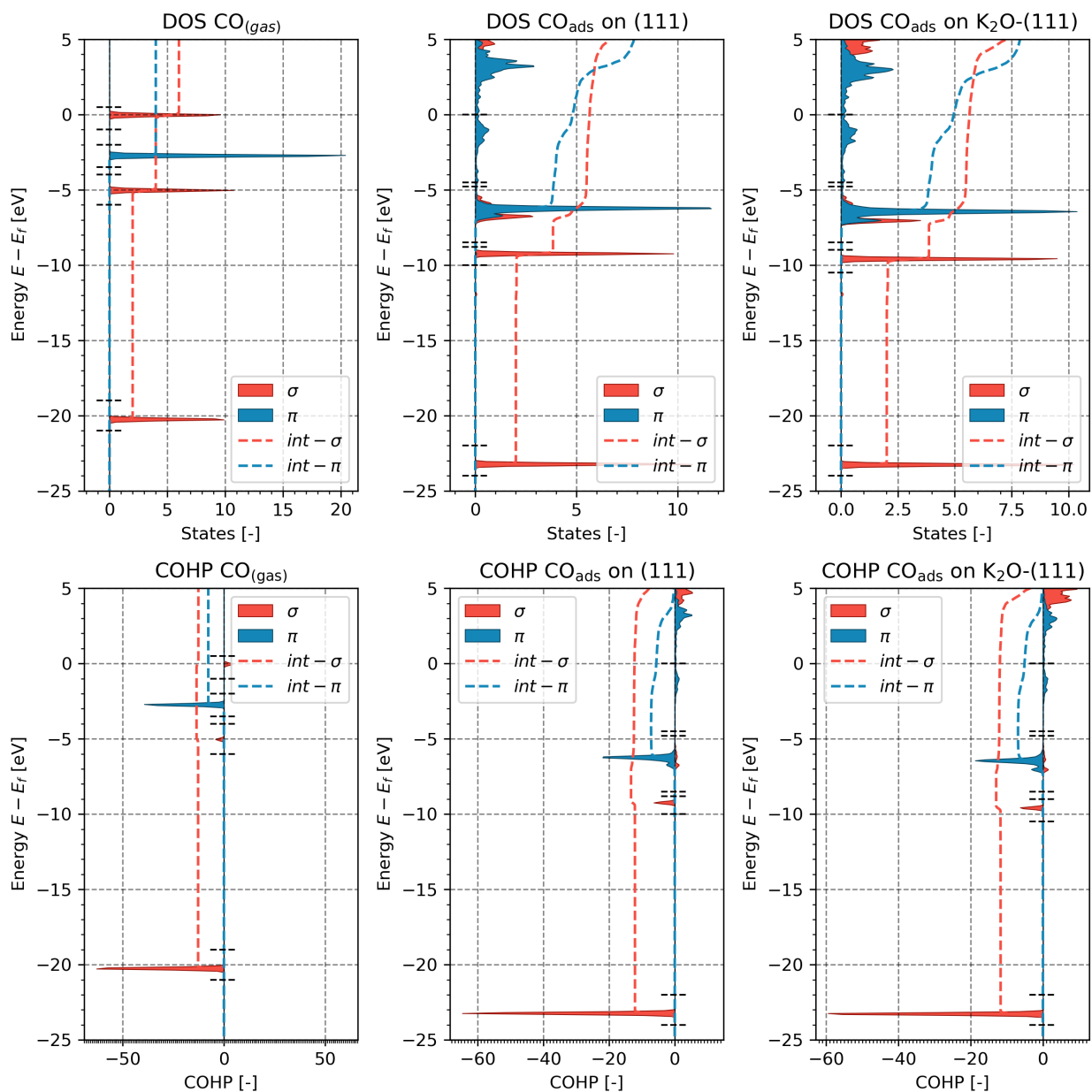


Figure A20. DOS and COHP of C-O bond of CO in the gas phase, CO adsorbate on the (111) and K₂O-promoted (111) surfaces of χ -Fe₅C₂.

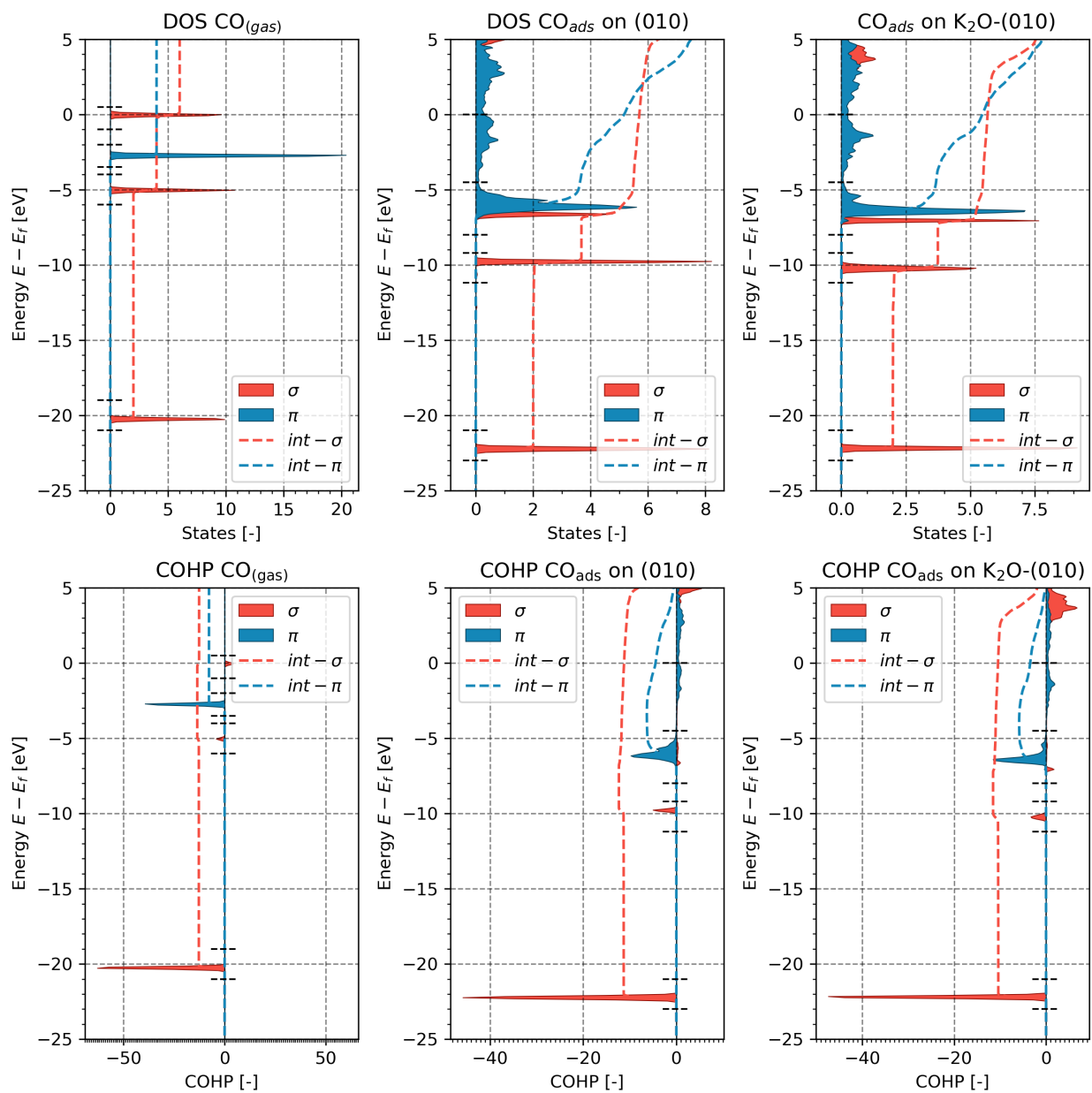


Figure A21. DOS and COHP of C-O bond of CO in the gas phase, CO adsorbate on the (010) and K₂O-promoted (010) surfaces of χ -Fe₅C₂.

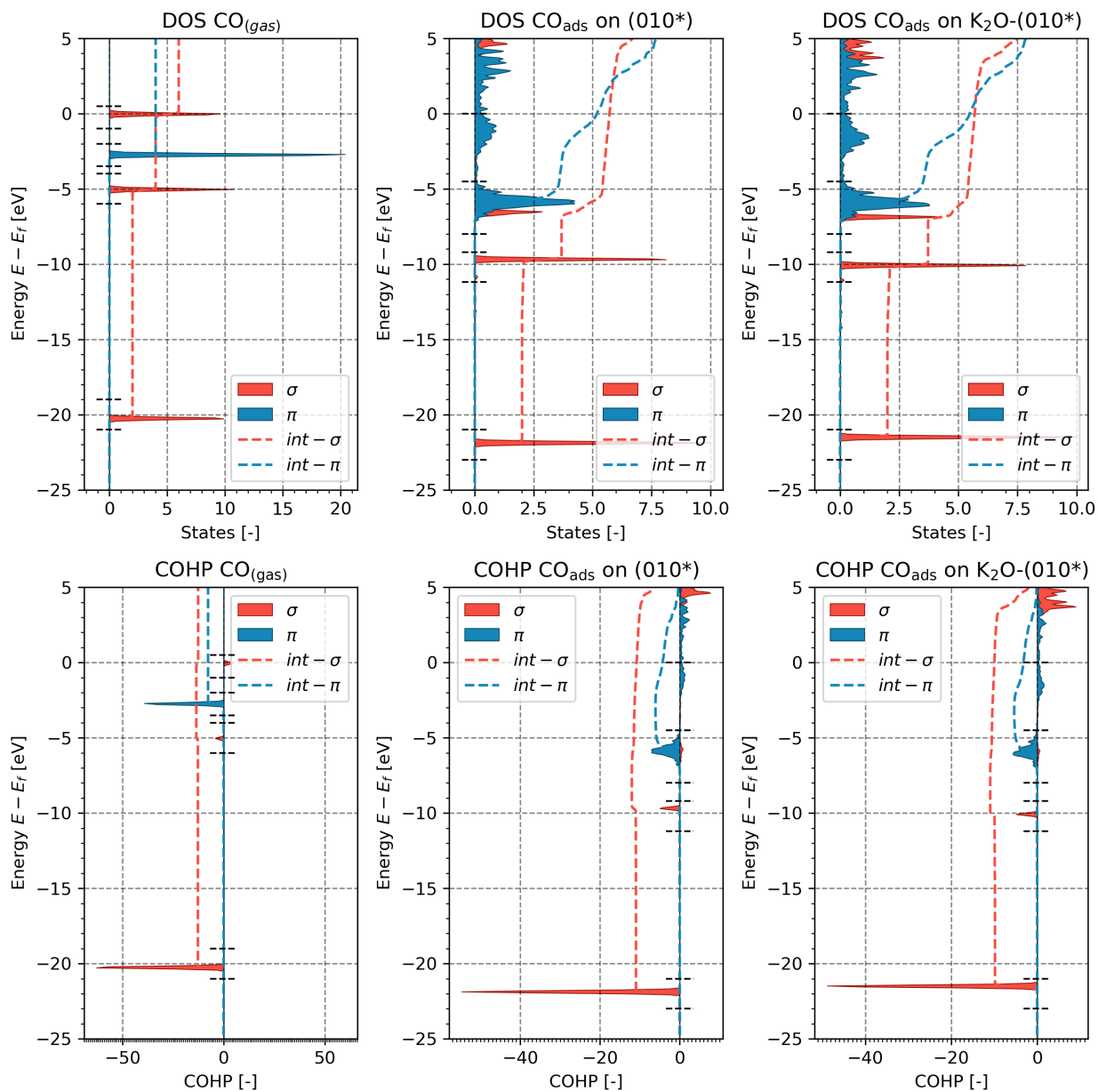


Figure A22. DOS and COHP of C-O bond of CO in the gas phase, CO adsorbate on the (010*) and K₂O-promoted (010*) surfaces of χ -Fe₅C₂.

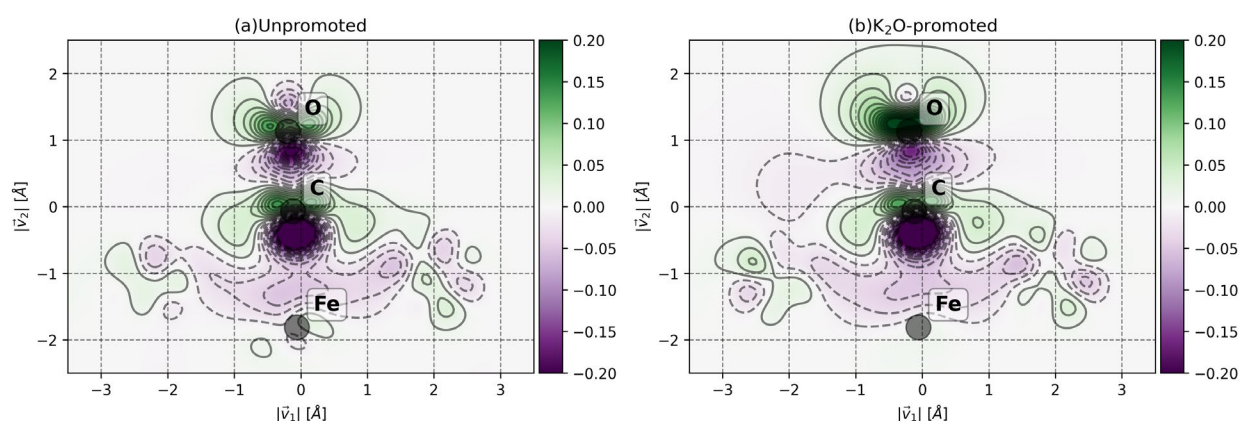


Figure A23. Charge density difference upon CO adsorption on the (010) and K₂O-promoted (010) surfaces of χ -Fe₅C₂.

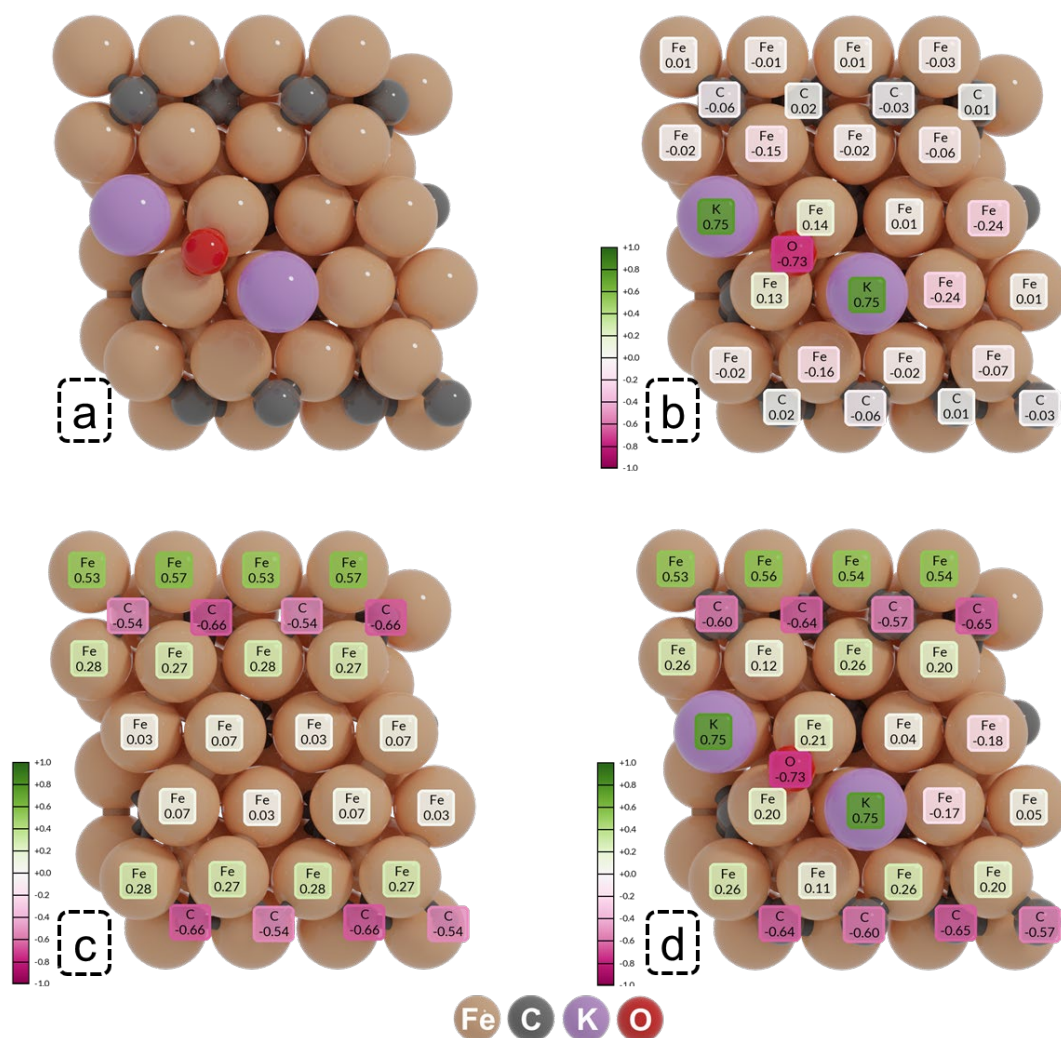


Figure A24. (a) K₂O promoted (010) surface of χ -Fe₅C₂. (b) Charge difference of surface Fe atoms on the (010) surface upon K₂O adsorption (Negative values indicate increased electron density upon adsorption). (c) Charge of surface Fe atoms on the pristine (010) and (d) K₂O-promoted (010) surfaces of χ -Fe₅C₂.

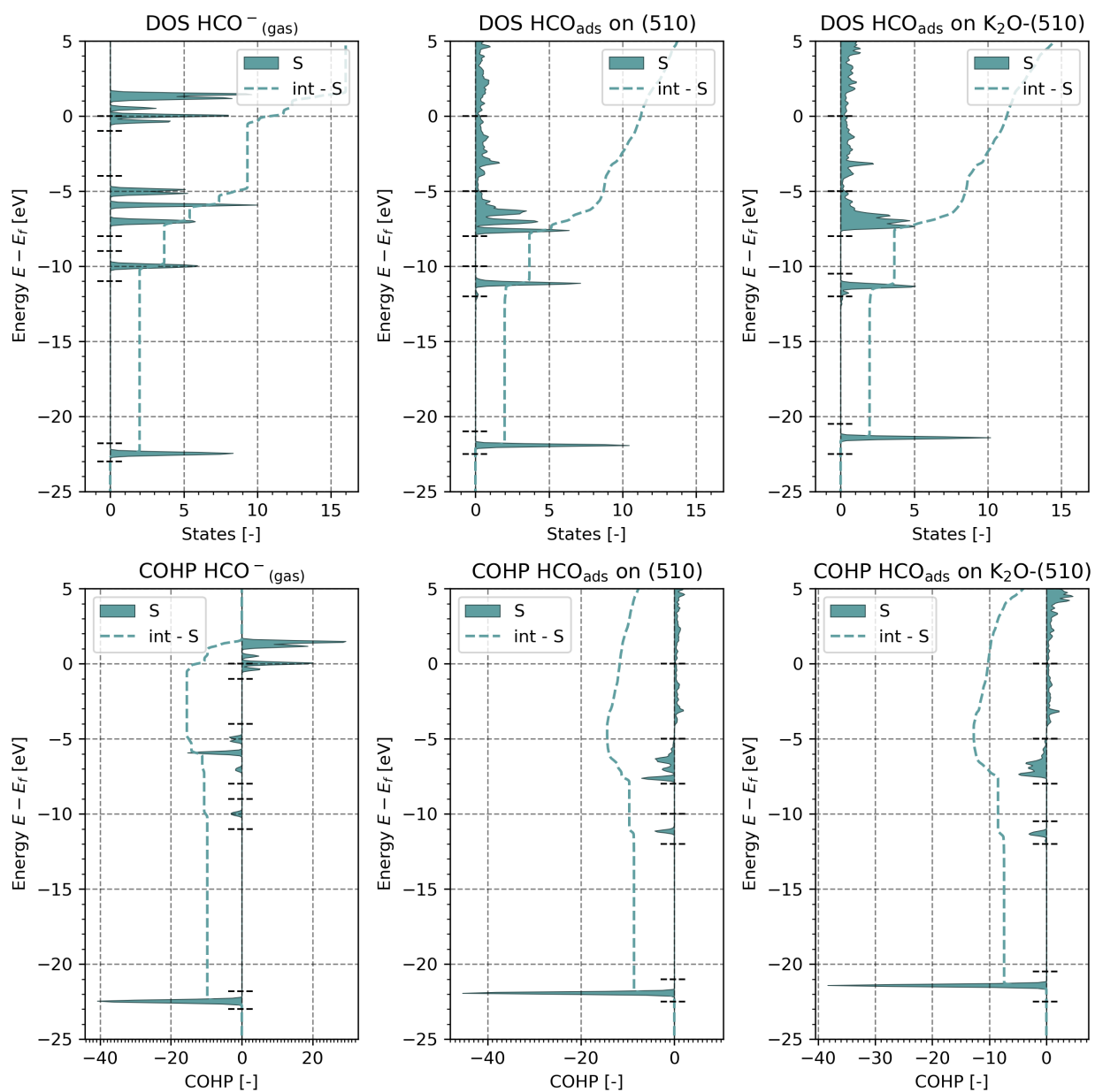


Figure A25. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO adsorbate on the (510) and K_2O -promoted (510) surfaces of $\chi\text{-Fe}_5\text{C}_2$.

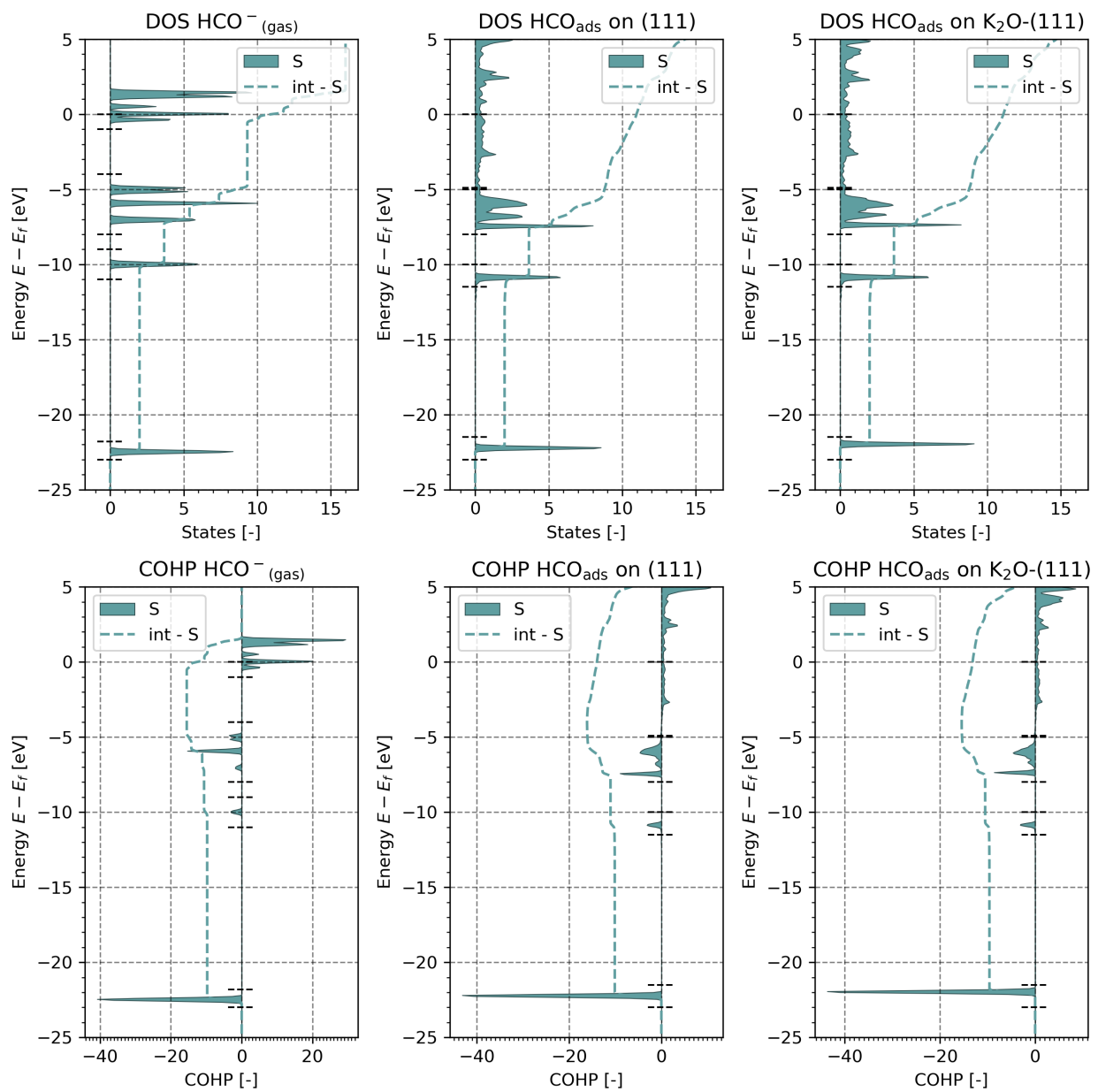


Figure A26. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO adsorbate on the (111) and K_2O -promoted (111) surfaces of $\chi\text{-Fe}_5\text{C}_2$.

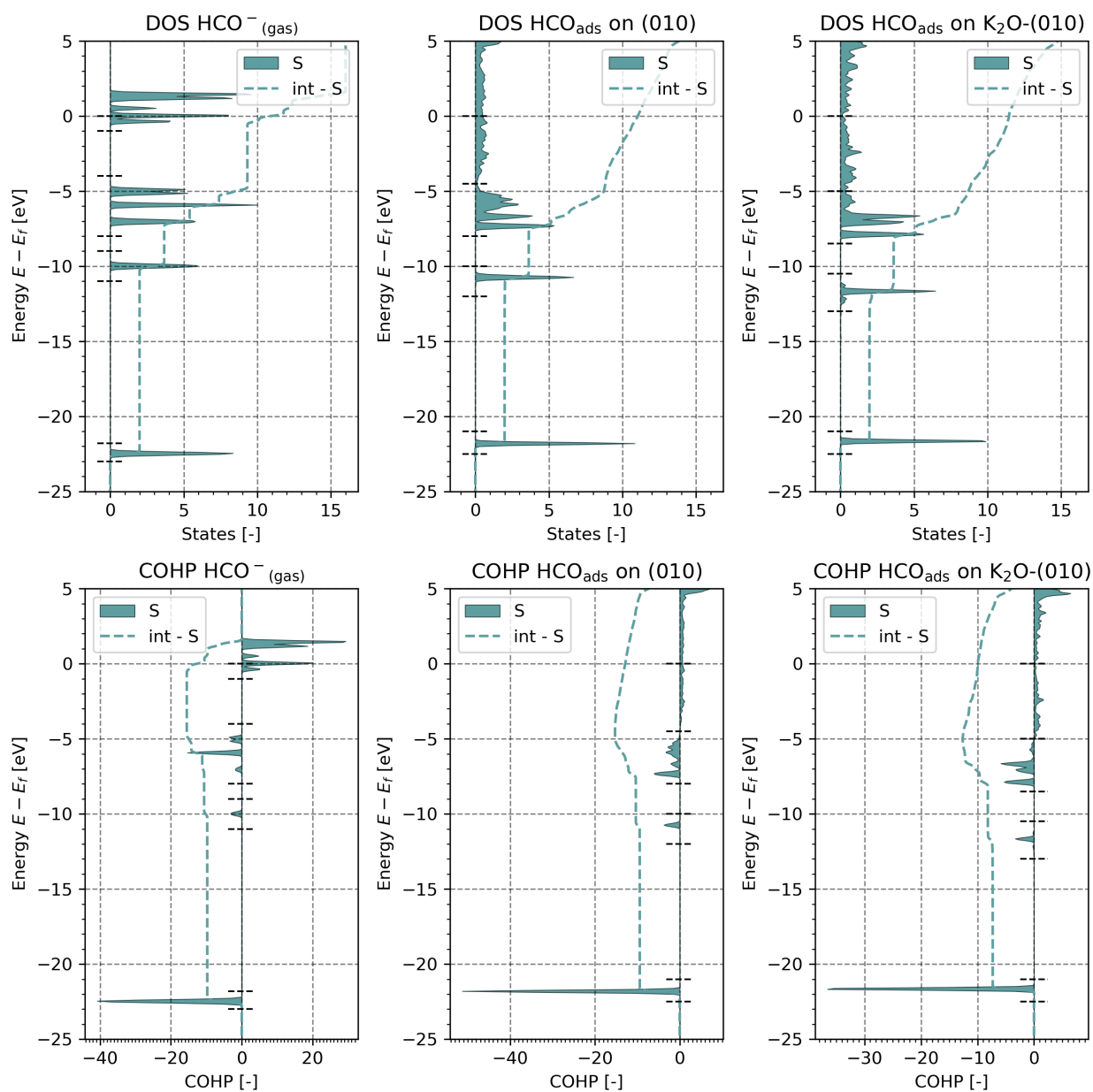


Figure A27. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO adsorbate on the (010) and K_2O -promoted (010) surfaces of $\chi\text{-Fe}_5\text{C}_2$.

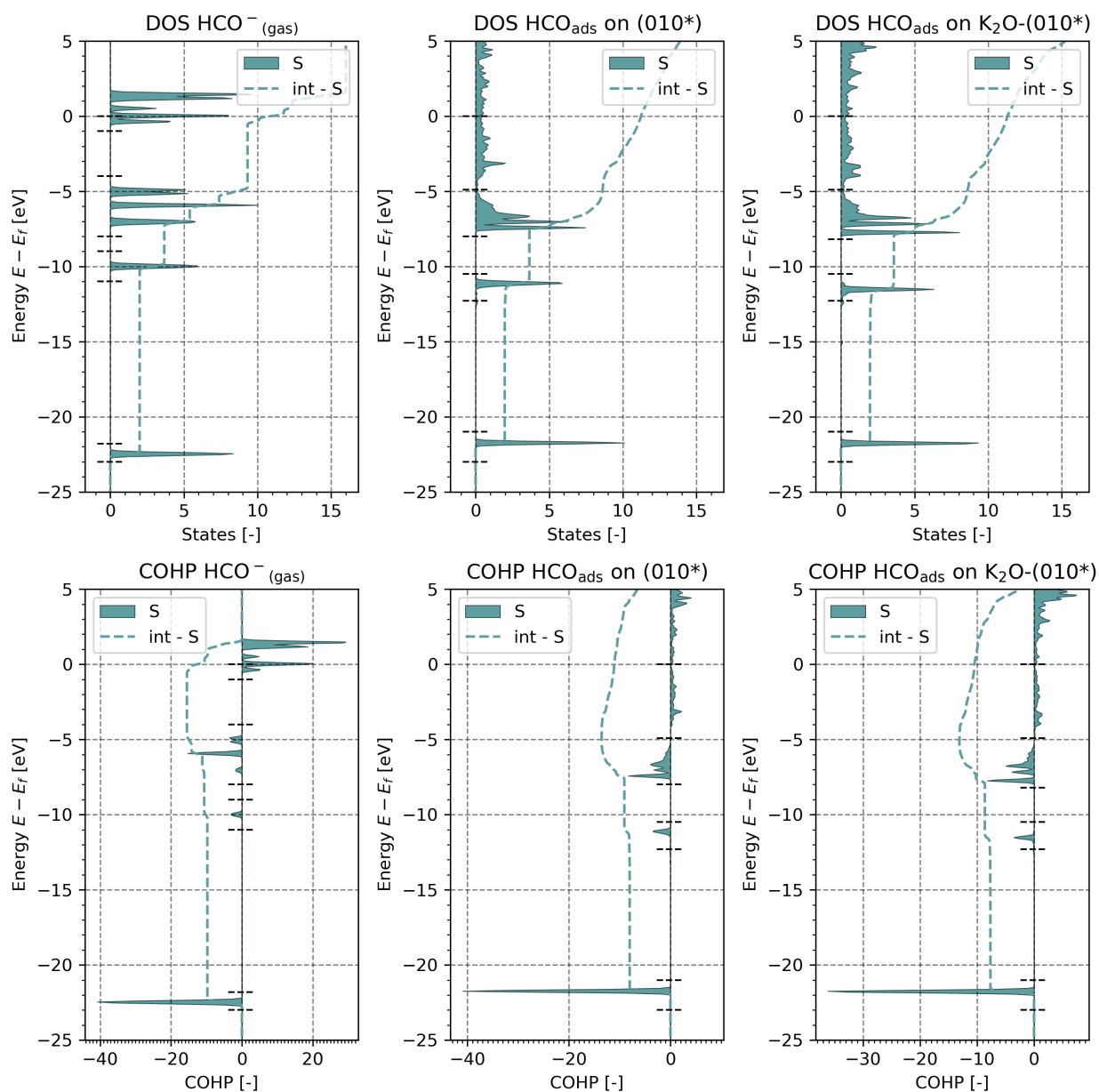


Figure A28. DOS and COHP of C-O bond of HCO^- in the gas phase, HCO adsorbate on the (010^*) and K_2O -promoted (010^*) surfaces of $\chi\text{-Fe}_5\text{C}_2$.

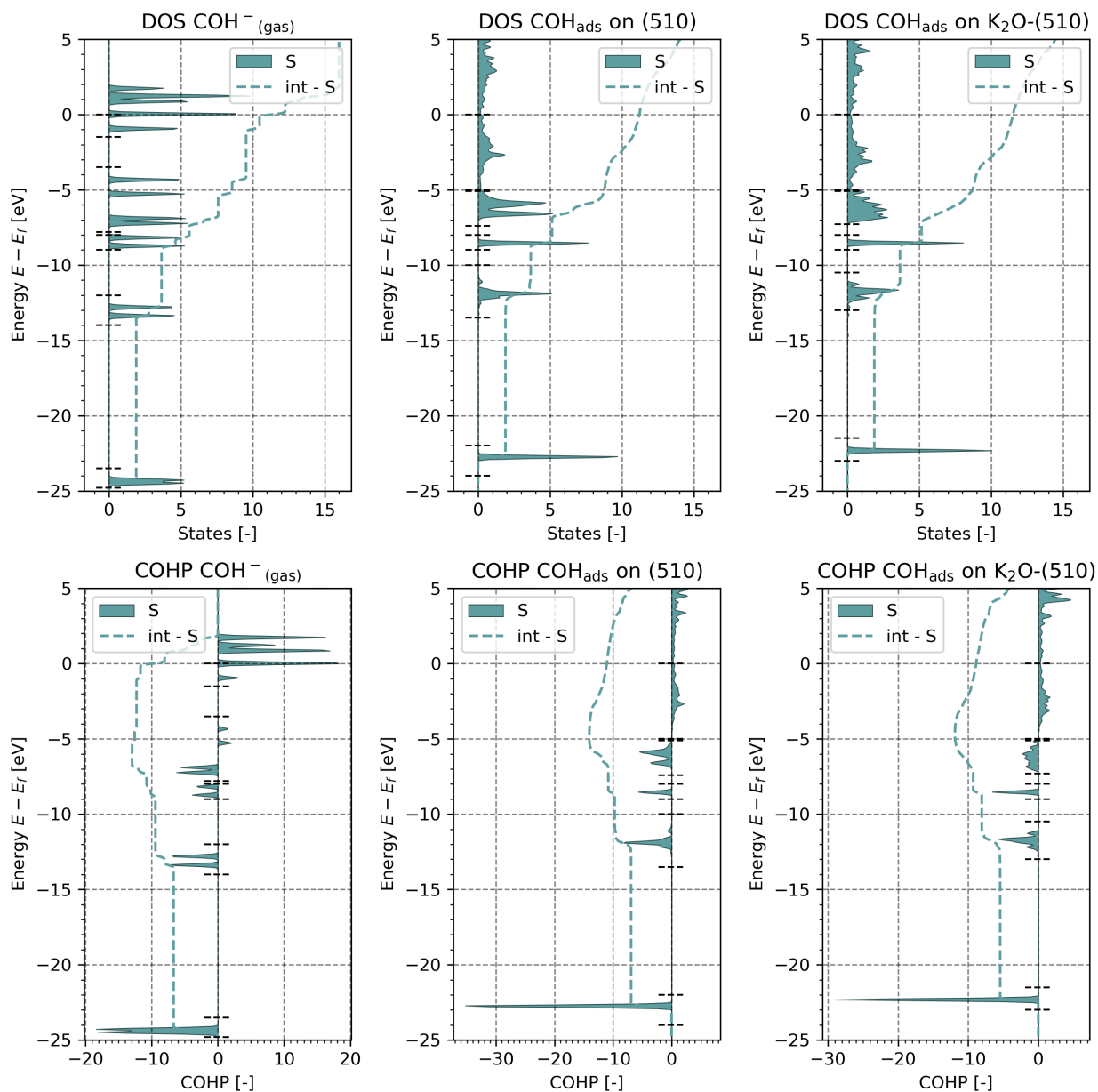


Figure A29. DOS and COHP of C-O bond of COH^- in the gas phase, COH adsorbate on the (510) and K_2O -promoted (510) surfaces of $\chi\text{-Fe}_5\text{C}_2$.

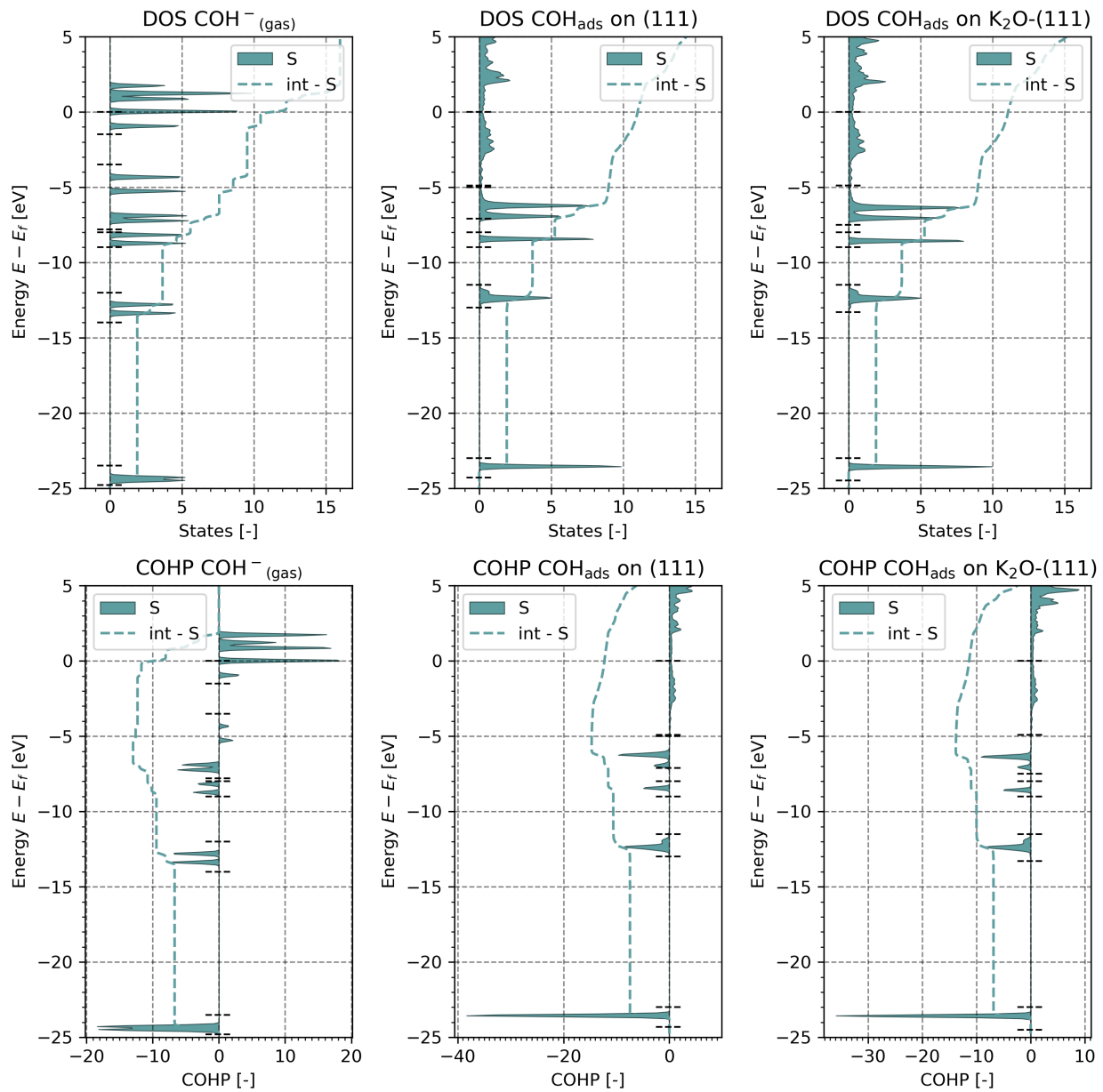


Figure A30. DOS and COHP of C-O bond of COH^- in the gas phase, COH adsorbate on the (111) and K_2O -promoted (111) surfaces of $\chi\text{-Fe}_5\text{C}_2$.

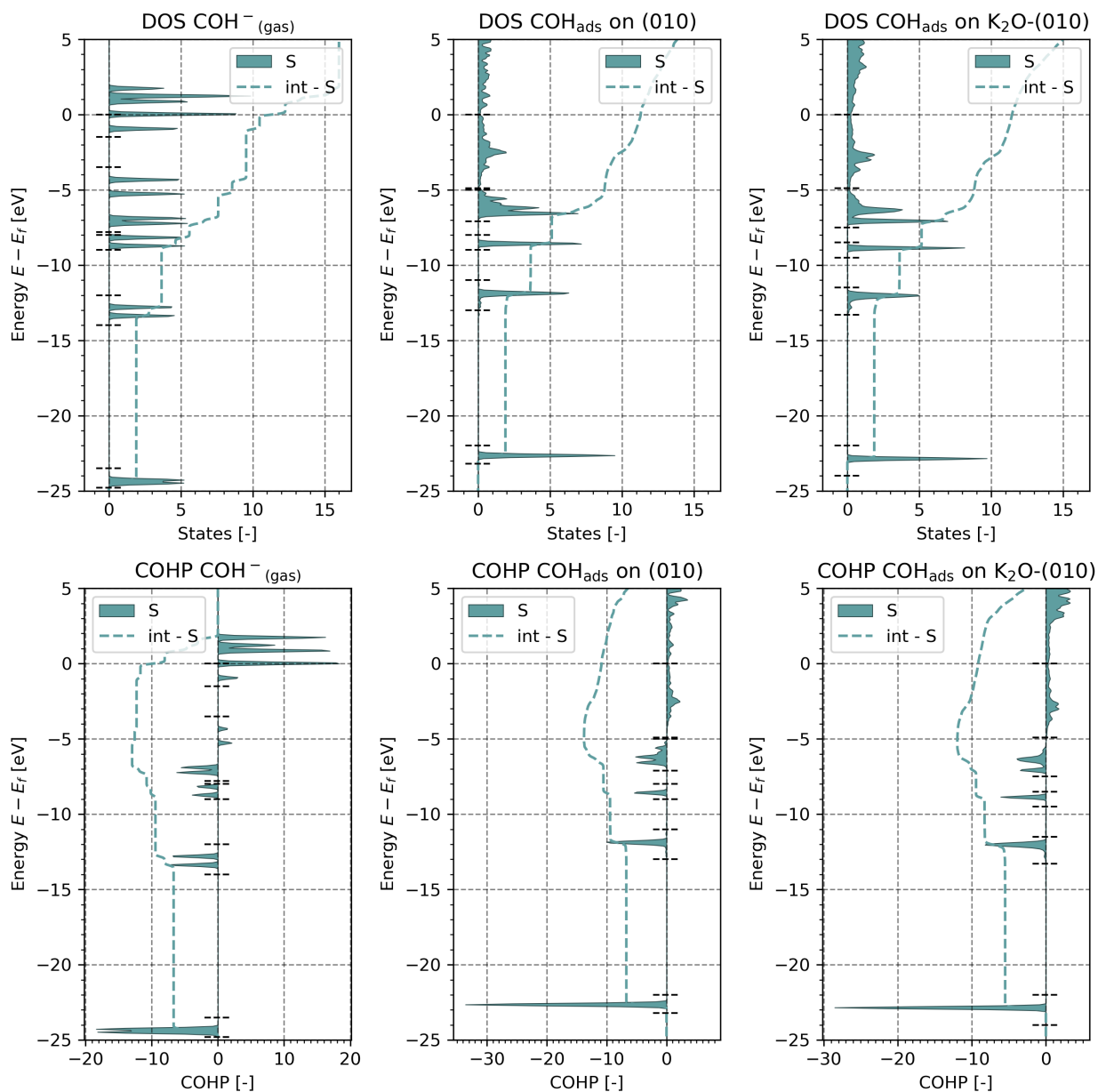


Figure A31. DOS and COHP of C-O bond of COH^- in the gas phase, COH adsorbate on the (010) and K_2O -promoted (010) surfaces of $\chi\text{-Fe}_5\text{C}_2$.

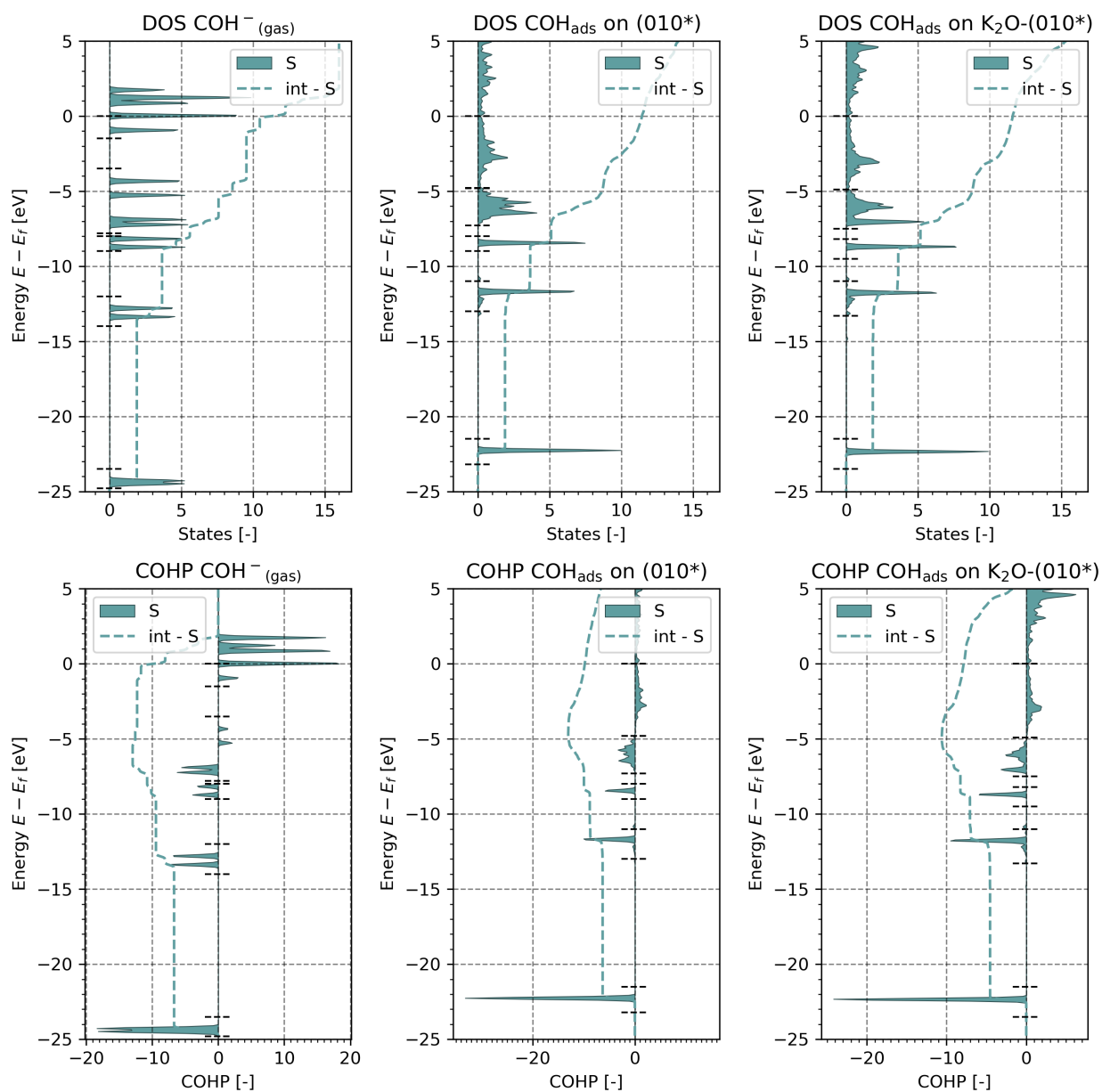


Figure A32. DOS and COHP of C-O bond of COH⁻ in the gas phase, COH adsorbate on the (010*) and K₂O-promoted (010*) surfaces of χ -Fe₅C₂.

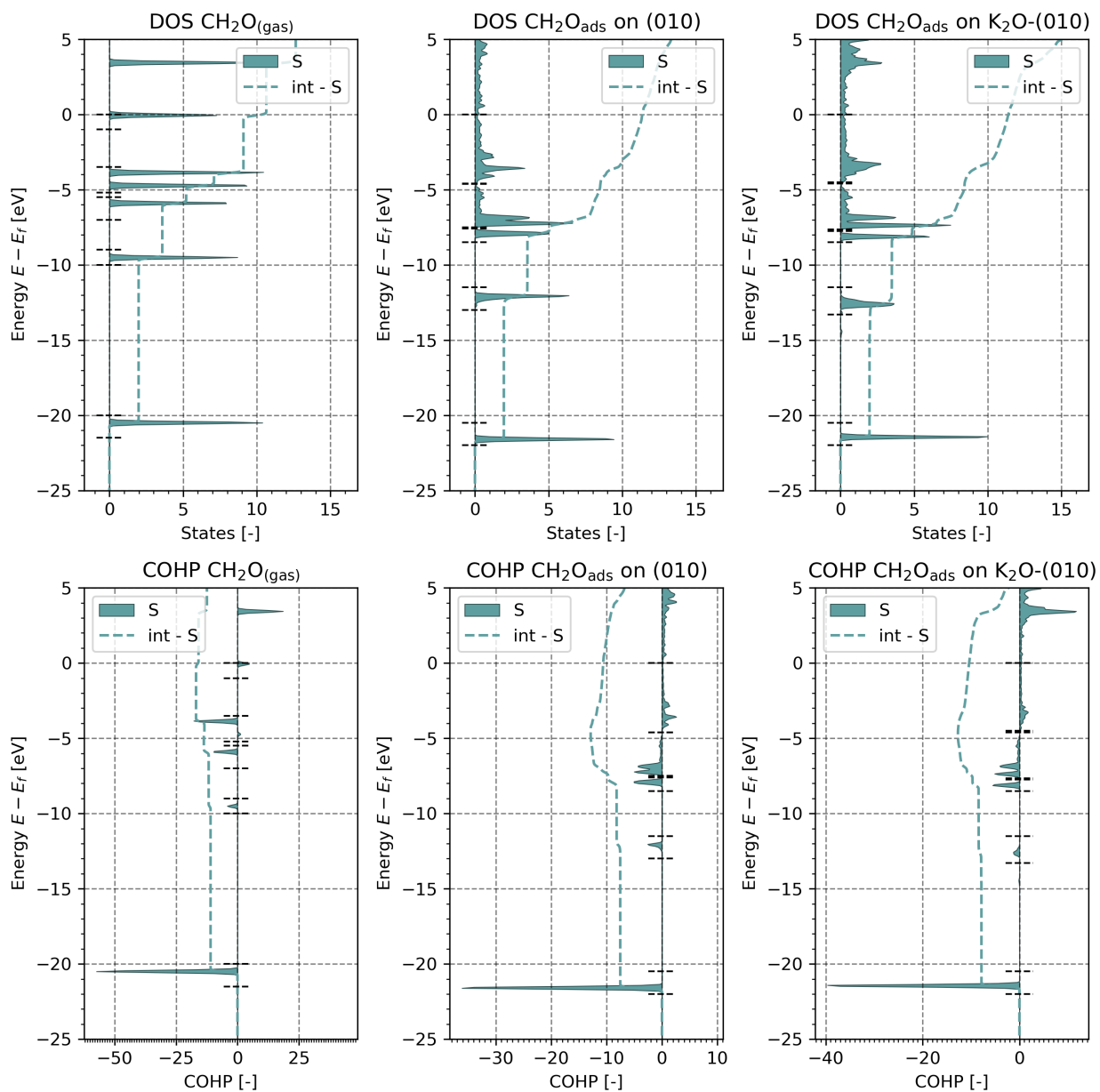


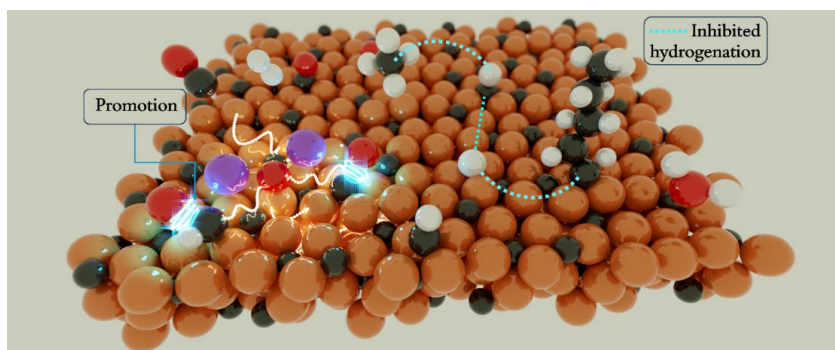
Figure A33. DOS and COHP of C-O bond of CH_2O in the gas phase, CH_2O adsorbate on the (010) and K_2O -promoted (010) surfaces of $\chi\text{-Fe}_5\text{C}$.

Chapter 4. The Nature of K Promotion of χ -Fe₅C₂ for High Chain-Growth Probability in the Fischer-Tropsch Reaction

Abstract

Potassium (K) is widely used as a promoter in industrial Fe-based Fischer-Tropsch (FT) catalysts to enhance CO conversion and increase the chain-growth probability while decreasing CH₄ selectivity. We deployed density functional theory calculations and microkinetics simulations to elucidate the mechanistic role of K promotion on χ -Fe₅C₂ (Hägg carbide). The preferred state of K under reaction conditions, K₂O, on the reactive (010) surface strengthens the adsorption of CO, H, C, and CH. This results in faster C-O bond dissociation and slower hydrogenation reactions. The main FT reaction mechanism involves HCO dissociation, O removal as H₂O, CH+CR (R = alkyl group) coupling reactions, and termination by α -CH hydrogenation to olefins. Microkinetics were determined to study the impact of K on the FT reaction catalyzed by the χ -Fe₅C₂(010) surface. Irrespective of the presence of K, the FT reaction operates at the interface of chain growth-limiting and oxygen removal-limiting regimes, with CCH₂ hydrogenation and OH disproportionation controlling the overall CO conversion rate. On the unpromoted surface, CO hydrogenation and CHO dissociation control the chain-growth process and slightly inhibit the overall CO conversion rate. Simulations of the K-promoted surface demonstrate that K promotion removes the kinetic limitation of CHO dissociation in the chain-growth process. Overall, K₂O increases the chain-growth probability while decreasing the CH₄ selectivity because the impact of the promoter is stronger for CH₄ formation than the hydrogenation reactions of olefinic surface precursors. The main effect of K₂O on the intrinsic FT chemistry is electronic, involving electron transfer to Fe surface atoms. The main kinetic consequences are a lower overall barrier of CHO dissociation and higher barriers for the hydrogenation of carbon-containing surface intermediates.

Keywords: Fischer-Tropsch synthesis, Hägg carbide, potassium promoter, density functional theory, microkinetics simulations



4.1 Introduction

Fischer–Tropsch (FT) synthesis is an industrial chemical process to convert syngas, derived from natural gas, biomass, and coal by gasification or reforming, into clean fuels and chemical building blocks,¹⁻³ providing an economically attractive way to monetization of non-petroleum feedstock.⁴

⁵ Regarding the production of chemical building blocks, a challenge remains the low selectivity of light olefins,⁶ which is intrinsic to the FT synthesis reaction.⁷⁻⁹ A high light olefins selectivity implies a relatively high contribution of low-value methane in the product slate. Therefore, improving the selectivity for light olefins while simultaneously suppressing methane production is crucial for the effective optimization of the FT synthesis catalyst.¹⁰

Co and Fe are the predominant catalysts used in industrial FT synthesis due to their cost-effectiveness and versatility.¹⁰⁻¹² Co catalysts are typically used in low-temperature FT synthesis for synthesis gas mixtures generated from natural gas. The benefits of Fe are its very low price, high selectivity to lower olefins and activity in the water-gas shift (WGS) reaction. This latter aspect is especially advantageous when utilizing synthesis gas primary active phases, such as those obtained from coal and biomass.¹³⁻¹⁷ In the practical FT synthesis process, Fe-based catalysts undergo inevitable carburization, transforming into a mixture of various carbide phases that include ϵ -Fe₂C, δ -Fe_{2.2}C, χ -Fe₅C₂, θ -Fe₃C, and Fe₇C₃.¹⁸⁻²⁰ X-ray diffraction (XRD) and Mössbauer spectroscopy have been pivotal in elucidating the FT activity to these Fe-carbide phases.²¹⁻²⁵ Among these, Hägg iron carbide (χ -Fe₅C₂) has been identified as a primary active phases for CO activation and chain growth in FT synthesis.^{16, 24, 26}

Promoters can improve the performance of Fe-based catalysts: they can increase the CO conversion rate, decrease the formation of undesired CH₄ or increase the formation of valuable long-chain hydrocarbons.^{27, 28} Promoters such as Zn, Cu, S and alkali metals increase the CO conversion rate and the selectivity to lower olefins.²⁹⁻³⁴ Among these, K is often used as it is effective in enhancing the chain-growth probability of Fe-carbide catalysts. Another role of K is to promote the WGS reaction, which is often crucial when synthesis gas with low H₂/CO ratios needs to be converted.¹³⁻¹⁵ Moreover, K also helps in Fe carburization.^{27, 35-37}

Given the critical role of K in commercial catalyst formulation, the state and mechanistic role of K in Fe-catalyst FT synthesis has been widely investigated. Amoyal et al. found that K renders χ -Fe₅C₂ more resistant against oxidation, which was their explanation for the higher CO conversion.³⁷ Zhao et al. showed that K increases the rate of Fe carburization by facilitating CO dissociation.³⁸ An increased rate of Fe carburization by K was also among the conclusions in the

work of Cheng et al.,²⁷ who identified a linear relationship between the Hägg carbide content and the basicity as a result of increasing K loading. Ma et al. reported that K enhances both the rate of FT synthesis and the WGS reaction.³⁹ At an optimum K loading, the formation of CH₄ and CH₃OH is suppressed, favoring the formation of heavy hydrocarbons. Yang et al. reported that the optimal K loading of 0.7 wt.% resulted in the highest activity for both Fischer–Tropsch synthesis (FTS) and the water-gas shift (WGS) reaction, along with the minimal oxygenate formation.³⁵ Most theoretical investigations focused on the effect of K on adsorption energies, with only a few studies reporting decreased barriers for CO dissociation and lower CH₄ formation barriers due to K. Petersen et al. reported that K increased CO and O adsorption energies on Hägg carbide (χ -Fe₅C₂).⁴⁰ Zhao et al. also found K lowers the CO dissociation barrier on the Hägg carbide.⁴¹ Sorescu mentioned that enhanced CO activation is due to interactions between the K promoter and the O atom of adsorbed CO in the transition state for C-O bond dissociation.⁴² Jiao et al. studied the impact of K₂O on CH₄ formation on the (111), (100) and (110) surfaces of χ -Fe₅C₂. Despite these insights, the nature of K species under FT conditions and their mechanistic role in promoting chain growth reactions on Fe-carbide surfaces has not been resolved yet.

Here, we adopted a theoretical approach, DFT in conjunction with microkinetics simulations, to study the impact of K in the FT synthesis reaction on χ -Fe₅C₂. The stable (010) surface of χ -Fe₅C₂ is used for these simulations, due to its high activity toward CO dissociation.⁴³ The reaction mechanism considered included synthesis CO dissociation via direct and H-assisted pathways, O removal via H₂O and CO₂, CH₄ formation and chain-growth reactions to obtain olefins and paraffins. We first established that K₂O is the most stable form of the K promoter on the (010) surface. K₂O promotes the Fe-catalyzed FT synthesis by pre-activating the surface through electron injection, stabilizing the adsorption of key species (CO, H, C, CH), and enhancing C-O bond dissociation in CO and its intermediates. It suppresses CH₄ formation by inhibiting CH_x hydrogenation and increases C₅⁺ selectivity. This shift is driven by both the increased CO conversion and the suppression of hydrogenation for chain termination of C_n intermediates. While K₂O generally increases the barriers for C₂ and C₃ formation and hydrogenation, the dominant pathways for chain growth and polymerization remain unchanged. The insights gained in this study are key towards fundamentally understanding the role of promoters in FT synthesis, potentially leading to the efficient catalyst formulations relevant to syngas conversion derived from more exotic feedstocks such as biomass and plastics.

4.2 Computational Methods

4.2.1 Density Functional Theory Settings

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP), wherein the effective ion cores are described by projector-augmented wave (PAW) potentials.⁴⁴⁻⁴⁶ The exchange and correlation energies were computed by the Perdew-Burke-Ernzerhof (PBE) functional.⁴⁷ Dispersion corrections were implemented using the PBE+D3 method.⁴⁸ The cut-off energy of the plane wave basis was set to 400 eV. Geometry optimization was conducted using the conjugate gradient method with a force-based stopping criterion of 0.02 eV/Å for each cartesian direction and for each atom. The climbing-image nudged elastic band method (CI-NEB) was used to identify transition states.^{49, 50} A frequency analysis was performed to evaluate the nature of the extrema on the potential energy surface and to verify stable and first-order transition states. On the basis of the frequency analysis, zero-point energy corrections were applied to all states. The Brillouin zone was sampled using a 1×1×1 Monkhorst-Pack grid (Γ-point only). For the slab model, a vacuum layer of 15 Å was introduced in order to avoid spurious interactions between neighbouring slabs. During geometry optimization, the bottom two layers were frozen, while all other atoms were allowed to relax.

Crystal Orbital Hamilton Population (COHP) and Density of States (DOS) analyses were performed using the Lobster software (version 4.1.0).^{51, 52} DDEC6 charge analysis was carried out using the Chargemol program (version 3.5).^{53, 54} Electronic density difference between slab, adsorbate and adsorbate-on-slab configurations were constructed using the VTST set of electronic tools (version 5.4).⁵⁴ Electronic structure analysis using electron density differences was performed by projecting the three-dimensional scalar fields onto two-dimensional planes. Analysis and visualization of the electron density are conducted using the EDP program (version 2.0.3).⁵⁵

4.2.2 Microkinetic Modelling

Based on the energetics of the elementary reaction steps, a microkinetic model was constructed to investigate the kinetics of CO activation and hydrogenation using the MKMCXX software suite.⁵⁶ The set of elementary reaction steps in the microkinetic model is composed of a coupled set of ordinary differential equations (ODE). Time-integration of the differential equations was conducted using the backward differentiation formula (BDF)^{57, 58} method until a steady-state solution was achieved.⁵⁹

For each elementary reaction step, as expressed as



a corresponding rate expression, i.e. an ordinary differential equation in time, can be constructed as follows by

$$r_A = - \frac{d[A]}{dt} = v_a (k^+ [A]^{v_a} [B]^{v_b} - k^- [C]^{v_c} [D]^{v_d}), \quad (4.2)$$

where v_a is the stoichiometric coefficient of the component x and $k^{+/-}$ is the rate constant for the forward and backward reaction. The ODEs are time-integrated until steady state is reached using a relative and absolute tolerance of 10^{-8} . For the initial condition, we set $\theta_* = 1$ corresponding to an empty catalytic surface.

In the adsorption process, the net absorption rate of gas-phase species i is calculated by

$$r_i = k_{i,\text{ads}} \theta_* p_i - k_{i,\text{des}} \theta_i \quad (4.3)$$

where θ^* and θ_i are the fraction of free sites and fractional coverage of species i , respectively. $k_{i,\text{ads/des}}$ corresponds to the rate constant for the adsorption/desorption process and p_i is the partial pressure of species i .

For the description of adsorption/desorption steps, each adsorbate is assumed to lose one translational degree of freedom in the transition state with respect to the initial gas-phase state. Under this assumption, the rate constant of adsorption and desorption is given by

$$k_{\text{ads}} = \frac{p A_{\text{st}}}{\sqrt{2\pi m_i k_B T}}, \quad (4.4)$$

where $k_{i,\text{ads}}$ is the rate constant for adsorption of the adsorbate, p the partial pressure, A_{st} the effective surface area for adsorption, m_i the molar mass of the gas species, k_B the Boltzmann constant and T is the temperature.

The gas-phase entropy of the adsorbates is calculated by the thermochemical Shomate equation as shown in Equation 5.

$$S^0 = A \cdot \ln(T) + B \cdot T \frac{C \cdot T^2}{2} + \frac{D \cdot T^3}{3} - \frac{E}{2 \cdot T^2} + G \quad (4.5)$$

In this equation, S^0 is the standard molar entropy⁶⁰ and A-G refer to the thermochemical parameters as obtained from the NIST Chemistry Webbook.⁶¹

For the desorption, the rate constant k_{des} is given by

$$k_{\text{des}} = \frac{pA_{\text{st}}}{\sqrt{2\pi m_i k_B T}} \cdot \exp\left(-\frac{\Delta H_{\text{ads}}}{RT}\right) \cdot \exp\left(\frac{S_{\text{gas}}}{R}\right) \cdot \frac{1}{q_{\text{vib,ads}}}, \quad (4.6)$$

where ΔH_{ads} and R are the desorption energy and gas constant, respectively. S_{gas} is the entropy of gaseous product, derived from Equation (5). The term of $q_{\text{vib,ads}}$ refers to the vibrational partition functions of adsorbed products, introduced as not all entropy of the molecule is lost upon adsorption process.

For an elementary reaction step over the catalytic surface, the rate constant (k) is calculated from the Eyring equation as given by

$$k = \nu \cdot \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) \quad (4.7)$$

Herein, ΔE_{act} is the electronic activation energy including the ZPE-correction and ν is the pre-exponential factor. The pre-exponential factors are evaluated for the forward and backward reaction using the following equations

$$\nu_{\text{forward}} = \frac{k_B T}{h} \left(\frac{q_{\text{vib}}^{TS}}{q_{\text{vib}}^{IS}} \right) \quad (4.8)$$

$$\nu_{\text{backward}} = \frac{k_B T}{h} \left(\frac{q_{\text{vib}}^{TS}}{q_{\text{vib}}^{FS}} \right) \quad (4.9)$$

where q_{vib} pertains to the vibrational partition functions of the activated complex and the corresponding reactants/products. For surface reactions, we only considered vibrational contributions which are calculated from the frequency calculations.

To evaluate the chain-growth probability (α), which is defined as the ratio between the rates of chain propagation (r_p) over the sum of the rate of chain propagation and termination (r_t), the chain-growth probability (α) is determined by the slope of Anderson-Schulz-Flory (ASF) distribution for carbon numbers (n) 5 to 15.

The chain-growth probability (α) is determined, assuming an ASF distribution, by means of a linear fit via Equation (10).⁶²

$$\alpha = \frac{r_p}{r_p + r_t} \cong \exp\left(\frac{\partial \ln F_{C_n}^{\text{out}}}{\partial n}\right) \quad (4.10)$$

In this equation, r_p and r_t are the rates for chain-propagation and -termination, n the number of monomers in the hydrocarbon chain and $F_{C_n}^{out}$ the molar rate of production of a chain with length n .

To identify the contribution of each reaction step to the overall rate and product distribution, we used the concepts of the degree of rate control (DRC) as proposed by Campbell⁶³ as well as the degree of selectivity control (DSC).⁶³⁻⁶⁵

For each elementary reaction step, a DRC coefficient is assigned as given by

$$X_{RC,i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (4.11)$$

which at zero conversion and under steady-state obeys the following sum-rule

$$\sum X_{RC,i} = 1 \quad (4.12)$$

In the above equations, $X_{RC,i}$ corresponds to the DRC coefficient, K_i is the equilibrium constant, k_i is the reaction rate constant and r corresponds to the overall reaction rate.

The DSC is used to measure the influence of a particular elementary reaction steps on the selectivity of the overall reaction. The DSC of a key component (product) c is given by

$$X_{SC,i,c/r} = \left(\frac{\partial \ln \eta_{c/r}}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (4.13)$$

where $X_{SC,i,c/r}$ corresponds to the DSC of the product c with respect to reactant r due to a change in the barrier height of elementary reaction step i , and $\eta_{c/r}$ being the selectivity towards product c with respect to reactant r . The relationship between DRC and DSC coefficients is given by

$$X_{SC,i,c} = \eta_{c/r} (X_{c,i} - X_{r,i}). \quad (4.14)$$

To evaluate the impact of individual elementary reaction steps on the chain-growth probability, we also used the concept of the degree of chain-growth control (DCGC),⁶⁶ which is calculated via

$$DCGC^i = \left(\frac{\partial \alpha}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (4.15)$$

4.3 Results and Discussion

4.3.1 Surface Models

The monoclinic unit cell (space group C2/c) relevant to bulk χ -Fe₅C₂ was first optimized. The computed lattice parameters of $11.53 \text{ \AA} \times 4.50 \text{ \AA} \times 4.95 \text{ \AA}$ and angles of $\beta = 97.75^\circ$ ($\alpha = \gamma = 90^\circ$) are in good agreement with the experimental values for Hägg carbide ($a = 11.588 \text{ \AA}$, $b = 4.579 \text{ \AA}$, $c = 5.059 \text{ \AA}$, and $\beta = 97.75^\circ$).⁶⁷ The optimized unit cell is shown in the Supporting Information (Figure A1). As a model system in this study, we used the (010) surface termination, as this surface is stable and the CO dissociation exhibits one of the lowest CO dissociation barriers.⁴³ The (010) surface layer was terminated at a relative height of $z = 0.25$ with respect to the optimized bulk χ -Fe₅C₂ unit cell. This slab model contains 40 Fe atoms and 16 C atoms and has dimensions of $9.98 \text{ \AA} \times 11.53 \text{ \AA} \times 18.93 \text{ \AA}$. A schematic depiction of the model system is shown in Figure 4.1.

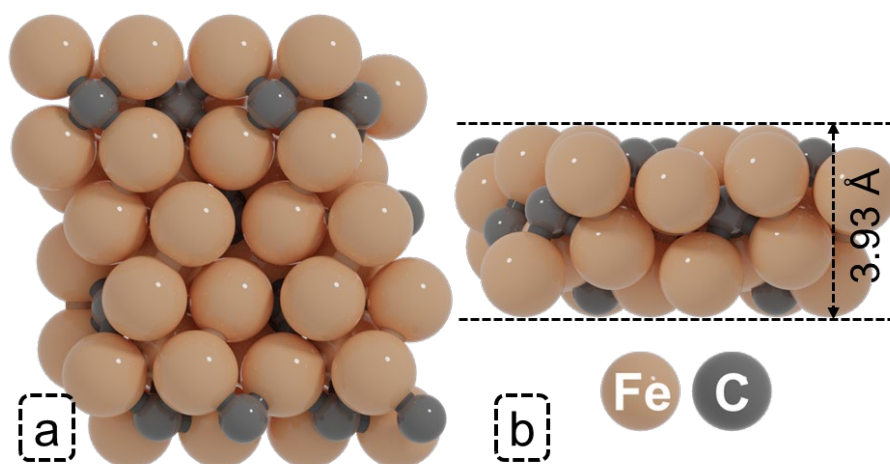


Figure 4.1. Top and side view of χ -Fe₅C₂(010) surface. The dotted lines correspond to the top and bottom edges of the periodic supercell.

To understand the effect of K promotion in χ -Fe₅C₂-catalyzed Fischer-Tropsch synthesis, we first investigated the thermodynamically most stable state of the K promotor, *i.e.*, its preferred oxidation state, its coordination to the surface and the stability of the oxygen atom bonded to K. Based on the known valence states of K and O, it is reasonable that K resides on the catalytic surface in the form of K₂O. To investigate the stability of this complex, we calculated the energetics of K-O bond scission *via* the formation of CO₂ from CO and H₂O from H₂ on the (010) surface. The potential energy diagrams of these processes are shown in Figure B1. The conversion of K₂O to K is associated with very high barriers. Thus, the most stable configuration of adsorbed K is as K₂O, in good agreement with previous studies.^{37, 68-70}

The χ -Fe₅C₂(010) surface termination offers various locations for K₂O adsorption. Figure B2 depicts the considered adsorption configurations and the corresponding adsorption energies. Among these, K₂O adsorbed on a semi-fourfold site corresponds to the most stable configuration with an adsorption energy of -613 kJ/mol with respect to gaseous K₂O (Figure 4.2a). To understand how K₂O promotion affects the electron density distribution of the surface, a Bader charge analysis highlights the charges on the surfaces before and after K₂O adsorption on the (010) surface (Figure 4.2b-d). For the surface without the promoter, Fe has a slightly positive charge, while C carries a slight excess of negative charge, in line with their difference in electronegativity. The Fe atoms directly in contact with lattice C show a higher (less negative) charge in comparison to the Fe atoms further distanced from C. Upon K₂O adsorption, we observe that the Fe atoms to which O is bonded increase in charge. In contrast, the Fe atoms in the vicinity of K decrease in charge, *i.e.*, they become more negatively charged.

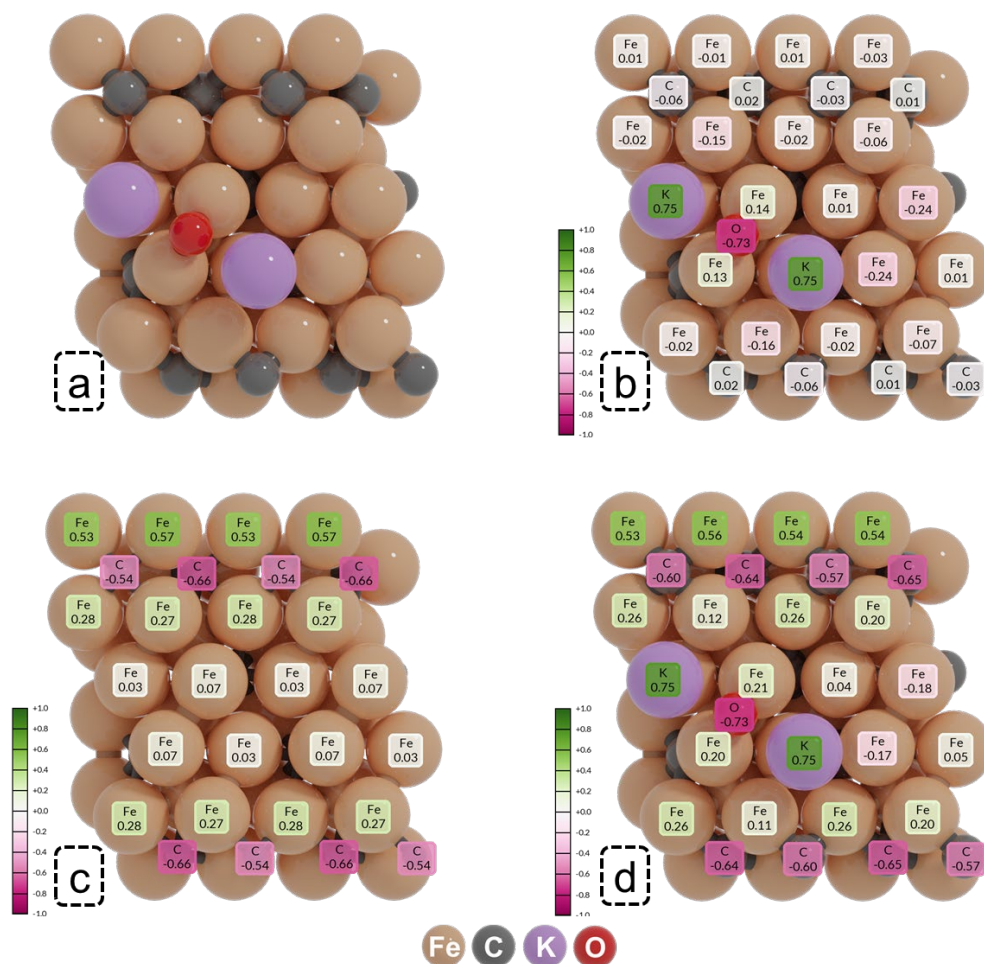


Figure 4.2. (a) Structure of K₂O-promoted (010) surface of χ -Fe₅C₂. (b) Charge difference of surface Fe atoms on the (010) surface upon K₂O adsorption (negative values indicate increased electron density compared to the promoter-free (010) surface). Charge on the surface Fe atoms on the (c) (010) and (d) K₂O-promoted (010) surfaces of χ -Fe₅C₂.

4.3.2 Adsorption of Reaction Intermediates

The adsorption energy of the reactants and the stability of the reaction intermediates critically determine the surface composition under reaction conditions and, by extent, the reaction rate. As such, we investigate how K₂O promotion influences the adsorption energy and stability of intermediates relevant to the FT synthesis reaction. We compare the adsorption energy of CO, H, C, CH, CH₂ and CH₃ adsorption for the (010) and K₂O-promoted (010) surface terminations. The most stable geometries of the surface intermediates and the corresponding adsorption energies with respect to the gas phase are shown in Figure 4.3. We first consider the adsorption of CO and H₂. For both surfaces, CO preferentially adsorbs on a 4-fold site, wherein the C atom of CO binds to 4 Fe atoms. In the presence of K₂O, the CO adsorption energy is significantly increased to -256 kJ/mol from -204 kJ/mol. Molecular H₂ readily dissociates over the unpromoted and K₂O-promoted surfaces upon adsorption. The dissociated H* fragment preferentially adsorbs on a threefold site with an adsorption energy of -72 kJ/mol on the unpromoted surface and -73 kJ/mol for the K₂O-promoted surface.

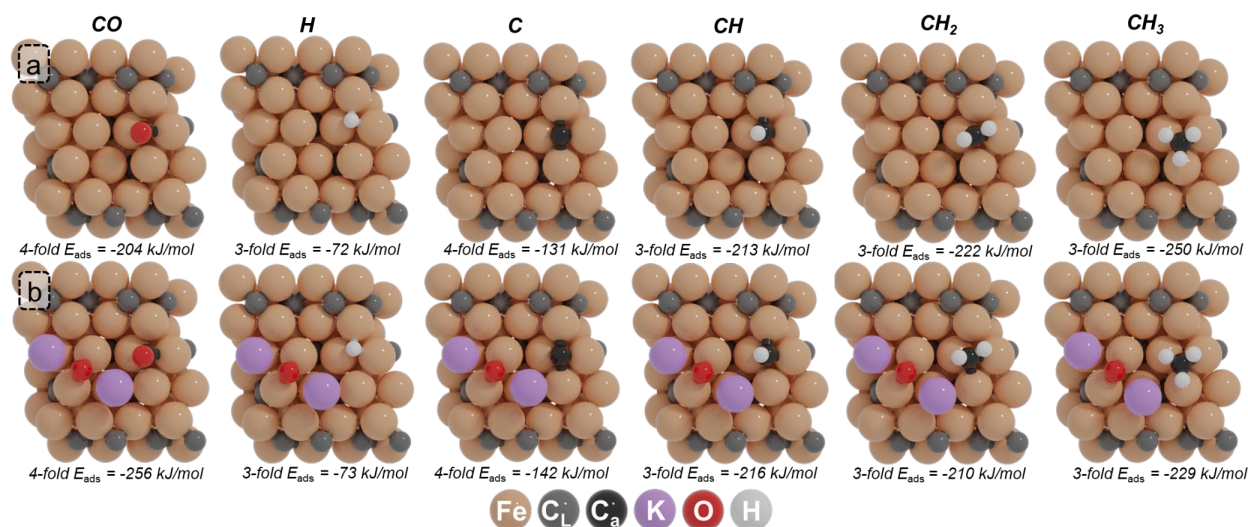


Figure 4.3. ZPE-corrected adsorption energies of CO, C, CH, CH₂, CH₃ and H on the (a) (010) and (b) K₂O-promoted (010) surfaces of χ -Fe₅C₂.

Next, we consider the carbon-containing reaction intermediates C, CH, CH₂ and CH₃. Similar to CO, the C, CH, CH₂ and CH₃ fragments prefer to reside in the semi-fourfold site. The adsorption energies of these surface intermediates were references to gaseous CO, H₂, and H₂O. For instance, the adsorption energy of CH₂ is calculated via the chemical reaction of $\text{CO} + \frac{3}{2}\text{H}_2 + * \rightleftharpoons \text{CH}^* + \text{H}_2\text{O}$. The relevant equations can be found in the supporting information (equations Appendix B. E1-4). This approach allows comparing the stability of various intermediates and the impact of K₂O on these stabilities. The adsorption energies of C, CH, CH₂ and CH₃ on the unpromoted

surface are -131, -213, -222 and -250 kJ/mol, respectively. Upon K promotion, the adsorption energies of C and CH become more exothermic, i.e., -142 and -216 kJ/mol, respectively, whereas a decrease in the CH₂ and CH₃ adsorption energies to -210 and -229 kJ/mol, respectively, is noted. Overall, however, the changes are minor. While the presence of K₂O facilitates favorable charge injection into the surface (Figure 4.2), stabilizing slightly C and CH, this advantage is countered by stronger steric repulsion between K₂O and CH₂ and CH₃, leading to their decreased stability.

4.3.3 CO Activation

4.3.3.1 CO Activation Pathways

The activation of adsorbed CO is a crucial step and often found to be rate-limiting in the overall FT synthesis reaction. CO dissociation can proceed either in a direct manner or assisted by hydrogen wherein first the C or O atom of adsorbed CO is hydrogenated before C-O bond scission takes place.⁷¹ Figure 4.4 shows the reaction energy diagrams corresponding to these pathways for the unpromoted and promoted surfaces. The corresponding forward and backward barriers for the involved elementary reaction steps are provided in Table 4.1. The geometries of the initial, transition and final states are presented in Figures B3 and B4.

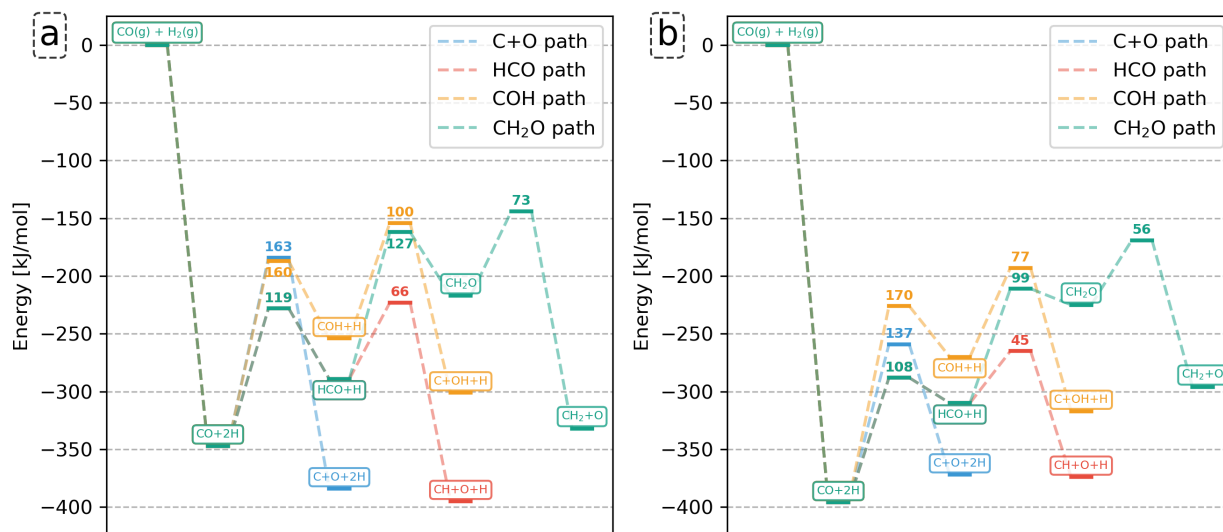


Figure 4.4. Reaction energy diagrams of the direct and H-assisted dissociation of CO starting from co-adsorbed H and CO on the (a) (010) and (b) K₂O-promoted (010) surfaces of χ -Fe₅C₂ (indicated values are ZPE-corrected barriers).

Table 4.1. Forward reaction barrier (E_f) and backward reaction barrier (E_b) of CO dissociation on (010) and K₂O-(010) surfaces of χ -Fe₅C₂, along with the energy difference in the forward reaction barrier (ΔE_f) between these surfaces.

Elementary steps	(010)		K ₂ O-(010)		ΔE_f
	E_f	E_b	E_f	E_b	
CO* + * $\rightarrow$ C* + O*	163	200	137	113	-26
CO* + H* $\rightarrow$ HCO* + *	119	61	108	22	-11
CO* + H* $\rightarrow$ COH* + *	160	67	170	44	10
HCO* + * $\rightarrow$ CH* + O*	66	172	45	110	-21
COH* + * $\rightarrow$ C* + OH*	100	148	77	124	-23
HCO* + H* $\rightarrow$ CH ₂ O* + *	127	49	99	15	-28
CH ₂ O* + * $\rightarrow$ CH ₂ * + O*	73	188	56	127	-17

Figure 4.4a and Table 4.1 show that the H-assisted CO dissociation pathway, involving the HCO surface intermediate, is energetically favored on the unpromoted surface, exhibiting the lowest overall barrier of 124 kJ/mol. The direct CO dissociation and COH pathways involve substantially higher overall barriers of 163 and 193 kJ/mol, respectively. Furthermore, CH₂O formation via further hydrogenation of HCO is unfavorable: its barrier of 127 kJ/mol is much higher than the barrier of HCO dissociation (66 kJ/mol).

The effect of K₂O on these elementary reaction steps is shown in Figure 4.4b and Table 4.1. The numerical data in Table 4.1 show that K₂O has a promoting effect on nearly all steps related to CO dissociation, except the formation of COH. The direct CO dissociation barrier is lowered by 26 kJ/mol by the presence of K₂O. The barriers of the formation and dissociation for HCO are decreased by 11 and 21 kJ/mol, respectively. K₂O also reduces the barrier for CH₂O formation and dissociation by 28 and 17 kJ/mol, respectively. Although the barrier of COH formation is increased in the presence of K₂O (170 kJ/mol versus 161 kJ/mol without K₂O), the subsequent barrier to cleave COH into C and OH is reduced by 23 kJ/mol. K₂O promotion affects the preferred CO dissociation pathways. K₂O decreases the overall barrier of direct CO dissociation from 164 kJ/mol to 137 kJ/mol, while the overall barrier for the HCO pathway increases slightly from 124 kJ/mol to 131 kJ/mol. Thus, while the HCO pathway is preferred on the non-promoted surface, the addition of K₂O results in competition between the HCO pathway and direct CO dissociation. The COH pathway is the least favorable mode of CO dissociation, irrespective of the presence of K₂O. Another important consequence of K₂O promotion is that HCO formation becomes more endothermic ($\Delta E_{R,CO+H \rightarrow HCO}^{unpromoted} = 58$ kJ/mol vs. $\Delta E_{R,CO+H \rightarrow HCO}^{promoted} = 86$ kJ/mol), whereas direct CO dissociation changes from being an exothermic reaction ($\Delta E_{R,CO \rightarrow C+O}^{unpromoted} = -37$ kJ/mol) to an endothermic one ($\Delta E_{R,CO \rightarrow C+O}^{promoted} = +24$ kJ/mol). As will be shown in microkinetic simulations (*vide infra*), this changes the CO hydrogenation pathway.

4.3.3.2 O Removal

The removal of O atoms derived from C-O bond scission proceeds by the production of H₂O or CO₂. The first step in H₂O formation is O* hydrogenation to OH*. H₂O can then be produced by direct OH* hydrogenation (OH* + H* → H₂O* + *) and by OH disproportionation (OH* + OH* → H₂O* + O*). We investigated the impact of K₂O on both H₂O formation pathways on the (010) surface. The results are shown as reaction energy diagrams in Figure 4.5. The corresponding geometries are provided in Figure B5, while the forward and backward barriers are listed in Table B1.

On the unpromoted surface, O* hydrogenation to form OH* has a barrier of 143 kJ/mol and is endothermic by 83 kJ/mol. Further hydrogenation to H₂O* has a barrier of 154 kJ/mol. Alternatively, a second OH* can be involved in the disproportionation of OH*, resulting in the formation of H₂O* and O*. This OH* disproportionation step has a barrier of only 44 kJ/mol and is more favorable in comparison to direct hydrogenation of OH* (154 kJ/mol). Figure 4.5 shows that the presence of K₂O results in a decrease of the O* hydrogenation barrier from 143 kJ/mol to 113 kJ/mol. Furthermore, the reaction becomes less endothermic in the presence of K₂O. Direct OH* hydrogenation to H₂O* remains difficult with a barrier of 161 kJ/mol. OH* disproportionation only involves a barrier of 49 kJ/mol on the promoted surface. Irrespective of the presence of K₂O, it is expected that H₂O formation via OH* disproportionation remains a favorable pathway noting that K₂O promotes this pathway slightly.

We also considered CO₂ formation as a pathway for O removal. This reaction involves much higher barriers of 151 kJ/mol and 146 kJ/mol on the unpromoted and promoted surfaces, respectively, than the H₂O formation pathways (143 and 113 kJ/mol, respectively). This implies that H₂O formation is likely preferred over CO₂ formation.

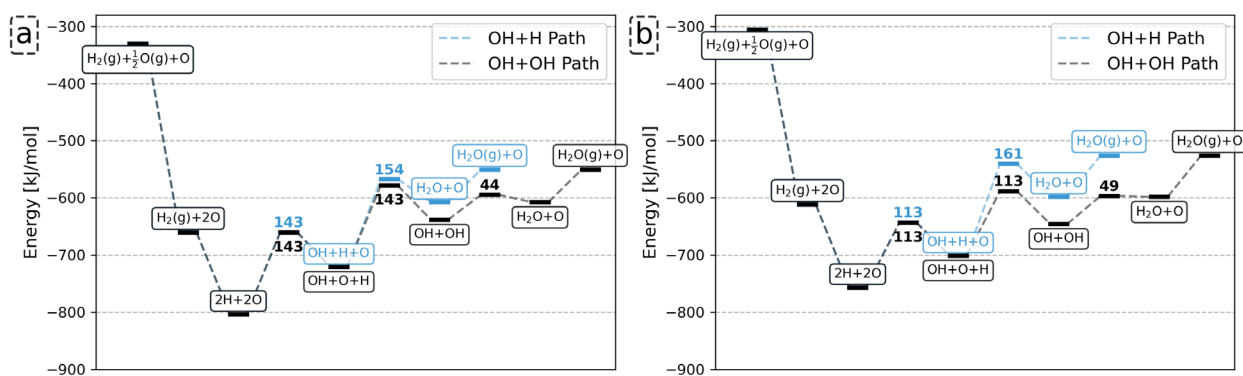


Figure 4.5. Reaction energy diagram of H₂O formation via OH hydrogenation and disproportionation pathways on the (a) (010) and (b) K₂O-promoted (010) surfaces of χ -Fe₅C₂.

4.3.4 CH₄ Formation

CH₄ is a significant but undesirable byproduct of the FT synthesis process. It has been experimentally established that CH₄ not only derives from C atoms obtained by dissociation of adsorbed CO but also from lattice C species.⁷² We therefore examined the impact of K₂O on both of these pathways for the (010) surface. Figure 4.6 shows the reaction energy diagrams. The corresponding transition state structures can be found in Figures B6 and B7. The forward and backward barriers are listed in Table B1.

The data for the hydrogenation of lattice C are shown in Figure 4.6a. For the unpromoted surface, hydrogenation reactions of lattice C, CH, CH₂ and CH₃ have barriers of 106, 99, 74 and 93 kJ/mol, respectively. K₂O increases the respective hydrogenation barriers to 121, 116, 80 and 93 kJ/mol. This increase is mainly caused by the stronger adsorption of H on the K₂O-promoted surface (72 kJ/mol vs. 62 kJ/mol for the unpromoted surface). Figure 4.6b depicts the reaction energy diagrams for CH₄ formation from adsorbed C. As shown earlier, C-O bond scission via HCO is preferred from the kinetic point of view on both surfaces, irrespective of the presence of K₂O. The stability of CH between the unpromoted surface is nearly the same as the promoted surface. Hydrogenation of CH to CH₂ is endothermic with barriers of 70 and 81 kJ/mol for the unpromoted and promoted surfaces, respectively. Subsequent hydrogenation steps to form CH₃ and CH₄ are also endothermic. Like CH hydrogenation, the barriers for CH_x ($x = 2, 3$) hydrogenation are slightly higher for the promoted surface. Thus, K₂O has a slightly inhibiting effect on CH₄ formation.

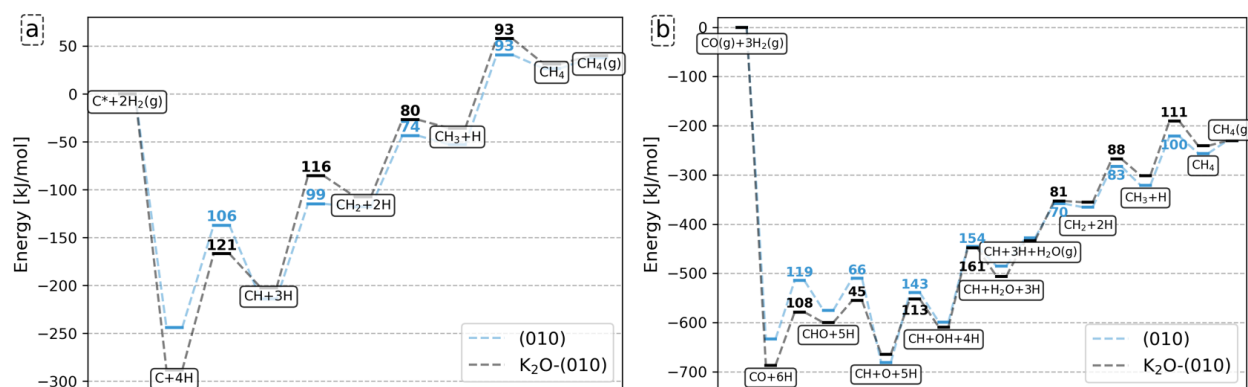


Figure 4.6. Reaction energy diagram of CH₄ formation of (a) lattice C and (b) adsorbed C on the (010) and K₂O-promoted (010) surfaces of χ -Fe₅C₂.

4.3.5 Hydrocarbon Chain Growth

4.3.5.1 C₂ Hydrocarbon Formation

We determined the impact of K₂O on the energetics of CH_x + CH_y coupling reactions and the hydrogenation of resulting C_xH_y intermediates to ethylene and ethane formation. The computed

energetics are shown in Figures 4.7 and 4.8. The corresponding transition states and reaction energy diagrams are given in Figures B8 - B15 and Table B1.

The CH_x+CH_y coupling steps occur at the 4-fold site of the unpromoted surface where also CO dissociation takes place. Figure 4.7a shows that CH + CH coupling has the lowest barrier (66 kJ/mol), followed by C + CH coupling (80 kJ/mol), CH₂ + CH₂ coupling (82 kJ/mol), C + CH₂ coupling (103 kJ/mol) and CH + CH₂ coupling (105 kJ/mol). As the C and CH species are more stable than CH₂ and CH₃, it is likely that C + CH and CH + CH reactions are most relevant to chain growth. This interpretation is consistent with the preferred reaction routes proposed for the (510) surface of χ -Fe₅C₂ by Pham et al.¹⁷ and Liu et al.⁷³ The formation of ethylene and ethane proceeds through a series of endothermic hydrogenation steps. The reaction energy diagrams show that the pathway with the lowest overall barrier goes through CHCH, followed by hydrogenation to CHCH₂ and CH₂CH₂. The further hydrogenation of ethylene to ethane exhibits relatively high overall barriers (>150 kJ/mol), suggesting that ethane formation is not favourable on this surface.

Figure 4.7b shows the corresponding data for the K₂O-promoted surface. Similar to the unpromoted surface, CH_x + CH_y coupling occurs on the 4-fold site, albeit that the barriers are higher by ~10 – 30 kJ/mol. The hydrogenation barriers of C₂ intermediates are also higher than the corresponding ones on the unpromoted surface, except for CCH + H → CHCH and CCH + H → CCH₂. The overall barrier for ethylene hydrogenation to ethane is substantially increased, implying that ethane formation is even more difficult for the promoted surface. The increase in hydrogenation barriers is due to the stabilization of CH_x and H species by K₂O. The most favourable pathway for C-C coupling and hydrogenation is CHCH to CHCH₂ to CH₂CH₂. Although the pathway is unaffected by K₂O, the overall barrier for ethylene formation increases from 196 kJ/mol for the unpromoted surface to 206 kJ/mol for the promoted one.

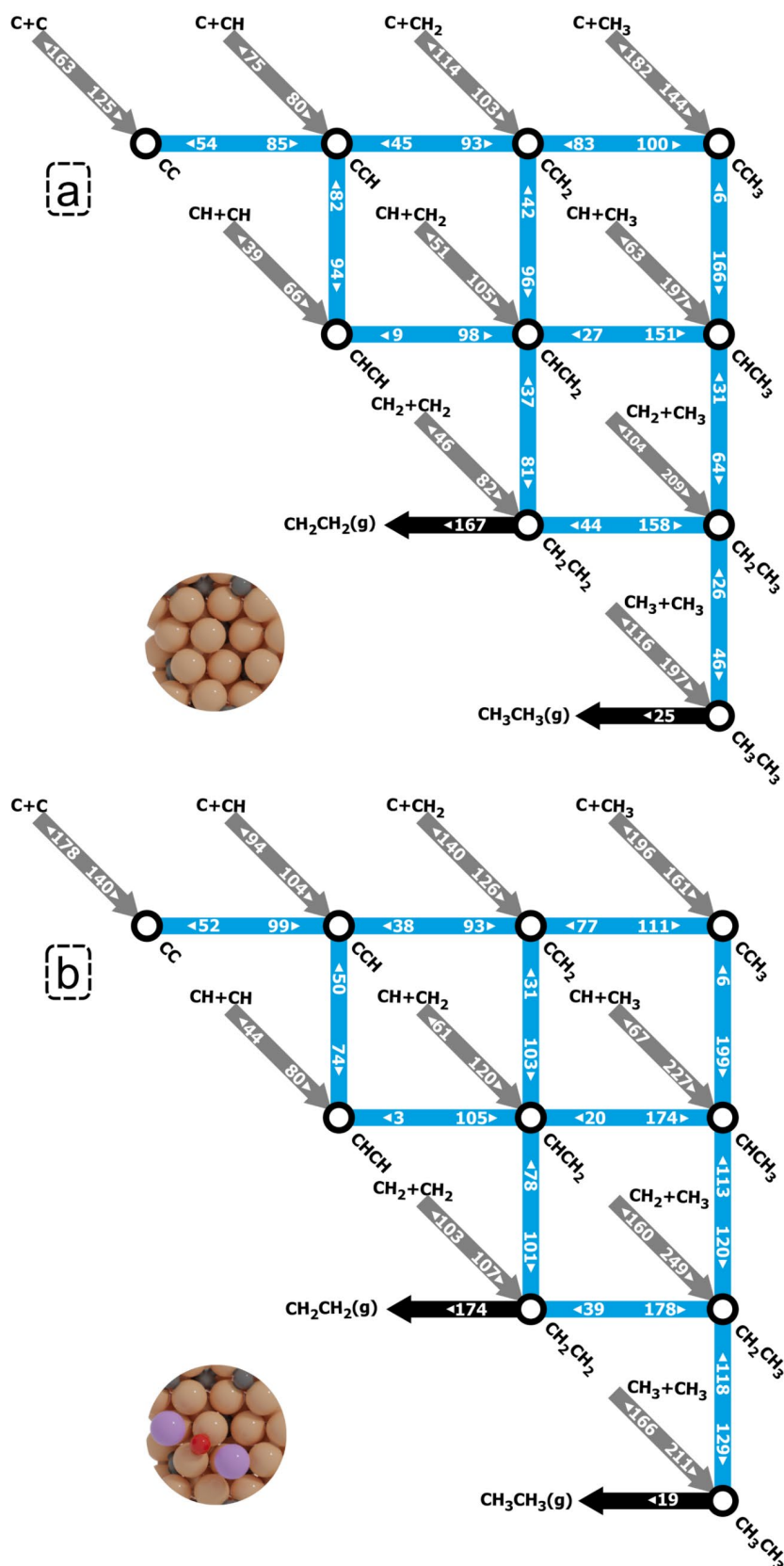


Figure 4.7. Reaction network for C₂ hydrocarbon formation on the (a) (010) and (b) K₂O-promoted (010) surfaces of χ -Fe₅C₂ (energies in kJ/mol; colors: grey - C-C coupling pathways, blue - hydrogenation pathways, black - C₂ product desorption).

4.3.5.2 C₃ Hydrocarbon Formation

To properly describe chain growth, it is necessary to include C₃ hydrocarbon formation when modeling the FT synthesis reaction.⁷⁴⁻⁷⁶ For chain growth beyond 3 carbon atoms, the reaction center at the terminal end is sufficiently far away from the dangling hydrocarbon chain that further coupling and hydrogenation reaction steps are not significantly affected by the length of the hydrocarbon chain.⁷⁶ Figure 4.8 shows the reaction energetics for C₃ formation at the 4-fold site for both surfaces. These C-C coupling steps for C₃ formation can be considered analogues of those for C₂ formation, by replacing a H atom in one of the reacting species for C₂ formation by a CH₃ group.

Figure 4.8a presents the energetics of C₃ formation for the unpromoted surface. The most favorable C-C coupling steps in C₂ and C₃ formation are similar. While C + CH and CH + CH reactions are preferred for C₂ formation, their C₃-analogues, i.e. C+CCH₃ and CH + CCH₃, are the most favourable pathways for C₃ formation with respective barriers of 131 and 134 kJ/mol. Although CH_x ($x = 0-3$) coupling with CHCH₃ proceeds with relatively low barriers (60, 43, 25 and 66 kJ/mol for $x = 0, 1, 2$, and 3), the formation of CHCH₃ is very difficult on both surfaces, as CH + CH₃ coupling and CCH₃ hydrogenation reactions have barriers higher than 160 kJ/mol. Thus, chain growth beyond C₂ will predominantly proceed via C+CCH₃ and CH+CCH₃ coupling. Hydrogenation reactions of the resulting C₃ intermediates exhibit slightly lower barriers than those computed for C₂ intermediates. These reactions are endothermic. Propylene formation goes through a CHCHCH₃ surface intermediate. Further hydrogenation of propylene to propane is endothermic by 123 kJ/mol and exhibits an overall barrier of 129 kJ/mol.

Figure 4.8b shows that K₂O increases the barriers of the C+CCH₃ and CH+CCH₃ coupling pathways by 17 and 18 kJ/mol, respectively. This is due to the stronger adsorption of C and CH in the vicinity of K₂O. These reactions remain the dominant coupling reactions, as CHCH₃ formation through CH + CH₃ coupling, CCH₃ hydrogenation, and CH_x ($x = 0-3$) coupling with CHCH₃ also exhibit high barriers on the promoted surface. Thus, it is likely that K₂O does not strongly affect the main coupling pathways. This also holds for the pathway to propylene, although its overall barrier increases slightly by 9 kJ/mol. The overall barrier for propane formation is increased by 70 kJ/mol compared to the unpromoted surface, indicating that K₂O further suppresses propane formation on the promoted surface.

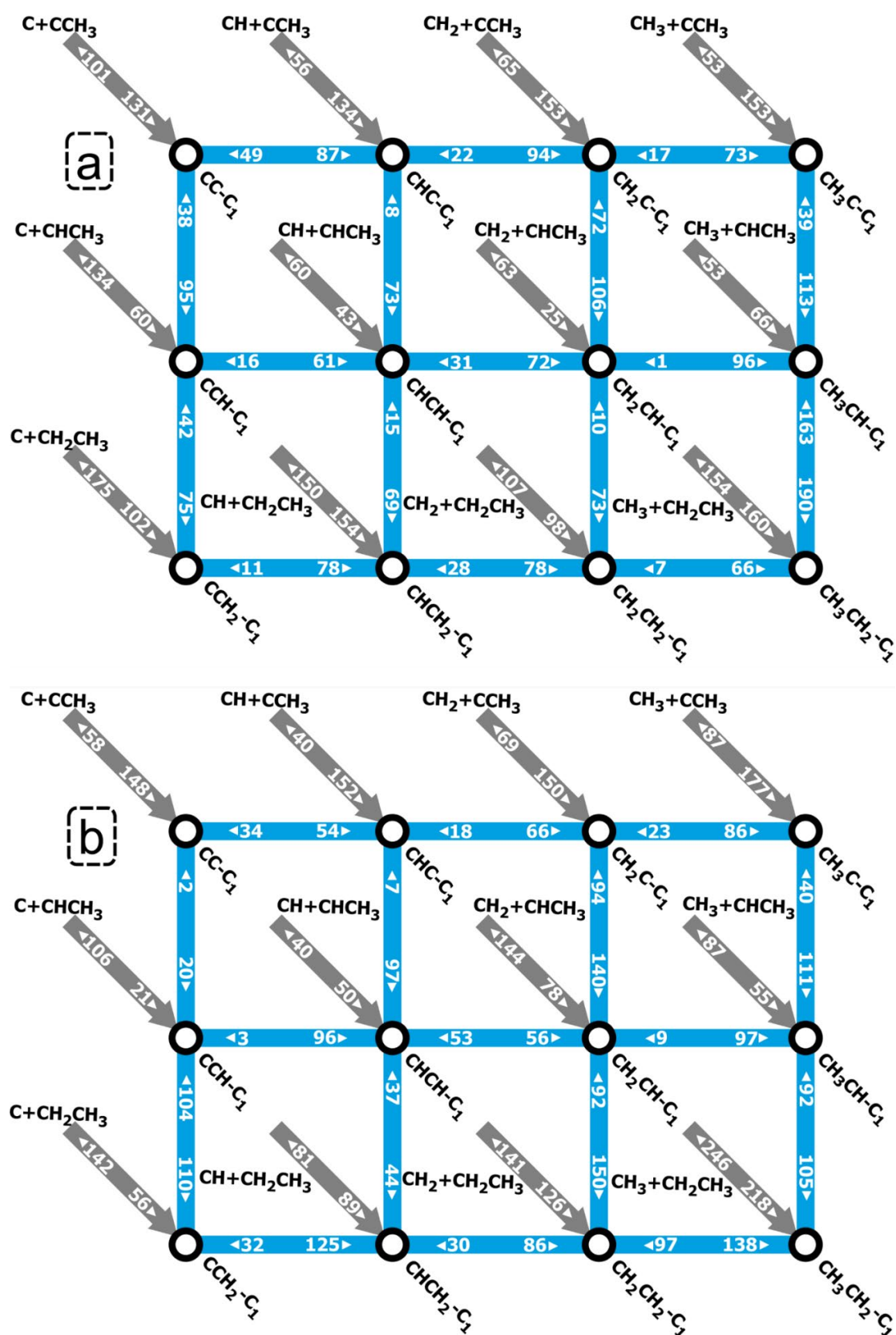


Figure 4.8. Reaction network for C₃ hydrocarbon formation on the (a) (010) and (b) K₂O-promoted (010) surfaces of χ -Fe₅C₂ (energies in kJ/mol; colors: grey - C-C coupling pathways, blue - hydrogenation pathways, black - C₂ product desorption).

4.3.6 Microkinetics Simulations

Microkinetics simulations were performed to assess the impact K₂O on χ -Fe₅C₂-catalyzed FT synthesis. We considered chains up to 15 carbon atoms, with reaction barriers for the formation of hydrocarbons with 4 or more carbons being equal to the reaction barriers for C₃ hydrocarbon formation. The kinetic parameters used in microkinetics simulations, i.e., forward reaction barriers (E_f), backward reaction barriers (E_b), and pre-exponential factors, of all elementary steps, are listed in Table B1. The simulated reaction conditions were a total pressure of 20 bar and a H₂/CO ratio of 2, which corresponds to typical experimental conditions for the FT synthesis reaction.^{77, 78} The reaction temperature was varied between 500 and 600 K. A comparison to experimental data uses predicted activity data at a temperature of 520 K, close to temperatures used in medium-temperature FT synthesis.⁷⁹

4.3.6.1 Unpromoted (010) Surface

The temperature dependence of the main reaction parameters is shown in Figure 4.9. Figure 4.9a shows the CO reaction rate and formation rates of CH₄, C₂-C₄ and C₅₊ hydrocarbons as a function of the temperature, while Figures 4.9b and 4.9c report the ASF and product distribution plots, respectively. The predicted CO turnover frequency (TOF) of $8.1 \times 10^{-4} \text{ s}^{-1}$ aligns well the experimental values of $2.6 \times 10^{-4} \text{ s}^{-1}$ for a phase-pure χ -Fe₅C₂ catalyst⁷⁹ and $3.4 \times 10^{-4} \text{ s}^{-1}$ for a graphene oxide-supported Fe-carbide catalyst.²⁷ These and other reaction parameters are compared to available experimental data in in Table S2 and S3. Notably, the predicted CO₂ selectivity is much lower (< 1%) than observed in experimental works. As outlined in the works of Wang et al.,^{25, 79} this is primarily due to the WGS reaction on Fe-oxide impurity phases, typically present in these catalysts. The hydrocarbon product distribution is in reasonable agreement with the experimental data. Experimental chain-growth probabilities are between 0.4 and 0.8.⁸⁰⁻⁸² The predicted chain-growth probability of 0.42 aligns well with the value of 0.39 reported by Torris Galvis et al.⁸³ The predicted CH₄ selectivity is below the expected value based on the chain-growth probability determined for hydrocarbons with 3 and more C atoms. This finding is similar to simulated product distributions for Ru⁵⁹ and Co⁸⁴ catalysts and has been linked to higher CH₄ formation rates on less reactive surface sites with lower C binding energies.⁸⁵ Likewise, the present simulations show a lower ethylene selectivity than expected based on the ASF plot, which is in line with experiment and has been understood in terms of a different reactivity of C₂ surface intermediates.⁸⁴ The chain-growth probability decreases with temperature, as chain termination has a higher activation energy than chain growth. Figure 4.9d reports the steady-state surface coverages for the unpromoted (010) surface. The surface contains a small amount of H species and

a significant amount of O and hydrocarbon species, mostly CH, CCH and CHCH. The surface also contains longer hydrocarbon chains, which can be hydrogenated to longer hydrocarbons. As an example, the two most abundant C₃ surface intermediates are CCCH₃ and CHCCH₃ have a much lower coverage than the C₁ and C₂ intermediates. With increasing temperature, the O coverage slightly increases, likely due to the faster removal of carbon-containing intermediates due to hydrogenation and desorption of olefinic reaction products. The decrease in CHCH* coverage goes together with a slight increase in CH* coverage. The coverage of CO is very low (<0.001), which can be explained by CO dissociation being fast relative to chain-growth reactions. The rate-controlling steps were determined using a degree of rate control (DRC) analysis (Figure 4.9e). At low temperatures, the hydrogenation of CCH₂* to CCH₃*, which is part of the overall chain-growth process, and the OH disproportionation reaction are the main rate-controlling steps. To a lesser extent, CH₃ hydrogenation to CH₄ also contributes to the rate control. CO* hydrogenation to CHO* and its dissociation to CH* and O* are mildly inhibiting the rate. Together, these data show that C-O bond dissociation is fast compared to chain growth, in line with predictions made by Filot et al.⁵⁹ While chain-growth reactions control the overall rate at typical reaction temperatures below 573 K, higher reaction temperatures lead to stronger competition with OH disproportionation, shifting the operation of this surface to the interface between chain growth- and O removal-controlled regimes.⁵⁹ The DRC coefficient for CCH₂ hydrogenation decreases with temperature, which is due to the decreasing contribution of chain growth in the overall reaction: with increasing temperature, the CH₄ selectivity increases and the chain-growth probability decreases.

The reaction orders with respect to CO and H₂ and the apparent activation energies ($E_{\text{act}}^{\text{app}}$) are presented in Figure 4.9f. The predicted CO reaction orders are negative, which agrees with experimental data.⁸⁶⁻⁸⁸ The slightly negative reaction order is consistent with the negative DRC value for CO dissociation. The H₂ reaction order is higher than 1, which is reasonable as a higher H coverage will accelerate several rate-controlling steps in the mechanism, namely CH₃ hydrogenation, CCH₂ hydrogenation and OH formation, that depend on the H coverage. The predicted apparent activation energy ($E_{\text{act}}^{\text{app}}$) of 118 kJ/mol is in the range of values experimentally reported (86-121 kJ/mol).^{30, 89}

We also analyzed the sensitivity of the results to reactions that control the CH₄ selectivity (degree of selectivity control, DSC) and the chain-growth probability (degree of chain-growth control, DCGC). The results of these analyses are shown in Figures 4.9g and 4.9h, respectively. Figure 4.9g demonstrates the dependence of CH₄ selectivity on the hydrogenation step of CH₃*. The CH₄

selectivity decreases by lowering the barriers for CCH₂ hydrogenation to CCH₃, (a key step in chain growth) and CO dissociation via CHO. The latter can be explained by the higher coverage of growth monomers, which increases the rate of chain growth compared to that of CH₄ formation. Note that higher CO coverage still suppresses the overall rate. The main result of Figure 4.9h is that lowering the barrier of H-assisted CO dissociation benefits chain growth, as indicated by the positive DCGC value of CO dissociation. On the other hand, a lower CCH₂ hydrogenation barrier decreases the chain-growth probability, while simultaneously lowering the selectivity to CH₄. To understand this aspect better, we performed an additional simulation where only the CCH₂ barrier was decreased by 5 kJ/mol. Figure B17 highlights the rate differences for all elementary steps involved in C₂-C₅ formation compared to the results based on the unchanged kinetics. The resulting higher rate of CCH₃ formation increases the CH+CCH₃ coupling rate. This leads to an increased rate of C₃ olefin formation. which can desorb from the surface, an enhanced CCH₂ hydrogenation rate favors C₃-olefin formation. Figure B18 confirms this by showing that, among the C₁-C₅ products, only the C₃ selectivity is increased, while the selectivity of the other hydrocarbons with more than 3 C atoms is decreased. This explains the decrease in the chain-growth probability.

Chapter 4. The Nature of K Promotion of χ -Fe₅C₂ for High Chain-Growth Probability in the Fischer-Tropsch Reaction

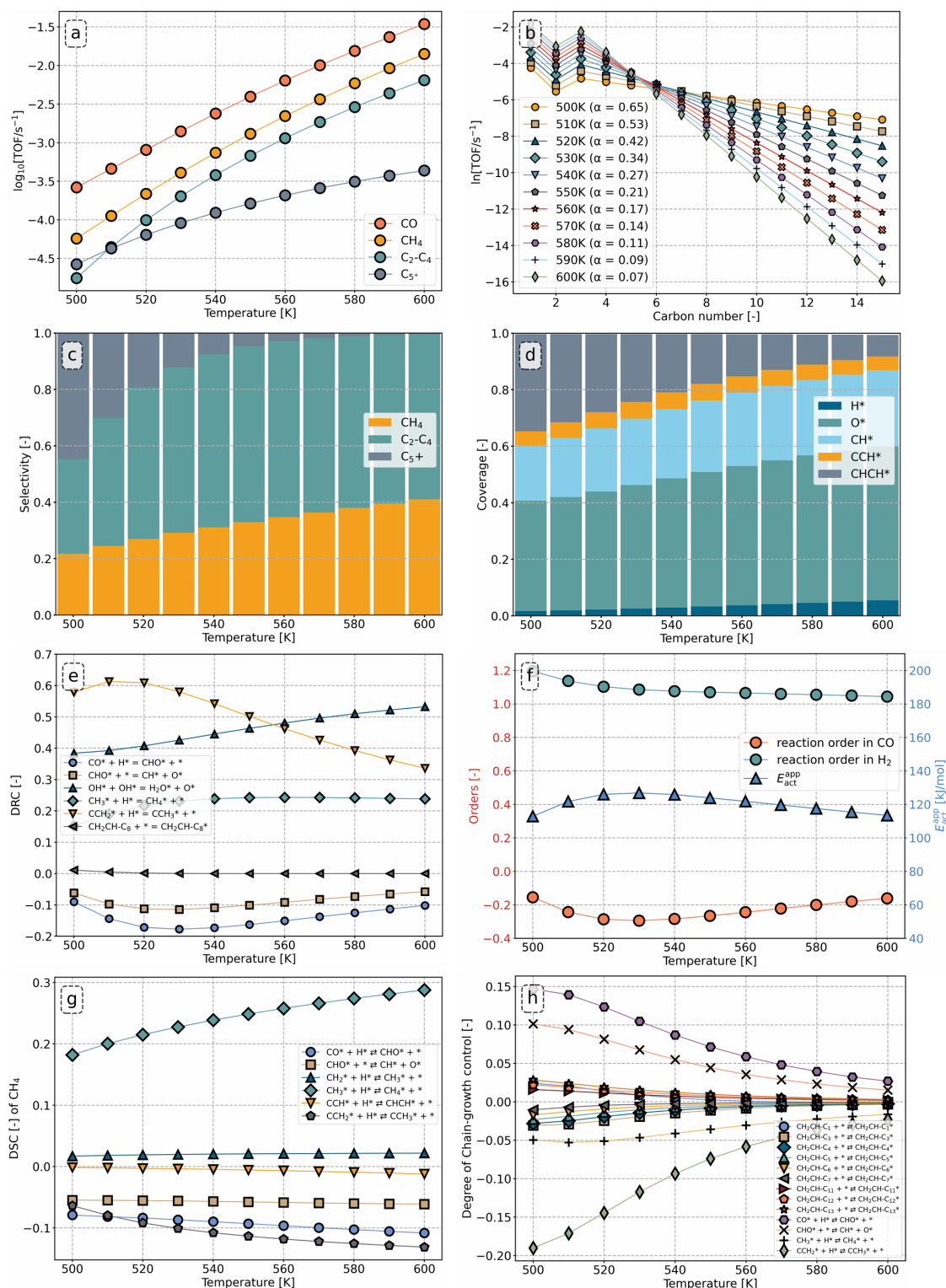


Figure 4.9. Microkinetics simulations for FT synthesis reaction on the (010) surface of χ -Fe₅C₂. (a) CO reaction rate (s^{-1}) and CH₄, C₂-C₄ olefines and C₅⁺ olefines formation rates, (b) ASF distribution and corresponding chain-growth probability values (α), (c) Carbon-based product distribution, (d) Surface coverages, (e) DRC, (f) Reaction orders with respect to CO and H₂ and apparent activation energies (E_{act}^{app}), (g) DSC for CH₄, and (h) DCGC as a function of temperature ($p = 20$ bar, H₂/CO ratio = 2).

Next, we conducted a comprehensive analysis of the reaction network to identify the main reaction pathways. The rates of chain-growth steps, including coupling and hydrogenation reactions, were lumped together to simplify the presentation of the results. The results given in Figure 4.10 show HCO dissociation is the dominant pathway for C-O bond dissociation. The formation of H₂O proceeds through OH disproportionation and olefins are the dominant hydrocarbon reaction products. In our simulations, we identified distinct branches within the kinetic network involving chain growth and chain depolymerization reactions. The dominant chain-growth pathway involves the coupling of CH* with CR* (R = H or alkyl) to CHCR, which is hydrogenated to CHCHR. Subsequently, CHCHR undergoes hydrogenation to CHCH₂CR* and, to a lesser extent, CH₂CHCR*. Dehydrogenation of the former into CCH₂CR leads to the precursor for further chain elongation, while desorption of the latter produces an olefin. Depolymerization occurs simultaneously through CHCR* dehydrogenation to form CCR* via two pathways: (i) CHCR* → CCR* and (ii) CHCR* → CHCHR* → CCHR* → CCR*. Both these pathways can lead to depolymerization through CCR* conversion to C* + CR*. This reaction is possible due to the relatively low barriers for the dehydrogenation of CCHR* and CHCHR* and subsequent dissociation of CCR* into C* + CR*. There also exists a chain-growth pathway originating from CHCR*, which proceeds through CHCR* → CHCHR* → CHCH₂R* → CCH₂R*, the latter species being equivalent to CR, which allows for another CH insertion.

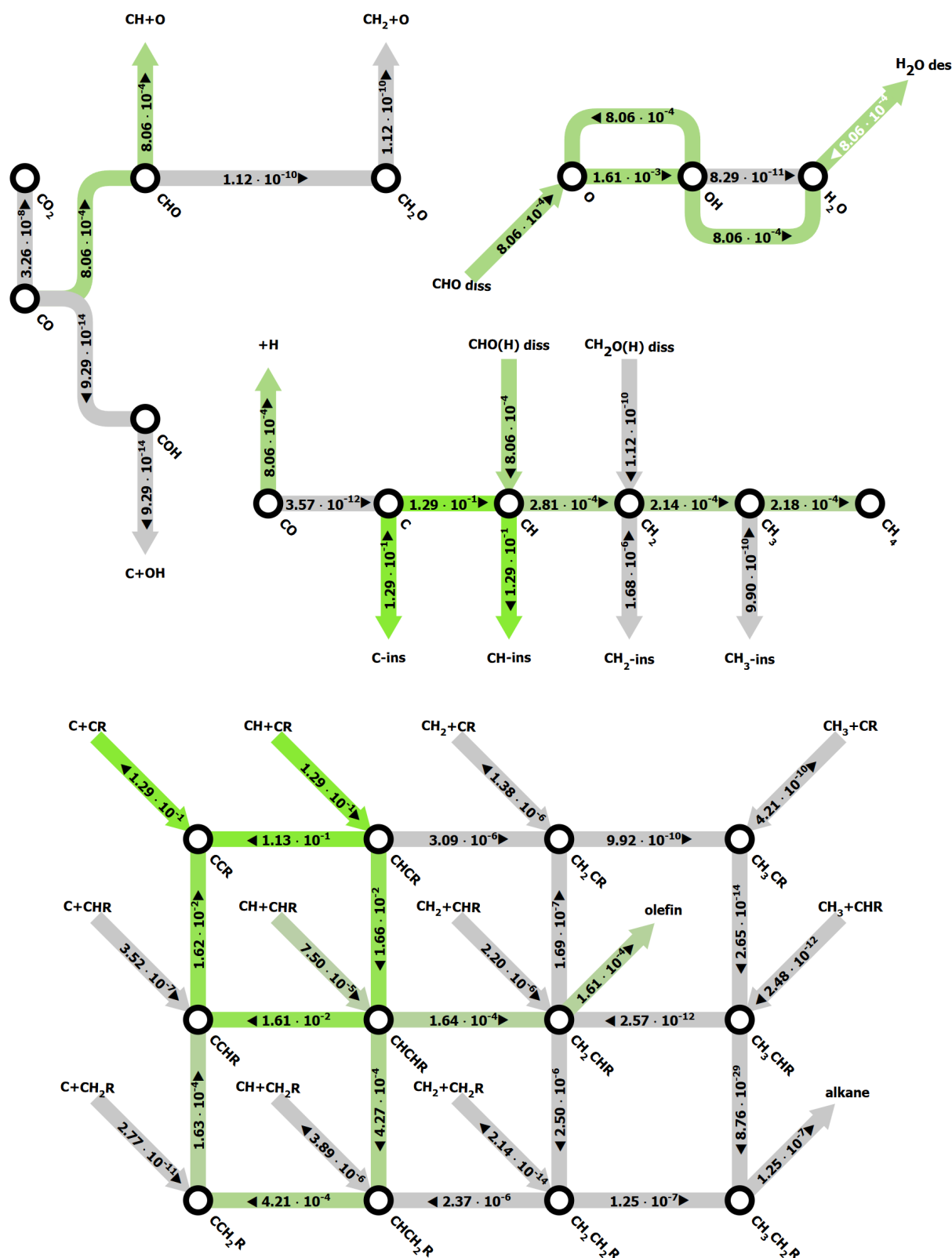


Figure 4.10. Reaction network analysis of the FT synthesis reaction on the (010) surface of χ -Fe₅C₂ ($T = 520\text{K}$, $p = 20\text{ bar}$, H_2/CO ratio = 2). The values indicated in the pathways are the molar flux (the difference between the forward and back rates for the elementary reaction steps) of dissociation, hydrogenation, desorption and coupling. The intensity of the color indicates the magnitude of the molar flux value. The black triangles indicate the direction of the molar fluxes.

To further investigate the details of simultaneous chain propagation and chain depolymerization, we investigated in detail the segment of the kinetic network pertaining to C₈ chains. The molar fluxes of the relevant reaction steps are indicated in Figure 4.11. The reaction temperature is 520 K. Chain growth occurs by CH into C-C₆ to CHC-C₆, which is predominantly hydrogenated to CHCH-C₆. The hydrogenation of the α -CH group in CHCH-C₆ to CH₂CH-C₆ has a rate of $1.22 \times 10^{-6} \text{ s}^{-1}$, leading to chain-growth termination as linear α -C₈-olefin is formed upon desorption. Alternatively, the hydrogenation of the β -CH group in CHCH-C₆ with a rate of $3.4 \times 10^{-6} \text{ s}^{-1}$ results in a C₉ surface species. The chain termination rate (r_t), which is the sum of the desorption rates of olefin (C₈⁻) and alkane (C₈), is $1.2 \times 10^{-6} \text{ s}^{-1}$. The chain-propagation rate (r_p) is the rate difference between the total in- and outflux for the C₈ segment of the kinetic network, which is $8.8 \times 10^{-7} \text{ s}^{-1}$. Thus, the chain-growth probability for C₈ corresponds to 0.42 (cf. equation (4.10)). From the net rate of CCH₂-C₆, we know that more than half of the CCH₂-C₆ species formed ($2.5 \times 10^{-6} \text{ s}^{-1}$) undergo two dehydrogenation steps to form CC-C₆, which can dissociate into C* and C-C₆*. CCH₂-C₆ also participates in chain growth to C₉ by coupling with CH species at a rate of $1.46 \times 10^{-6} \text{ s}^{-1}$. This analysis confirms that chain growth is a process involving simultaneous polymerization and depolymerization reaction steps, where the insertion of CH extends the chain and C species can be removed in subsequent steps. The reversibility of chain growth has been described before computationally for FT synthesis on a Ru step-edge model⁵⁹ and both theoretically⁸⁴ and experimentally for Co catalysts.¹²

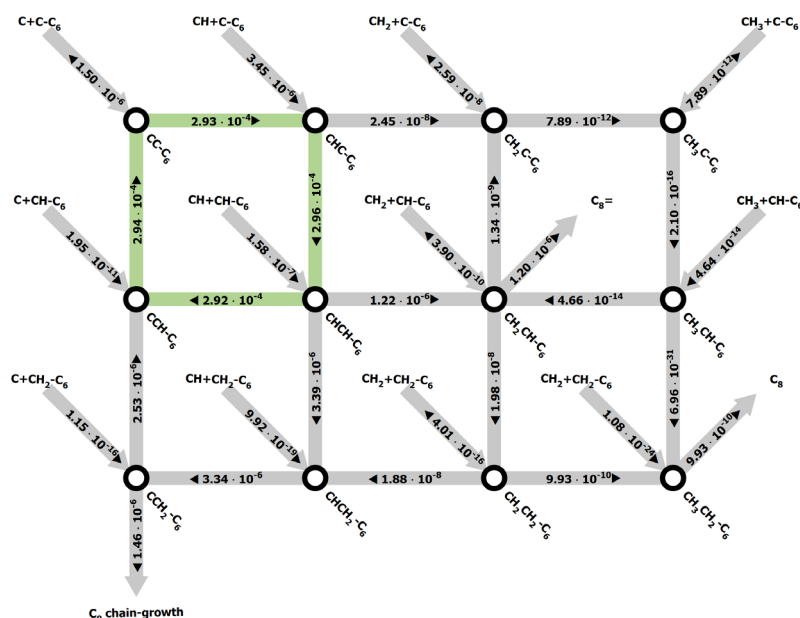


Figure 4.11. Reaction network analysis for the C₈ segment in the kinetic ($T=520\text{K}$, $p=20\text{ bar}$, H_2/CO ratio = 2). The values indicated in the pathways are the molar flux of dissociation, hydrogenation, desorption and coupling. The intensity of the color corresponds to the magnitude of the molar flux value.

4.3.6.2 Promoted (010) Surface

Figure 4.12a presents the CO reaction rate and CH₄, C₂-C₄ and C₅₊ formation rates as a function of temperature for the K₂O-promoted surface, while Figures 4.12b and 4.12c plot the ASF and the product distribution, respectively. At the reference conditions (Table B2), the CO reaction rate is slightly increased for the promoted surface, while the impact on the product distribution is more substantial. Several experimental studies of the reaction kinetics of K-promoted Fe-carbides also reported an increase in the CO conversion at low K content, although a higher K content led to a decreasing CO conversion.^{27, 36, 39} Overall, the CH₄ selectivity decreased from 27% for the unpromoted surface to 10% for the promoted one. Concomitantly, this leads to an increase in the selectivity to C₅₊ hydrocarbons from 19% to 48% and the chain-growth probability from 0.42 to 0.67. This shift in the product distribution is in good agreement with the experimental reports, which often discuss this by K promotion suppressing hydrogenation reactions presence.^{35, 86 39, 90, 91} This can be linked to the increased hydrogenation barriers in the presence of K₂O. Similar to the unpromoted surface, the CO₂ selectivity is negligible, implying that most of the O atoms are removed as H₂O.

Figure 4.12d presents the steady-state surface coverage for the K₂O-promoted surface. At low temperatures, this surface contains more H* than the unpromoted surface, which is due to lower rates of hydrogenation reactions. The surface also contains O* and OH* species, although their combined coverage is lower than on the unpromoted surface. This is likely due to the higher H* coverage and the decreased O* hydrogenation barriers. Moreover, the surface contains a higher amount of CO. This is an intrinsic effect of K₂O promotion of CO adsorption. The CH* coverage is lower on this surface, which is likely due to the increased chain-growth probability.

Figure 4.12e shows the DRC analysis for the promoted surface. Like the unpromoted surface, CCH₃* formation via CCH₂* hydrogenation and the OH disproportionation reactions are the dominant rate-controlling steps. This shows that also the K-promoted surface operates in a transient regime where chain growth and O removal control the overall rate. The DRC of CH₃ hydrogenation to CH₄ is lower due to the lower CH₄ selectivity caused by higher hydrogenation barriers. Another difference is that, while CO dissociation was inhibiting the overall reaction rate on the unpromoted surface and slightly controlling the formation rate of longer hydrocarbons, the dissociation of CHO becomes slightly rate-controlling at low temperatures, thereby determining the availability of C₁ growth monomers. Some of the hydrogenation steps involved in the formation of C₃-C₅ surface intermediates also displayed a significant rate control compared to the unpromoted surface. With increasing temperature, the DRC of the OH* disproportionation

increases, whereas the DRC of CCH₂ hydrogenation decreases. This shift is due to the increased rate of hydrocarbon product desorption at higher temperatures, which enhances CH₄ selectivity and reduces the impact of CCH₂ hydrogenation in chain-growth steps. With increasing temperature, the rate of O* formation increases, which results in OH* disproportionation, the most challenging step in the O-removal pathway, controlling the rate more. Notably, at the highest simulated temperature, this even leads to the direct CO dissociation step having a slightly rate-inhibiting nature, as hydrogenation events are unable to keep up with C* and O* production. While the hydrogenation of C₃-C₅ intermediates decreases as the decreased chain-growth probability reduces the dependence on these species, the DRC of the CH₃ hydrogenation increases with temperature due to the increasing CH₄ selectivity.

The reaction orders with respect to CO and H₂ and the apparent activation energies ($E_{\text{act}}^{\text{app}}$) for the promoted surface are shown in Figure 4.12f. The presence of K₂O results in positive CO reaction orders, consistent with experimental results⁸⁶ and with the DRC for CO dissociation reactions becoming positive compared to the unpromoted surface. A higher CO coverage will increase the reaction rate by increasing the abundance of C₁ chain-growth monomers. The H₂ reaction order is lower than the one on the unpromoted surface, although it remains positive. This difference is also observed experimentally.⁸⁶ The decrease in the H₂ reaction order can be attributed to the shift in product distribution towards long-chain hydrocarbons, which decreases the dependence on H* for hydrogenation. Despite this, the H₂ reaction order remains positive as the three most dominant rate-controlling require H* species. The hydrogenation of CH₃* and CCH₂ requires H*, while OH* disproportionation favors a high OH* coverage, which increases with H₂ pressure. Finally, the apparent activation energy ($E_{\text{act}}^{\text{app}}$) is lower for the K₂O-promoted surface, which is also typically observed in experimental studies.⁸⁶ The decrease in the apparent activation energy is due to a shift in the product distribution towards longer hydrocarbons and faster removal of O*, with the later being the dominant rate-controlling step at high temperature.

Figure 4.12g presents the degree of selectivity control (DSC) for CH₄ for the promoted surface. A lower barrier of CH₃* hydrogenation increases the CH₄ selectivity. Higher reaction temperatures increase the DSC for CH₄, as its selectivity becomes higher. On the contrary, lowering the barrier of CCH₂ hydrogenation leads to less CH₄ selectivity and more chain growth. A lower barrier of OH* disproportionation also decreases the CH₄ selectivity, as easier O removal via H₂O benefits CO dissociation, resulting in more C₁ chain-growth monomers. We also explored the DCGC for the promoted surface (Figure 4.12h). Many elementary reaction steps contribute to the DCGC, which can be lumped into two types with a few exceptions. The first one belongs to the

hydrogenation of growing hydrocarbon chains, exhibiting a mildly positive DCGC. For instance, the hydrogenation of the β -CH group in C_n intermediates exhibits a positive value, as increasing the rate of such steps enhances the availability of CR for the CH insertion during chain growth. In contrast, the hydrogenation of α -CH group leads to the termination of chain growth, which explains the negative DCGC for the hydrogenation of CHCH-C₆ and CHCH-C₇ to CH₂CH-C₆ and CH₂CH-C₇, respectively. The other type corresponds to desorption steps of longer hydrocarbons, exhibiting a slightly negative DCGC. Increasing the rate of desorption decreases the availability of CR for the chain-growth reactions.

Both simulations operate at the interface of chain growth-limiting and oxygen removal-limiting regimes, as follows from the CCH₂ hydrogenation and OH disproportionation reactions being the rate-controlling steps. For the unpromoted surface, the DCGC plot in Figure 4.9h shows that CHO formation and dissociation control the chain-growth rate, whereas they are rate-inhibiting steps for CH₄ formation. This indicates that lowering the barrier of these two steps leads to faster chain growth but inhibits CH₄ formation. K₂O decreases the barriers of CHO formation and dissociation to such an extent that these steps no longer control the chain-growth rate (Figure 4.12h). The enhanced CHO dissociation rate should result in an increased availability of the main CH chain-growth intermediate on the promoted surface, which is however not observed. This relates to the preference for chain growth over CH₄ formation due to the strong impact of the inhibition of hydrogenation reactions that lead to CH₄. Together, these effects cause a slightly higher CO conversion rate, a significantly lower CH₄ selectivity and a higher chain-growth probability. This insight underscores the role of enhanced CO dissociation in facilitating chain growth on the K-promoted catalyst.^{30, 37, 38}

Another important difference between simulated kinetics of the two surfaces is that CHO dissociation is not a rate-limiting step for the unpromoted surface. This is caused by the fact that CO dissociation is a strong rate-inhibiting step to CH₄ formation while it controls the rate of chain growth. The high CH₄ selectivity on the unpromoted surface results in an overall slightly inhibiting effect of CHO dissociation. For the promoted surface, it is observed that CHO dissociation controls the overall rate slightly. This is due to the shift in the product distribution to longer hydrocarbons, which is the consequence of the slower rate of hydrogenation reactions, affecting CH₄ formation more profoundly than olefin formation.

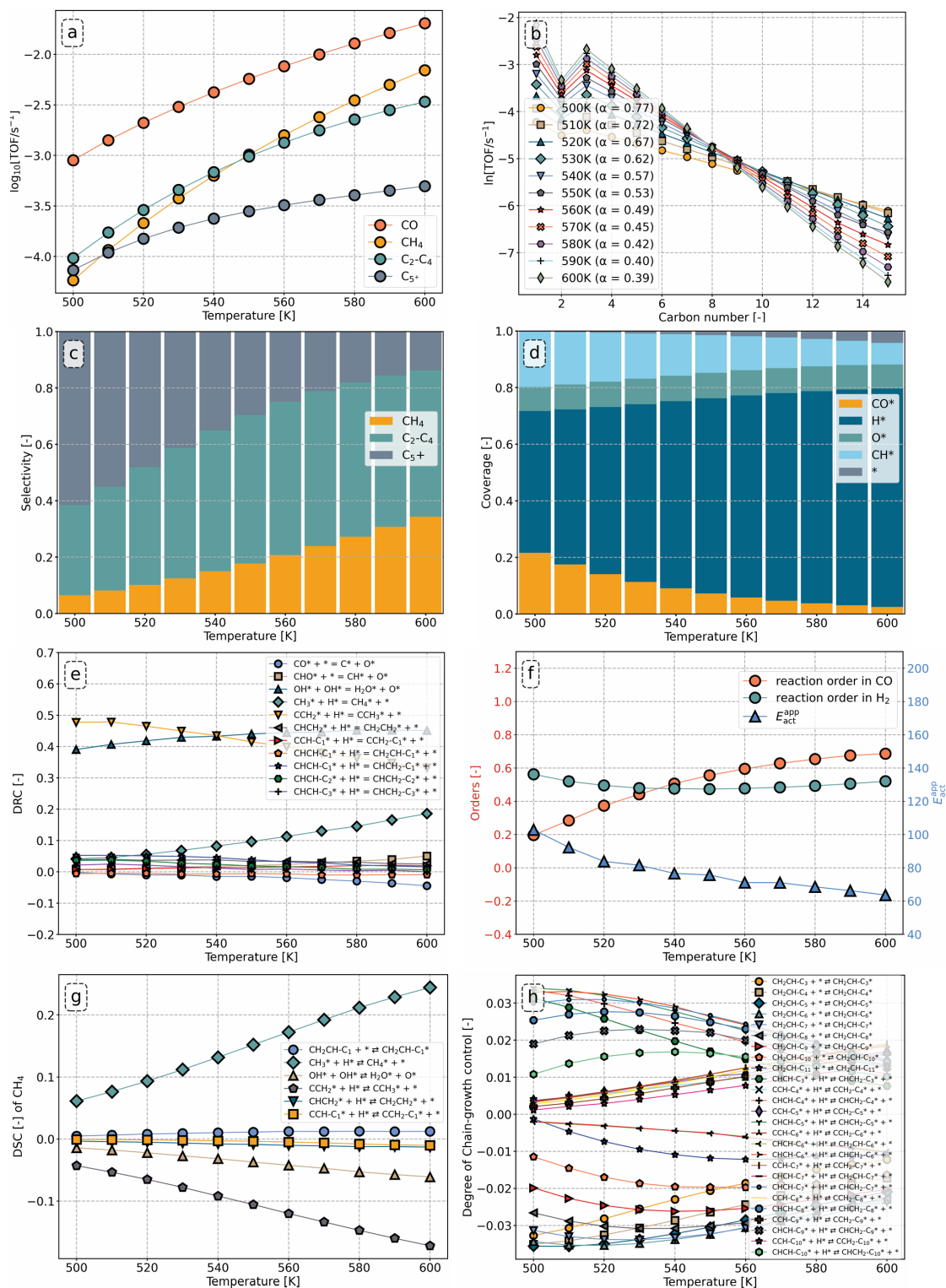


Figure 4.12. Microkinetics simulations for FT synthesis reaction on the K₂O-promoted (010) surface of χ -Fe₅C₂. (a) CO reaction rate (s⁻¹) and CH₄, C₂-C₄ olefines and C₅⁺ olefines formation rates, (b) ASF distribution and corresponding chain-growth probability values (α), (c) Carbon-based product distribution, (d) Surface coverages, (e) DRC, (f) Reaction orders with respect to CO and H₂ and apparent activation energies ($E_{\text{act}}^{\text{app}}$), (g) DSC for CH₄, and (h) DCGC as a function of temperature ($p = 20$ bar, H₂/CO ratio = 2).

Figure 4.13 depicts the reaction network at a temperature of 520 K for the promoted surface. A comparison of the data for the promoted and unpromoted surfaces shows that HCO* dissociation and OH* disproportionation remain the dominant routes for CO dissociation and H₂O formation, respectively. The presence of K₂O does not change the dominant chain-growth pathway. Moreover, chain growth and decoupling reactions still occur for the promoted surface. The CH formation rate is also increased due to faster CO dissociation, leading to a higher CH availability. Likewise, the formation rate of olefins significantly increases at the expense of the formation rate of paraffins in comparison with the unpromoted surface. In our simulations, this shift in selectivity can be attributed to K₂O inhibiting the hydrogenation of most intermediates. In summary, the increase in chain-growth probability by K₂O stems from enhanced CO conversion and suppressed hydrogenation of C_n intermediates, resulting faster formation of CH chain-growth monomers and a decreased rate of chain-growth termination, collectively increasing the chain-growth probability.

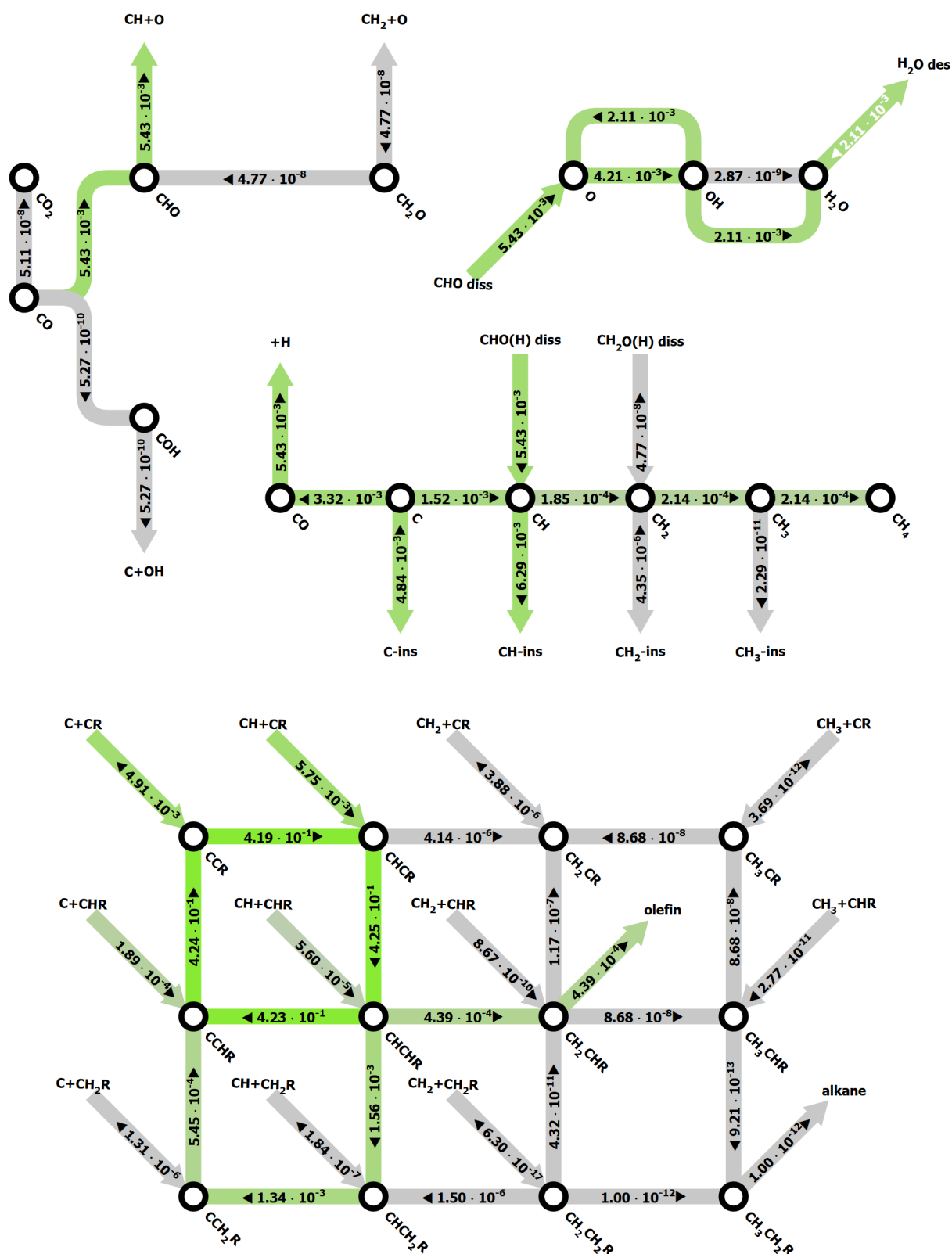


Figure 4.13. Reaction network analysis of FT synthesis reaction on the K₂O-promoted (010) surface of χ -Fe₅C₂ ($T=520$ K, $p=20$ bar, H_2/CO ratio = 2). The values indicated in the pathways are the molar flux of dissociation, hydrogenation, desorption and coupling. The intensity of the color indicates the magnitude of the molar flux value.

4.4 General Discussion

Comparison of the microkinetics of the χ -Fe₅C₂ (010) surfaces with and without K provide deeper understanding about the mechanistic role of K in FT synthesis. We established that K₂O is the most likely state of the K promotor on the surface, consistent with experimental indications.⁶⁸⁻⁷⁰ Electronic structure analysis shows that K₂O increases the reactivity of the surface by electron transfer from K₂O to surface Fe atoms. K₂O leads to stronger adsorption of the reactants CO and H as well as surface species relevant to chain growth such as C and CH. This effect of K is in broad agreement with the trend predicted by theoretical calculations of Petersen et al.⁴⁰ We found that steric repulsion with K₂O leads to destabilization of CH₂ and CH₃.

We then investigated the influence of K₂O on CO dissociation, a critical step in the FT synthesis mechanism, which produces the monomers for chain growth. K₂O reduces C-O bond dissociation barriers of CO, HCO, COH, and CH₂O intermediates, by injecting electrons to the surface sites involved in C-O bond dissociation. The additional electron density on the Fe atoms destabilizes low-lying bonding orbitals due to the increased electron-electron repulsion and enhances occupation of high-lying anti-bonding orbitals, overall leading to a weakening of the C-O bond. A more detailed electronic analysis for this and other surfaces has been discussed in **Chapter 3**. The H-assisted HCO pathway is the dominant CO dissociation pathway for the unpromoted (010) surface with lowest overall barrier, consistent with previous theoretical results.⁴³ K₂O lowers the barriers for direct CO and H-assisted CO dissociation pathways, the latter route via CHO remaining the dominant one for the promoted surface. The O atoms derived from CO dissociation is nearly exclusively removed by hydrogenation to H₂O, involving OH disproportionation instead of OH hydrogenation. These results are qualitatively the same for the unpromoted and promoted surfaces. Overall, the barrier for CO₂ formation is higher than that of H₂O formation.

CH₄ formation was considered from lattice C atoms of the χ -Fe₅C₂ surface and adsorbed C from CO dissociation. K₂O increase hydrogenation barriers of both types of C atoms due to the stronger adsorption of C and H, consistent with earlier DFT calculations for the (100) and (110) surfaces of χ -Fe₅C₂.⁷⁰ This result aligns with the experimentally observed decrease in CH₄ selectivity upon K promotion.^{35-37, 70} Such inhibition of C hydrogenation can increase the coverage with C and CH, which can act as a precursor for carbonaceous deposits due to C-C coupling reactions. Experimentally, it has been observed that K promotion can lead to a higher coverage with carbonaceous species.^{40, 68}

Chain growth initiates with C+CH and CH+CH coupling reactions, aligning with earlier theoretical studies.^{17, 73} Hydrogenation of C₂ surface intermediates is endothermic, with ethylene formation being much easier than ethane. K₂O increases most of the barriers involved in C₂ formation, which can be ascribed to the stronger adsorption of C-containing species and H due to K₂O. Despite these changes, the dominant pathway for C-C coupling and hydrogenation is unaffected by K₂O. We also explored the effect of K₂O on the formation of C₃ surface intermediates as a proxy for further chain growth. This reveals that C+CHCH₃ and CH+CHCH₃ coupling reactions, which are the equivalent of C+CH and CH+CH, are preferred, irrespective of the presence of K₂O.

The impact of all these changing reaction energetics due to K₂O promotion was explored by microkinetics simulations. We took into account the formation of hydrocarbon chains up to 15 C atoms to avoid too significant cut-off errors.⁷⁴ The kinetic predictions for the unpromoted (010) surface compare well with experimental observations. They demonstrate that this surface likely contributes significantly to the high FT synthesis activity of χ -Fe₅C₂ catalysts with a relatively low CH₄ selectivity, a reasonable chain-growth probability and negligible CO₂ formation. K₂O increases the CO conversion rate, which is in line with activity data obtained for catalysts with a low K content.^{30, 37, 38} The experimentally observed decrease at high K content is likely due to the decreased amount of active sites caused by increased particle size and carbon deposition,²⁷ which is not considered explicitly in our modelling. The simulations show that CO dissociation proceeds via the CHO pathway. While CO dissociation is rate-inhibiting for the overall CO conversion rate, it limits the chain growth on the unpromoted surface, as follows from the DCGC in Figure 4.9h. The overall rate-inhibiting nature of CO dissociation stems from the significant CH₄ selectivity, which is inhibited by this step (Figure 4.9g). K₂O lowers the overall barrier for CHO dissociation. Then, CO dissociation via CHO pathway is no longer limiting the rate of chain growth (Figure 4.12h). The faster CHO dissociation step leads to a higher coverage with the CH chain-growth monomer, which contributes to a higher chain-growth probability. Key to the increased rate of CO dissociation is the stronger adsorption of CO and C intermediates due to K₂O. K₂O also strengthens the bonds of carbon-containing surface intermediates and H atoms, resulting in higher barriers for hydrogenation. This effect is more pronounced for CH₄ formation than the formation of olefins, which also contributes to the higher chain-growth probability. This understanding aligns with the experimental observation that small amounts of K enhance the chain-growth probability.^{30, 37, 38} Overall, the combination of these effects of K₂O leads to a slight increase in the CO conversion rate, a lower CH₄ selectivity and a higher C₅₊ selectivity, consistent with experiments studies.^{36, 39,}

⁹⁰⁻⁹² Finally, we emphasize the dominance of CH* + CR* coupling pathway and the reversible nature of chain-growth reactions, regardless of the presence of K₂O.

4.5 Conclusions

DFT and microkinetic simulations investigated the mechanistic role of K on the FT synthesis reaction on the (010) surface of χ -Fe₅C₂. As the most stable form under FT reaction conditions, K₂O renders the surface more active by electron transfer to the surface Fe atoms, effectively enhancing the adsorption of CO, C, H and other carbon-containing surface intermediates. Overall, this results in a lower overall CO dissociation barrier, which is understood in terms of an electronic structure analysis. For O removal, H₂O is the main product with OH* disproportionation being the dominant pathway. The contribution of CO₂ is negligible due to high recombination barriers, irrespective of the presence of K₂O. K₂O suppresses CH₄ formation by increasing the hydrogenation barriers of lattice C atoms and adsorbed C due to the stronger adsorption of C and H. This also affects other hydrogenation barriers of fragments with two or more C atoms, effectively increasing the barriers for chain growth and chain-growth termination. Separate coupling reaction kinetics for C₂ and C₃ formation are computed, with the C₃ energetics being taken as a proxy for all hydrocarbons forming with more than 3 C atoms. Overall, the main coupling reactions are those between CH and CR (R = alkyl) intermediates. The microkinetics simulations reveal that the unpromoted and promoted surfaces operate at the interface of chain growth-limiting and oxygen removal-limiting regimes: the main rate-controlling steps are CCH₂ hydrogenation and OH disproportionation, the former being dominant at realistic FT temperatures. Simulations of the unpromoted surface show that CO hydrogenation and CHO dissociation control chain growth, although this step slightly inhibits the overall CO conversion rate due to its large impact on CH₄ formation. The simulations of the promoted surface demonstrate that these kinetic barriers for CHO dissociation with respect to chain growth are removed. Overall, K₂O increases the chain-growth probability due to higher barriers for hydrogenation reactions that impact CH₄ formation stronger than the hydrogenation of surface intermediates to olefin products. This explains the simultaneous strong decrease in CH₄ selectivity.

4.6 References

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Appendix B

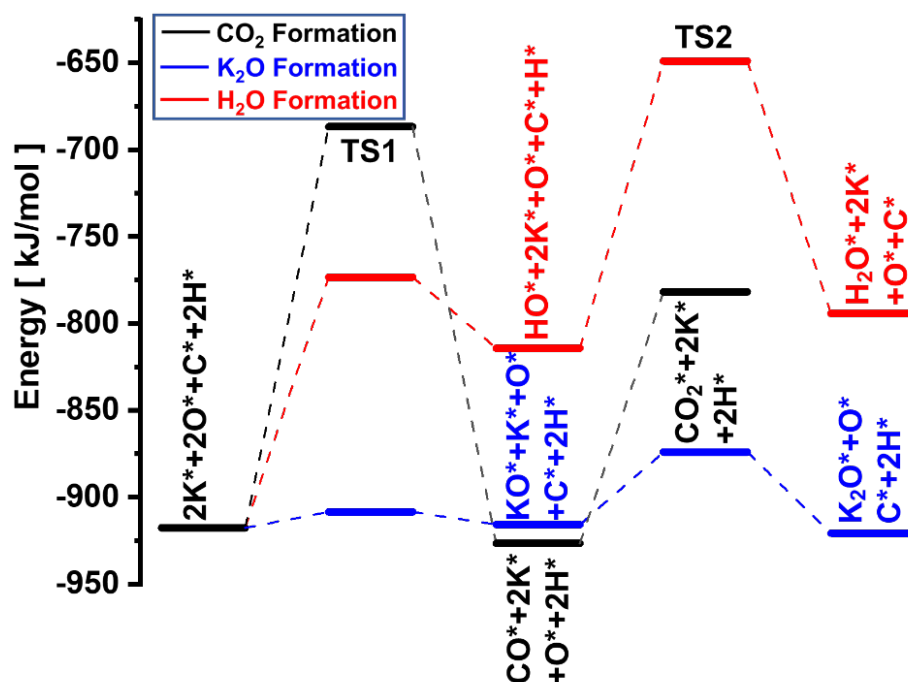


Figure B1. K₂O, CO₂ and H₂O formation on the (010) surface of χ -Fe₅C₂.

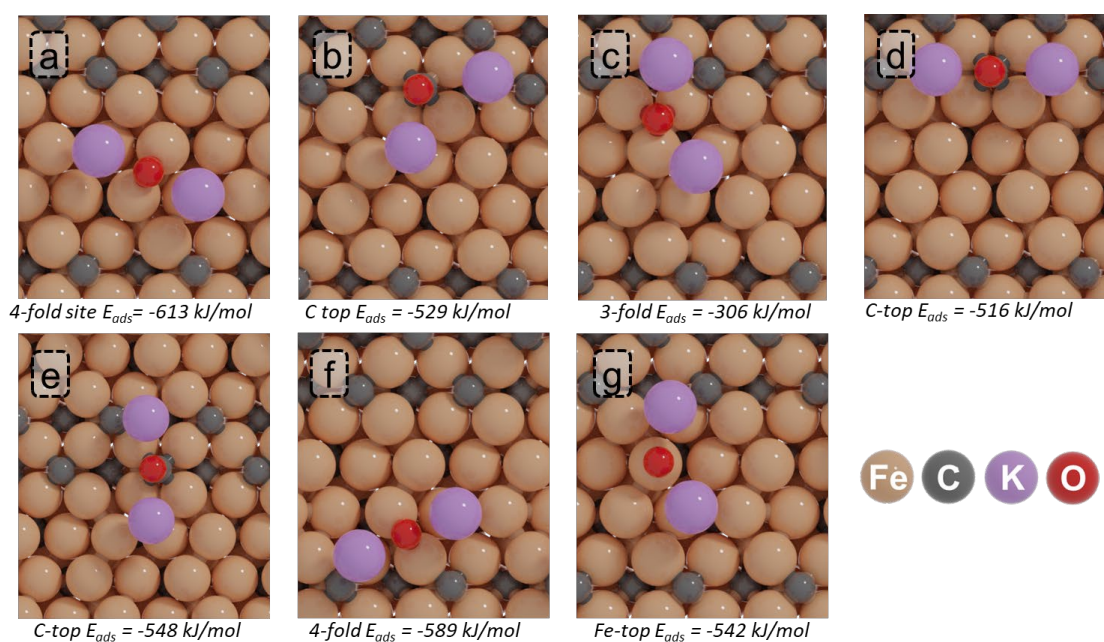


Figure B2. Optimized structures and energies of K₂O adsorption on the (010) surface of χ -Fe₅C₂.

In the adsorption process, the adsorption energy of C is calculated following the reaction ($\text{CO} + \text{H}_2 + * \rightleftharpoons \text{C}^* + \text{H}_2\text{O}$)

$$E_{\text{ads}(\text{C})} = E_{\text{C}^*} - E_* - E_{\text{CO}} - E_{\text{H}_2} + E_{\text{H}_2\text{O}} \quad (\text{B. E1})$$

Similarly, the adsorption energies of CH, CH₂ and CH₃ are calculated following reactions ($\text{CO} + \frac{3}{2}\text{H}_2 + * \rightleftharpoons \text{CH}^* + \text{H}_2\text{O}$), ($\text{CO} + 2\text{H}_2 + * \rightleftharpoons \text{CH}_2^* + \text{H}_2\text{O}$) and ($\text{CO} + \frac{5}{2}\text{H}_2 + * \rightleftharpoons \text{CH}_3^* + \text{H}_2\text{O}$), respectively.

$$E_{\text{ads}(\text{CH})} = E_{\text{CH}^*} - E_* - E_{\text{CO}} - \frac{3}{2}E_{\text{H}_2} + E_{\text{H}_2\text{O}} \quad (\text{B. E2})$$

$$E_{\text{ads}(\text{CH}_2)} = E_{\text{CH}_2^*} - E_* - E_{\text{CO}} - 2E_{\text{H}_2} + E_{\text{H}_2\text{O}} \quad (\text{B. E3})$$

$$E_{\text{ads}(\text{CH}_3)} = E_{\text{CH}_3^*} - E_* - E_{\text{CO}} - \frac{5}{2}E_{\text{H}_2} + E_{\text{H}_2\text{O}} \quad (\text{B. E4})$$

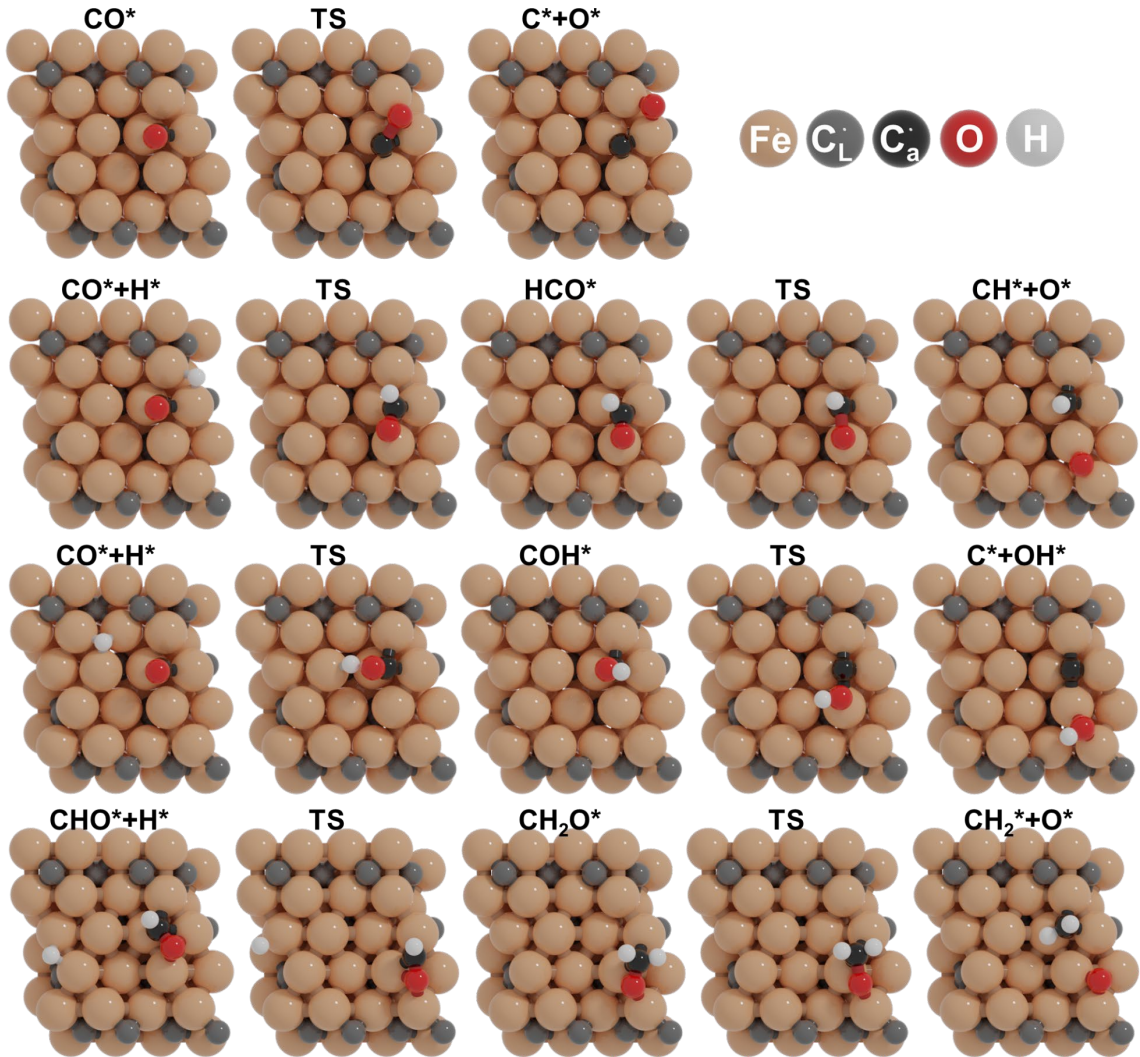


Figure B3. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (010) surface of χ -Fe₅C₂.

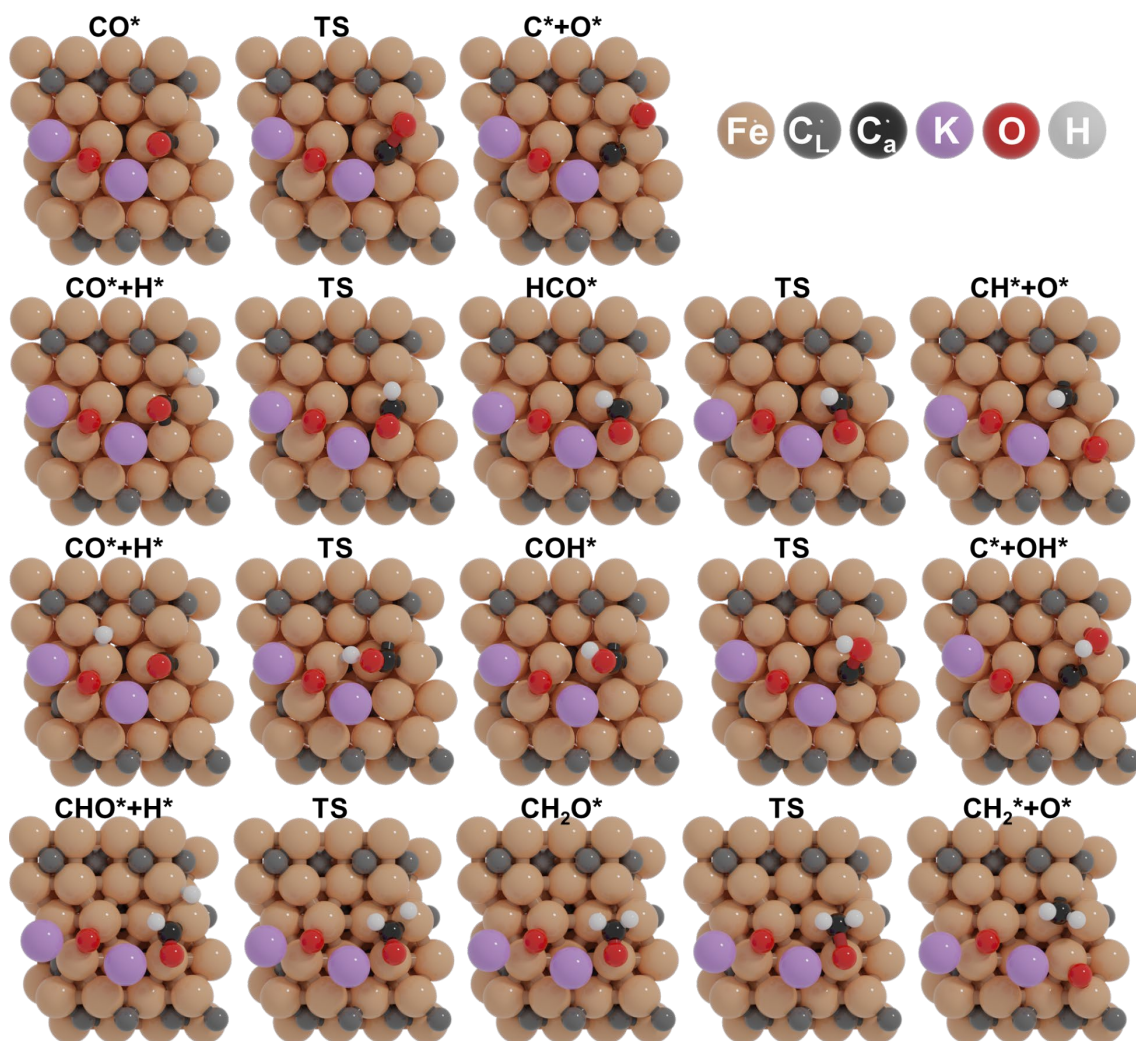


Figure B4. Configurations of IS, TS and FS for the direct or H-assisted dissociation of CO on the K₂O-promoted (010) surface of χ -Fe₅C₂.

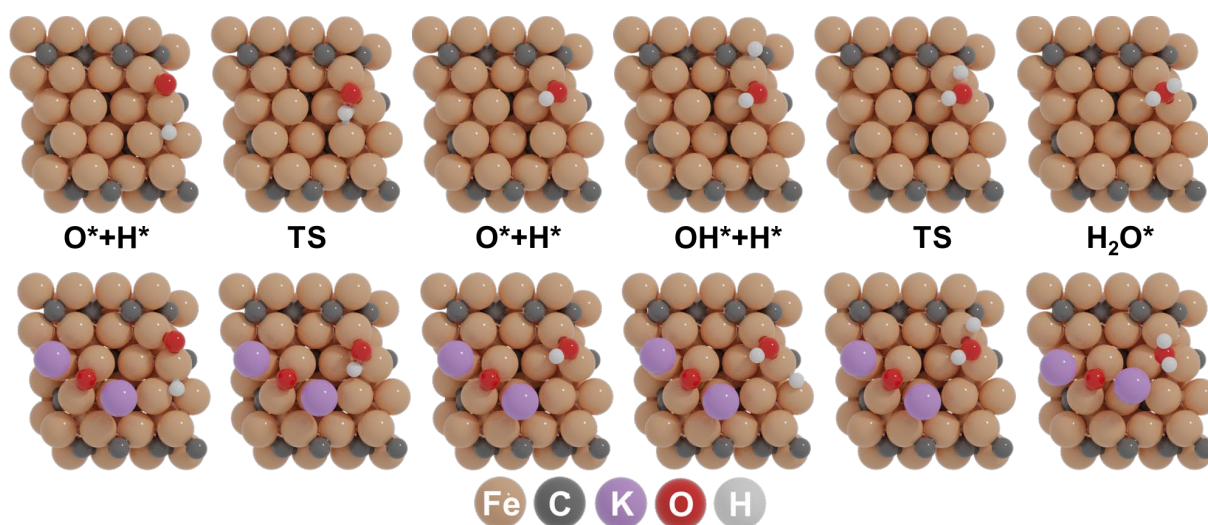


Figure B5. Configurations of IS, TS and FS for H₂O formation on the pristine (up) and K₂O-promoted (010) surface (down) of χ -Fe₅C₂.

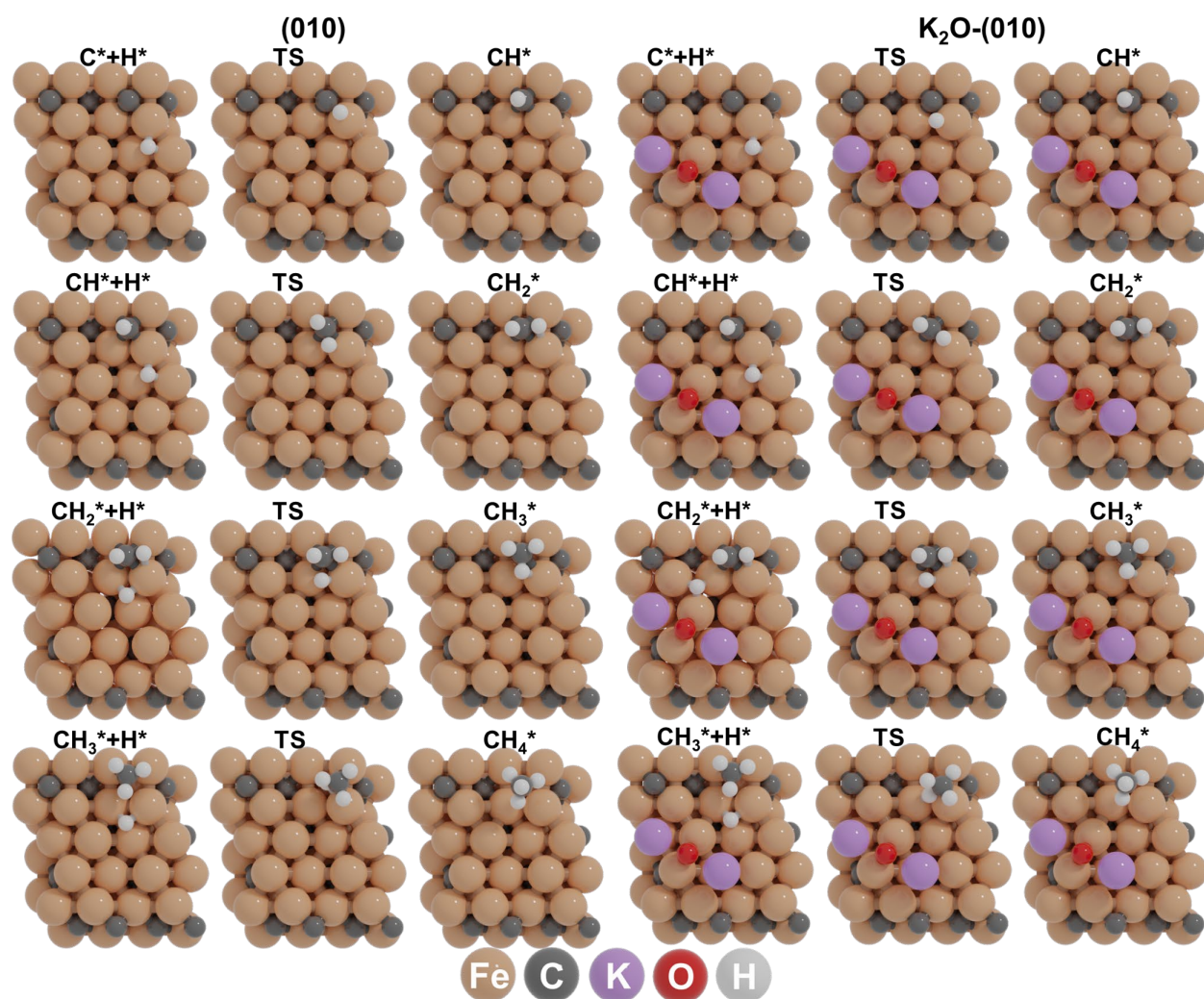


Figure B6. Configurations of IS, TS and FS for CH₄ formation of lattice C on the pristine (left) and K₂O-promoted (010) surface (right) of χ -Fe₅C₂.

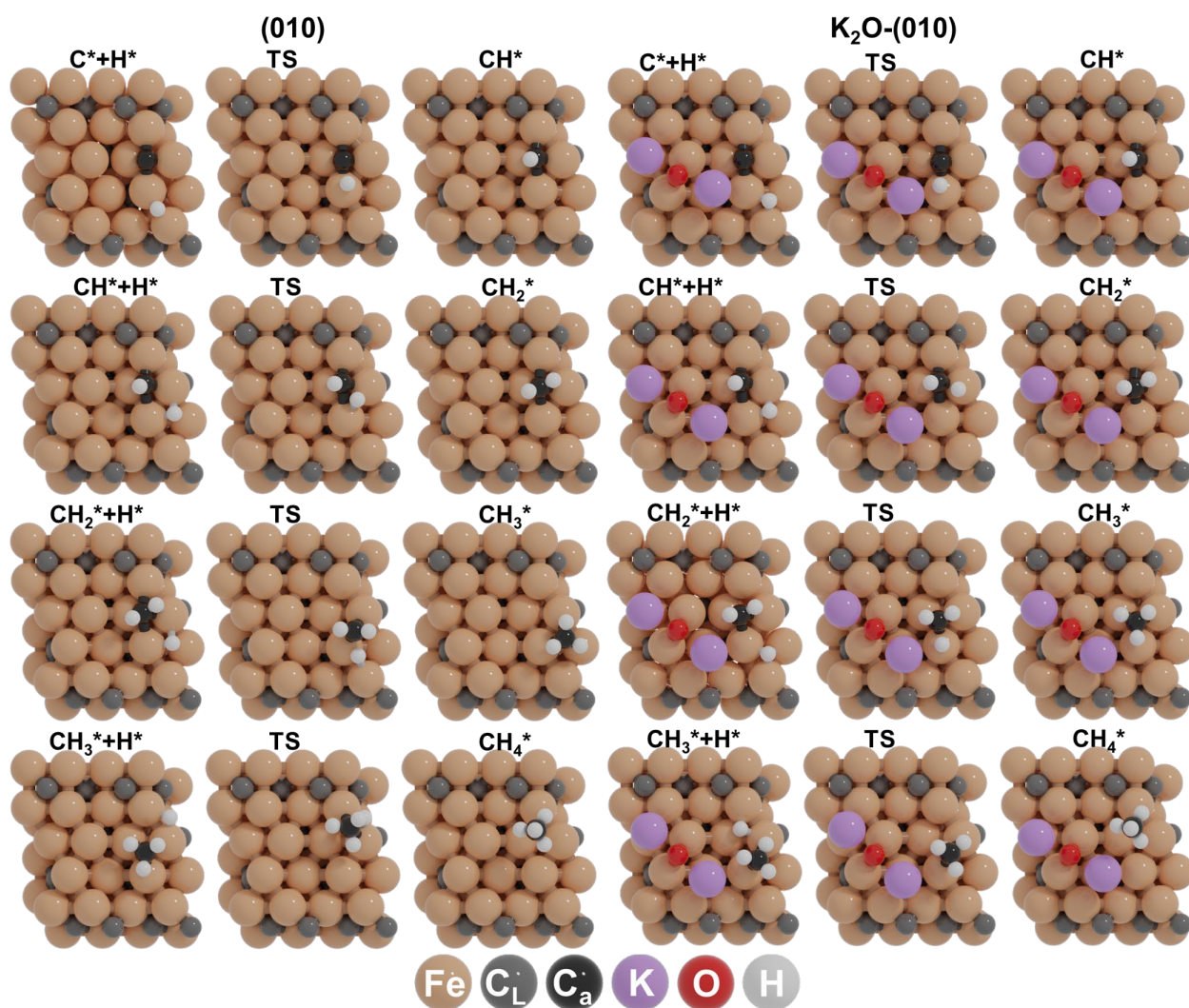


Figure B7. Configurations of IS, TS and FS for methane formation of absorbed C on the pristine (left) and K₂O-promoted (010) surface (right) of χ -Fe₅C₂.

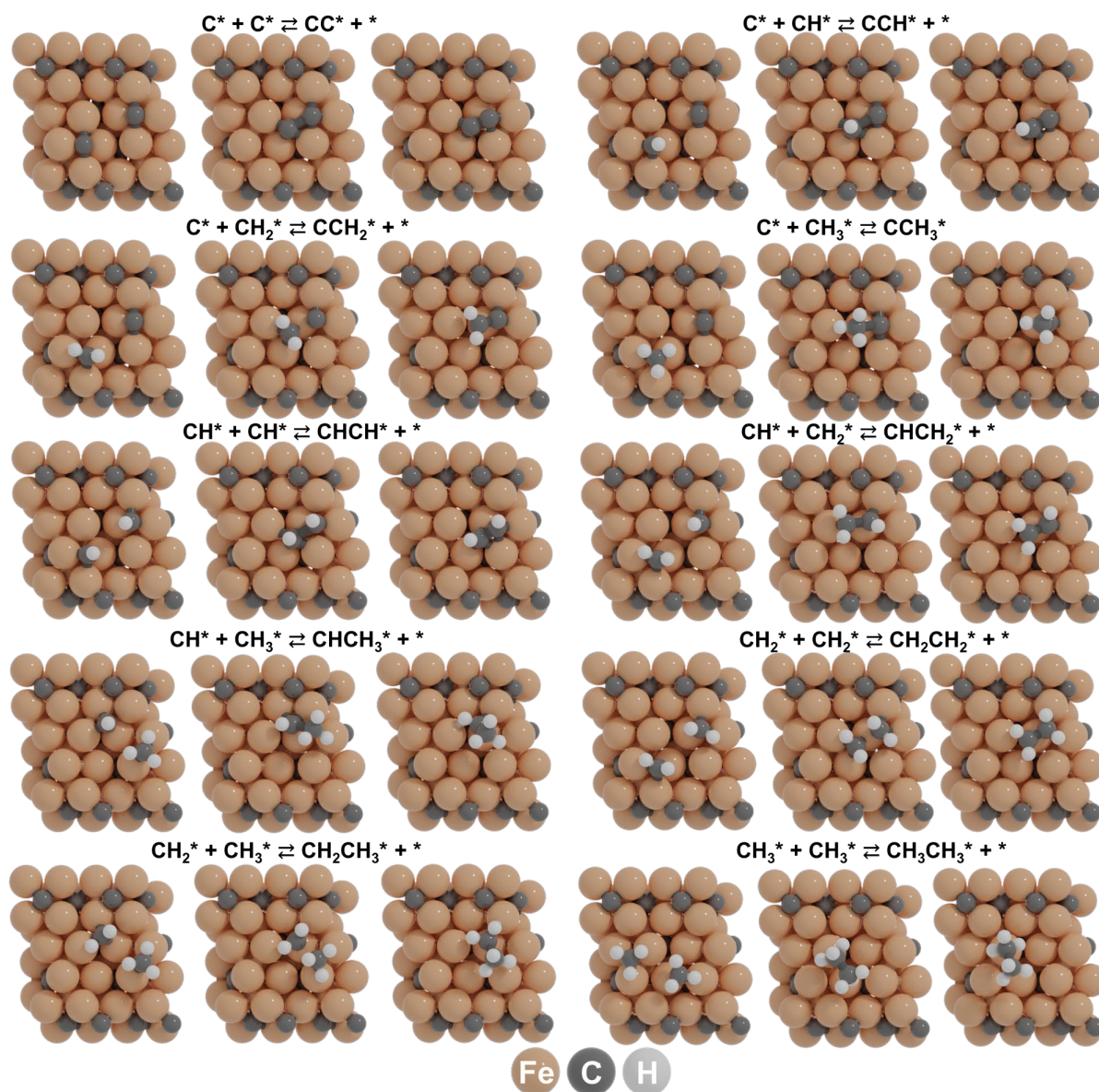


Figure B8. Configurations of IS, TS and FS for C₂ formation on the (010) surface of χ -Fe₅C₂.

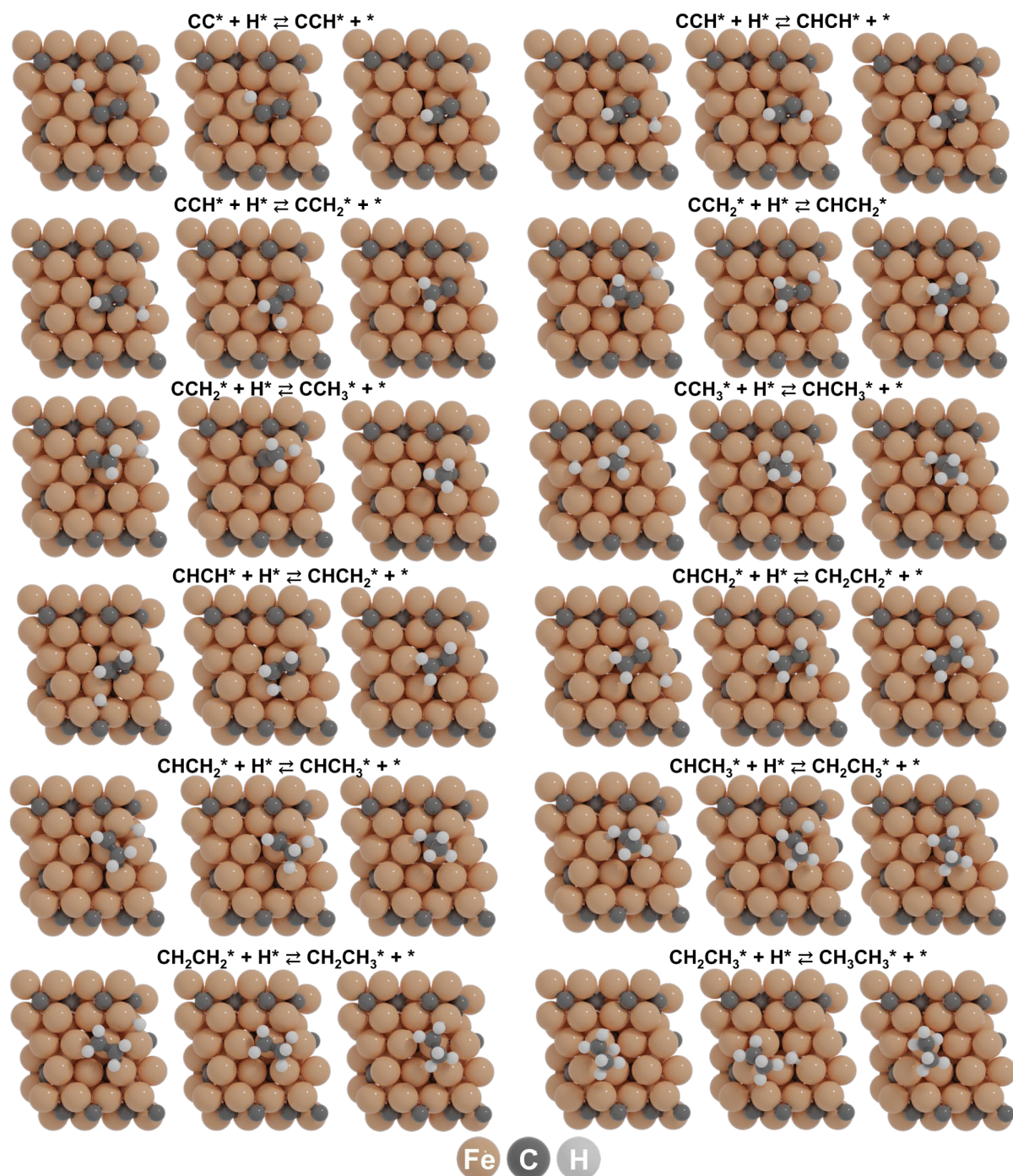


Figure B9. Configurations of IS, TS and FS for C₂ hydrogenation on the (010) surface of χ -Fe₅C₂.

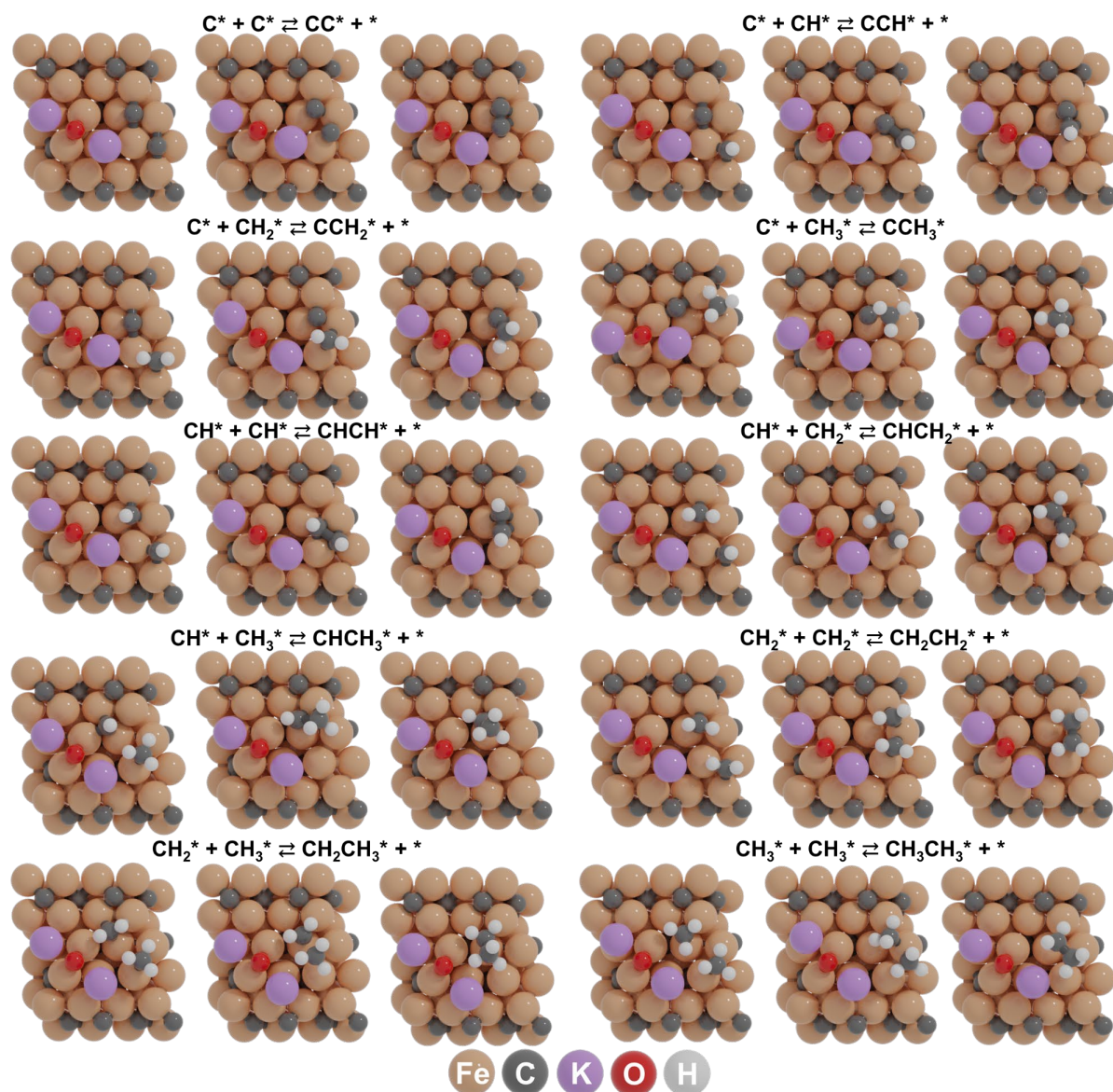


Figure B10. Configurations of IS, TS and FS for C₂ formation on the K₂O-promoted (010) surface of χ -Fe₅C₂.

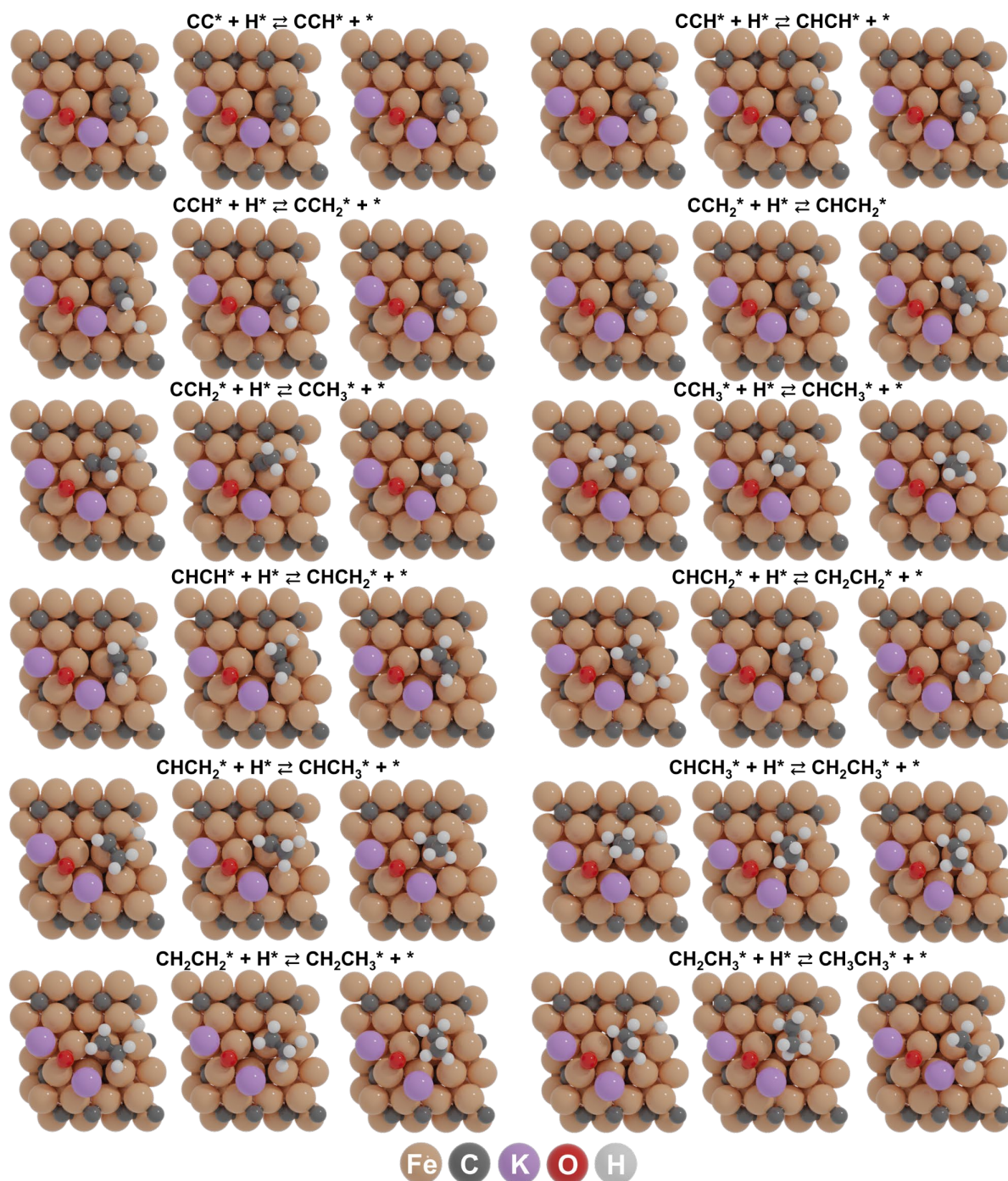


Figure B11. Configurations of IS, TS and FS for C₂ hydrogenation on the K₂O-promoted (010) surface of χ -Fe₅C₂.

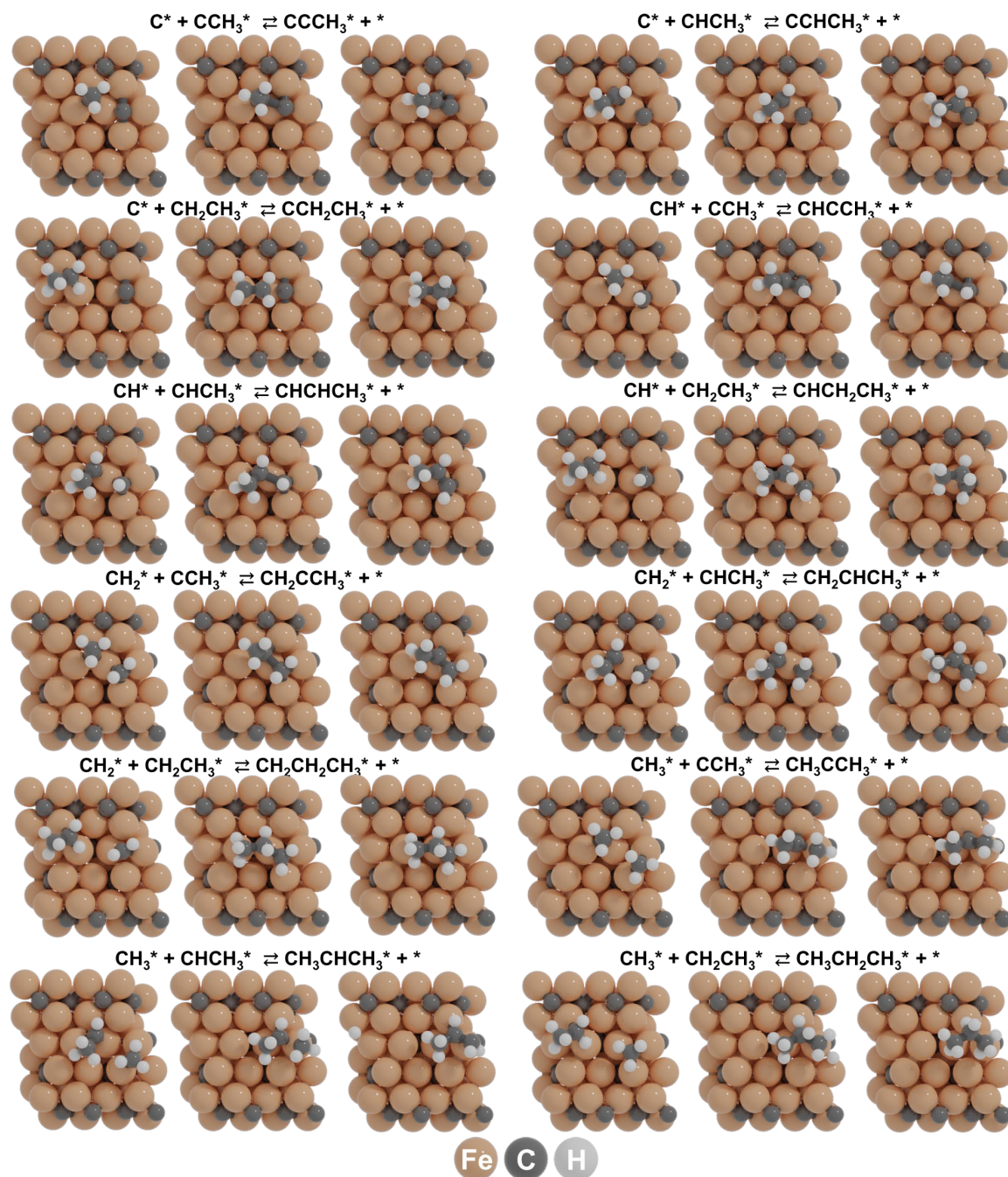


Figure B12. Configurations of IS, TS and FS for C₃ formation on the (010) surface of χ -Fe₅C₂.

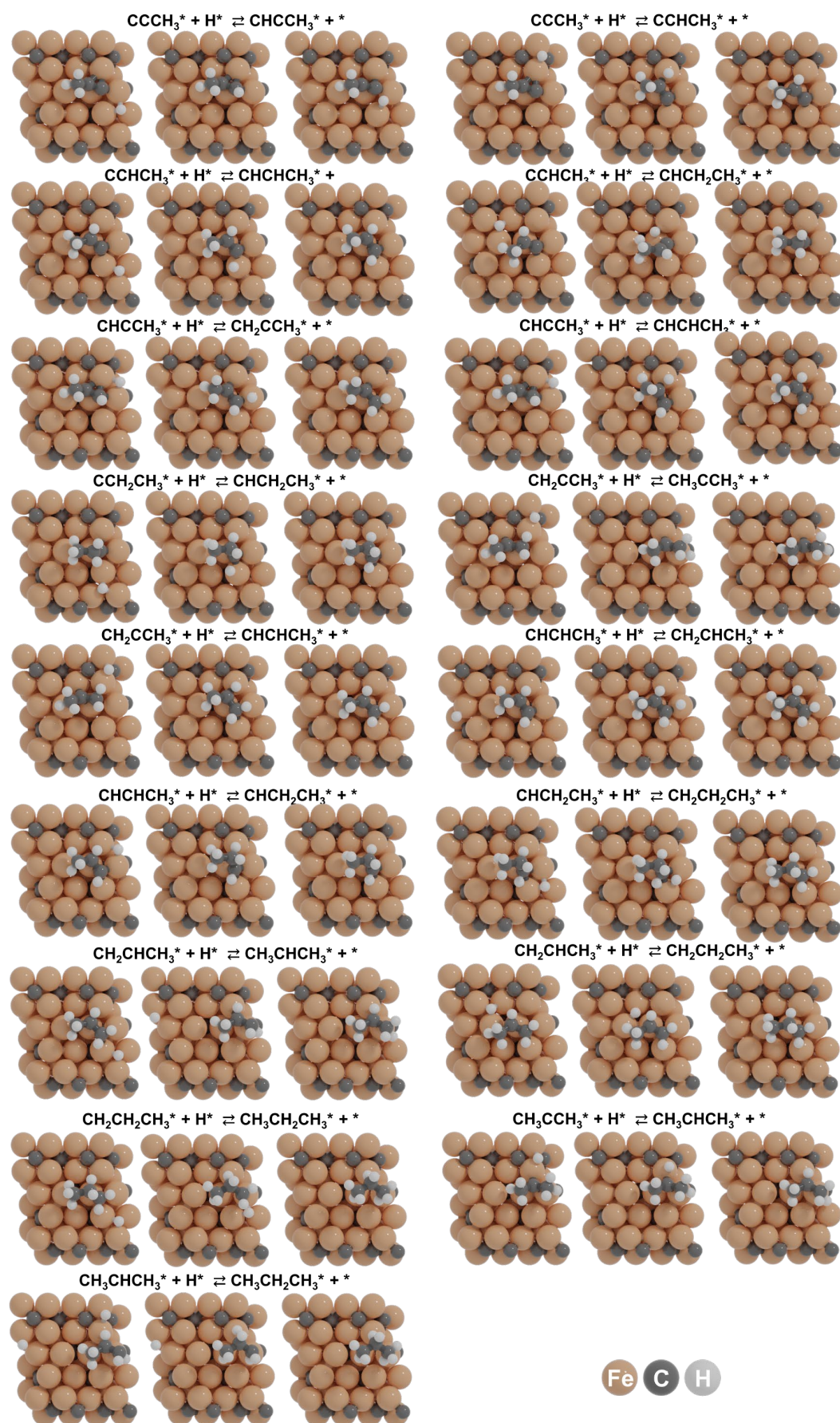


Figure B13. Configurations of IS, TS and FS for C₃ hydrogenation on the (010) surface of χ -Fe₅C₂.

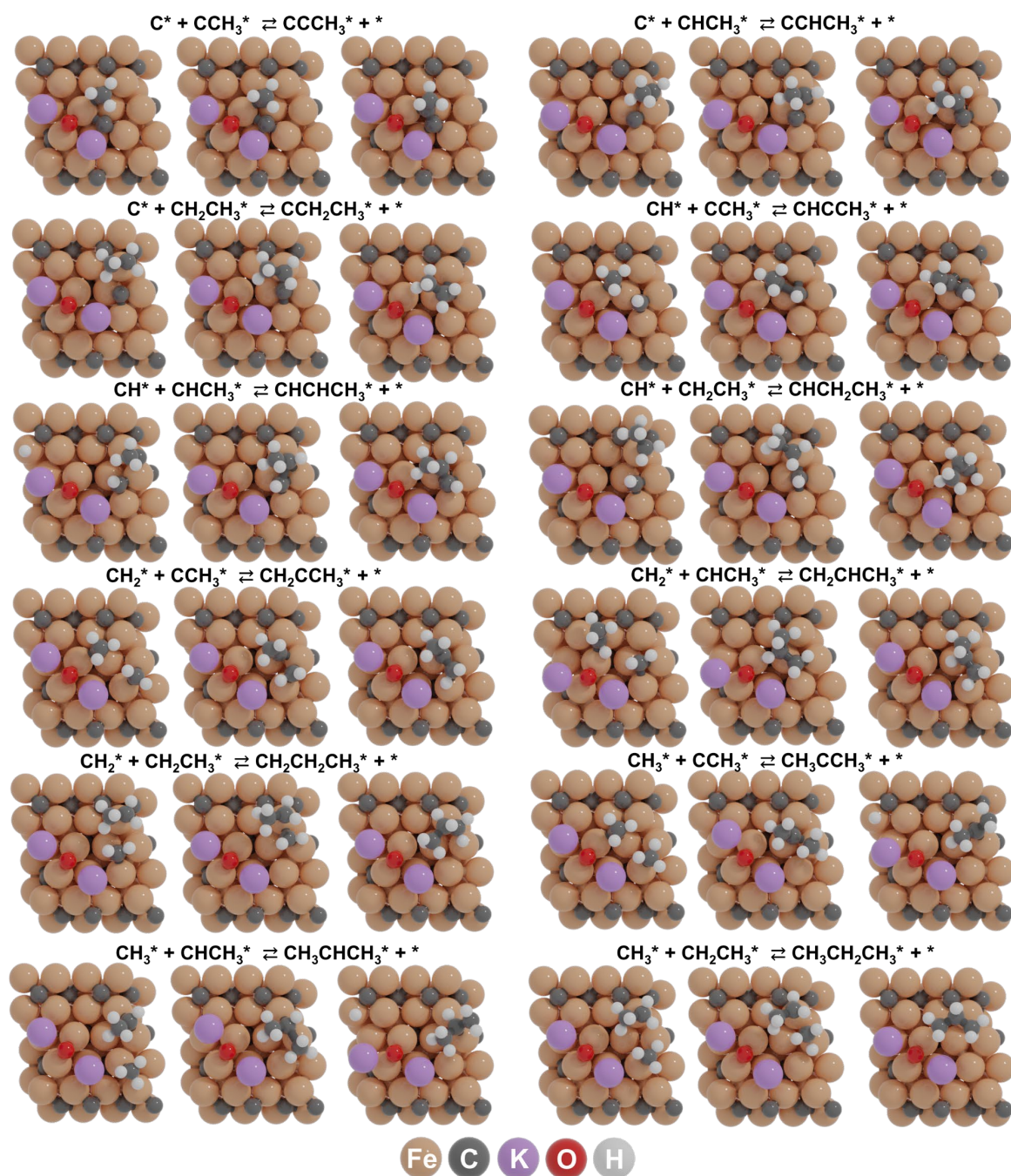


Figure B14. Configurations of IS, TS and FS for C₃ formation on the K₂O-promoted (010) surface of χ -Fe₅C₂.

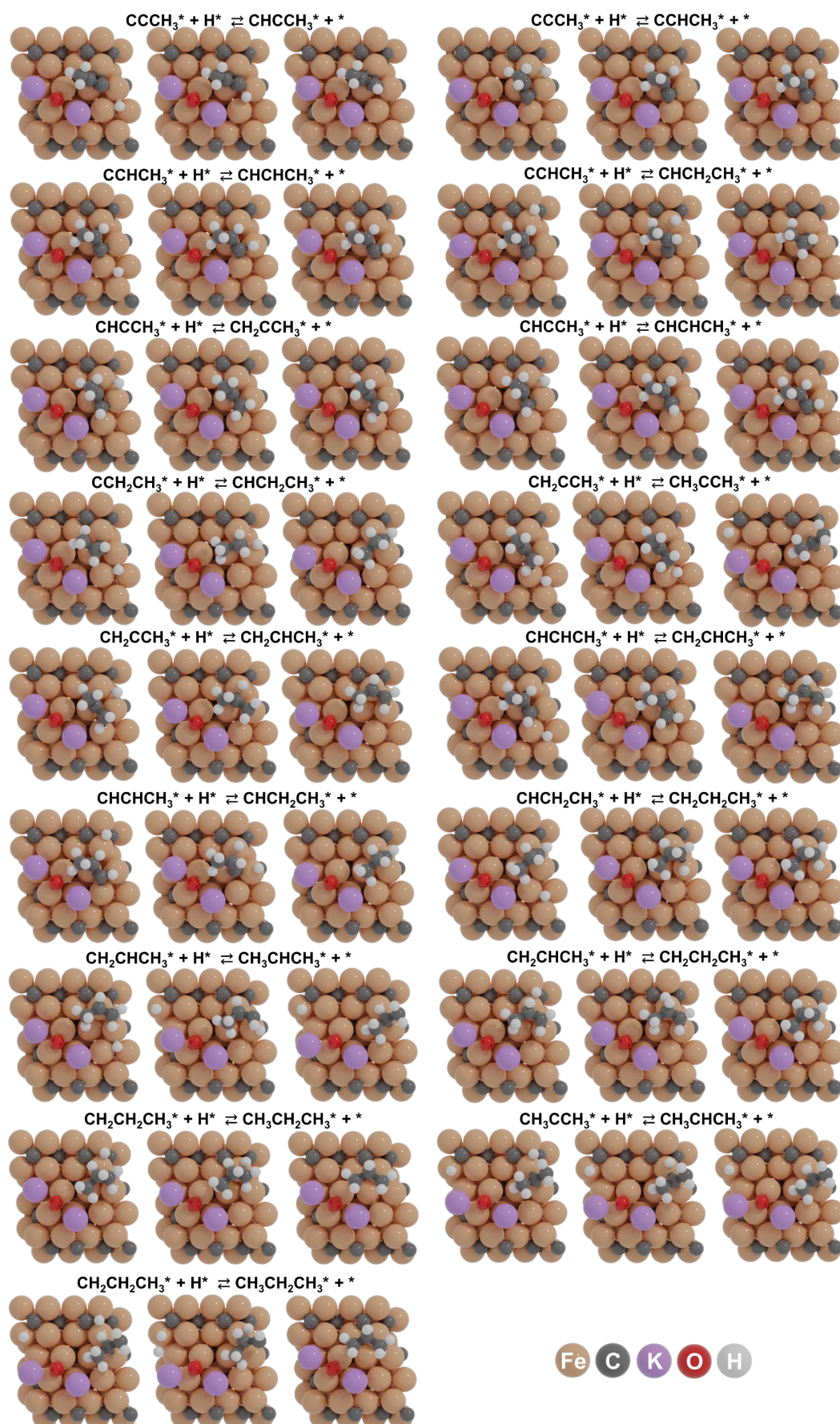


Figure B15. Configurations of IS, TS and FS for C₃ hydrogenation on the K₂O-promoted (010) surface of χ -Fe₅C₂.

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Table B1. Forward reaction barrier (E_f), backward reaction barrier (E_b) and pre-exponential factors of All Elementary Steps Examined in the Pathways of FTS on pristine and K₂O-promoted (010) surface of χ -Fe₅C₂.

Energy / kJ/mol	(010)				K ₂ O-(010)			
Elementary steps	E_f	ν_f	E_b	ν_b	E_f	ν_f	E_b	ν_b
$\text{CO}^* + * \rightleftharpoons \text{C}^* + \text{O}^*$	163	5.7×10^{11}	200	6×10^{12}	137	7.5×10^{12}	113	9.5×10^{12}
$\text{CO}^* + \text{H}^* \rightleftharpoons \text{HCO}^* + *$	119	9.2×10^{13}	61	1×10^{12}	108	9.4×10^{12}	22	3.7×10^{13}
$\text{CO}^* + \text{H}^* \rightleftharpoons \text{COH}^* + *$	160	5.0×10^{12}	67	4.7×10^{13}	170	2.1×10^{11}	44	4.6×10^{11}
$\text{HCO}^* + * \rightleftharpoons \text{CH}^* + \text{O}^*$	66	5.3×10^{12}	172	2.4×10^{12}	45	2.1×10^{13}	110	2.2×10^{12}
$\text{COH}^* + * \rightleftharpoons \text{C}^* + \text{OH}^*$	100	4.6×10^{12}	148	1.8×10^{12}	77	5.5×10^{12}	124	4.4×10^{11}
$\text{HCO}^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{O}^* + *$	127	1.7×10^{12}	49	2.4×10^{11}	99	1.6×10^{13}	15	4.9×10^{13}
$\text{CH}_2\text{O}^* + * \rightleftharpoons \text{CH}_2^* + \text{O}$	73	4.9×10^{11}	188	1.8×10^{12}	56	5.7×10^{12}	127	1.4×10^{12}
$\text{O}^* + \text{H}^* \rightleftharpoons \text{OH}^* + *$	143	5.7×10^{13}	60	1.3×10^{13}	113	5.6×10^{12}	57	4.4×10^{12}
$\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$	154	1.4×10^{13}	40	6.0×10^{11}	161	3.4×10^{13}	58	1.6×10^{12}
$\text{OH}^* + \text{OH}^* \rightleftharpoons \text{H}_2\text{O}^* + \text{O}^*$	44	3.4×10^{13}	13	1.2×10^{13}	49	3.9×10^{13}	1	1.8×10^{13}
$\text{CO}^* + \text{O}^* \rightleftharpoons \text{CO}_2^* + *$	151	1.1×10^{11}	64	2.6×10^{10}	146	2.6×10^{11}	45	1.3×10^{12}
$\text{C}^* + \text{H}^* \rightleftharpoons \text{CH}^* + *$	80	9.3×10^{12}	91	4.9×10^{12}	105	5.6×10^{12}	107	4.4×10^{12}
$\text{CH}^* + \text{H}^* \rightleftharpoons \text{CH}_2^* + *$	70	9.3×10^{12}	7	4.9×10^{12}	81	4.3×10^{13}	3	5.7×10^{12}
$\text{CH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_3^* + *$	83	1.5×10^{13}	38	6.6×10^{11}	88	2.3×10^{13}	34	8.0×10^{11}
$\text{CH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_4^* + *$	100	4.2×10^{13}	35	5.2×10^{12}	111	5.7×10^{14}	50	2.4×10^{13}
C ₂ formation								
$\text{C}^* + \text{C}^* \rightleftharpoons \text{CC}^* + *$	125	5.0×10^{13}	163	6.1×10^{12}	140	6.8×10^{12}	178	1.6×10^{13}
$\text{C}^* + \text{CH}^* \rightleftharpoons \text{CCH}^* + *$	80	5.5×10^{12}	75	5.8×10^{12}	104	9.0×10^{12}	94	6.9×10^{12}
$\text{C}^* + \text{CH}_2^* \rightleftharpoons \text{CCH}_2^* + *$	103	8.7×10^{12}	114	7.0×10^{12}	126	8.7×10^{13}	140	6.2×10^{13}
$\text{C}^* + \text{CH}_3^* \rightleftharpoons \text{CCH}_3^* + *$	144	5.1×10^{12}	182	3.2×10^{11}	161	1.6×10^{13}	196	3.2×10^{13}
$2\text{CH}^* \rightleftharpoons \text{CHCH}^* + *$	66	5.5×10^{12}	39	6.5×10^{12}	80	7.5×10^{13}	44	2.0×10^{13}
$\text{CH}^* + \text{CH}_2^* \rightleftharpoons \text{CHCH}_2^* + *$	105	1.4×10^{12}	51	7.9×10^{11}	120	5.1×10^{13}	61	3.1×10^{13}
$\text{CH}^* + \text{CH}_3^* \rightleftharpoons \text{CHCH}_3^* + *$	198	4.6×10^{13}	63	1.2×10^{14}	227	4.1×10^{12}	67	2.6×10^{12}
$2\text{CH}_2^* \rightleftharpoons \text{CH}_2\text{CH}_2^* + *$	82	4.9×10^{12}	46	6.7×10^{12}	107	9.7×10^{12}	103	3.3×10^{12}
$\text{CH}_2^* + \text{CH}_3^* \rightleftharpoons \text{CH}_2\text{CH}_3^* + *$	209	2.4×10^{11}	104	9.6×10^{10}	249	1.5×10^{12}	160	1.1×10^{12}
$\text{CH}_3^* + \text{CH}_3^* \rightleftharpoons \text{CH}_3\text{CH}_3^* + *$	197	2.3×10^{12}	116	2.6×10^{13}	211	1.9×10^{12}	166	1.7×10^{12}
C ₂ hydrogenation								
$\text{CC}^* + \text{H}^* \rightleftharpoons \text{CCH}^* + *$	85	1.2×10^{13}	54	4.6×10^{12}	99	1.7×10^{13}	52	8.6×10^{12}
$\text{CCH}^* + \text{H}^* \rightleftharpoons \text{CHCH}^* + *$	94	1.0×10^{13}	82	1.1×10^{13}	74	2.3×10^{13}	50	6.8×10^{12}
$\text{CCH}^* + \text{H}^* \rightleftharpoons \text{CCH}_2^* + *$	93	1.6×10^{13}	45	1.0×10^{13}	93	1.2×10^{13}	38	1.0×10^{13}
$\text{CCH}_2^* + \text{H}^* \rightleftharpoons \text{CCH}_3^* + *$	100	7.5×10^{13}	83	5.4×10^{13}	111	7.6×10^{13}	57	1.5×10^{13}
$\text{CCH}_2^* + \text{H}^* \rightleftharpoons \text{CHCH}_2^* + *$	96	7.9×10^{13}	42	2.3×10^{13}	103	8.1×10^{13}	31	7.1×10^{12}
$\text{CCH}_3^* + \text{H}^* \rightleftharpoons \text{CHCH}_3^* + *$	166	1.0×10^{11}	6	1.1×10^{10}	199	7.6×10^{13}	6	1.5×10^{13}
$\text{CHCH}^* + \text{H}^* \rightleftharpoons \text{CHCH}_2^* + *$	98	1.4×10^{13}	8	5.3×10^{12}	105	5.7×10^{13}	3	4.7×10^{12}
$\text{CHCH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_2^* + *$	81	8.6×10^{12}	37	7.7×10^{12}	101	6.1×10^{13}	78	1.9×10^{12}
$\text{CHCH}_2^* + \text{H}^* \rightleftharpoons \text{CHCH}_3^* + *$	151	6.6×10^{11}	27	1.8×10^{11}	174	8.3×10^{12}	20	1.4×10^{13}
$\text{CHCH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_3^* + *$	64	1.9×10^{11}	31	1.2×10^{11}	178	2.4×10^{13}	39	3.1×10^{12}
$\text{CH}_2\text{CH}_2^* + \text{H}^* \rightleftharpoons \text{CH}_2\text{CH}_3^* + *$	158	3.2×10^{11}	44	1.5×10^{12}	120	8.9×10^{11}	113	7.8×10^{11}
$\text{CH}_2\text{CH}_3^* + * \rightleftharpoons \text{CH}_3\text{CH}_3^* + *$	46	2.8×10^{10}	26	1.5×10^{11}	129	2.9×10^{12}	118	4.2×10^{12}

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C ₃ formation								
$C^* + CCH_3^* \rightleftharpoons CCCH_3^* + ^*$	131	5.0×10^{13}	101	6.0×10^{12}	148	2.9×10^{13}	58	2.2×10^{13}
$C^* + CHCH_3^* \rightleftharpoons CCHCH_3^* + ^*$	60	7.6×10^{12}	134	1.1×10^{11}	21	4.5×10^{12}	106	2.3×10^{13}
$C^* + CH_2CH_3^* \rightleftharpoons CCH_2CH_3^* + ^*$	102	4.6×10^{12}	175	4.5×10^{13}	56	9.3×10^{11}	142	4.8×10^{13}
$CH^* + CCH_3^* \rightleftharpoons CHCCH_3^* + ^*$	134	2.8×10^{14}	56	2.1×10^{12}	152	8.1×10^{14}	41	4.7×10^{12}
$CH^* + CHCH_3^* \rightleftharpoons CCHCH_3^* + ^*$	43	1.7×10^{13}	60	8.4×10^{12}	50	4.0×10^{13}	40	6.5×10^{12}
$CH^* + CH_2CH_3^* \rightleftharpoons CHCH_2CH_3^* + ^*$	154	5.3×10^{12}	150	9.3×10^{12}	89	5.1×10^{12}	81	4.4×10^{12}
$CH_2^* + CCH_3^* \rightleftharpoons CH_2CCH_3^* + ^*$	153	4.0×10^{13}	65	1.5×10^{13}	150	5.7×10^{13}	69	2.9×10^{12}
$CH_2^* + CHCH_3^* \rightleftharpoons CH_2CHCH_3^* + ^*$	25	1.1×10^{13}	63	5.8×10^{12}	78	8.4×10^{12}	144	9.9×10^{12}
$CH_2^* + CH_2CH_3^* \rightleftharpoons CH_2CH_2CH_3^* + ^*$	98	1.7×10^{13}	107	9.0×10^{13}	126	4.1×10^{11}	141	1.3×10^{12}
$CH_3^* + CCH_3^* \rightleftharpoons CH_3CCH_3^* + ^*$	153	1.7×10^{11}	53	2.7×10^{12}	177	4.1×10^{12}	87	2.3×10^{13}
$CH_3^* + CHCH_3^* \rightleftharpoons CH_3CHCH_3^* + ^*$	66	1.7×10^{13}	53	2.5×10^{13}	55	8.3×10^{13}	87	4.8×10^{13}
$CH_3^* + CH_2CH_3^* \rightleftharpoons CH_3CH_2CH_3^* + ^*$	160	6.2×10^{12}	154	9.6×10^{12}	218	4.9×10^{12}	246	4.2×10^{13}
C ₃ hydrogenation								
$CCCH_3^* + H^* \rightleftharpoons CHCCH_3^* + ^*$	87	3.7×10^{13}	49	4.1×10^{12}	54	8.9×10^{11}	34	2.4×10^{12}
$CCCH_3^* + H^* \rightleftharpoons CCHCH_3^* + ^*$	95	1.3×10^{13}	38	1.8×10^{12}	20	2.5×10^{13}	2	8.3×10^{12}
$CCHCH_3^* + H^* \rightleftharpoons CHCHCH_3^* + ^*$	61	3.1×10^{13}	16	2.1×10^{11}	91	2.3×10^{13}	3	9.4×10^{12}
$CCHCH_3^* + H^* \rightleftharpoons CCH_2CH_3^* + ^*$	75	1.8×10^{14}	42	2.7×10^{14}	110	2.8×10^{13}	104	7.0×10^{12}
$CCH_2CH_3^* + H^* \rightleftharpoons CHCH_2CH_3^* + ^*$	78	2.7×10^{14}	11	2.1×10^{14}	125	3.1×10^{14}	32	1.2×10^{13}
$CHCCH_3^* + H^* \rightleftharpoons CHCHCH_3^* + ^*$	73	2.5×10^{13}	8	1.1×10^{13}	96	1.5×10^{13}	7	2.3×10^{13}
$CHCCH_3^* + H^* \rightleftharpoons CH_2CCH_3^* + ^*$	94	3.7×10^{13}	22	7.2×10^{12}	66	2.3×10^{12}	18	1.8×10^{11}
$CH_2CCH_3^* + H^* \rightleftharpoons CH_2CHCH_3^* + ^*$	106	4.1×10^{12}	72	7.3×10^{12}	140	5.7×10^{12}	94	8.6×10^{11}
$CH_2CCH_3^* + H^* \rightleftharpoons CH_3CCH_3^* + ^*$	73	3.7×10^{12}	17	6.2×10^{12}	86	1.3×10^{13}	23	4.7×10^{12}
$CHCHCH_3^* + H^* \rightleftharpoons CH_2CHCH_3^* + ^*$	72	7.1×10^{13}	31	1.6×10^{12}	56	9.0×10^{13}	53	8.2×10^{12}
$CHCHCH_3^* + H^* \rightleftharpoons CHCH_2CH_3^* + ^*$	69	3.5×10^{13}	14	7.7×10^{12}	44	5.5×10^{11}	37	2.7×10^{11}
$CH_2CHCH_3^* + H^* \rightleftharpoons CH_2CH_2CH_3^* + ^*$	73	3.8×10^{13}	10	1.3×10^{13}	150	8.3×10^{12}	92	1.6×10^{12}
$CH_2CHCH_3^* + H^* \rightleftharpoons CH_3CHCH_3^* + ^*$	96	1.1×10^{13}	1	7.9×10^{14}	97	2.9×10^{12}	9	1.8×10^{12}
$CHCH_2CH_3^* + H^* \rightleftharpoons CH_2CH_2CH_3^* + ^*$	78	4.7×10^{13}	28	3.9×10^{13}	86	2.2×10^{12}	30	7.2×10^{13}
$CH_2CH_2CH_3^* + H^* \rightleftharpoons CH_3CH_2CH_3^* + ^*$	66	1.8×10^{13}	7	4.2×10^{13}	138	1.1×10^{14}	97	1.0×10^{13}
$CH_3CCH_3^* + H^* \rightleftharpoons CH_3CHCH_3^* + ^*$	113	1.6×10^{13}	39	2.9×10^{13}	111	1.6×10^{13}	40	1.1×10^{13}
$CH_3CHCH_3^* + H^* \rightleftharpoons CH_3CH_2CH_3^* + ^*$	190	1.3×10^{11}	163	9.8×10^{10}	105	4.2×10^{12}	92	3.0×10^{12}

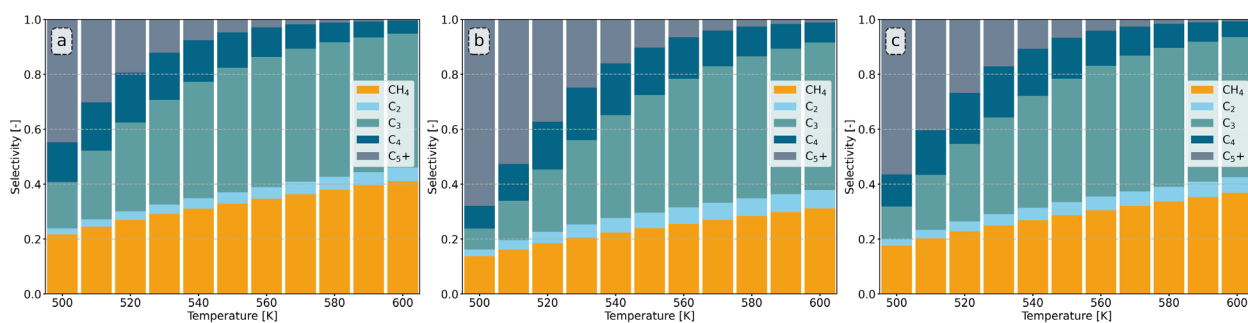


Figure B16. Selectivity of three models: (a) initial model, the modulated models where the barrier is manually decreased by 5 kJ/mol for (b) HCO formation ($CO^* + H^* \rightleftharpoons CHO^* + ^*$) or (c) HCO dissociation ($HCO^* + ^* \rightleftharpoons CH^* + O^*$), on the (010) surface of χ -Fe₅C₂ ($p = 20$ bar, H_2/CO ratio = 2).

Chapter 4. The Nature of K Promotion of χ -Fe₅C₂ for High Chain-Growth Probability in the Fischer-Tropsch Reaction

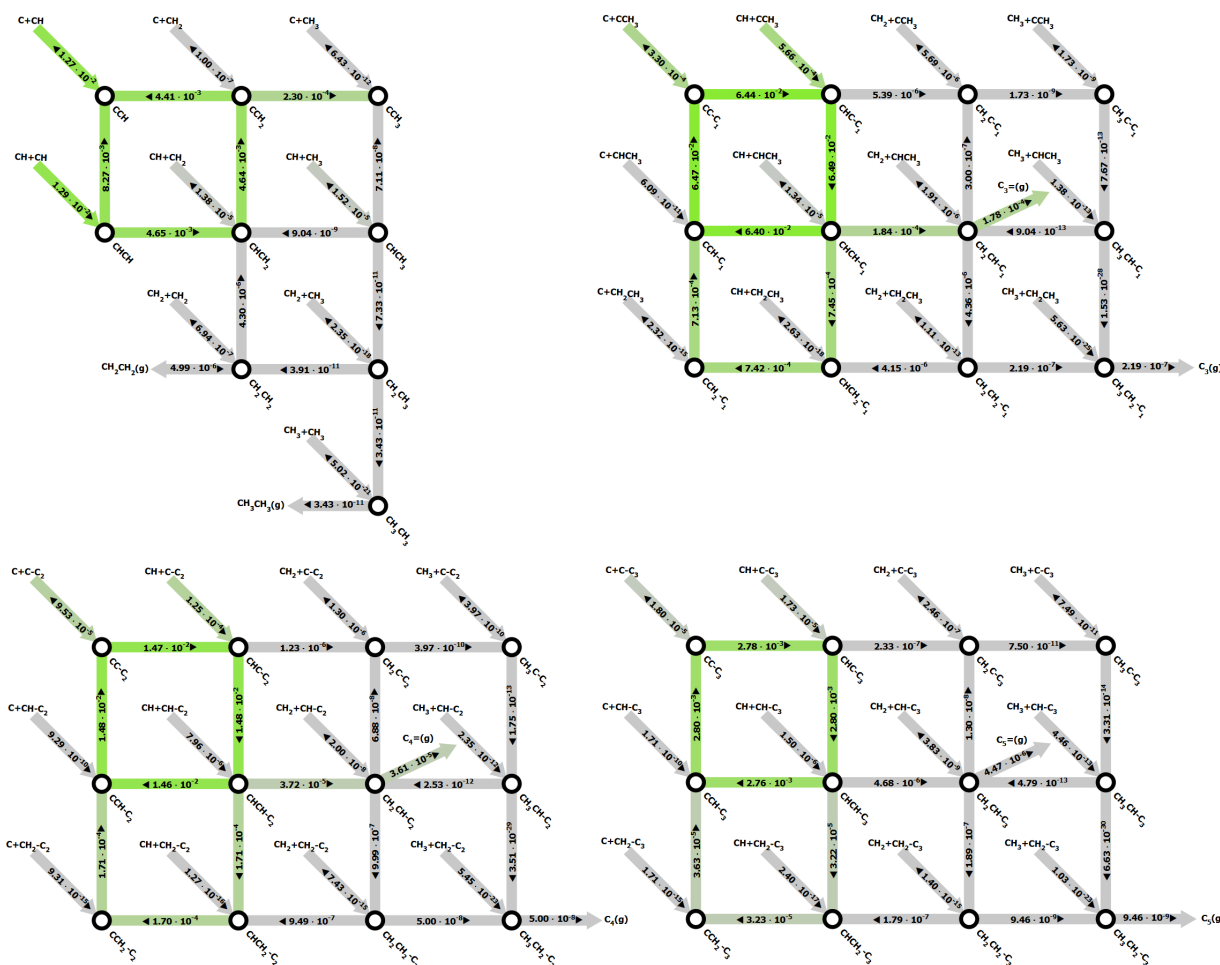


Figure B17. Molar Flux difference in C₂-C₅ formation between the reaction networks of the initial and modulated models for the (010) surface of χ -Fe₅C₂ ($T=520\text{K}$, $p = 20\text{ bar}$, H_2/CO ratio = 2). To build the modulated system, we manually decreased the barrier of CCH₃* formation ($\text{CCH}_2^* + \text{H}^* \rightleftharpoons \text{CCH}_3^*$) by 5 kJ/mol. This comparison is conducted to explain the negative value of degree control of chain growth for CCH₃* formation. The values indicated in the pathways are the difference in the molar flux of dissociation, hydrogenation, desorption and coupling. The intensity of the color indicates the magnitude of the molar flux value.

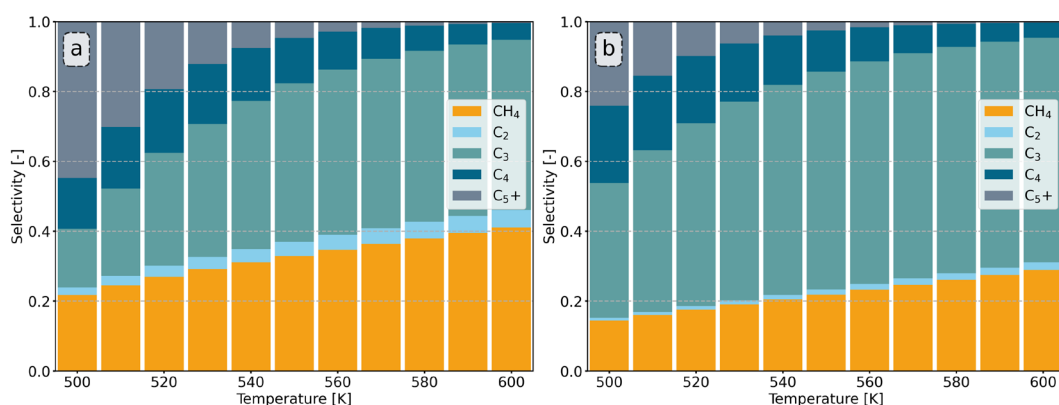


Figure B18. Selectivity of the (a) initial and (b) modulated models for the (010) surface of χ -Fe₅C₂ ($p = 20\text{ bar}$, H_2/CO ratio = 2).

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Table B2. Microkinetics simulations for FT synthesis reaction on the (010) and K₂O-promoted (010) surface of χ -Fe₅C₂. ($T = 520$ K, $p = 20$ bar, H_2/CO ratio = 2).

Microkinetics simulations Outputs at T = 520 K	(010)	K ₂ O-(010)
CO TOF/ s ⁻¹	8.06×10 ⁻⁴	2.11×10 ⁻³
CO ₂ selectivity	4.04×10 ⁻⁵	2.43×10 ⁻⁵
CH ₄ selectivity	2.70×10 ⁻¹	1.02×10 ⁻¹
C ₂ -C ₄ selectivity	5.37×10 ⁻¹	4.17×10 ⁻¹
C ₅ + selectivity	1.93×10 ⁻¹	4.81×10 ⁻¹
Alpha (α)	0.42	0.67

Table S3. Turn over frequency (TOF) of CO and selectivity based on C in Fischer-Tropsch Process on the unpromoted and K-promoted iron-based catalysts.

Catalyst	TOF (mol g _{cat} ⁻¹ s ⁻¹)	Selectivity (%)				Alpha (α)	Reference
		CO ₂	CH ₄	C ₂ -C ₄	C ₅ +		
Fe/rGO	3.4 × 10 ⁻⁴	49.7	48.0 ^a	51 ^a	0.3 ^a	0.14	Cheng et al. [27]
FeK _{0.5} /rGO	5.6 × 10 ⁻⁴	49~52	31.0 ^a	65 ^a	3.3 ^a	0.18	Cheng et al. [27]
FeK ₁ /rGO	6.5 × 10 ⁻⁴	49~52	26.0 ^a	69.9 ^a	4.4 ^a	0.23	Cheng et al. [27]
FeK _{1.5} /rGO	2.7 × 10 ⁻⁴	49~52	22.0 ^a	73.8 ^a	5.0 ^a	0.26	Cheng et al. [27]
FeK ₂ /rGO	2.2 × 10 ⁻⁴	49~52	20.0 ^a	74.2 ^a	6.7 ^a	0.29	Cheng et al. [27]
ε-Fe _{2.2(2)} C	-	5.0	18.0	29.0	48.0	-	Peng et al. [25]
Mn- χ -Fe ₅ C ₂	2.6 × 10 ⁻⁴	9.3	8.0	47	35.7	0.61	Peng et al. [79]
Fe/K ₍₀₎	-	35.9	23.0 ^a	39.9 ^a	37.1 ^a	-	Yang et al. [79]
Fe/K _(0.2)	-	35.6	15.4 ^a	33.8 ^a	50.8 ^a	-	Yang et al. [35]
Fe/K _(0.7)	-	40.4	10.6 ^a	27.8 ^a	61.6 ^a	-	Yang et al. [35]
Fe/K _(1.5)	-	22.8	8.6 ^a	27.4 ^a	64.0 ^a	-	Yang et al. [35]
Fe/K _(3.0)	-	20.6	8.0 ^a	27.0 ^a	65.0 ^a	-	Yang et al. [35]
χ -Fe ₅ C ₂	1.4 × 10 ⁻⁴	33.0	38.5 ^a	54 ^a	7.5 ^a	-	Park J C et al. [36]
K _(0.05) - χ -Fe ₅ C ₂	1.6 × 10 ⁻⁴	31.0	11.5 ^a	33.6 ^a	54.9 ^a	-	Park J C et al. [36]
Fe/AC	-	30.1	18.4 ^a	51.1 ^a	30.6 ^a	0.64	Ma et al. [39]
Fe/0.9 K/AC	-	45.5	7.80 ^a	41.7 ^a	50.5 ^a	0.75	Ma et al. [39]
Fe/ α -Al ₂ O ₃	8.5 × 10 ⁻⁵	-	24.0 ^a	56 ^a	10.0 ^a	0.39	Torris Galvis et al. [83]
Fe-Ti-Zn-K	1.12 × 10 ⁻⁵	-	23.0 ^a	57 ^a	10.0 ^a	0.43	Torris Galvis et al. [83]
Supported Fe	-	10-14	30.0 ^a	36 ^a	34.0 ^a	-	Eliason et al. [86]
Supported K/Fe	-	12.0	11.0 ^a	25 ^a	63.0 ^a	-	Eliason et al. [86]
Fe/rGO	3.4 × 10 ⁻⁴	49.7	42.3 ^a	56.6 ^a	1.1 ^a	0.23	Cheng et al. [90]
FeMg/rGO	2.5 × 10 ⁻⁴	40.7	35.6 ^a	59.9 ^a	4.5 ^a	0.32	Cheng et al. [90]
FeMgK0.5/rG	1.1 × 10 ⁻³	40.5	31.4 ^a	62.7 ^a	5.9 ^a	0.35	Cheng et al. [90]
FeMgK1/rGO	1.7 × 10 ⁻³	41.1	27.1 ^a	66.5 ^a	6.4 ^a	0.37	Cheng et al. [90]
FeMgK2/rGO	1.4 × 10 ⁻³	40.8	20.3 ^a	71.2 ^a	8.5 ^a	0.40	Cheng et al. [90]
FeMgK5/rGO	6.2 × 10 ⁻⁴	40.5	19.6 ^a	70.1 ^a	10.3 ^a	0.45	Cheng et al. [90]
FeK2/rGO	5.5 × 10 ⁻⁴	49.0	22.0 ^a	70.1 ^a	7.9 ^a	-	Cheng et al. [90]
Fe/K-free	-	-	11.1 ^a	25.3 ^a	63.3 ^a	-	Zhao et al. [91]
Fe/K-ZSM-5	-	-	9.1 ^a	22.9 ^a	68.0 ^a	-	Zhao et al. [91]

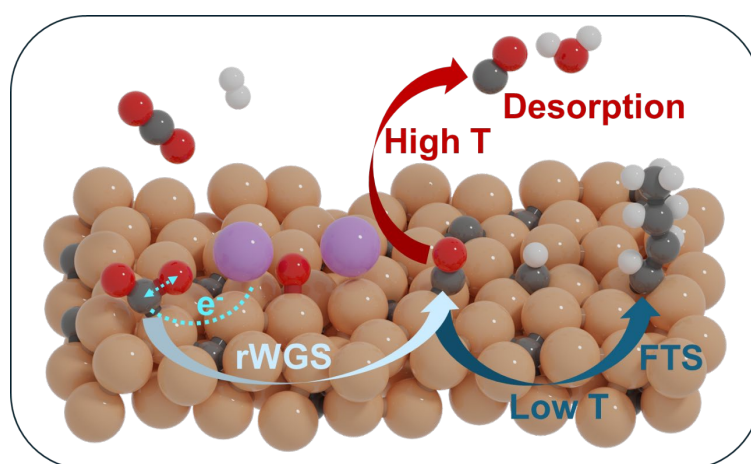
a: Hydrocarbon selectivity (normalized without CO₂).

Chapter 5. A Theoretical Study of the Role of K on the Reverse Water-Gas Shift Reaction on Hägg Carbide

Abstract

Potassium (K) is known to enhance the catalytic performance of Fe-based catalysts in the reverse water-gas shift (rWGS) reaction, which is highly relevant during Fischer–Tropsch (FT) synthesis of CO₂-H₂ mixtures. To elucidate the mechanistic role of K promoter, we employed density functional theory (DFT) calculations in conjunction with microkinetic modelling for two representative surface terminations of Hägg carbide (χ -Fe₅C₂), i.e., (010) and (510). K₂O results in stronger adsorption of CO₂ and H₂ on Hägg carbide and promotes C-O bond dissociation of adsorbed CO₂ by increasing the electron density on Fe atoms close to the promoter oxide. The increased electron density of the surface Fe atoms results in an increased electron-electron repulsion with bonding orbitals of adsorbed CO₂. Microkinetics simulations predict that K₂O increases the CO₂ conversion during CO₂-FT synthesis. K₂O also enhances CO adsorption and dissociation, facilitating the formation of methane, used here as a proxy for hydrocarbons formation during CO₂-FT synthesis. CO dissociation and O removal via H₂O compete as the rate-controlling steps in CO₂-FT.

Keywords: Fischer-Tropsch synthesis, Hägg carbide, reverse water-gas shift, potassium, density functional theory



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5.1 Introduction

The huge amount of greenhouse gases released into the atmosphere by human activities is expected to lead to serious changes in the climate.^{1, 2} Utilizing CO₂ as a source of carbon to manufacture fuels and chemicals is a way to lower the atmospheric CO₂ concentration and close the carbon cycle, thereby replacing the use of fossil feedstock such as oil, gas and coal.³⁻⁵ This explains the interest in the conversion of CO₂ with H₂ generated from water using renewable energy.^{6, 7} It leads to significant research and development efforts in water electrolysis to generate green H₂,⁸ driven by the availability of cheap green electricity.⁹ The hydrogenation of CO₂ with H₂ leads to valuable products such as carbon monoxide,^{10, 11} methane,^{12, 13} methanol,¹⁴ light olefins¹⁵ and other hydrocarbons.¹⁶ Fischer-Tropsch synthesis is a versatile technology to convert synthesis gas, a mixture of CO and H₂, into fuels and chemicals. Besides the indirect route involving the conversion of CO₂ to CO, there is growing interest in the direct hydrogenation of CO₂ with H₂ to fuels and chemicals, i.e., CO₂ Fischer–Tropsch (CO₂-FT) synthesis.¹⁷

FT synthesis catalysts typically contain Co or Fe as the active transition metals.^{18, 19} With CO₂ as the carbon-containing reactant, FT catalysts should have sufficient activity in the reverse water-gas shift (rWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) to form hydrocarbons. As the water-gas shift (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) activity of Co is very low, the formation of CO intermediate, from which CH_x monomers are in situ formed, is too slow during CO₂-FT synthesis. This explains why CH₄ is the main reaction product of CO₂-FT synthesis on Co catalysts.²⁰ CH₄ has a lower economic value than hydrocarbons containing carbon-carbon bonds, as long-chain paraffins can be used as fuels and olefins are common chemical building blocks. In contrast, catalysts containing Fe are known for their high activity in the WGS reaction, which is advantageous when processing synthesis gas with a low H₂/CO ratio typically obtained from coal or biomass.²¹⁻²⁵ Besides, Fe is a much cheaper metal than Co. The considerable WGS activity of Fe also helps to form sufficient CO reactant during CO₂-FT synthesis, explaining the promise of Fe catalysts in the direct hydrogenation of CO₂ into fuels and chemicals.²⁶ Under typical FT synthesis conditions, the Fe-containing precursor phases in such FT catalysts undergo carburization, resulting in Fe-carbides, such as $\epsilon\text{-Fe}_2\text{C}$, $\epsilon'\text{-Fe}_{2.2}\text{C}$, $\chi\text{-Fe}_5\text{C}_2$, $\theta\text{-Fe}_3\text{C}$, or Fe_7C_3 .²⁷⁻²⁹ X-ray diffraction (XRD) and Mössbauer spectroscopy have been instrumental in establishing the strong correlation between the catalytic performance and such Fe-carbide phases.^{19, 30-33} Among them, Hägg carbide ($\chi\text{-Fe}_5\text{C}_2$) is usually regarded as one of the dominant and most active phases for CO activation and chain growth.^{24, 33,}

Alkali metals are widely used as promoters in large-scale industrial processes, such as ammonia synthesis³⁵ and Fischer-Tropsch synthesis.³⁶ Besides, it can also promote the active MoS₂ phase in the hydrogenation of CO to higher alcohols³⁷ and, with H₂S, to methanethiol.^{38, 39} Alkali promoters are used to tune the performance of Fe-based catalysts, i.e., they typically increase the CO conversion and the selectivity to long-chain hydrocarbons at the expense of undesired methane.⁴⁰⁻⁴³ Among alkali metals, K is usually reported to be the most effective one for inhibiting methane selectivity, presumably by decreasing hydrogenation rates.⁴⁴⁻⁴⁷ K is also known to significantly enhance the rate of the WGS reaction.⁴⁸

Given the widespread use as a promoter for Fe-based FT catalysts, the role of K in the FT reaction has already been the topic of several investigations.^{46, 49-56} Studies into the mechanistic role of K in the WGS reaction are relatively scarce. While some WGS activity in the CO-FT reaction of synthesis gas is important to increase the low H₂/CO ratio, the reverse WGS (rWGS) reaction is likely the essential first step in CO₂-FT synthesis. According to Amoyal et al.,⁴⁶ the addition of K renders Fe-carbide less prone to oxidation, explaining the increased CO conversion compared to non-promoted catalysts. Huo et al. attributed enhanced CO conversion to the ability of K to stabilize the active Fe-carbide surfaces, as followed from transmission electron microscopy (TEM) and XRD studies supported by density functional theory (DFT) calculations.⁵² It has also been reported that the introduction of K facilitates CO dissociation, which in turn increases the rate of Fe carburization.⁵⁰ Faster carburization due to the presence of K was also concluded in the work of Cheng et al.,⁵¹ who observed a linear relationship between the amount of Hägg carbide and the surface basicity, which was related to K and involved in CO and CO₂ activation. Theoretical investigations mainly focused on the effect of K on adsorption, with only a few studies reporting enhanced CO and CO₂ dissociation. Petersen et al. reported that the presence of a K atom on Hägg carbide leads to stronger adsorption of CO and O.⁵³ Zhao et al. found that K₂O promotes CO dissociation by lowering dissociation barriers of intermediates such as COH, CHOH and CH₂OH.⁵⁴ Sorescu attributed easier CO dissociation to the interaction of atomic K with the O atom of the dissociating CO molecule⁵⁵. A similar interaction between adsorbed CO₂ and K was reported by Nie et al.⁵⁶ Such interactions were identified for several Fe-containing surfaces, including metallic Fe and oxidized and carburized Fe. Despite these insights, the nature of K species under FT reaction conditions and their mechanistic role in promoting the WGS reaction remain unclear.

In this work, we aimed at a deeper insight into the mechanistic role of K in the rWGS reaction in the context of CO₂-FT synthesis. We employed DFT calculations to study candidate K-containing

surface structures on two representative surface models of χ -Fe₅C₂, i.e., (010) and (510). It was first established that the most stable structure form of K on these surfaces is K₂O. Using this as a model for K-promoted χ -Fe₅C₂, we found that the adsorption of CO₂, H and CO is stronger in the vicinity of K₂O. K₂O promotes CO₂ dissociation by injecting electrons into the surface, leading to increased occupation of anti-bonding orbitals and increased electron-electron repulsion in bonding orbitals of the C-O bond in adsorbed CO₂. This results in the weakening of the C-O bond and lower C-O dissociation barriers. We then conducted microkinetics simulations of the rWGS reaction on the more active (510) surface, where CO₂ dissociation exhibited a significantly lower barrier than on the (010) surface, which was furthermore more strongly affected by the presence of K. Given the relevance of the rWGS reaction in CO₂-FT, we also considered the formation of CH₄ as a hydrocarbon product, serving as a proxy for the formation of hydrocarbons. The results show that K₂O increases the rate of CO₂ conversion. K₂O facilitates methane formation by enhancing the adsorption and dissociation of both CO₂ and CO and decreasing C-O bond dissociation barriers.

5.2 Computational Methods

5.2.1 Density Functional Theory

All density functional theory (DFT) calculations were conducted by using generalized gradient approximation (GGA) ⁵⁷ with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,⁵⁷ and carrying out spin-polarization as implemented in the Vienna Ab Initio Simulation Package (VASP 5.4.4). A dispersion correction for Van der Waals interaction was applied by using the PBE+D3 method.⁵⁸ Wherein the effective ion core-electrons and nucleus were described by projector-augmented wave (PAW) potentials.⁵⁹⁻⁶¹ The plane-wave basis was set with a cut-off energy of 400 eV. Geometry optimizations were performed using the conjugate gradient method with a force-based stopping criterion of 0.05 eV/Å for each cartesian direction and each atom. The Brillouin zone was sampled using a 1×1×1 Monkhorst-Pack grid (Γ-point only). The climbing-image nudged elastic band method (CI-NEB) was used to find the transition state.^{62, 63} A frequency analysis was employed for all states, where stable states were verified to have no imaginary frequencies, while all transition states were confirmed to have a single imaginary frequency in the direction of the reaction coordinate. A finite difference approach was applied to determine the Hessian matrix for frequency analysis by perturbing the atomic positions by 0.01 Å in each Cartesian direction. The corresponding normal mode vibrations were used to calculate the zero-point energy (ZPE) and vibrational partition functions.

As a model system in this study, we selected two representative models for CO₂ activation on the Fe₅C₂ catalyst. i.e., (i) a quasi-fourfold rectangle (FR) and (ii) the planar five-fold site (P5) on Fe₅C₂(510) representing active sites with different reactivities on the surface of χ -Fe₅C₂ under FTS conditions. The first two layers with the adsorbed molecules were allowed to relax while the bottom layers were kept frozen for these four models in all geometry optimization. A vacuum layer of 15 Å was added perpendicular to the surface to mitigate spurious interactions between neighbouring slabs.

A Crystal Orbital Hamilton Population (COHP) and Density of States (DOS) analysis is conducted using the Lobster software (version 4.1.0) to investigate the electronic structures.^{64, 65} DDEC6 charge analysis was applied to calculate net charges on atoms using the Chargemol software (version 3.5).^{66, 67} Electronic structure analysis using electron density differences was performed by projecting the three-dimensional scalar fields onto two-dimensional planes. Analysis and visualization of the electron density are conducted using the open-source EDP package (version 2.0.3).⁶⁸

5.2.2 Microkinetics Modelling

Based on the energetics of the elementary reaction steps, a microkinetic model was constructed to investigate the kinetics of CO₂ activation and hydrogenation to methane. The kinetic network was modeled using a set of ordinary different equations (ODE) involving the surface coverages, the reaction rate constants of the elementary reaction steps, and the partial pressures of the gas-phase species. Each ODE corresponds to the time derivative of a surface compound. Time-integration of the ODEs was conducted using relative and absolute tolerances of 10⁻⁸. At $t = 0$, the surface was empty. All the microkinetic simulations were performed using the MKMCXX software suite.⁶⁹

In the adsorption process, the net absorption rate of gas-phase species i is calculated by

$$r_i = k_{i,\text{ads}}\theta^*p_i - k_{i,\text{des}}\theta_i \quad (5.1)$$

where θ^* and θ_i are the fraction of free sites and fractional coverage of species i , respectively. $k_{i,\text{ads/des}}$ corresponds to the rate constant for the adsorption/desorption process and p_i is the partial pressure of species i .

For the description of adsorption/desorption steps, each adsorbate is assumed to lose one translational degree of freedom in the transition state with respect to the initial gas-phase state. Under this assumption, the rate of adsorption and desorption is given by

$$k_{\text{ads}} = \frac{p A_{\text{st}}}{\sqrt{2\pi m_i k_B T}} \quad (5.2)$$

$$k_{\text{des}} = \frac{k_B \cdot T^3}{h^3} \cdot \frac{A_{\text{st}}(2\pi m_i k_B)}{\sigma \theta_{\text{rot}}} \cdot \exp\left(\frac{-\Delta E_{\text{des}}}{RT}\right) \quad (5.3)$$

where k_{ads} is the rate constant for adsorption of the absorbate, P and A_{st} are the corresponding partial pressure and the effective surface area, m_i is the molar mass of the gas species, k_B is the Boltzmann constant, T is the temperature, k_{des} is the constant for desorption of the absorbate, h is the Planck constant, σ is the symmetry number, θ_{rot} is the rotational temperature, and finally ΔE_{des} and R are the desorption energy and gas constant.

For an elementary reaction step over the catalytic surface, the rate constant (k) is calculated from the Eyring equation as given by

$$k = v \cdot \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) \quad (5.4)$$

Herein, ΔE_{act} is the electronic activation energy including the ZPE-correction and v is the pre-exponential factor. The pre-exponential factors are evaluated for the forward and backward reaction using the following equations

$$v_{\text{forward}} = \frac{k_B T}{h} \left(\frac{Q_{\text{TS}}^*}{Q_{\text{IS}}} \right) \quad (5.5)$$

$$v_{\text{backward}} = \frac{k_B T}{h} \left(\frac{Q_{\text{TS}}^*}{Q_{\text{FS}}} \right) \quad (5.6)$$

where Q_{TS}^* is the total of translational, rotational, and vibrational partition functions of the transition state excluding the partition function corresponding to the imaginary frequency. $Q_{\text{IS/FS}}$ correspond to the products of the motional partition functions for the initial and final state, respectively.

To further evaluate the contribution of each reaction step to the overall rate and product distribution, we used the concepts of the degree of rate control (DRC) as proposed by Campbell.⁷⁰ For each elementary reaction step, a DRC coefficient is assigned as given by

$$X_{\text{RC},i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (5.7)$$

which at zero conversion and at steady state obeys the following sum rule

$$\sum X_{\text{RC},i} = 1 \quad (5.8)$$

In the above equations, $X_{RC,i}$ corresponds to the DRC coefficient, K_i is the equilibrium constant, k_i is the reaction rate constant and r corresponds to the overall reaction rate.

5.3 Results and Discussion

5.3.1 Surface Models

Optimization of the monoclinic unit cell (space group C2/c) of bulk χ -Fe₅C₂ by DFT yielded as unit cell parameters $a \times b \times c = 11.53 \text{ \AA} \times 4.50 \text{ \AA} \times 4.95 \text{ \AA}$ and unit cell angles $\beta = 97.75^\circ$ and $\alpha = \gamma = 90^\circ$, in good agreement with the experimental values of Hägg carbide ($a = 11.588 \text{ \AA}$, $b = 4.579 \text{ \AA}$, $c = 5.059 \text{ \AA}$, and $\beta = 97.75^\circ$).⁷¹ The optimized unit cell is shown in the Appendix C (Figure A1). Starting from this optimized bulk structure, two representative surface slab models were built, exposing the (010) and (510) surface facets. As shown in Figure 5.1, these surfaces exhibit distinct active site configurations, named FR and P5 sites. These active configurations were selected because they were earlier found to exhibit high activity for CO dissociation by respectively direct CO dissociation and H-assisted CO dissociation under typical FT conditions.^{54, 72-74}

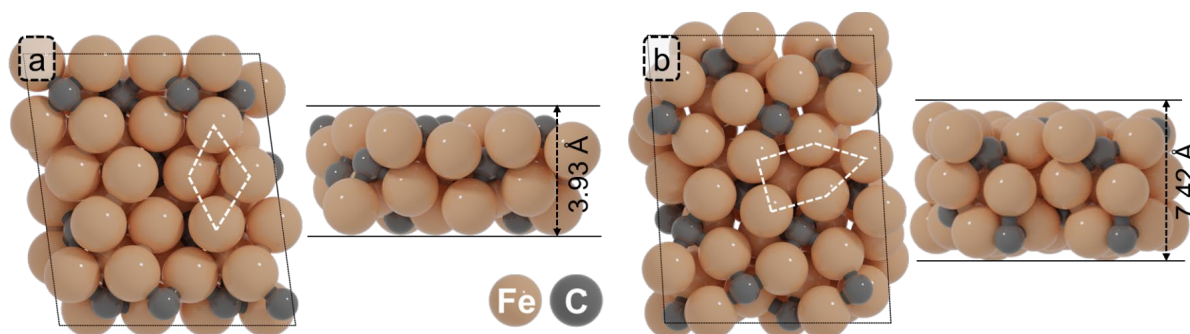


Figure 5.1. Top and side view of (a) the (010) and (b) the (510) surfaces models of Hägg carbide. The solid lines correspond to the top and bottom edges of the periodic supercell. The FR and P5 sites are indicated by dotted white lines.

We next explored the most stable state of K on these surfaces by evaluating the stability of K, KO, KOH, K₂O and K₂CO₃ as candidate surface species. Energy diagrams linking these species through transition states are shown in Figure 5.2. K₂O is significantly more stable than the other surface species with barriers for the interconversion between K, KO, and K₂O being low. The formation of KOH from KO and K₂CO₃ from K₂O involves higher barriers. For instance, metallic K is oxidized to KO with no barriers on the (010) and (510) surfaces. On the (010) surface, KO is easier oxidized to K₂O with a barrier of 23 kJ/mol than hydrogenated to KOH ($E_{\text{act}} = 81 \text{ kJ/mol}$). Likewise, on the (510) surface, KO is oxidized to K₂O without a much lower barrier rather than

being hydrogenated to KOH ($E_{\text{act}} = 149$ kJ/mol). On the (510) surface, K_2CO_3 formation is not favourable due to its much higher barrier (112 kJ/mol) than CO_2 dissociation (14 kJ/mol). Similarly, the difference between these two reactions is 94 kJ/mol on the (010) surface, indicating that the formation of K_2CO_3 is unfavourable. Therefore, the most stable configuration of adsorbed K is in its K_2O form, aligning well with other studies.^{45, 47, 75, 76}

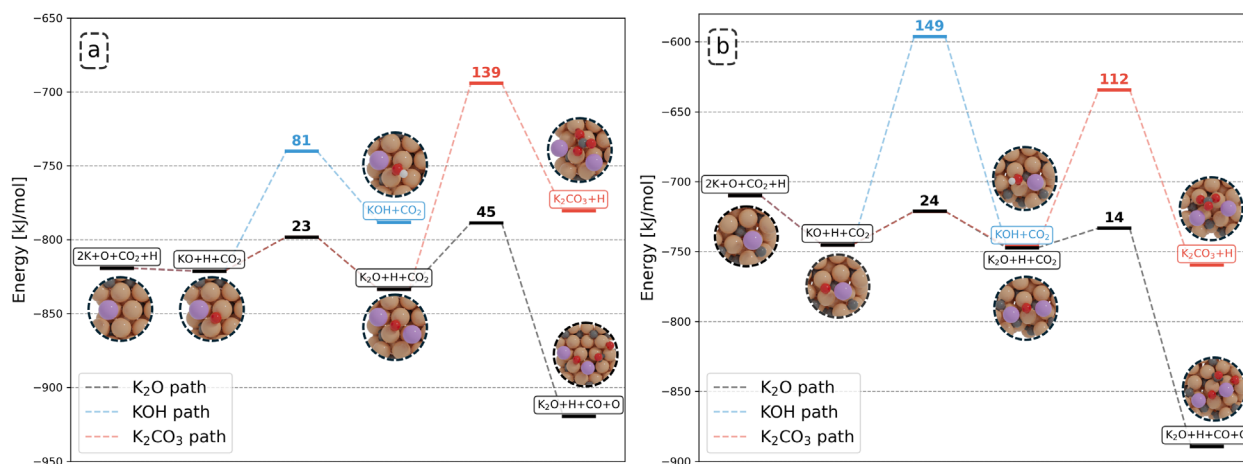


Figure 5.2. Reaction energy diagrams of the formation of KOH, K_2O and K_2CO_3 on (a) the (010) surface and (b) the (510) surface of $\chi\text{-Fe}_5\text{C}_2$.

5.3.2 Reactant Adsorption and Activation

5.3.2.1 Adsorption

The adsorption energies of CO_2 and H_2 and the stability of reaction intermediates critically determine the surface composition under FT reaction conditions and, by extent, the reaction rate. Therefore, we investigated the influence of K_2O on the adsorption of CO_2 and H in these two models. Top, bridge, three-fold, four-fold and five-fold adsorption modes were considered for CO_2 and H. The most stable adsorption geometries and their corresponding adsorption energies of CO_2 and H on the two considered Hägg carbide surfaces, with and without the K_2O promoter, are provided in Figure 5.3.

On the (010) surface, the most stable adsorption configuration of CO_2 is obtained at the FR site with an adsorption energy of -152 kJ/mol (Figure C1). The presence of K_2O strengthens this adsorption mode by 8 kJ/mol. On the (510) surface, CO_2 is most stably adsorbed at a four-fold site, partially covering the P5 site, with an adsorption energy of -97 kJ/mol (Figure C2). Adsorption on this site is stronger (-107 kJ/mol) in the presence of K_2O . Upon CO_2 adsorption, the K atoms on the (010) surface slightly shift towards the adsorbate, resulting in a longer K-O bond (2.67 Å) in K_2O than the initial K-O bond distance (2.61 Å) before CO_2 adsorption. A similar trend is observed on the promoted (510) surface. Irrespective of the surface under consideration, we

observe stronger CO₂ adsorption in the presence of K₂O. Stronger CO₂ adsorption has also been observed in experiments.⁷⁷

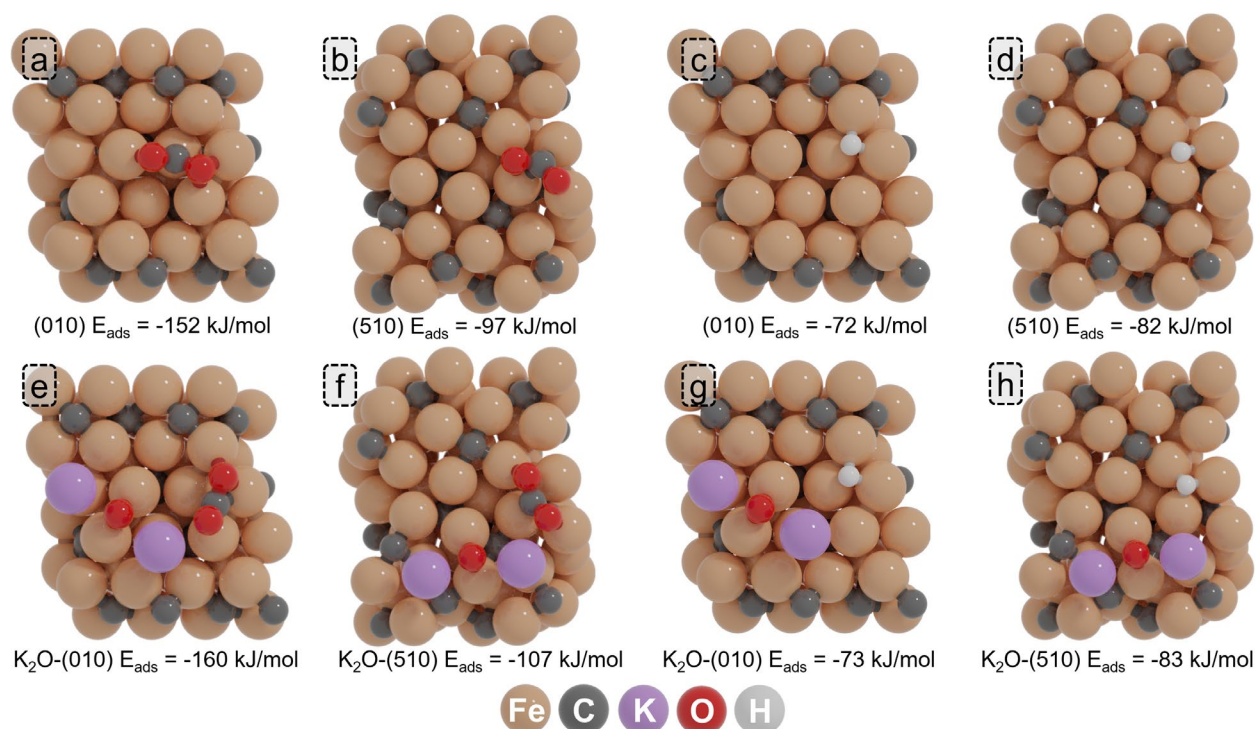


Figure 5.3. The most stable adsorption configurations of CO₂ and H on the (top row) unpromoted and (bottom row) K₂O-promoted (010) and (510) surfaces.

Molecular H₂ readily dissociates upon adsorption on the unpromoted and promoted surfaces, consistent with previous DFT results.⁷⁸ On the (010) surface, the H adsorption energy is -72 kJ/mol referenced against gaseous H₂. A nearly similar value of -73 kJ/mol is found with K₂O. In both cases, the H atom is in a threefold site within the FR site. For the (510) surface, the H atom preferentially adsorbs in a threefold site within the P5 site with an adsorption energy of -82 kJ/mol. In the presence of K₂O, H is adsorbed with nearly the same energy (-83 kJ/mol).

5.3.2.2 CO₂ Activation

C-O bond dissociation in adsorbed CO₂ can proceed either in a direct manner or in a H-assisted fashion. In the latter case, the C or O atom is first hydrogenated before one of the C-O bonds is cleaved.⁷⁹ We investigated how K₂O influences the dissociation of CO₂ on the (010) and (510) surfaces. The computed barriers of CO₂ dissociation are listed in Table 5.1. The energy diagrams for these pathways are given in Figures C3-4. The corresponding geometries of the initial state (IS), transition state (TS) and final state (FS) on the 4 considered surfaces are provided in Figures C5-8.

Table 5.1 shows that K₂O decreases the barrier for direct CO₂ dissociation from respective values of 56 and 33 kJ/mol on the (010) and (510) surfaces to 45 and 14 kJ/mol on the same surfaces containing K₂O. On the K₂O-containing surfaces, the O atom obtained by C-O bond dissociation moves close to one of the K atoms of K₂O, effectively stabilizing the O adatom. For H-assisted CO₂ dissociation, K₂O affects the barriers of the formation of HCOO and COOH intermediates. The barrier of HCOO formation decreases from values of 103 and 79 kJ/mol for (010) and (510), respectively, to 63 and 71 kJ/mol in the presence of K₂O. On the other hand, K₂O increases the subsequent dissociation barrier of HCOO by 36 kJ/mol on (010), but decreases this barrier by 29 kJ/mol on (510). The formation of COOH is hardly affected by K₂O on (010) in the presence of K₂O, while it becomes more difficult on the (510) surface. The impact of K₂O on COOH dissociation is very small on both surfaces.

Table 5.1. Forward reaction barriers (E_f), backward reaction barriers (E_b) and reaction energies (E_{rxn}) of CO dissociation via direct and H-assisted pathways, along with the difference in forward barrier (ΔE_f) between the unpromoted and promoted surfaces for the (010) and (510) of χ -Fe₅C₂.

Surface	Elementary steps	Unpromoted			K ₂ O Promoted			ΔE_f (kJ/mol)
		E_f (kJ/mol)	E_b (kJ/mol)	E_{rxn} (kJ/mol)	E_f (kJ/mol)	E_b (kJ/mol)	E_{rxn} (kJ/mol)	
(010)	CO ₂ * + * → CO* + O*	56	142	-86	45	146	-101	-11
(010)	CO ₂ * + H* → HCOO* + *	103	23	80	63	9	54	-40
(010)	CO ₂ * + H* → COOH* + *	122	44	78	118	32	86	-4
(010)	HCOO* + * → HCO* + O*	28	136	-108	64	133	-69	36
(010)	COOH* + * → CO* + OH*	34	115	-81	36	168	-132	2
(510)	CO ₂ * + * → CO* + O*	33	171	-138	14	156	-142	-19
(510)	CO ₂ * + H* → HCOO* + *	79	25	54	71	3	68	-8
(510)	CO ₂ * + H* → COOH* + *	57	4	53	115	61	54	58
(510)	HCOO* + * → HCO* + O*	55	115	-60	26	113	-87	-29
(510)	COOH* + * → CO* + OH*	68	171	-103	70	153	-83	2

From Table 5.1 and the energy diagrams (Figures C4-5), it can be found that the direct CO₂ dissociation pathway exhibits the lowest overall barrier for both surfaces, irrespective of the presence of K₂O. K₂O decreases the overall barrier for CO₂ dissociation from 56 to 45 kJ/mol on (010) and from 33 to 14 kJ/mol on (510).

5.3.2.3 Electronic Structure Analysis

To understand the way K₂O lowers the barrier for direct CO₂ dissociation, a density of states (DOS) and a crystal orbital Hamilton population (COHP) analysis^{64, 65} were conducted. Figure 5.4 compares the electronic structure of CO₂ in the gas phase with CO₂ adsorbed on the (010) surface, in the presence and absence of the K₂O promoter. The Kohn-Sham states of CO₂ are categorized into distinct energy ranges, as indicated by the dashed horizontal lines in the DOS and COHP analyses. By projecting the Kohn-Sham states onto localized atomic orbitals, we attempted to

deconvolute these interactions and distinguish between σ and π contributions for bonds in linear geometries, based on the procedure outlined by Krösschell et al.⁸⁰ As the non-linear geometry of the CO₂ adsorbate prevents a distinction in σ and π contributions, we labeled the distinct energy ranges as S1, S2, S3, S4, S5 and S6 with increasing energy (Figures 5.4a and 5.4b).

From the DOS displayed in Figures 4a-4c, the S1, S2 and S3 molecular orbitals (MOs) shift to lower energies with respect to the Fermi level upon CO₂ adsorption. The retention of the sharpness of the DOS features implies that these orbitals do not readily mix with the d -states of the surface Fe atoms. This finding is expected as the S1-S3 orbitals are compact in size (Figure C9). In contrast, the S4 and S5 MOs are seen to broaden slightly, which is a consequence of their more diffuse nature, allowing for better mixing with the d -states on the metal. At energies above the energy range of the S5 MO, a new set of occupied states is formed upon CO₂ adsorption. These S6 states predominantly correspond to the mixing of previously unoccupied orbitals with the Fe $3d$ -states, resulting in their downshift below the Fermi level.

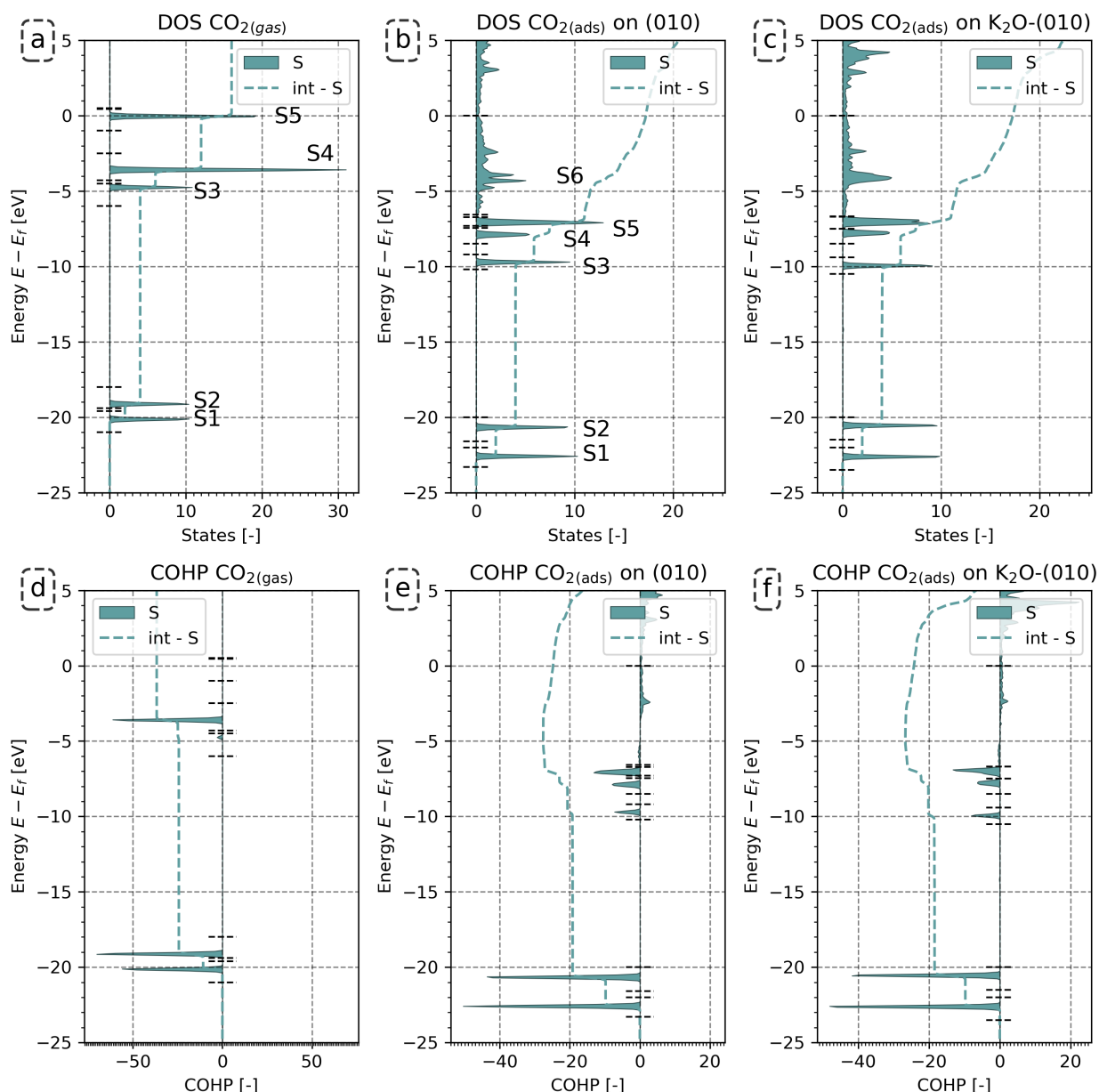


Figure 5.4. DOS of C-O bond of CO₂ (a) in the gas phase and on (b) the (010) surface, and (c) on the K₂O-promoted (010) surface of χ -Fe₅C₂; COHP of the C-O bonds in CO₂ (d) in the gas phase; (e) on the (010) surface, and (f) on the K₂O-promoted (010) surface of χ -Fe₅C₂.

The COHP plots in Figure 5.4d-5.4f show how the redistribution of the electron density of CO₂ upon adsorption affects the C-O bonds in CO₂. To quantify the changes in bonding characteristics, the COHP features are integrated using the previously defined energy ranges for the S1-S6 MOs. The dashed curves show the integrated COHP as a function of the state energy. The integrated COHP (iCOHP) and the integrated DOS (iDOS) per energy range for gaseous and adsorbed CO₂ for the (010) surface are collected in Figures 5.5a and 5.5c. In a similar fashion, the iDOS and iCOHP values for the (510) surface are shown in Figures 5.5b and 5.5d. The original DOS and COHP diagrams for the (510) surface are provided in Figure C10.

From Figure 5.5a-5.5b, it is found that the CO₂ molecule accumulates extra electron density upon adsorption. CO₂ in the gas phase has 16 valence electrons. In the PAW method, the core electrons are retained but treated with an effective frozen-core approximation, meaning they do not contribute explicitly to the DOS/COHP analyses. Upon adsorption, the number of valence electrons of CO₂ increases by 1.12 on (010) and 1.23 on (510), respectively. In the presence of K₂O, the electron density of CO₂ further increases by 0.11 and 0.08 electrons, respectively. We observe that the number of electrons corresponding to the S1 and S2 states remains almost constant upon CO₂ adsorption, while the electron density in S3, S4 and S5 decreases upon adsorption. The S6 orbital, which is unoccupied in gaseous CO₂, gains electron density upon adsorption, and more so with K₂O promotion. We also observe that the number of electrons (states) gained by the S6 MO is larger than the number of electrons lost by the other orbitals. For instance, it is found that S6 gains 1.12 and 1.23 more electrons than the combined number of states lost in S3-S5, for the unpromoted and promoted (510) surfaces, respectively.

To understand how the redistribution of the electron density affects the stability of the C-O bonds and how the presence of K₂O affects this, we consider Figure 5.5c-5.5d. For CO₂ in the gas phase, the S1, S2 and S4 orbitals are strongly bonding with iCOHP values of -10.77, -13.57 and -11.81, respectively, whereas the S3 exhibits a very small contribution with an iCOHP value of -0.55. For S5, the bonding feature is negligible, with iCOHP being close to zero. The S5 orbital is considered non-bonding for the C-O bonds, because the electron density resides mainly on the O atoms and not on C, as visualized in Figure C10. Upon CO₂ adsorption, however, the bonding orbitals become less bonding, and the unoccupied anti-bonding feature becomes more anti-bonding. First, the bonding S1 orbital becomes less bonding upon CO₂ adsorption, indicated by an increase in iCOHP value by 0.99 and 1.13 for the (010) and (510) surfaces, respectively. K₂O further increases this value by 0.05 and 0.04 for (010) and (510) surfaces, respectively. Likewise, the iCOHP value of S2 increases even more by 4.15 and 3.92 for (010) and (510) surfaces, respectively. In the presence of K₂O, the iCOHP further increases by 0.73 and 0.34 for (010) and (510) surfaces, respectively. As these two orbitals (S1-S2) show minimal change and broadening upon adsorption, mixing of these two orbitals with *d*-orbitals of surface Fe is regarded as negligible. Instead of the mixing effect, the decrease of the bonding character of orbitals S1-S2 is assigned to the increased electron-electron repulsion due to the increased proximity of these orbitals with the electron density of the surface. This repulsion is further enhanced by the addition of K₂O, because K₂O increases the electron density in the surface. For S4, the bonding character strongly decreases upon CO₂ adsorption, reflected by a 9.50 decrease in the absolute value of iCOHP. This value is further

decreased by 0.25 in the presence of K_2O . In contrast to the S1-S3 orbitals, the decreased bonding character in S4 is considered due to the mixing of S4 with the surface states. This can be readily assessed from the slight peak broadening and decrease of intensity of S4 (Figure 5.4 and Figure C10). The DOS (Figures 5.5a and 5.5b) also shows that S4 loses electron density upon adsorption, indicative of an interaction with the surface. Besides the decrease in the bonding character of S1-S4, the occupation of the anti-bonding S6 state further destabilizes the C-O bonds, as shown by their positive iCOHP values.

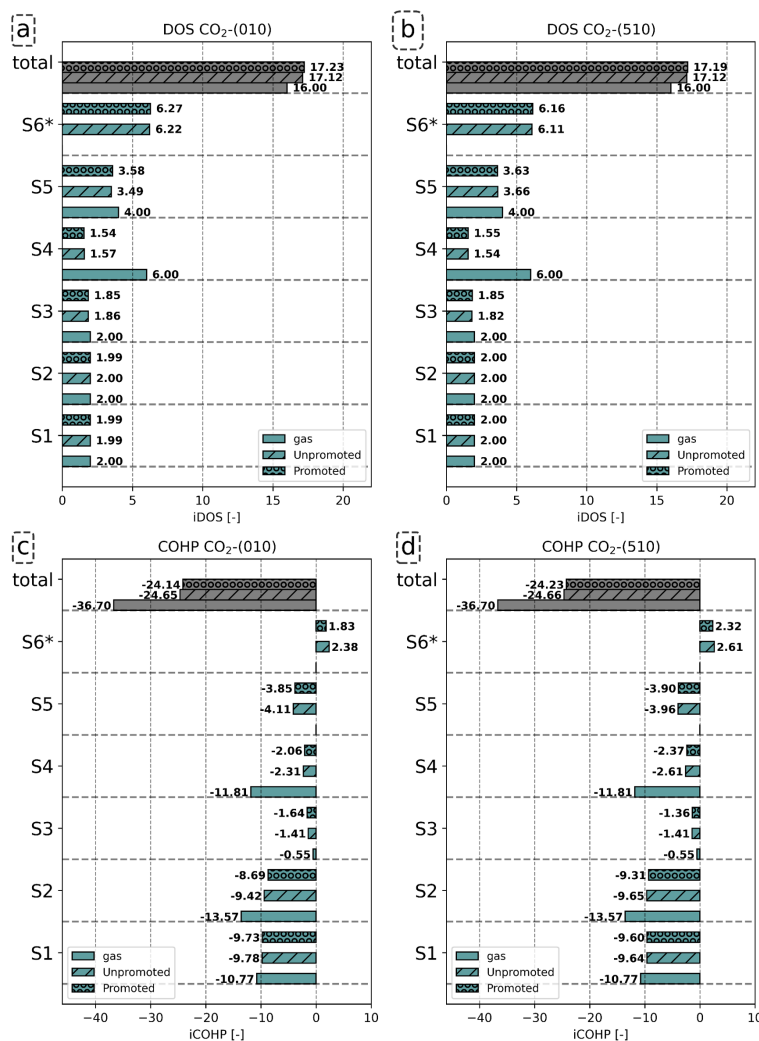


Figure 5.5. (a) - (b) iDOS and (c) - (d) iCOHP of C-O bond of CO_2 in the gas phase, on the unpromoted surfaces; and the K_2O -promoted surfaces. The results for the unpromoted and K_2O -promoted surfaces are indicated by hashed and dotted bars, respectively.

Based on these results, we conclude that the weakening of the C-O bonds in CO_2 by the surface is manifested in two aspects, *i.e.*, destabilizing low-lying bonding orbitals (S1, S2 and S4) due to increased electron-electron repulsion and increasing occupation of high-lying anti-bonding orbitals S6. We attribute the enhanced weakening of the C-O bonds in CO_2 by K_2O to the injection

of extra electrons into the surface by K₂O, as shown in Figures C11 and C12. This electron injection results in enhanced electron-electron repulsion between the S1, S2 and S4 MOs and the surface electrons, as is reflected in their decrease in bonding character for the promoted surface cases. This results in pre-activation of the CO₂ adsorbate, leading to a decrease in the dissociation barrier of CO₂.

5.3.3 Water Formation

The rWGS reaction involves the removal of O obtained by CO₂ dissociation as H₂O with H₂. H₂O formation can occur by direct OH* hydrogenation ($\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^* + *$) or OH disproportionation ($\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}^* + \text{O}^*$). Given the higher CO₂ dissociation activity on the (510) surface, we investigated these H₂O formation pathways on this surface in the presence and absence of K₂O. The resulting reaction energy diagrams are given in Figure 5.6, with the corresponding geometries provided in Figure C13. The forward and backward barriers are provided in Table C1.

On the unpromoted surface, the hydrogenation of O* to OH* is highly endothermic with a high barrier of 144 kJ/mol. Subsequent OH* hydrogenation to H₂O* is associated with a barrier of 138 kJ/mol, which agrees well with the previously theoretical value of 136 kJ/mol obtained on the (100) surface⁸¹. The barrier for the alternative disproportionation of OH* has a barrier of only 80 kJ/mol, lower than the barrier of 118 kJ/mol on the (100) surface⁸¹, rendering the overall process more favorable than direct hydrogenation. In the presence of K₂O, we observe a minor increase in the barrier of O* hydrogenation to OH* from 144 kJ/mol to 149 kJ/mol, while the reaction also becomes more endothermic. Direct OH* hydrogenation to H₂O* remains difficult with a barrier of 141 kJ/mol. On the other hand, OH* disproportionation is facilitated by K₂O with a barrier of 54 kJ/mol. Irrespective of the presence of K₂O, H₂O formation via OH* disproportionation is the most favorable pathway, with K₂O promoting this step slightly.

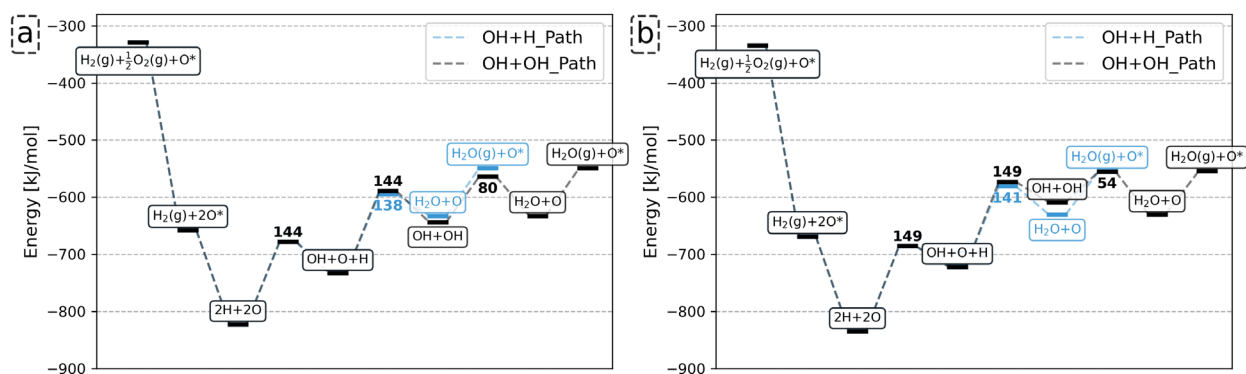


Figure 5.6. Reaction energy diagrams of H₂O formation through O* hydrogenation followed by OH* hydrogenation or OH* disproportionation pathways on the (a) (510) and (b) K₂O-promoted (510) surfaces of χ -Fe₅C₂.

5.3.4 Methane Formation

We next investigated CH₄ formation on both (510) surfaces as a proxy for hydrocarbon formation in the FT synthesis reaction. CH₄ formation starts from the CO product of the rWGS reaction. The energy diagrams for CH₄ formation are presented in Figure 5.7, with the corresponding geometries of the initial state (IS), transition state (TS) and final state (FS) being provided in Figures C14-16.

On the unpromoted (510) surface, CO dissociation occurs in a direct manner with a barrier of 116 kJ/mol (Figure C17), aligning well with the value of 118 kJ/mol on the (510) surface reported by Liu et al.⁷³. H-assisted CO dissociation pathways, involving HCO and COH intermediates, exhibit significantly higher overall barriers of 202 and 271 kJ/mol, respectively. In the presence of K₂O, the barrier for direct CO dissociation decreases significantly to 106 kJ/mol. Despite a decrease in the barriers of H-assisted pathways, these pathways still involve much higher barriers than direct CO dissociation. K₂O promotes the main direct CO dissociation pathway.

Figure 5.7 shows that the hydrogenation of C to CH is endothermic and involves barriers of 98 and 106 kJ/mol for the unpromoted and promoted surfaces, respectively. The subsequent hydrogenation steps to CH₂, CH₃, and CH₄ are also endothermic. Similar to C hydrogenation, all CH_x ($x = 1,2,3$) hydrogenation steps become slightly more difficult in the presence of K₂O, with barriers increasing less than 10 kJ/mol.

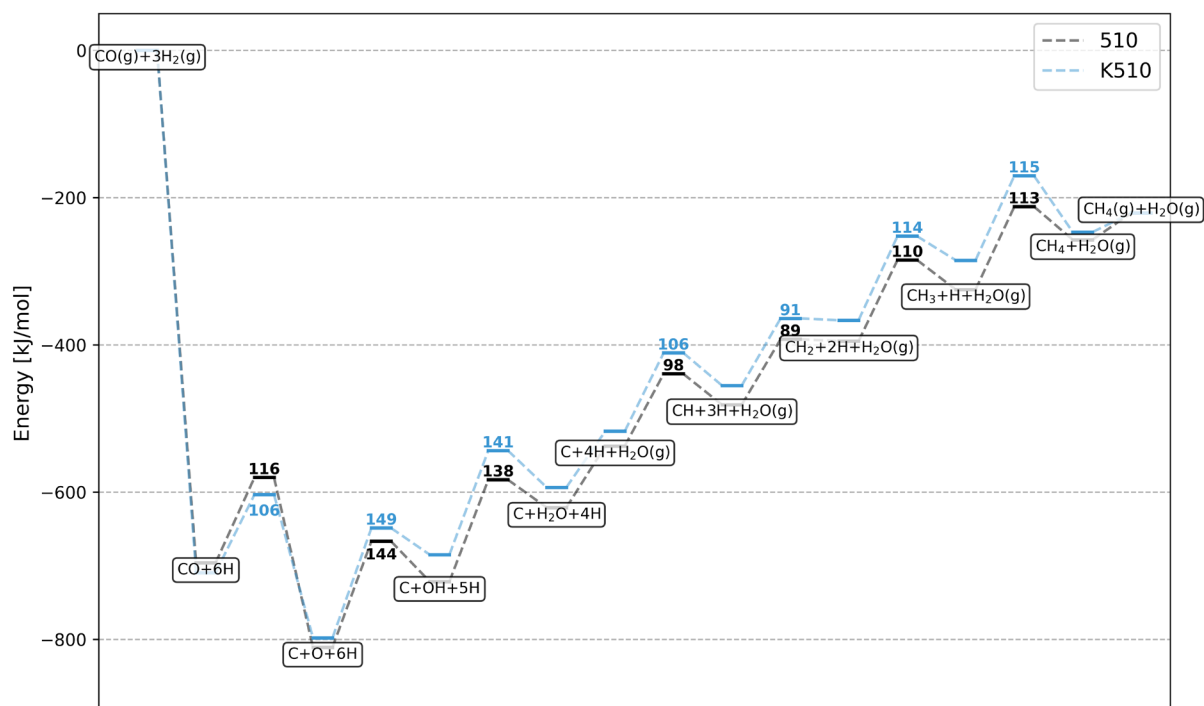


Figure 5.7. Reaction energy diagrams of CH₄ formation starting from gaseous CO and H₂ on the unpromoted and K₂O-promoted (510) surfaces of χ -Fe₅C₂.

5.3.5 Microkinetics Simulations

We employed microkinetics simulations to understand the role of the K₂O promoter on the rWGS reaction on the χ -Fe₅C₂(510) surface. CH₄ formation was included as a proxy for the formation of hydrocarbons from the CO product. The parameters used in microkinetic simulation, i.e., forward reaction barriers (E_f), backward reaction barriers (E_b) and pre-exponential factors of all elementary steps, are listed in Table C1. All simulations were conducted at a total pressure of 20 bar and a H₂:CO ratio of 4, corresponding to typical FT conditions.⁸²⁻⁸⁴

Figure 5.8 presents the CO₂ conversion rate and the reaction rates of CO and CH₄ as a function of the temperature. These rates for one active site per slab are expressed as turnover frequencies (TOFs). Figure 5.8a shows that the CO₂ conversion rate is higher in the presence of K₂O. The promoting effect of K₂O on the rWGS rate has been experimentally reported before.^{82, 85} Both the reaction rates of CO and CH₄ are increased by the addition of K₂O, as follows from Figure 5.8b. With increasing temperature, the CO rate increases faster than the CH₄ rate, the former becoming the dominant product above 585 K, irrespective of the presence of K₂O.

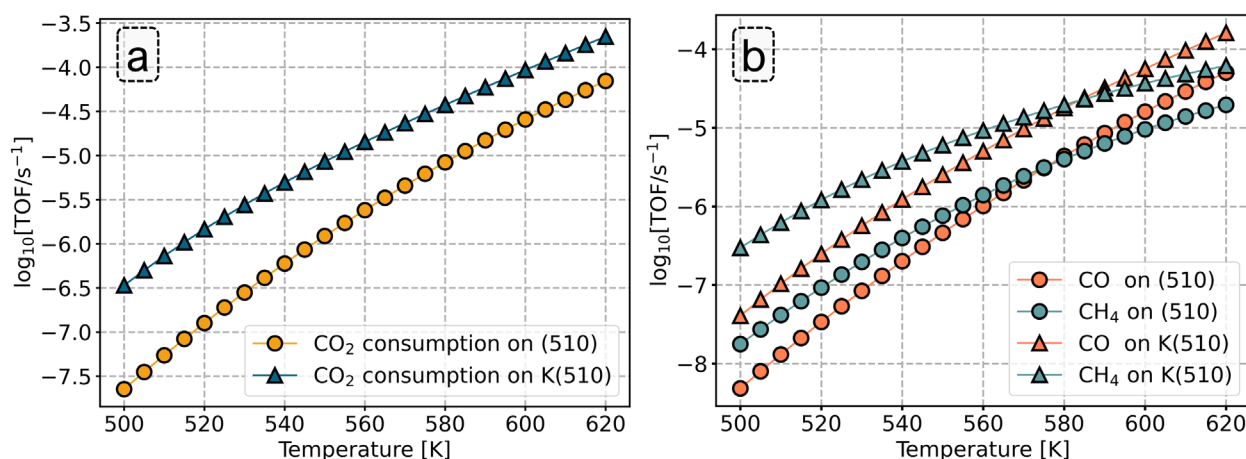


Figure 5.8. Microkinetics simulations on the unpromoted and K₂O-promoted (510) surfaces of χ -Fe₅C₂: (a) CO₂ conversion rate and (b) CO and CH₄ rates as a function of temperature ($p = 20$ bar, H₂/CO ratio = 4).

Figures 5.9a and 5.9b confirm the trend in the product distribution for both surfaces. With increasing temperature, desorption of CO leads to a lower CO coverage, resulting in a higher rate of CO formation compared to CH₄ formation. At low temperatures, the addition of K₂O increases the CH₄ selectivity due to an increased adsorption energy of CO and a decreased barrier of CO dissociation. We stress here that CH₄ formation is a proxy for the formation of hydrocarbons under FT synthesis conditions, where chain growth is generally favorable over methanation.⁸²

The steady-state coverages as a function of the temperature are displayed in Figures 5.9c-5.9d. At low temperatures, H*, O* and CO* are the dominant adsorbates on both surfaces. In the presence of K₂O, the C* coverage is significantly higher, which can be attributed to the lower CO dissociation barrier and the increased barrier for C* hydrogenation compared to the unpromoted surface. This could be an explanation for the experimental observation of more carbonaceous deposits on Fe-carbide promoted by K₂O.^{53, 75} With increasing temperature, the abundance of O* and C* increases as the rate of CO dissociation increases.

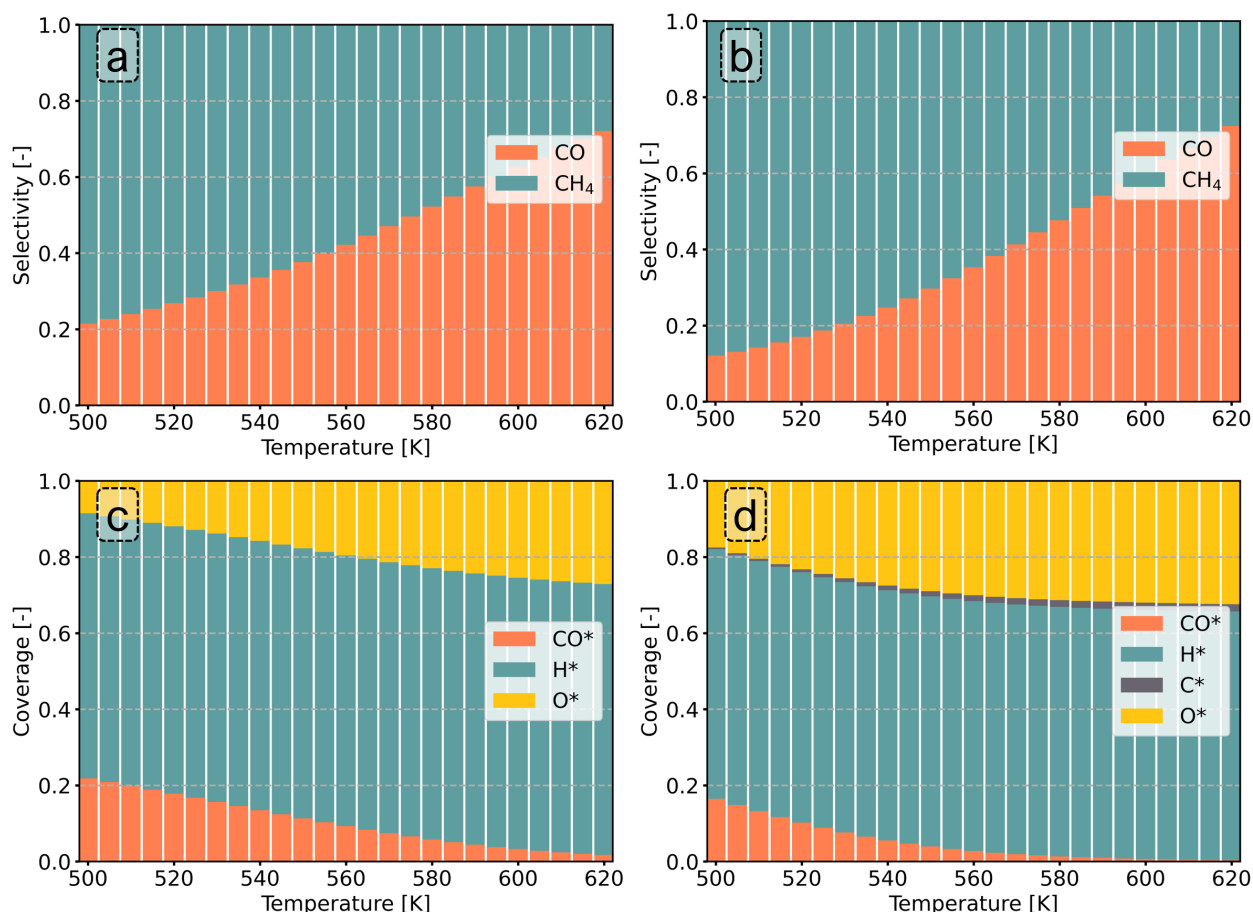


Figure 5.9. Microkinetics simulations on the (left) unpromoted and (right) K₂O-promoted (510) surfaces of χ -Fe₅C₂: (a)-(b) selectivity and (c)-(d) Coverage as a function of temperature ($p = 20$ bar, H₂/CO ratio = 4).

A degree of rate control (DRC) analysis was used to identify rate-controlling steps in the rWGS and methanation reactions on both surfaces. The results are given in Figures 5.10a-5.10b. For the unpromoted surface (Figure 5.10a), the dominant rate-controlling steps are direct CO dissociation ($\text{CO}^* + * \rightleftharpoons \text{C}^* + \text{O}^*$) and OH* hydrogenation ($\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$). Also, CO desorption, direct CO₂ dissociation, H-assisted CO dissociation via the HCO pathway and OH disproportionation contribute, to a lesser extent, to the overall rate control. With increasing temperature, the DRC value of direct CO dissociation decreases, while the DRC of OH hydrogenation increases. This is the result of a shift in the adsorbed layer composition containing less CO and more O at higher temperatures. For the promoted surface, direct CO dissociation, OH* hydrogenation and disproportionation are the main rate-controlling steps at low temperatures, as shown in Figure 5.10b. As temperature increases, the DRC value of direct CO dissociation gradually decreases and even becomes negative. This results in an increase in the DRC values of O removal steps, such as OH hydrogenation and OH disproportionation.

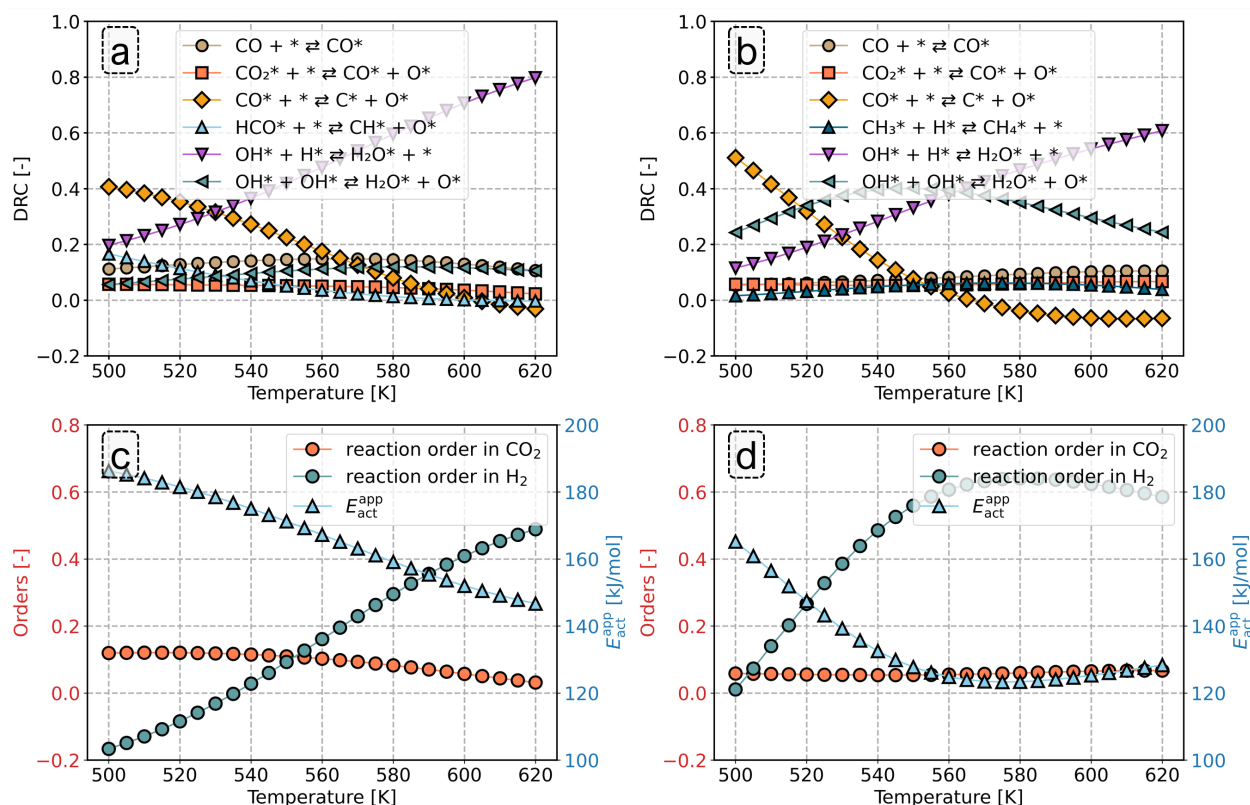


Figure 5.10. Microkinetics simulations on the (left) unpromoted and (right) K₂O-promoted (510) surfaces of χ -Fe₅C₂: (a)-(b) degree of rate control and (c)-(d) reaction order and apparent activation energy as a function of temperature ($p = 20$ bar, H_2/CO ratio = 4).

The reaction orders with respect to CO and H₂ and the apparent activation energies ($E_{\text{act}}^{\text{app}}$) are presented in Figures 5.10c-5.10d. For the unpromoted surface (Figure 5.10c), the reaction order of CO₂ exhibits a slightly positive value, which compares well with experimental data.⁸⁶ A higher CO₂ partial pressure increases the conversion rate, as it results in a higher coverage of the relatively weakly adsorbing CO₂ reactant. The reaction order of H₂ is slightly negative at low temperatures, which is due to the relatively high abundance of H* at the surface. With temperature rising, the reaction order of H₂ shifts to positive, which can be explained by the stronger contribution of H₂O formation as a rate-controlling step. This shift in the main rate-controlling steps is also reflected in the decrease in the apparent activation energy ($E_{\text{act}}^{\text{app}}$). For the promoted surface (Figure 5.10d), the reaction order of CO₂ and H₂ are both positive. Compared to the unpromoted surface, the CO₂ reaction orders are slightly lower, in line with experimental observations,⁴⁸ which is likely due to the stronger binding of CO₂ to the (510) surface close to K₂O. The higher coverage of CO₂ and adsorbates derived from its dissociation results in a lower H coverage, explaining the higher H₂ reaction order. The lower apparent activation energy ($E_{\text{act}}^{\text{app}}$) for the promoted surface reproduces the decrease in apparent activation energy for K-promoted Fe-based catalysts.^{48, 87}

Taken together, the presence of K_2O at the $\chi\text{-Fe}_5\text{C}_2(510)$ surface results in slightly stronger CO_2 adsorption and easier dissociation of the C-O bonds in CO_2 and CO, resulting in higher conversion rates. At low temperatures, CH_4 is the main product, serving as a proxy for the formation of hydrocarbons, while CO is the main product at higher temperatures. The promoted surface contains more C^* species, which may be a precursor to carbon deposits formed by C-C coupling reactions. The main rate-controlling steps are the dissociation of CO and the removal of O^* . Given that the barrier of CO_2 dissociation is significantly higher on the (010) surface and shows slight change with K_2O addition, the rWGS reaction is expected to exhibit higher activity on the (510) surface. This activity can be further enhanced by the presence of K_2O .

5.4 Conclusions

To investigate the mechanistic role of K in the rWGS reaction within the context of CO_2 -FT synthesis, we employed DFT in conjunction with microkinetics simulations. We identified K_2O to be the most stable structure of the K promoter. The impact of K_2O on two representative surfaces of Hägg carbide, i.e., (010) and (510), was explored for the reactant adsorption and activation. K_2O promotes C-O bonds dissociation in adsorbed CO_2 by increasing the electron density of the surface Fe atoms, weakening the C-O bonds through increased electron-electron repulsion. On both surfaces, direct CO_2 dissociation is more facile than H-assisted pathways involving HCOO and COOH intermediates, independent of K_2O addition. The (510) surface consistently exhibits lower barriers for CO_2 dissociation compared to the (010) surface, with or without the presence of K_2O . O Removal occurs via H_2O formation, with OH disproportionation showing a significantly lower barrier than direct hydrogenation. This process is further facilitated by K_2O addition. We next explored the CH_4 formation on the more active (510) surface as a proxy for hydrocarbon formation. K_2O reduces the barrier for CO dissociation while increasing the barriers for CH_x ($x = 0,1,2,3$) hydrogenation. Microkinetics simulations reveal that K_2O addition enhances CO_2 conversion. At low temperatures, CH_4 is the primary product, with K_2O promoting its formation. With increasing temperatures, the product shifts to CO due to the elevated CO desorption. Additionally, K_2O increases the abundance of C^* by facilitating the dissociation of CO_2 and CO while inhibiting the hydrogenation of C^* . A DRC analysis indicates that CO dissociation and O removal via H_2O formation compete as the rate-controlling steps, with the latter becoming more dominant with temperature at the expense of the former.

5.5 References

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Chapter 5. A Theoretical Study of the Role of K on the Reverse Water-Gas Shift Reaction on Hägg carbide

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Appendix C

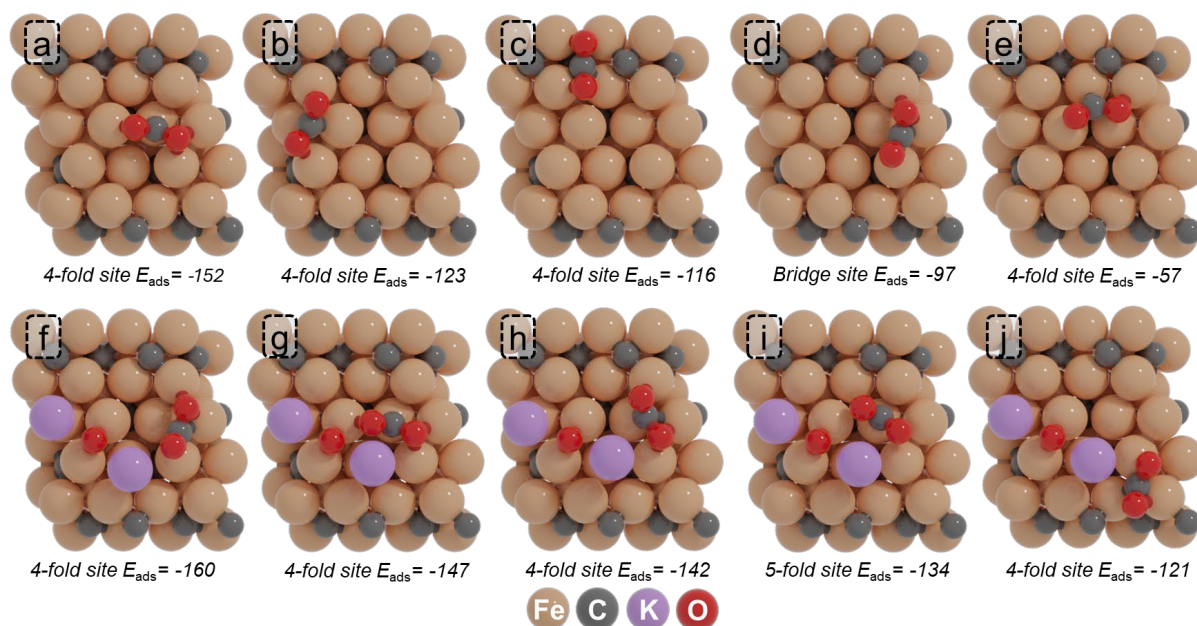


Figure C1. CO₂ adsorption configurations on the (a – e) (010) and (f - j) K₂O-promoted (010) surfaces of χ -Fe₅C₂. The adsorption energies are given in kJ/mol and include zero-point energy corrections.

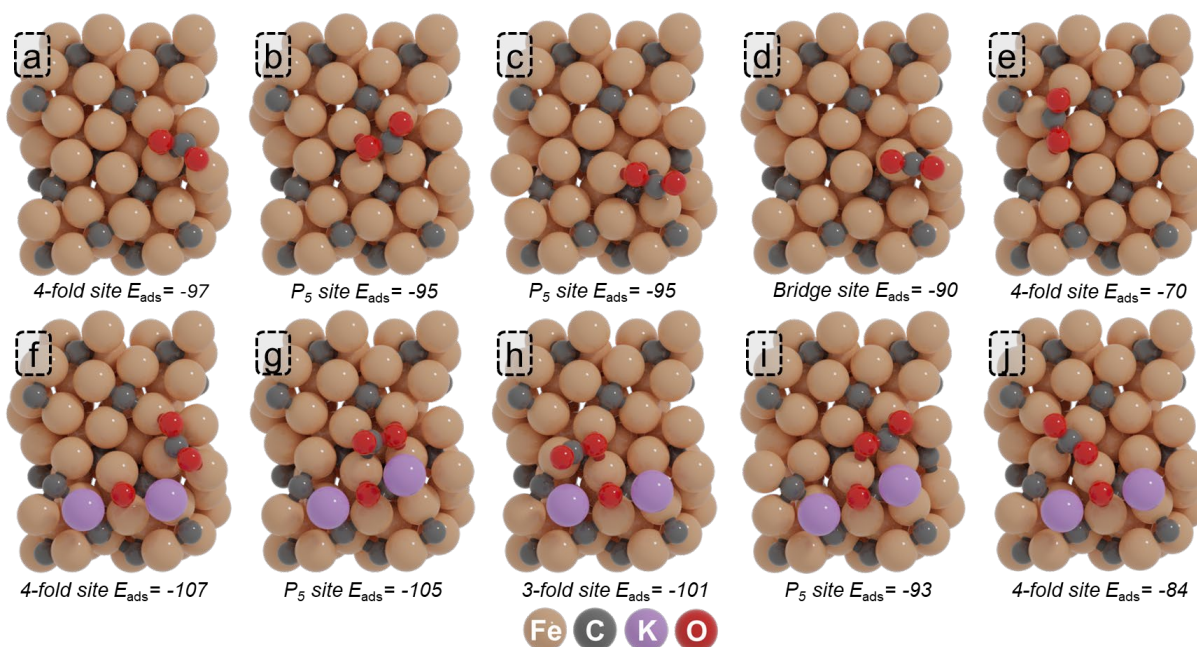


Figure C2. CO₂ adsorption configurations on the (a – e) (510) and (f - j) K₂O-promoted (510) surfaces of χ -Fe₅C₂. The adsorption energies are given in kJ/mol and include zero-point energy corrections.

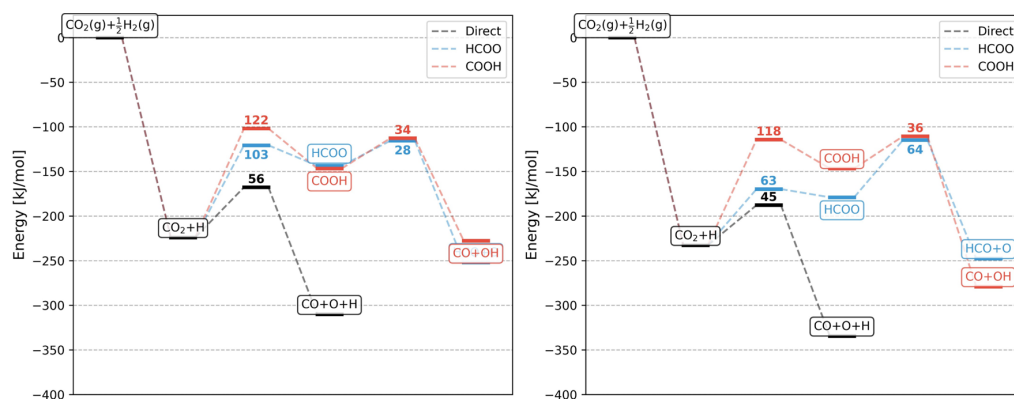


Figure C3. Reaction Energy diagrams for the direct or H-assisted dissociation of CO₂ from co-adsorbed H and CO on the (a) (010) and (b) K₂O-promoted (010) surfaces of χ-Fe₅C₂.

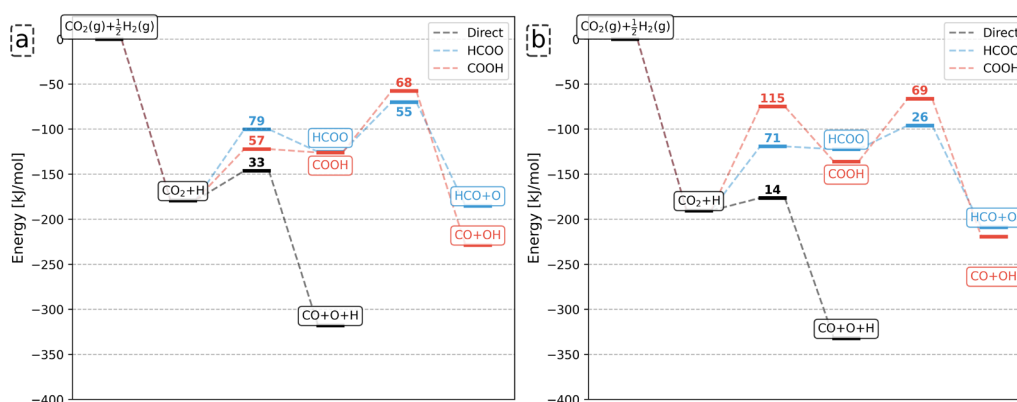


Figure C4. Reaction Energy diagrams for the direct or H-assisted dissociation of CO₂ from co-adsorbed H and CO on the (a) (510) and (b) K₂O-promoted (510) surfaces of χ-Fe₅C₂.

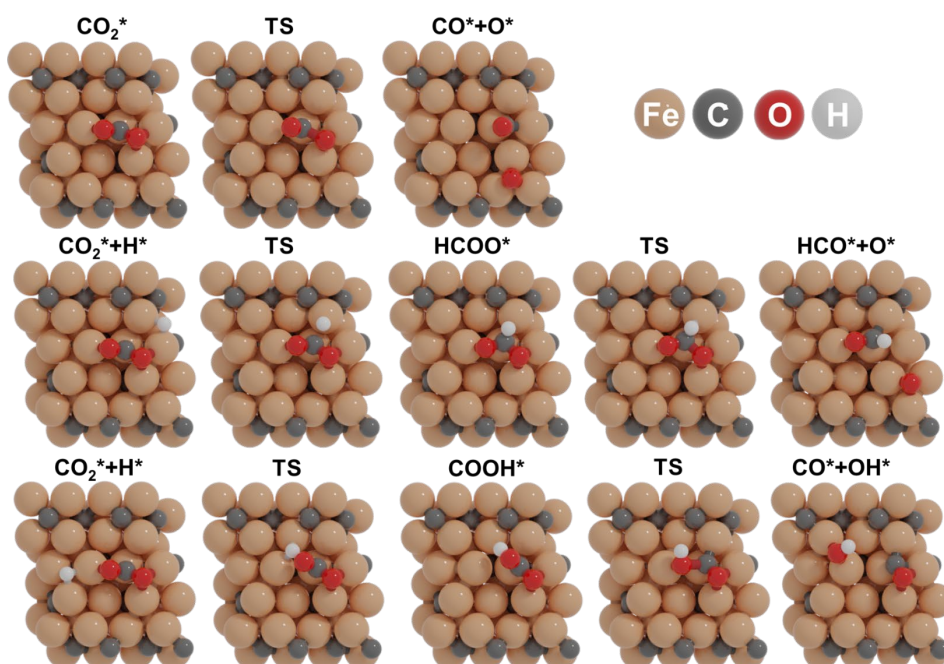


Figure C5. Configurations of IS, TS and FS for the direct or H-assisted dissociation of CO₂ on the (010) surface of χ-Fe₅C₂.

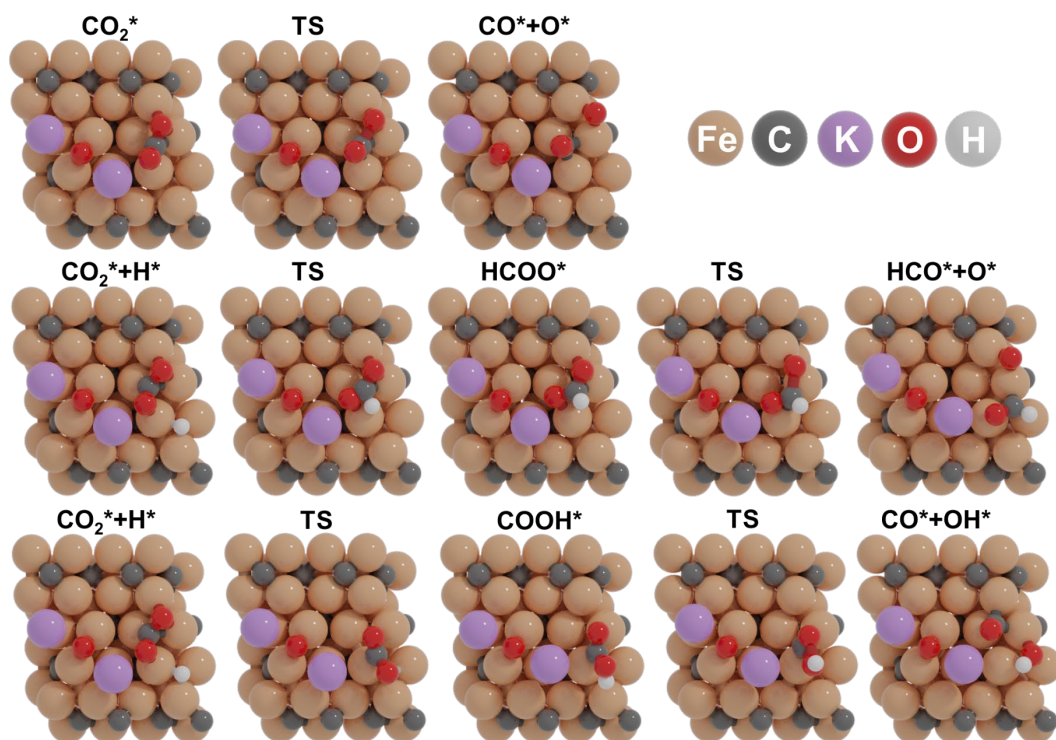


Figure C6. Configurations of IS, TS and FS for the direct or H-assisted dissociation of CO₂ on the K₂O-promoted (010) surface of χ -Fe₅C₂.

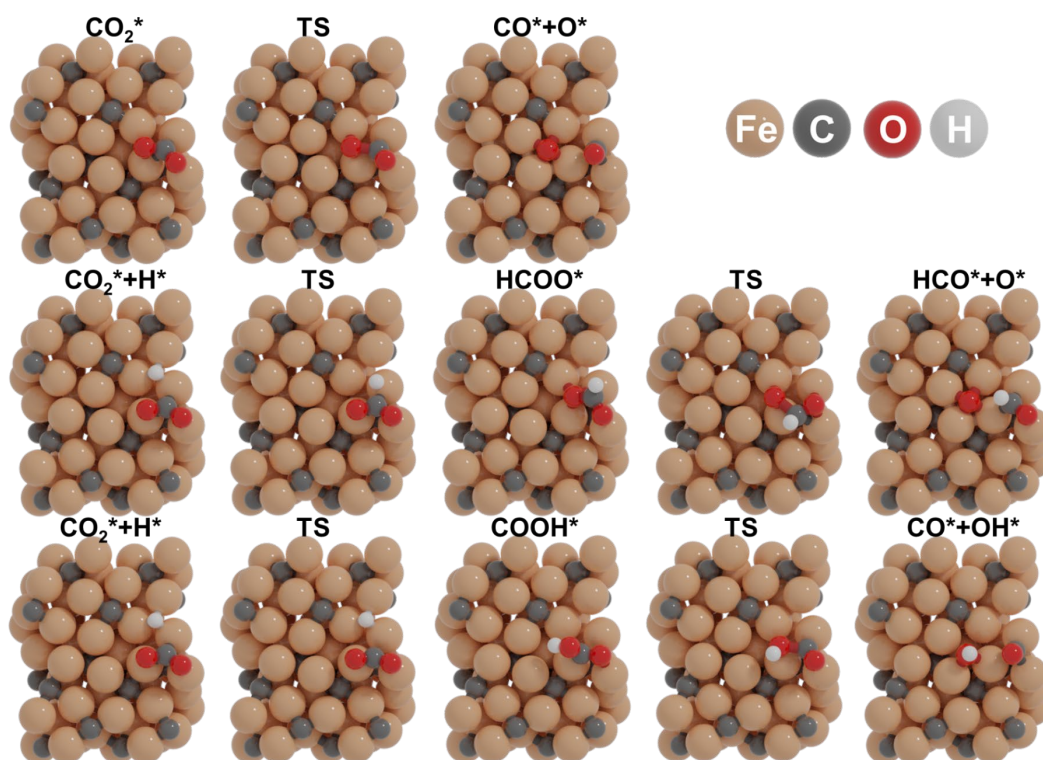


Figure C7. Configurations of IS, TS and FS for the direct or H-assisted dissociation of CO₂ on the (510) surface of χ -Fe₅C₂.

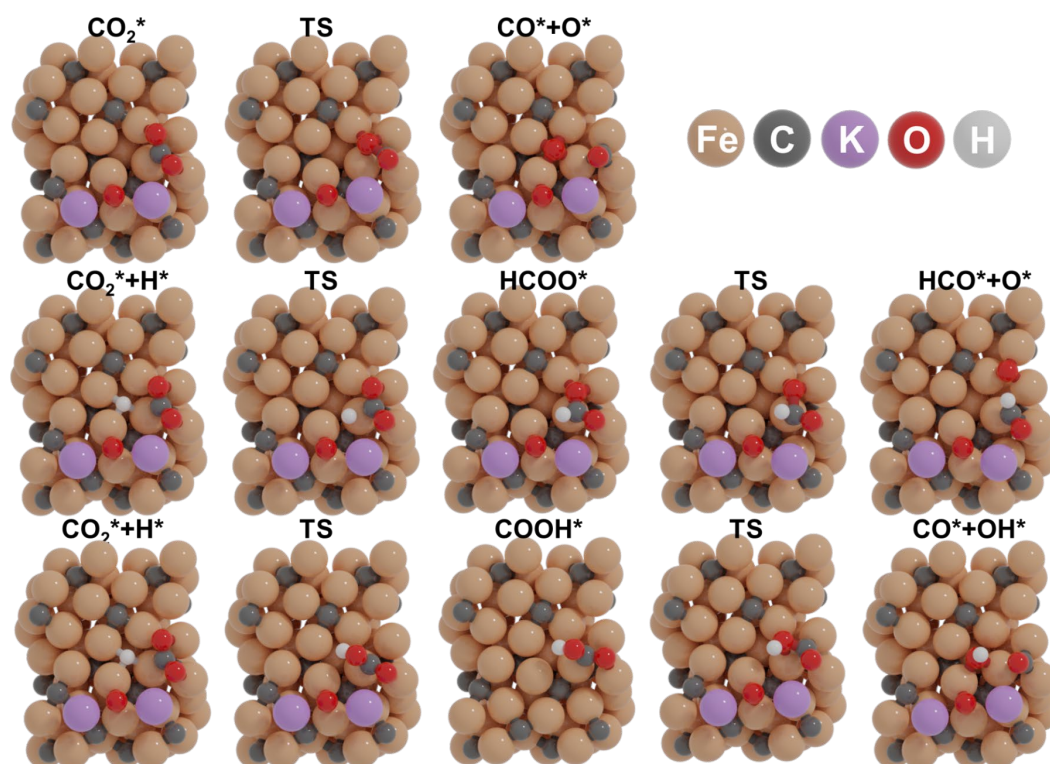


Figure C8. Configurations of IS, TS and FS for the direct or H-assisted dissociation of CO₂ on the K₂O-promoted (510) surface of χ -Fe₅C₂.

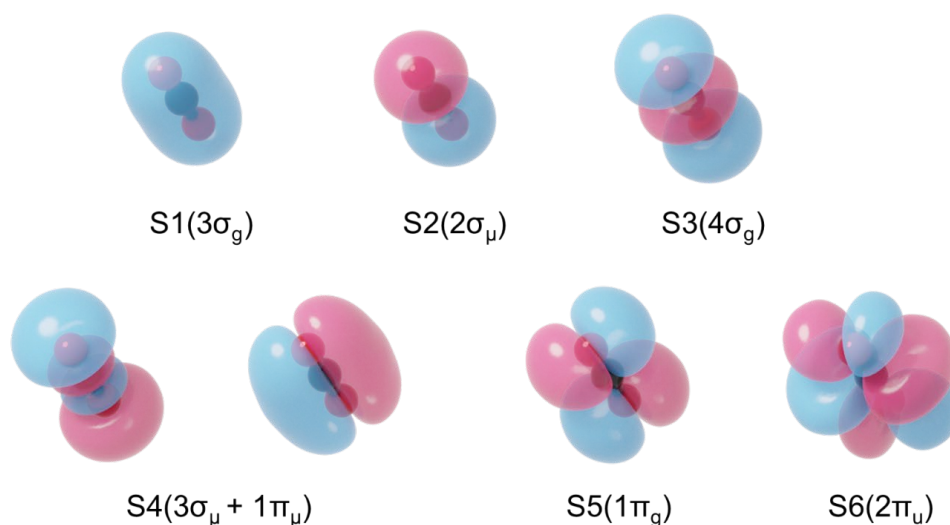


Figure C9. The canonical molecular orbital solutions of CO₂ in the gas phase. The orbital names given in brackets refers to the classical solution.¹ This figure is generated by Quantumsculpt suite.

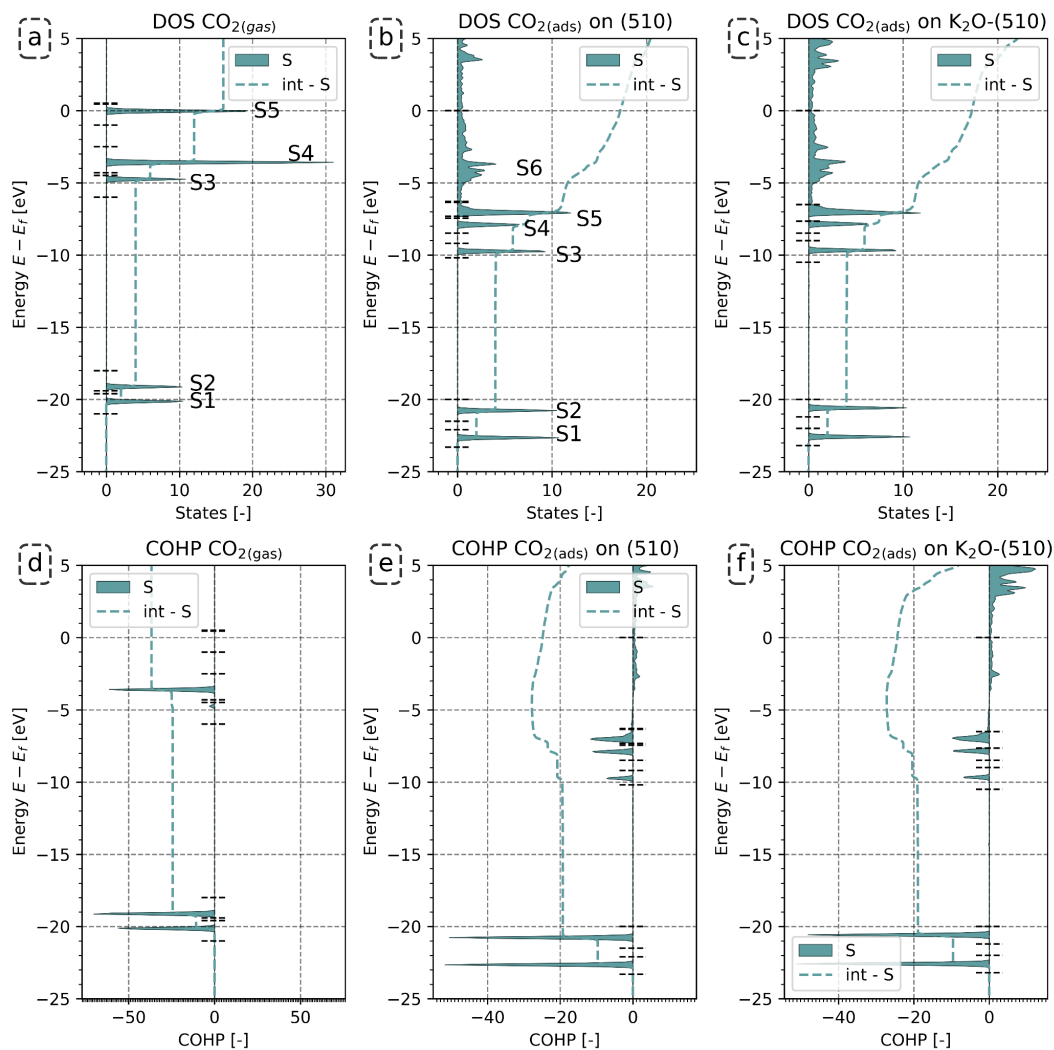


Figure C10. DOS of C-O bond of CO₂ (a) in the gas phase and (b) on the (510) surface, and (c) on the K₂O-promoted (510) surface of χ -Fe₅C₂; COHP of the C-O bonds in CO₂ (d) in the gas phase; (e) on the (510) surface, and (f) on the K₂O-promoted (510) surface of χ -Fe₅C₂.

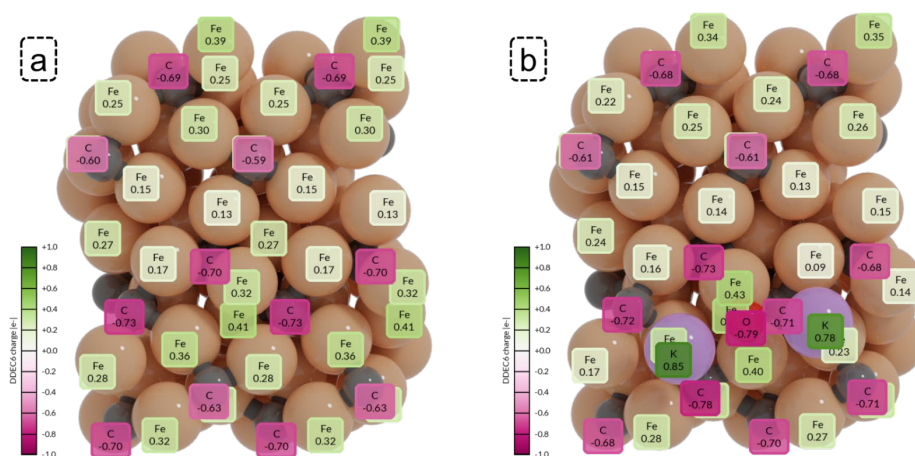


Figure C11. Charge of surface Fe atoms on the (a) the (510) surface and (d) K₂O-promoted (510) surface of χ -Fe₅C₂. The results show that K₂O improves the charge density of surface Fe atoms, especially for the 4-fold site for CO₂ activation.

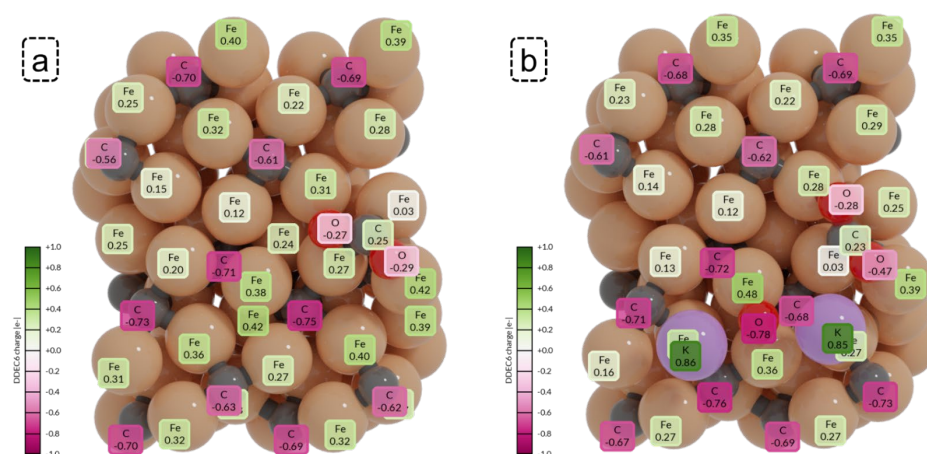


Figure C12. Charge of adsorbed CO₂ and surface Fe atoms on the (a) the (510) surface and (d) K₂O-promoted (510) surface of χ -Fe₅C₂. The results show that K₂O improves the charge density of surface Fe atoms, resulting in additional electron donation to the adsorbed CO₂.

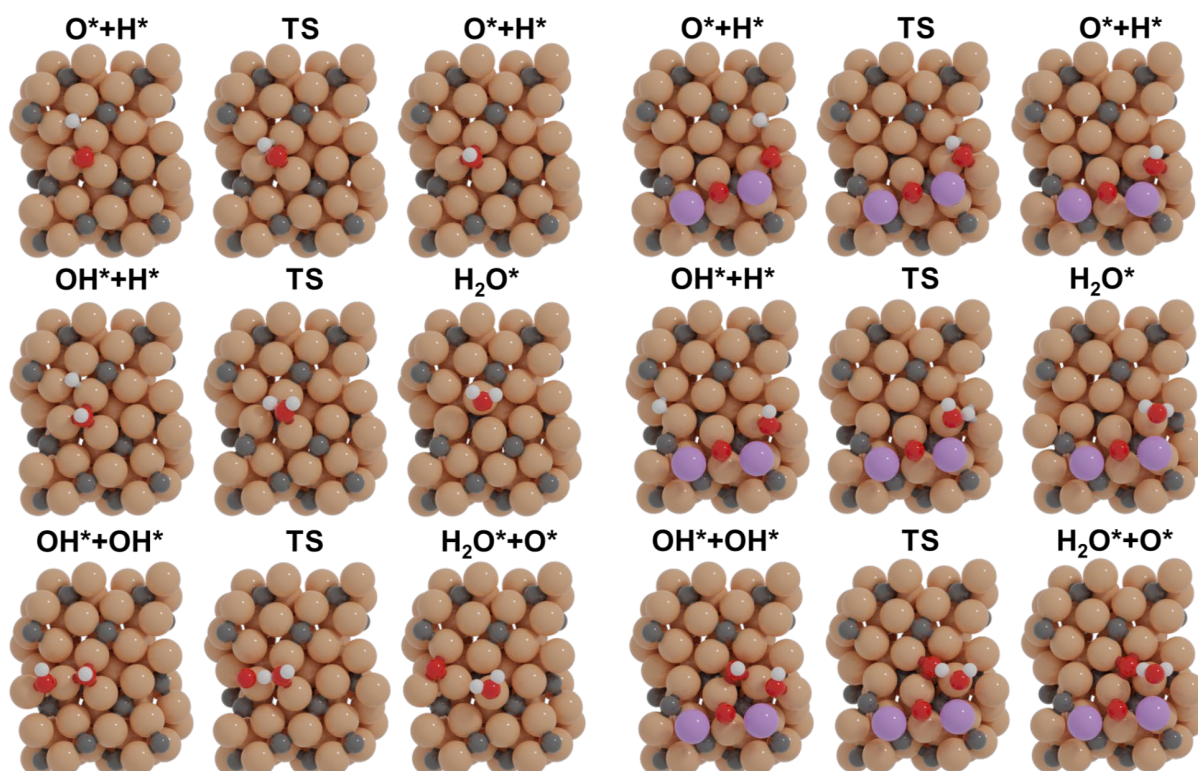


Figure C13. Configurations of IS, TS and FS for H₂O formation on the (510) (left) and K₂O-promoted (510) (right) surfaces of χ -Fe₅C₂.

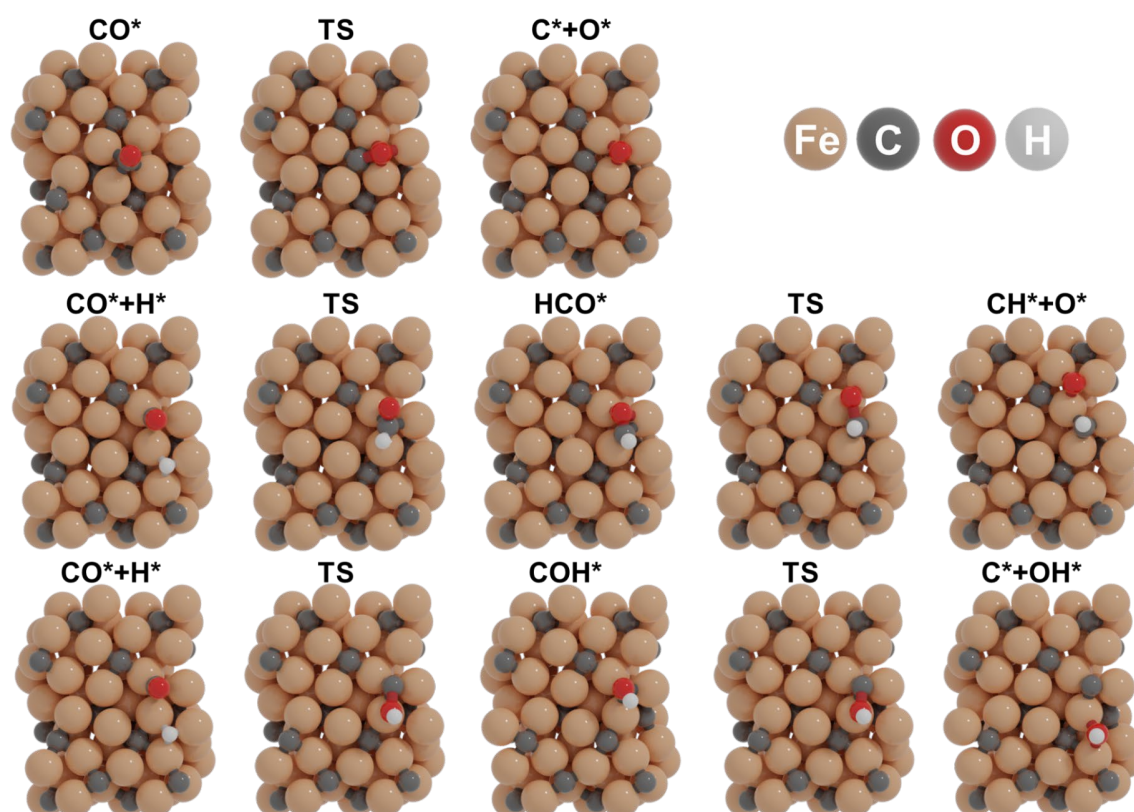


Figure C14. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the (510) surface of χ -Fe₅C₂.

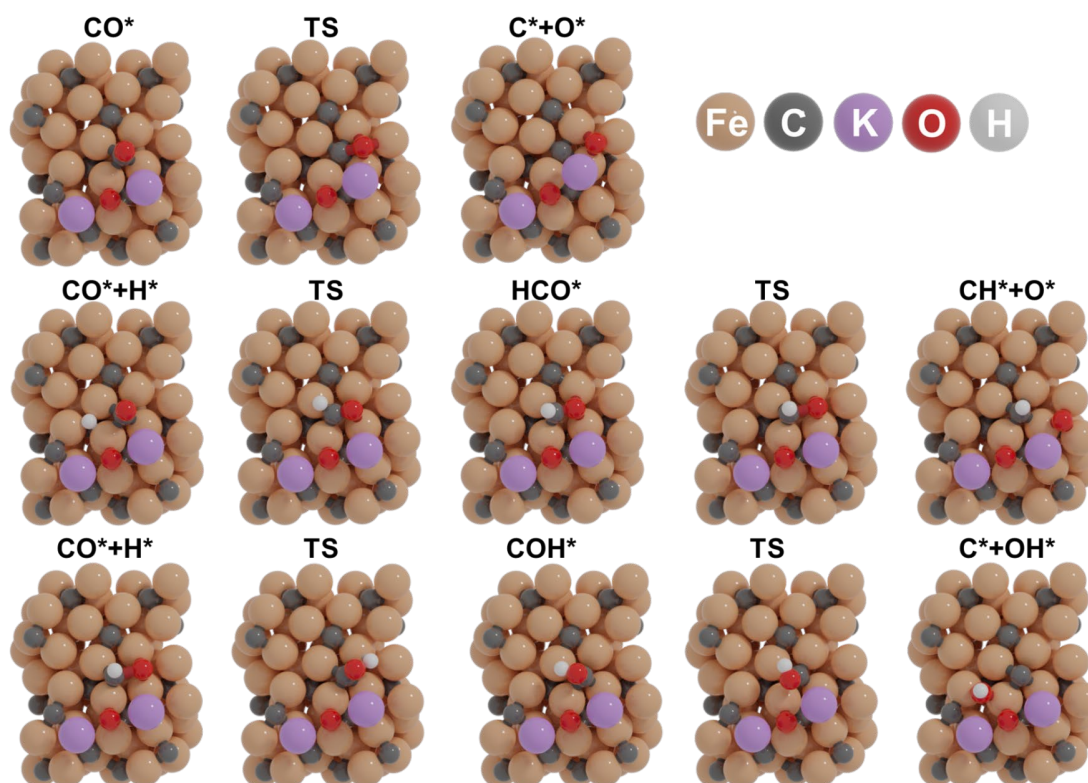


Figure C15. Configurations of IS, TS and FS for the direct and H-assisted dissociation of CO on the K₂O-promoted (510) surface of χ -Fe₅C₂.

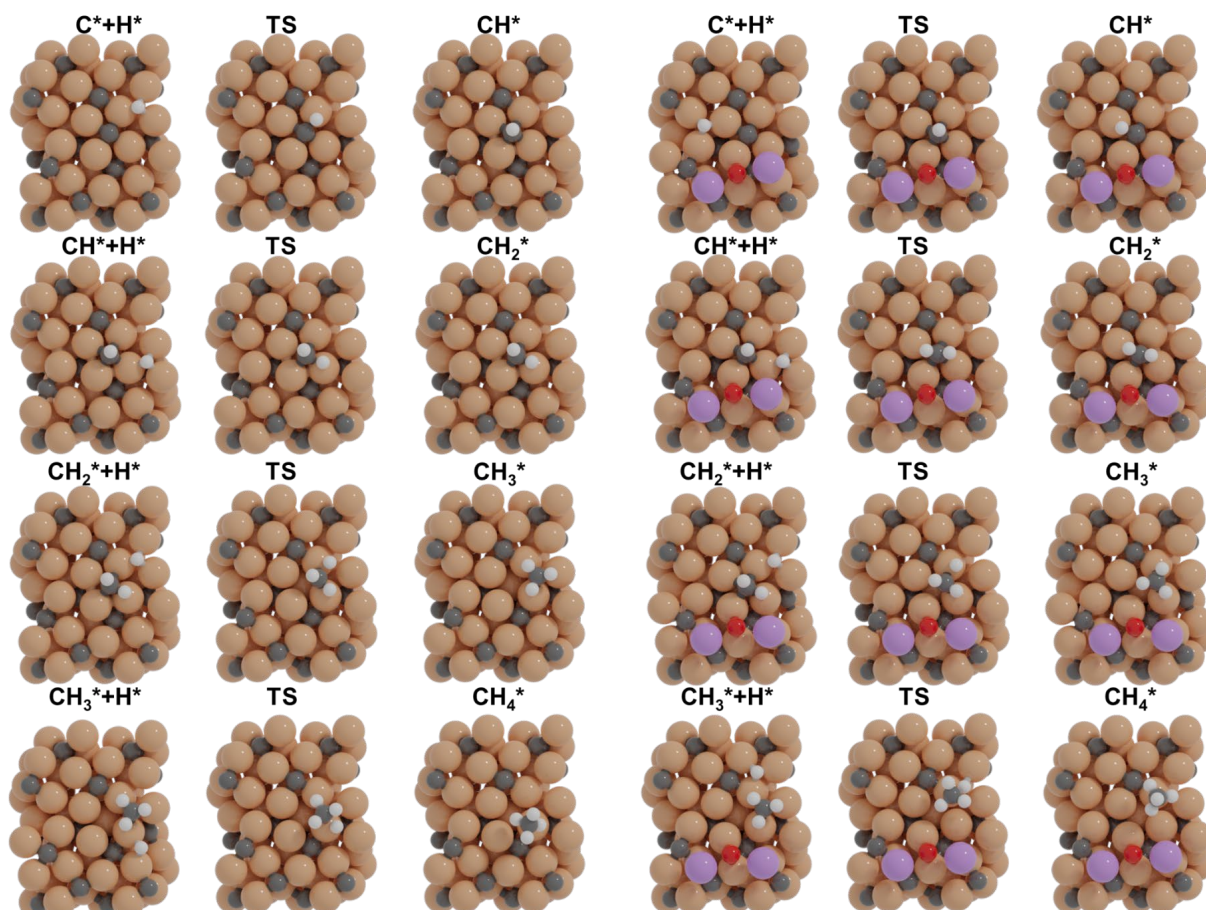


Figure C16. Configurations of IS, TS and FS for CH₄ formation on the (510) (left) and K₂O-promoted (510) (right) surfaces of χ -Fe₅C₂.

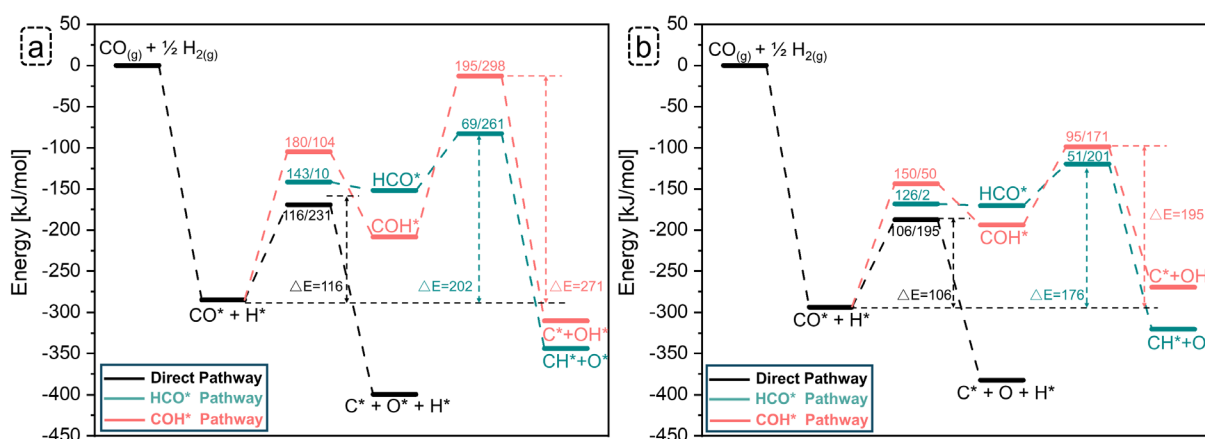


Figure C17. Reaction energy diagrams for the direct or H-assisted dissociation of CO on the (a) (510) and (b) K₂O-promoted (510) surfaces of χ -Fe₅C₂. The value upon the TS corresponds to the forward/backward activation barrier of each elementary step. ΔE refers to the overall barrier of each pathway.

Table C1. Forward reaction barrier (E_f), back-forward reaction barrier (E_b) and pre-exponential factors of All Elementary Steps Examined in the Pathways of CO₂ Conversion on the (510) and K₂O-promoted (510) surfaces of χ -Fe₅C₂.

Energy / kJ/mol Elementary steps	(510)				K ₂ O-(510)			
	E_f	ν_f	E_b	ν_b	E_f	ν_f	E_b	ν_b
CO ₂ * + * → CO* + O*	33	2.1×10 ¹³	171	6.7×10 ¹²	14	3.5×10 ¹³	156	5.1×10 ¹²
CO ₂ * + H* → HCOO* + *	79	1.0×10 ¹³	25	3.8×10 ¹²	71	9.8×10 ¹²	3	3.1×10 ¹³
CO ₂ * + H* → COOH* + *	57	1.5×10 ¹³	4	5.1×10 ¹²	115	3.2×10 ¹²	61	2.9×10 ¹³
HCOO* + * → HCO* + O*	55	3.7×10 ¹²	115	4.7×10 ¹²	26	6.6×10 ¹²	113	5.2×10 ¹²
COOH* + * → CO* + OH*	68	3.5×10 ¹³	171	8.4×10 ¹²	70	9.6×10 ¹²	153	5.0×10 ¹²
HCOO* + H* → HCOOH* + *	129	9.5×10 ¹²	18	1.9×10 ¹²	185	7.9×10 ¹³	89	1.3×10 ¹³
COOH* + H* → HCOOH* + *	126	5.5×10 ¹²	13	5.7×10 ¹²	119	9.1×10 ¹²	9	4.9×10 ¹²
HCOOH* + * → HCO* + OH*	34	2.3×10 ¹¹	116	5.6×10 ¹²	59	3.9×10 ¹³	129	6.9×10 ¹³
CO * → C*+O*	116	5.7×10 ¹¹	231	8.0×10 ¹²	106	6.8×10 ¹¹	195	1.1×10 ¹²
CO* + H* → HCO* + *	143	9.0×10 ¹²	10	8.3×10 ¹²	126	9.7×10 ¹²	2	2.9×10 ¹³
CO* + H* → COH* + *	180	1.7×10 ¹²	104	9.6×10 ¹²	150	3.2×10 ¹²	50	4.0×10 ¹²
HCO* + * → CH* + O*	69	2.5×10 ¹²	261	5.9×10 ¹²	51	8.1×10 ¹²	201	4.9×10 ¹²
COH* + * → C* + OH*	195	6.8×10 ¹²	298	1.3×10 ¹²	95	1.1×10 ¹³	171	1.2×10 ¹³
HCO* + H* → CH ₂ O* + *	67	6.1×10 ¹²	1	1.4×10 ¹³	68	1.6×10 ¹²	36	1.1×10 ¹³
CH ₂ O* + * → CH ₂ * + O	43	5.6×10 ¹²	214	1.1×10 ¹³	71	8.1×10 ¹²	165	1.4×10 ¹²
C* + H* → CH* + *	98	1.2×10 ¹²	42	9.7×10 ¹²	106	1.5×10 ¹³	44	1.2×10 ¹³
CH* + H* → CH ₂ * + *	89	7.6×10 ¹²	2	4.3×10 ¹²	91	1.1×10 ¹³	2	7.6×10 ¹²
CH ₂ * + H* → CH ₃ * + *	110	5.1×10 ¹³	40	2.9×10 ¹²	114	1.0×10 ¹³	33	1.5×10 ¹²
CH ₃ * + H* → CH ₄ * + *	113	8.4×10 ¹³	45	1.4×10 ¹²	115	5.9×10 ¹⁴	77	2.4×10 ¹²
O* + H* → OH* + *	144	1.8×10 ¹³	55	1.7×10 ¹²	149	2.4×10 ¹³	36	5.4×10 ¹²
OH* + H* → H ₂ O* + *	138	2.6×10 ¹³	37	1.7×10 ¹²	141	1.4×10 ¹³	49	7.9×10 ¹²
OH* + OH* → H ₂ O* + O*	80	1.8×10 ¹³	69	5.2×10 ¹¹	54	3.8×10 ¹³	76	1.3×10 ¹²

Pre-exponential factors of All Elementary Steps were estimated by transition state theory at $T = 500$ K. For a gas molecule adsorption, $P = 1.00$ bar and the effect adsorption area of $A = 1 \text{ \AA}^2$.

Appendix Reference

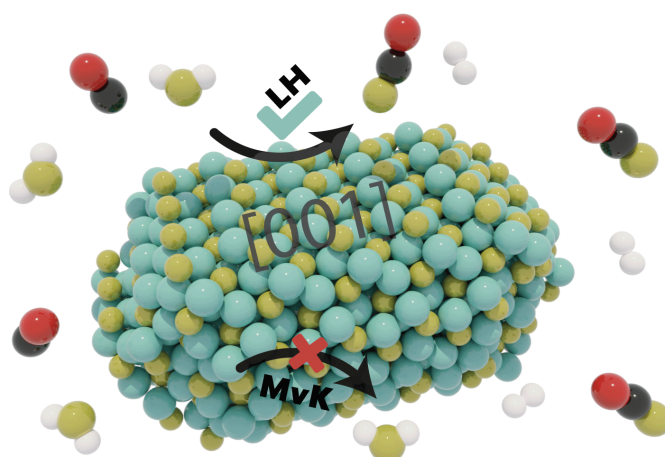
- (1) Jorgensen, W.; Salem, L., *The Organic Chemist's Book of Orbitals*. Elsevier Science: 1973.

Chapter 6. A Density Functional Theory Study of the Formation of COS from CO and H₂S on Cesium Sulfide

Abstract

Alkali metals can promote the performance of MoS₂ in methanethiol (CH₃SH) synthesis from CO/H₂/H₂S mixtures. Recently, it has been found that alkali sulfides and most prominently Cs₂S can also catalyze the reaction between CO and H₂S to COS and H₂, COS acting as an intermediate in CH₃SH formation (*M. Yu et al. J. Catal. 2022, 405, 116-128*). Here, we study the nature of the active sites and the mechanism of the CO + H₂S → COS + H₂ reaction for the 6 low-index Miller planes of Cs₂S. While CO adsorbs weakly, strong dissociative adsorption of H₂S results in HS* and H* intermediates, which further stabilize the (001) facet as the dominant surface termination. The main reaction pathway towards COS involves the association of CO* and SH* to COSH* followed by its dehydrogenation in a Langmuir-Hinshelwood mechanism. Reactions of CO* with lattice S atoms have prohibitively high barriers due to the strong Cs-S bonds in Cs₂S. Overall, the reaction rate is dominated by the (001) facet with small contributions of the (010), (011) and (101) surfaces. COSH* formation, its dehydrogenation to COS, and COS desorption compete as rate-controlling steps on these surfaces.

Keywords: alkali; sulfide; carbonyl sulfide; density functional theory; microkinetics simulations



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6.1 Introduction

Alkali metals are widely used in heterogeneous catalysts, mainly as promoters to metal-catalyzed reactions, such as ammonia synthesis, Fischer-Tropsch synthesis and higher alcohol synthesis.¹⁻⁵ In ammonia synthesis, K promotes N₂ activation on Fe and Ru metal catalysts via electronic promotion of the active sites.^{6, 7} K is also a common promoter in Fe-based Fischer-Tropsch catalysts, enhancing the CO conversion rate and improving the olefins selectivity, while Na is known to increase the rate of Fe carburization and the water-gas shift (WGS) reaction.^{8, 9} Alkali metals also find application as promoters in the WS₂-catalyzed thiolation of methanol to methanethiol (CH₃SH).¹⁰ Methanethiol (CH₃SH) is an important chemical intermediate in the manufacture of valuable organosulfur compounds, including pharmaceuticals and pesticides. Currently, CH₃SH is mainly produced by the thiolation of methanol (CH₃OH).¹¹ However, this multi-step process, involving the synthesis of CH₃OH from synthesis gas followed by thiolation, is costly, which is the main reason why a more efficient direct process for manufacturing CH₃SH is explored.

Olin et al. attempted to obtain CH₃SH directly from mixtures of synthesis gas and H₂S using alkali-promoted MoS₂ and found that K-promoted MoS₂ combines a high CO conversion rate with a high CH₃SH selectivity.¹²⁻¹⁴ Barrault et al. proposed that carbonyl sulfide (COS) is the main intermediate during CH₃SH formation in the reaction between CO, H₂ and H₂S.¹⁵ Gutierrez et al. exploited this insight by proposing a two-step approach, involving the formation of COS on K-promoted MoS₂, followed by its disproportionation into carbon dioxide (CO₂) and carbon disulfide (CS₂), the latter compound undergoing hydrogenation to CH₃SH on the hydrogenation function provided by MoS₂.¹⁶ Despite considerable research efforts, the nature of the active sites in MoS₂ catalysts remains unclear. MoS₂ can exhibit different crystal structures, namely the 1T (Mo in octahedral coordination), 2H (Mo in trigonal prismatic coordination), and 3R (Mo in rhombohedral coordination) polymorphs.¹⁷ An unresolved Mo-S-K phase was speculated to contain active sites in K₂MoS₄/SiO₂ and MoS₂/K₂CO₃/SiO₂ catalysts.¹⁸ On the other hand, MoS₂ was observed to be the only crystalline phase in a series of K-promoted MoS₂/SiO₂-Al₂O₃.^{13, 14, 16, 19} Cordova et al. employed XPS to demonstrate that 1T-MoS₂ is the dominant MoS₂ polymorph upon sulfidation of Mo-oxides in the presence of K. This led to the proposal that 1T-MoS₂ is the active phase for CH₃SH synthesis from a mixture of synthesis gas and H₂S.²⁰ However, Hensen's group showed that the 1T-MoS₂ phase formed during sulfidation (high H₂S/H₂ ratios) transformed into the more commonly observed 2H-MoS₂ phase during CH₃SH synthesis.²¹ These authors also found that this phase transformation did not impact the catalytic performance. Based on these

observations, it was concluded that both polymorphs of K-promoted MoS₂ exhibit similar catalytic performance, suggesting a direct role of K as the active sites. It was also found that the CH₃SH formation rate increased with the size of the alkali cation promoting MoS₂.²² Based on this, the role of alkali metals was investigated, leading to the insight that Cs-sulfide exhibited the highest catalytic performance, even without MoS₂. A possible role of MoS₂ is, therefore, to maintain a high dispersion of the alkali metal sulfide at the edges of MoS₂. A main insight of these works is that alkali sulfides, which were proven to be stable under the given reaction conditions by XPS, can catalyze the formation of CH₃SH from mixtures of synthesis gas and H₂S with COS as a main reaction intermediate.

To understand the role of alkali sulfide as an active catalyst for CH₃SH synthesis from CO/H₂/H₂S mixtures, we employed density functional theory (DFT) to calculate the key reaction steps that convert CO and H₂S into COS and H₂ ($\text{CO} + \text{H}_2\text{S} \rightleftharpoons \text{COS} + \text{H}_2$), COS being the key intermediate that yields CH₃SH upon further hydrogenation. The latter step was not studied here. DFT was used to calculate surface free energies of Cs₂S, adsorption energies of reactants and products, and the reaction energetics. These data were used as input to a microkinetic model to predict the reaction rate of different surface facets. The DFT results revealed that the most active surface facets comprise the simultaneous presence of Cs and S atoms in the first surface layer. Furthermore, it was inferred that adsorbed sulfur species (SH*) exhibited higher reactivity in reacting with adsorbed CO than lattice S atoms. Thus, a Langmuir-Hinshelwood mechanism is preferred over a Mars-Van Krevelen one. Microkinetics simulations show how the COS formation rate depends on the energy barriers. The overall reaction rate mainly derives from the (001) surface with a small contribution of the (010), (011) and (101) surfaces. At low temperatures, COS* desorption is the main rate-controlling step whereas at high temperatures, COSH* formation or dehydrogenation becomes increasing rate-controlling. The kinetics of the reaction are discussed in detail as well.

6.2 Computational Details

6.2.1 Density Functional Theory Calculations

All spin-polarized density functional theory (DFT) calculations were performed using the VASP software (version 5.4) with the Perdew-Burke-Ernzerhof of (PBE) exchange-correlation functional, wherein the effective ion cores are described by projector-augmented wave (PAW) potentials.²³⁻²⁶ The electronic wavefunctions for valence electrons were expanded into plane waves with a cut-off energy of 400 eV. Van-der-Waals interactions were taken into account by using the DFT-D3 method.²⁷ Geometry optimization was conducted by the conjugate gradient method with

a convergence criterion of 10^{-5} eV for the self-consistent electron interaction energy, while a force-based stop criterion of 0.05 eV/Å was employed. The climbing-image nudged elastic band method (CI-NEB) was employed to determine transition states for the elementary reaction steps.^{28, 29} A frequency analysis was performed for all states, where stable states were verified to have no imaginary frequencies, while all transition states were confirmed to have a single imaginary frequency in the direction of the reaction coordinate. The Hessian matrix for frequency analysis was determined using the finite difference approach in which individual atoms were displaced in each Cartesian direction. The corresponding normal mode vibrations were used to calculate the zero-point energy (ZPE) and vibrational partition functions. Brillouin zone sampling was performed using a $3 \times 3 \times 1$ Monkhorst–Pack k mesh.

Bulk Cs₂S with the orthorhombic crystal structure was first optimized (Figure D1 in Appendix D), yielding lattice parameters $a = 8.827$ Å, $b = 5.495$ Å, $c = 10.615$ Å. These lattice parameters agree reasonably well with the experimental values of $a = 8.541$ Å, $b = 5.365$ Å, $c = 10.354$ Å.^{30, 31} From the optimized bulk structure, we constructed six representative low-index Miller surface facets. A (1×2) supercell was used to model the (001), (010), (100), (101) and (111) facets, while a (2×2) supercell was used for the (011) facet. A vacuum layer of 15 Å was introduced perpendicular to the surface to avoid spurious interactions between neighbouring slabs. During geometry optimization, all the atoms in the bottom three layers were frozen, while all other atoms were allowed to relax.

The surface free energy of a facet (E_{surface}) is determined by

$$E_{\text{surface}} = \frac{E_n - n \cdot E_{\text{bulk}}}{2 \cdot A} \quad (6.1)$$

where E_n is the total energy of the slab containing n times the monoclinic bulk cell, E_{bulk} is the bulk energy and A is the surface area of the corresponding surface.

6.2.2 Microkinetics Simulations

Microkinetic simulations were conducted to investigate the kinetics of the $\text{CO} + \text{H}_2\text{S} \rightleftharpoons \text{COS} + \text{H}_2$ reaction. The energetics of the elementary reaction steps were determined by DFT. The kinetic network was modeled using a set of ordinary different equations (ODE) involving the surface coverages, the reaction rate constants of the elementary reaction steps, and the partial pressures of the gas-phase species. Each ODE corresponds to the time derivative of a surface compound. Time-integration of the ODEs was conducted using relative and absolute tolerances of 10^{-8} . At $t = 0$, the surface was empty.

For adsorption, the net rate of gas-phase species i was calculated by:

$$r_i = k_{i,ads}\theta_*P_i - k_{i,des}\theta_i \quad (6.2)$$

where θ_* and θ_i represent the fraction of free sites and the fractional coverage of species i , respectively. $k_{i,ads/des}$ corresponds to the rate constants for the adsorption/desorption processes of species i and P_i is the partial pressure of species i . The rate of desorption can be described by assuming that the transition state has two translational degrees of freedom. The rates of adsorption and desorption are then given by:

$$k_{i,ads} = \frac{p A_{st}}{\sqrt{2\pi m_i k_B T}} \quad (6.3)$$

$$k_{i,des} = \frac{k_B \cdot T^3}{h^3} \cdot \frac{A_{st}(2\pi m_i k_B)}{\sigma \theta_{rot}} \cdot \exp\left(\frac{-\Delta E_{des}}{RT}\right) \quad (6.4)$$

where $k_{i,ads}$ is the rate constant for adsorption of the absorbate, p and A_{st} are the corresponding partial pressure in Pa and the effective surface area in m², m_i is the molar mass of the gas species in kg, k_B is the Boltzmann constant in J/K, T is the temperature in K, $k_{i,des}$ is the constant for desorption of the absorbate, h is the Planck constant in m² kg/s, σ is the symmetry number, θ_{rot} is the rotational temperature of the gas-phase species in K, and ΔE_{des} and R are the desorption energy in J/mol and gas constant in J/K, respectively. For the adsorption process, a sticking coefficient of unity was assumed.

For each elementary step, the rate constant (k) is given by:

$$k = v \cdot e\left(\frac{-\Delta E_{act}}{RT}\right) \quad (6.5)$$

Herein, ΔE_{act} is the electronic activation energy including the ZPE correction in J/mol, while v is the pre-exponential factor in s⁻¹. The pre-exponential factor can be evaluated for the forward and backward reaction using the following equations:

$$v_{forward} = \frac{k_B T}{h} \left(\frac{Q_{TS}^*}{Q_{IS}} \right) \quad (6.6)$$

$$v_{backward} = \frac{k_B T}{h} \left(\frac{Q_{TS}^*}{Q_{FS}} \right) \quad (6.7)$$

where Q_{TS}^* is the total of translational, rotational, and vibrational partition functions of the transition state excluding the partition function corresponding to the imaginary frequency. $Q_{IS/FS}$

correspond to the products of the motional partition functions for the initial and final state, respectively.

To further evaluate the contribution of reaction steps to the reaction rate and product distribution, we used the concept of the degree of rate control (DRC), as proposed by Campbell.³²

$$X_{RC,i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (6.8)$$

which in the zero-conversion limit and under steady-state obeys the following sum rule

$$\sum X_{RC,i} = 1 \quad (6.9)$$

The $X_{RC,i}$ is the DRC coefficient. K_i is corresponding to the equilibrium constant. k_i is the reaction rate constant and r_i is the reaction rate of step i .

To account for the individual surface contributions of a particular surface facet j to the overall reaction rate, represented by f_j , on Cs₂S, we used the following equation which employs the fraction of the surface exposed (derived from the Wulff construction) by facet j (x_j),

$$f_j = \left(\frac{x_j \cdot r_j}{\sum_i x_i \cdot r_i} \right) \quad (6.10)$$

All the microkinetic simulations were conducted by the MKMCXX software suite.³³ Time-integration of the differential equations was conducted using the backward differentiation formula (BDF)^{34, 35} method until a steady-state solution was achieved.³⁶ From the steady-state coverages, the rates of the individual elementary reaction steps were computed.

6.3 Results and Discussion

6.3.1 Surface Model

The optimized models of the (001), (010), (011), (100), (101) and (110) facets of Cs₂S are shown in Figure 6.1. These surfaces differ in terms of exposed Cs and S atoms and surface atom topology. For instance, only S atoms are exposed at some of the surfaces, whereas the S atoms are below the exposed surface layer of Cs atoms in others. We first calculated the surface free energies for the 6 considered facets. The results compiled in Table 6.1 show that the (001) surface is the most stable one with $E_{\text{surface}} = -0.30 \text{ J/m}^2$. The surface free energies increase in the order (001) < (011) < (010) < (110) < (101) < (100). To have an estimate of the contributions of the various surface facets on a hypothetical Cs₂S nanoparticle, we employed the Wulff theorem. The results are included in

Table 6.1 and show substantial contributions of the (001), (010), (011), (101), and (110) facets to the surface with a negligible contribution of the (100) facet. As the contribution of these surfaces to the overall rate will also depend on their intrinsic activity, we next determined the energy diagrams for the reaction between CO and H₂S on all these facets.

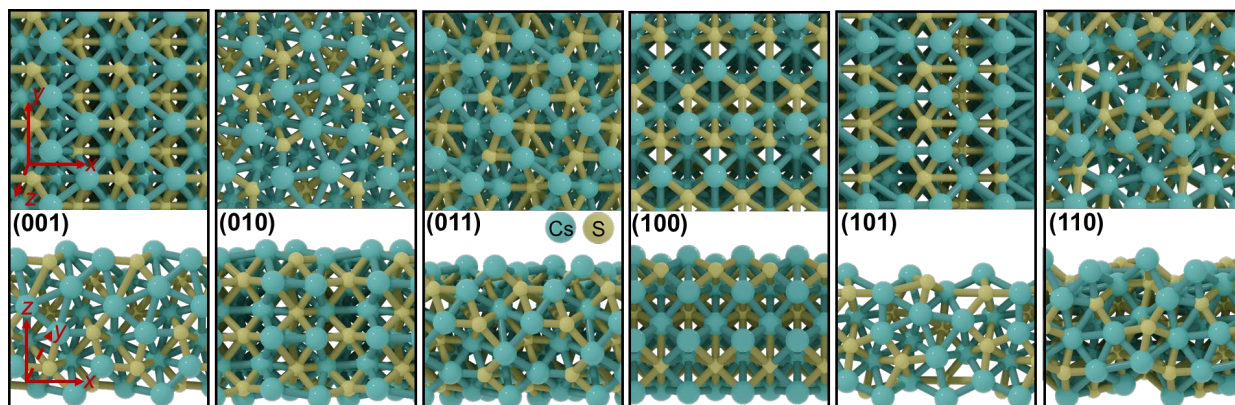


Figure 6.1. Top and side view of 6 low-index Miller planes of Cs₂S. (Cs atoms: light blue, S atoms: yellow).

6.3.2 Adsorption of CO and H₂S

Adsorption of CO and H₂S was considered on the optimized surface models. As adsorption sites, we considered top, bridge, 3-fold, 4-fold, and 5-fold positions. Figure 6.2 depicts the most stable adsorption configurations of CO and the corresponding adsorption energies. Although the various surfaces result in distinct stable CO adsorption sites, most of these adsorption modes represent weak binding, dominated by Van-der-Waals interactions. In the present DFT calculations, these are modeled by the D3 term. Examples of weak CO adsorption are the adsorption on lattice S atoms, such as CO on the 3-fold and 4-fold sites on the (001), (010), (011), (100), (101), and (110) surfaces.

On all the Cs₂S facets, H₂S undergoes spontaneous dissociative adsorption into HS* and H* species. The adsorption energies and geometries of the most stable states are provided in Figure 6.3. On the (001) surface, HS* preferentially adsorbs in a 3-fold site of Cs atoms. The H* species binds to an adjacent S atom with an S-H bond distance of 1.36 Å. Comparable adsorption geometries of HS* and H* were obtained for the (010), (100), and (110) surfaces. On the (011) surface, the most stable configuration of the H₂S dissociative adsorption was observed with HS* binding in the 4-fold site (4 Cs atoms) with H binding in the adjacent S site, the energy of dissociative adsorption being -133 kJ/mol. On the (101) surface, the most favorable adsorption site for HS* is a bridge Cs-Cs site, while H* is located on a nearby S site. While CO adsorbs very

weakly on the Cs₂S surface facets considered, dissociative adsorption of H₂S is strong, resulting in HS* and H* surface species.

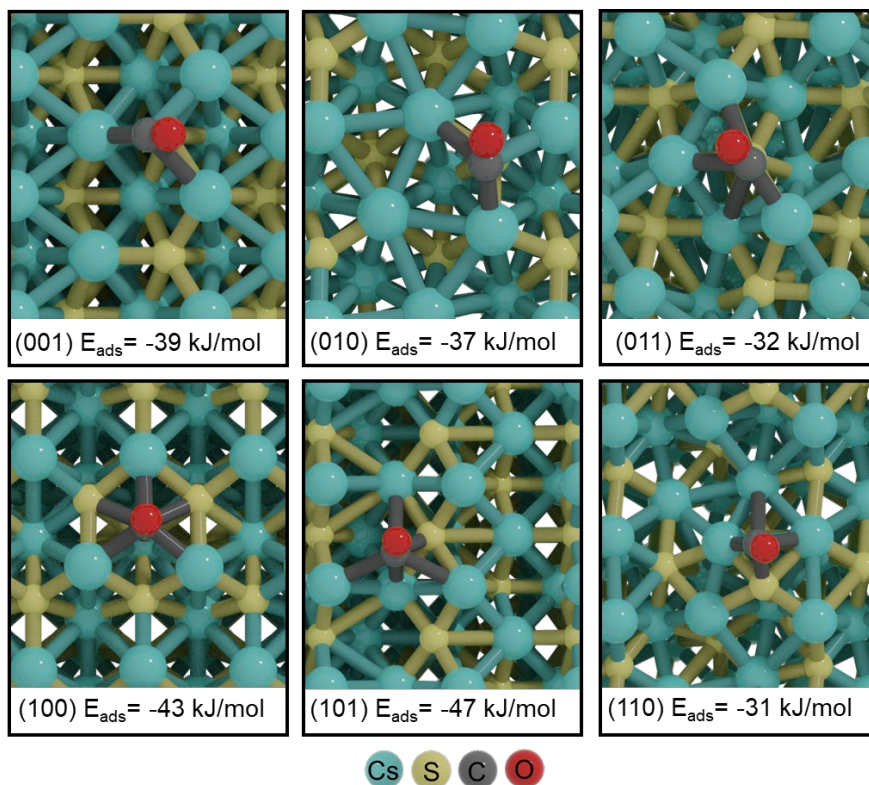


Figure 6.2. Most stable CO adsorption geometries and energies on the 6 considered Cs₂S facets.

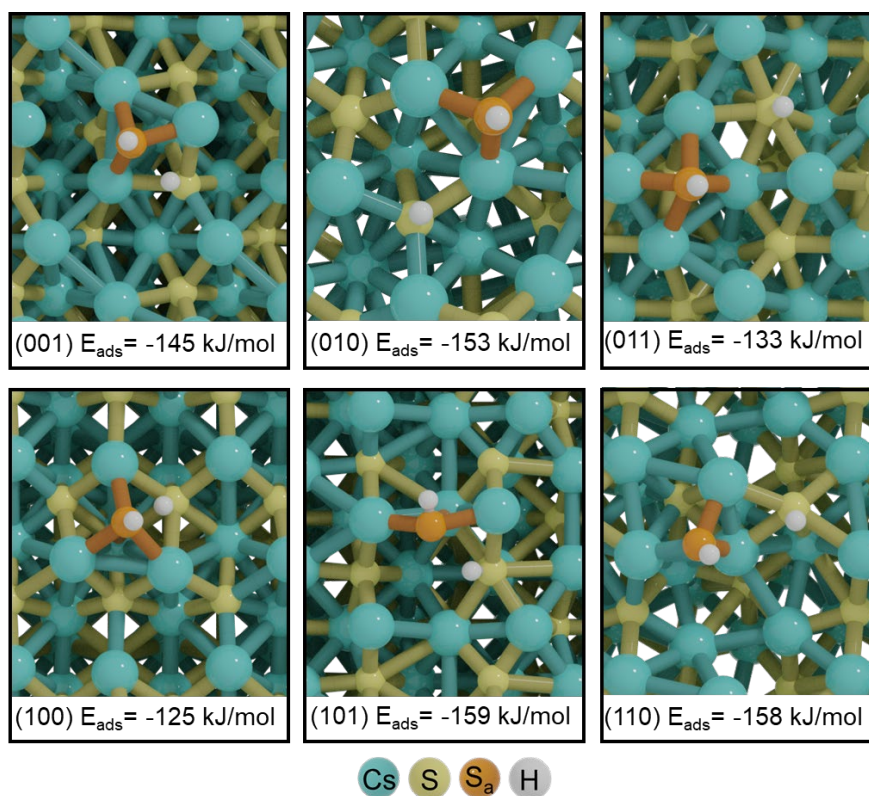


Figure 6.3. Most stable geometries upon dissociative adsorption of H₂S and the corresponding adsorption energies on the 6 considered Cs₂S facets.

Table 6.1. Free energies of empty surfaces and HS*+H* adsorbed surfaces facets at $T = 600$ K, $p = 10$ bar, and their contributions to the total surface of a hypothetical Wulff particle of Cs₂S.

Surface	Empty Surfaces		Surfaces with ¼ ML HS*+H*	
	Surface free energy/ J/m ²	Total amount of exposed surface (%)	Surface free energy/ J/m ²	Total amount of exposed surface (%)
(001)	0.30	21.9	0.23	26.0
(010)	0.34	0.7	0.26	2.8
(011)	0.32	29.8	0.25	23.7
(100)	0.68	<0.1	0.59	<0.1
(101)	0.42	23.7	0.36	16.9
(110)	0.37	23.9	0.28	30.6

Given the strong binding of H₂S, we explored the stabilization of surface facets by adsorbed H₂S using the ab initio thermodynamics approach introduced by Reuter and Scheffler.³⁷ For this purpose, we determined the surface free energies for all 6 surfaces containing 1/4 monolayer (ML) HS*+H* as a function of the temperature at a pressure of 10 bar H₂S. We compare these values to the surface free energies of the empty surfaces (Figure D2 in Appendix D). Dissociative adsorption of H₂S stabilizes all surfaces at typical reaction temperatures ($T < 700$ K). The order of stability of the surface facets remains unchanged. A phase diagram shows that the (001) surface is the most stable one in a wide temperature and pressure range (Figure D3). We extended our Wulff analysis to include the case including dissociative H₂S adsorption. The results show only minor changes in the fractions of the exposed surfaces (Table 6.1, Figure D4). We argue here that the Wulff analysis in the presence of H₂S is relevant for the shape of the catalytic particle, because Cs₂S is obtained by sulfidation of a Cs-oxide precursor in a H₂S atmosphere at 673 K.²² The data show that the shape of the Wulff particle does not strongly change without adsorbates. Accordingly, we used the surface facet contributions of the Wulff particle in the presence of H₂S to normalize site-specific reaction rates (vide infra).

6.3.3 Carbonyl Sulfide Formation

Carbonyl sulfide (COS) is considered a key intermediate in the formation of CH₃SH from CO and H₂S.¹⁵ Its formation can proceed through the reaction of CO with either (i) adsorbed S* obtained via dissociation of HS* from dissociative H₂S adsorption ($\text{CO}^* + \text{S}^* \rightleftharpoons \text{COS}^*$) and adsorbed HS* ($\text{CO}^* + \text{HS}^* \rightleftharpoons \text{COSH}^*$, $\text{COSH}^* \rightleftharpoons \text{COS}^* + \text{H}^*$), or (ii) lattice S. The two mechanisms under (i) are of the Langmuir-Hinshelwood type, the latter of the Mars-Van Krevelen type. The computed forward and backward barriers for S* generation are displayed in Figure 6.4, while the geometries of the initial state (IS), transition state (TS), and final state (FS) are provided in Figure D5. In this work, barriers of less than 50 kJ/mol are considered to be low, while barriers exceeding 100 kJ/mol

are regarded as high, considering the reaction occurs at relatively mild temperatures ($T < 700$ K). On the (001) surface, HS* obtained by dissociative adsorption of H₂S is in the 3-fold site. Subsequently, HS* dissociates into S* and H* with a moderate barrier of 71 kJ/mol. During HS* dissociation, S* stays in the 3-fold site, while H* migrates to a neighboring lattice S site. HS* undergoes a similar cleavage from the 3-fold sites on the (010) and (100) surfaces, with relatively high barriers of 100 kJ/mol and 98 kJ/mol, respectively. On the (011) surface, HS* in the 4-fold site dissociates into adsorbed S* remaining in this high-coordination site and H* binding to an adjacent lattice S site with a barrier of 107 kJ/mol. On the (101) and (110) surfaces, HS* can dissociate to adsorbed S* in a 5-fold site, with H* binding to a nearby lattice S site. The barriers for HS* dissociation on these two surfaces are 115 kJ/mol and 135 kJ/mol, respectively.

We next investigated the formation of COS through the reaction of CO* and S* and CO* and HS* (mechanism i). The reaction energy diagrams for these reactions are given in Figures 5 and 6 for CO*+S* and CO*+HS*, respectively. The corresponding IS, TS, and FS configurations for the pathway via CO* and S* are given in Figure D6. Figure 6.4 shows that the barrier for COS* formation substantially varies for the 6 Cs₂S surfaces. COS* formation is relatively easy on the (001) surface with a moderate barrier of 87 kJ/mol. For the (100) surface, this reaction has a barrier of 92 kJ/mol. The barriers for the other surface are much higher, with values of 140 kJ/mol, 130 kJ/mol, 134 kJ/mol, and 182 kJ/mol for the (010), (011), (101) and (110) surfaces, respectively. COS binds relatively strongly with values of 156 kJ/mol (001), 183 kJ/mol (010), 158 kJ/mol (011), 178 kJ/mol (100), 198 kJ/mol (101), and 136 kJ/mol (110). Finally, the catalytic cycle is closed by H₂ desorption, which is easy for all surfaces with barriers less than 30 kJ/mol.

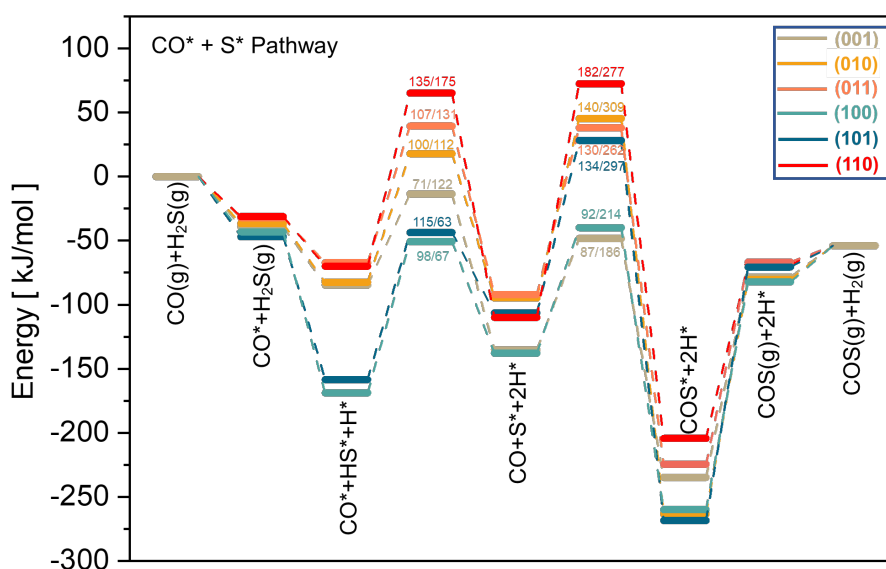


Figure 6.4. Reaction energy diagram for the formation of COS via CO* + S* association on the 6 Cs₂S surfaces.

Figure 6.5 shows the reaction energy diagram for COS formation via association of CO* and *HS, followed by COSH* dehydrogenation to COS*. The corresponding IS, TS, and FS configurations are given in Figures D7 and D8. COSH* formation is exothermic on all 6 Cs₂S surfaces. The reaction is most exothermic on the (100) surface, reflecting strong adsorption of COSH. As observed for COS* formation, the barriers for COSH* formation ($\text{CO}^* + \text{HS}^* \rightleftharpoons \text{COSH}^*$) vary substantially for the considered surfaces. The reaction is most facile on the (001) surface with a barrier of only 29 kJ/mol. The highest barrier of 90 kJ/mol is noted for the (110) surface, even though the product state is strongly favored on this surface. For the other surfaces, the barriers are 42 kJ/mol (010), 60 kJ/mol (011), 72 kJ/mol (100), and 83 kJ/mol (101). COSH* dehydrogenation ($\text{COSH}^* \rightleftharpoons \text{COS}^* + \text{H}^*$) is exothermic on most Cs₂S surfaces. The exception is the (100) surface, where the dissociation is only mildly exothermic due to the strong binding of COSH. The barriers of COSH* dehydrogenation to COS* are moderate for all surfaces. This elementary reaction is facile on the (101) and (001) surfaces with barriers of 56 kJ/mol and 63 kJ/mol, respectively. The barriers are slightly higher on the other surface, namely 82 kJ/mol (010), 86 kJ/mol (011), 88 kJ/mol (100) and 71 kJ/mol (110). Following COSH* dehydrogenation, the catalytic cycle is completed by desorption of COS and H₂.

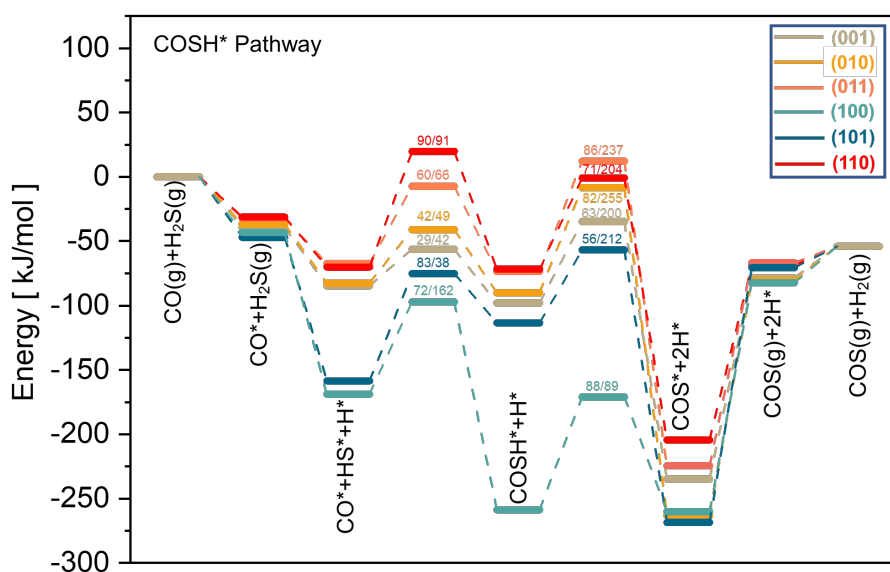


Figure 6.5. Reaction energy diagram for the formation of COS via CO* + HS* association on the 6 Cs₂S surfaces.

We also considered mechanism ii, which involves the reaction of adsorbed CO with lattice S atoms of the Cs₂S facets. We found that the reaction energies for the formation of COS and a surface S vacancy are highly endothermic. The associated reaction energies are 285 kJ/mol (001), 268 kJ/mol (010), 227 kJ/mol (011), 243 kJ/mol (100), 247 kJ/mol (101), and 251 kJ/mol (110). These energies are much higher than the barriers for COS formation through mechanism i, indicating that

COS formation will not occur via mechanism ii. Overall, these results indicate that the COS will be formed through mechanism i. As the reaction energy diagrams for mechanism i strongly depend on the surface facet, microkinetic simulations are needed to compare the intrinsic reaction rates.

6.3.4 Microkinetics Simulations

To investigate the contribution of each of the surface facets to the overall reaction rate for the reaction $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$, we carried out microkinetics simulations using the DFT-computed reaction energetics. In addition, these simulations aimed to explore the kinetic differences between the various facets, including the rate-controlling steps. Reaction barriers, reaction energies, and pre-exponential factors for all forward and backward elementary reaction steps are provided in Tables D1 and D2. The temperature in the simulations was varied between 570 and 670 K.²² Figure 6.6a presents the CO reaction rate, expressed as a turnover frequency (TOF), as a function of temperature. The (001) surface exhibits a significantly higher TOF than the other surfaces. While the (010), (011), (100) and (101) surfaces show intermediate activity, the (110) surfaces display a very low activity.

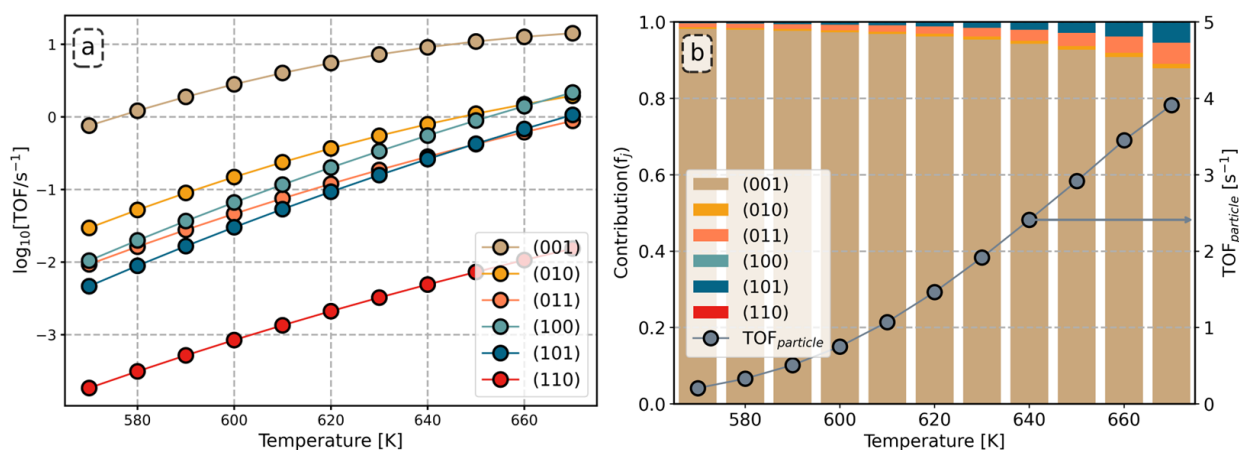


Figure 6.6. Microkinetics simulations of $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$ reaction on the 6 considered Cs₂S facets: (a) turnover frequency and (b) fractional contribution (f_i) of each surface facet to the turnover frequency of a Wulff particle as a function of the temperature ($p = 10$ bar, $\text{H}_2\text{S}/\text{CO}$ ratio = 1).

We employed Equation (6.10) to determine site-normalized rates of the Wulff particle in the presence of H₂S (TOF_{particle}) and the fractional contribution of each surface to this Wulff particle-based TOF as a function of the temperature (Figure 6.6b). The (001) surface contributes most to the particle-based TOF, while this surface makes up ~22% of the Wulff particle's surface. There is a small contribution of the (010), (011) and (101) surfaces to the overall rate. These contributions increase with temperature. The contributions of the (100) and (110) are negligible, although they

make up together ~24% of Wulff particle's surface. Thus, the overall activity of Cs₂S in the CO + H₂S → COS + H₂ reaction mainly derives from the (001) surface.

Figure 6.7 shows the steady-state surface coverages under the simulated reaction conditions in the temperature range 570–670 K. On the most reactive (001) surface, S* and COS* occupy the surface, which is consistent with the stronger binding of these intermediates compared to H* and CO*. The S* coverage increases with temperature due to H removal via H₂, while the COS* coverage decreases with temperature due to COS desorption. Similarly, COS* is the most abundant reaction intermediate on the (010), (011), (100) and (101) surfaces. Except for the (001) surface, all surfaces contain a considerable amount of HS*. The low HS* coverage on the (001) surface can be explained by the low barrier for COSH* formation. On the (100) surface, HS*, COS* and COSH* are the most abundant reaction intermediates due to the relatively high and comparable adsorption energies of COS* and COSH*.

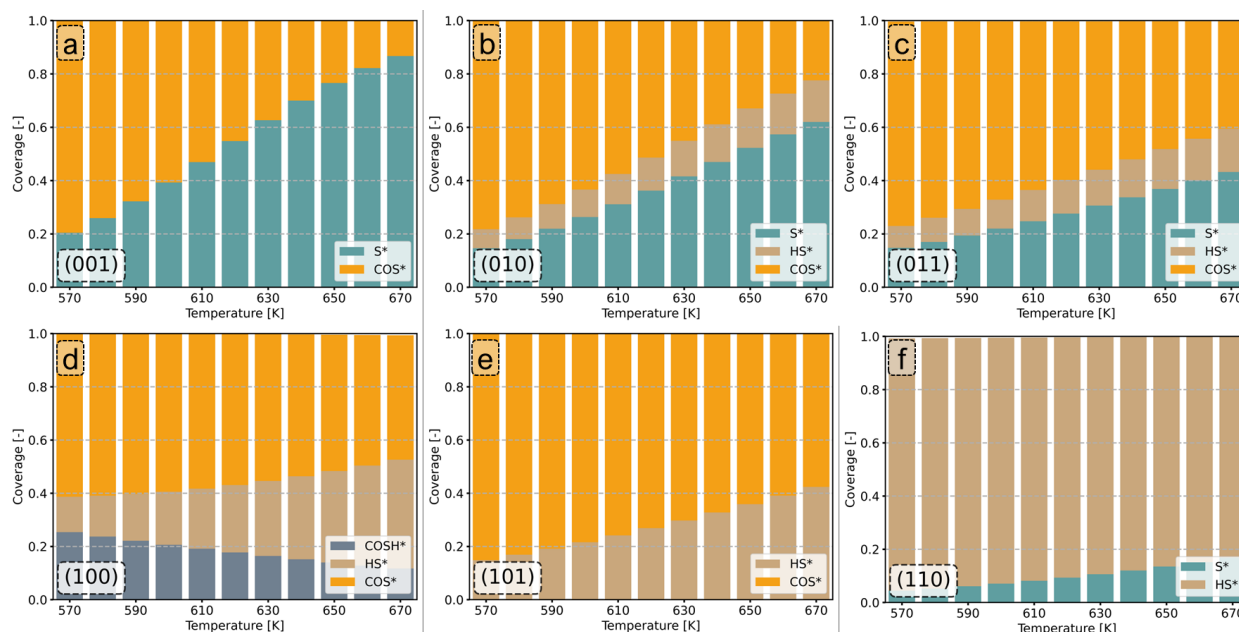


Figure 6.7. Surface coverage of the CO + H₂S → COS + H₂ reaction on the 6 considered Cs₂S facets ($p = 10$ bar, H₂S/CO ratio = 1).

A degree of rate control (DRC) was carried out to evaluate the rate-limiting step in COS formation (Figure 6.8). On the most active (001) surface, COS* desorption and COSH* formation (CO* + SH* ⇌ COSH* + *) control the reaction rate. The DRC of the latter reaction increases at the expense of the DRC of the former reaction with increasing temperature. This is caused by higher COS* desorption rates with increasing temperatures. The H₂ dissociation step has a negative DRC, which increases with the temperature. The negative DRC can be understood in terms of increased removal of H as H₂, resulting in a higher S* coverage. On the (100) surface, COS* desorption and COSH* formation control the reaction rate. On (010), (011) and (101) surfaces, COS* desorption

and COSH* dehydrogenation ($\text{COSH}^* + * \rightleftharpoons \text{COS}^* + \text{H}^*$) compete as main rate-controlling steps, where the latter increases at the expense of the former with increasing temperature due to the facile COS* desorption. On the least reactive surface (110), COSH* formation and dehydrogenation control the reaction rate, with their control degrees changing very slightly with temperature. The desorption of H₂ exhibits a negative value of DRC on (001), (010), (011) and (110) surfaces, as a higher rate of H₂ desorption leads to more HS* and S* derived from the H₂S dissociative adsorption, blocking surface sites for CO adsorption. H₂S dissociative adsorption shows a negative DRC for all surfaces, as this reaction decreases the number of free sites, required for CO adsorption.

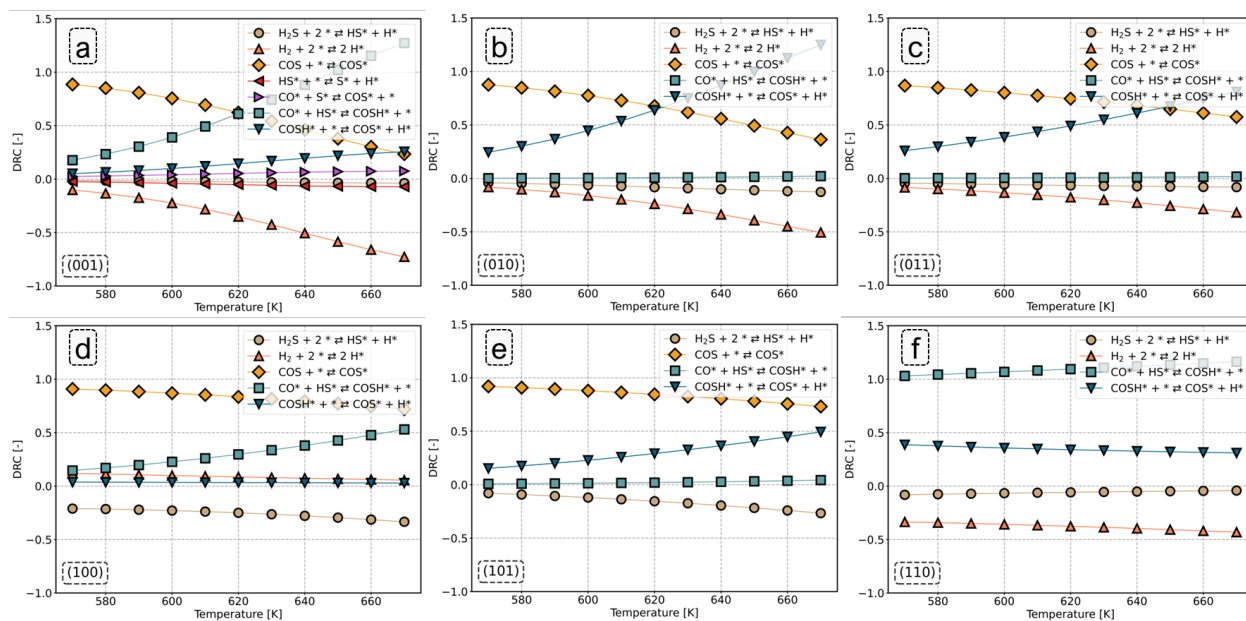


Figure 6.8. Degree of rate control (DRC) analysis of the $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$ reaction on the 6 considered Cs₂S facets ($p = 10$ bar, $\text{H}_2\text{S}/\text{CO}$ ratio = 1).

The reaction orders with respect to CO and H₂S and the apparent activation energies ($E_{\text{act}}^{\text{app}}$) are presented in Figure 6.9. Figure 6.9a shows positive CO reaction orders on all surface facets, consistent with the positive DRC values for the $\text{CO}^* + \text{SH}^* \rightleftharpoons \text{COSH}^* + *$ and $\text{COSH}^* + * \rightleftharpoons \text{COS}^* + \text{H}^*$ elementary steps. A higher CO partial pressure enhances the reaction rate, as it results in a higher coverage of CO, the surface component that limits the reaction. With the temperature rising, the CO reaction order increases, because CO will remove S or HS* species from the surface, providing vacancies for CO adsorption. On the contrary, the H₂S reaction orders are negative on all surfaces (Figure 6.9b). All surfaces contain a few vacant sites with high coverages of S* or SH*, meaning that a higher H₂S partial pressure further limits surface sites for CO adsorption.

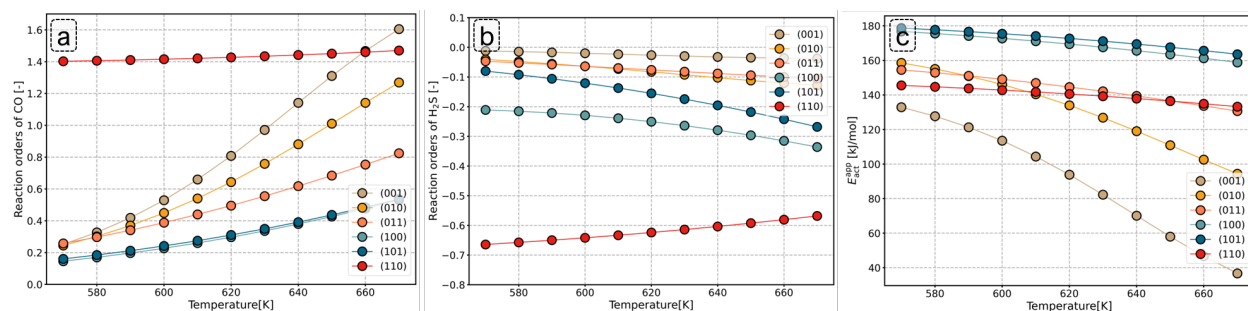


Figure 6.9. Microkinetics simulations of $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$ reaction on the 6 considered Cs₂S facets: reaction orders of (a) CO and (b) H₂S, and (c) apparent activation energy ($p = 10$ bar, H₂S/CO ratio = 1).

Figure 6.9c shows that the lowest apparent activation energy is obtained for the (001) surface, consistent with its highest reactivity. The apparent activation energy decreases with temperature due to the changing composition of the adsorbed layer. This decrease is also observed for the (010) surface. On the other surfaces, the apparent activation energies decrease slightly due to the slight shift in the main surface intermediate.

6.4 Conclusions

DFT was used to study the nature of the active sites and mechanism of the $\text{CO} + \text{H}_2\text{S} \rightleftharpoons \text{COS} + \text{H}_2$ reaction on Cs₂S, relevant to CO hydrogenation to methanethiol in H₂S-containing synthesis gas. Sites for CO and H₂S adsorption were identified on 6 lower Miller index planes. While CO adsorbs relatively weakly on the exposed S atoms of these surfaces, H₂S strongly adsorbs in a dissociative manner, yielding HS* and H* species. Strong adsorption of HS* and H* obtained by dissociative H₂S adsorption stabilizes the surfaces by lowering the free energy of all surfaces at typical reaction temperatures. The reconstruction due to strong dissociative H₂S adsorption compared to the case without adsorbates present on the surface is minimal. The main reaction pathways towards COS involve the reaction of adsorbed CO* with HS* and S* to respectively COSH* and COS*, the former reaction contributing the most to the overall reaction rate. COSH* dehydrogenation yields COS*. Such Langmuir-Hinshelwood mechanism is preferred over a Mars-Van Krevelen mechanism, as the barrier for reaction of CO with lattice S is very high. Among the Cs₂S facets considered, the (001) surface exhibits the lowest overall barrier for COS formation, which proceeds via COSH* formation and dehydrogenation. Microkinetics simulations were used to predict CO consumption rates, surface coverages, DRC values and other relevant kinetic parameters. Normalized to surface facet contributions based on the Wulff construction, the reaction rate is almost completely determined by CO conversion on the (001) surface with minor

contributions of the (010), (011) and (100) surfaces. Typically, COSH* formation or COSH* dehydrogenation compete with COS* desorption as rate-controlling steps. Our investigation provides atom-level insight into the active sites and mechanism of COS formation from CO and H₂S. As the metal-sulfur bond in other alkali metal sulfides will be stronger, it can be postulated that a similar Langmuir-Hinshelwood mechanism will likely be preferred as well.

6.5 References

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Appendix D

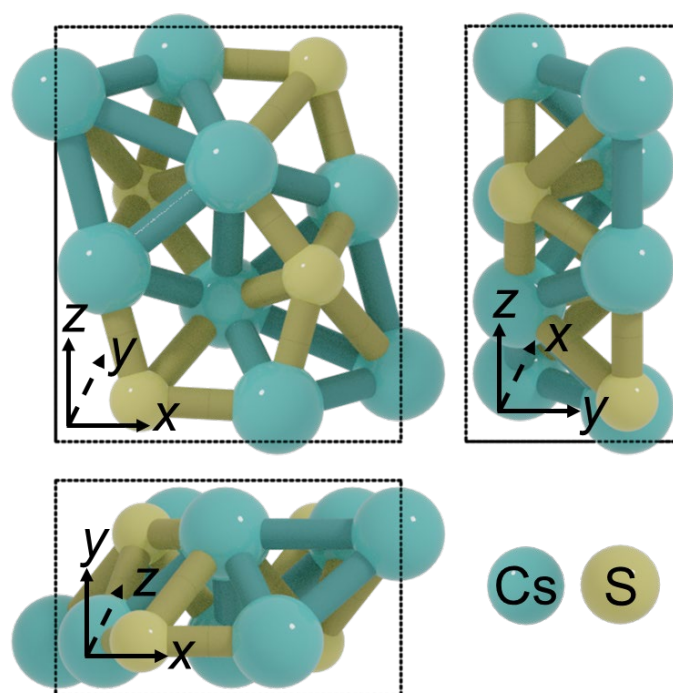


Figure D1. Optimized unit cell of bulk Cs₂S from different angles.

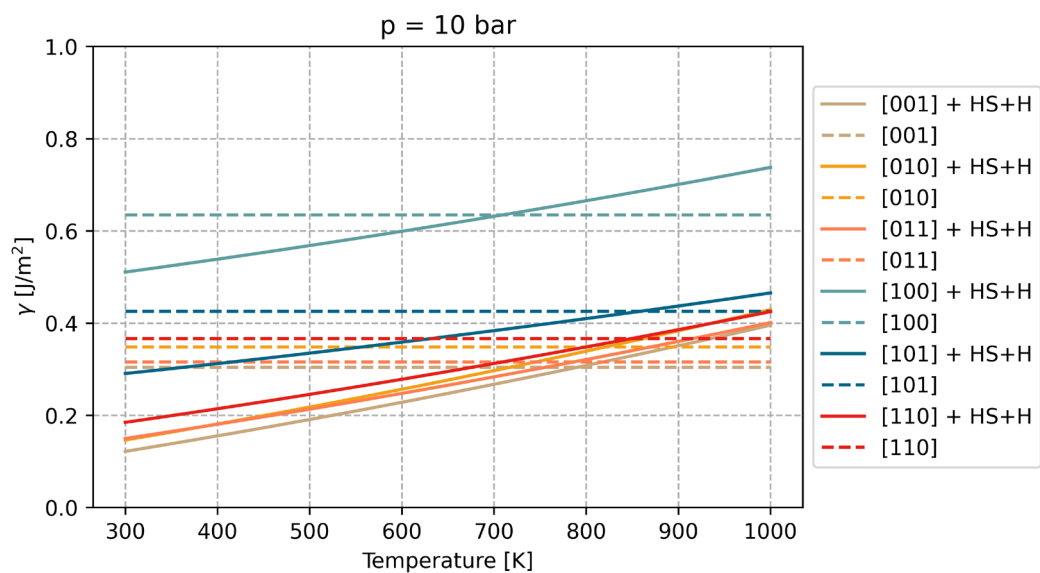


Figure D2. Surface free energies γ of the empty surfaces (dashed lines) and the surfaces containing HS*+H* as a function of the temperature at a H₂S pressure of 10 bar (full lines).

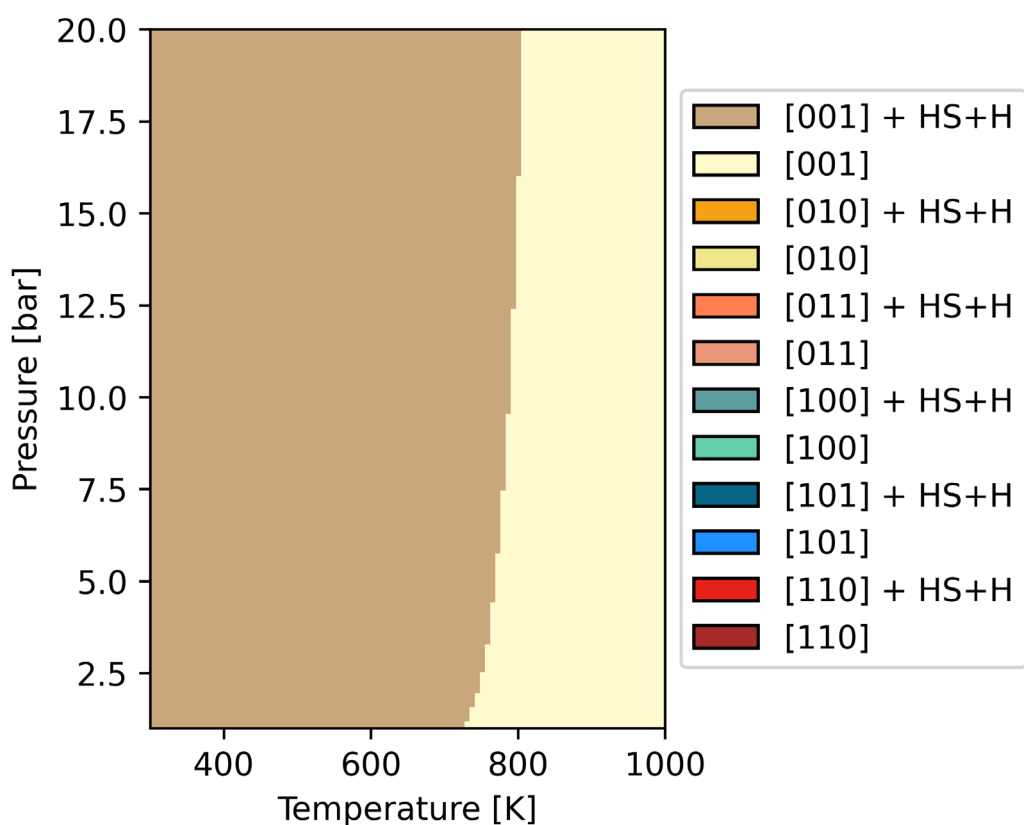


Figure D3. Phase diagram showing the most stable Cs₂S surface facets as a function of temperature and pressure. The (001) is the most stable surface facet. At relevant reaction conditions ($T < 700$ K), the surface is covered by HS* and H* species in a H₂S atmosphere. At higher temperatures, the surface is empty.

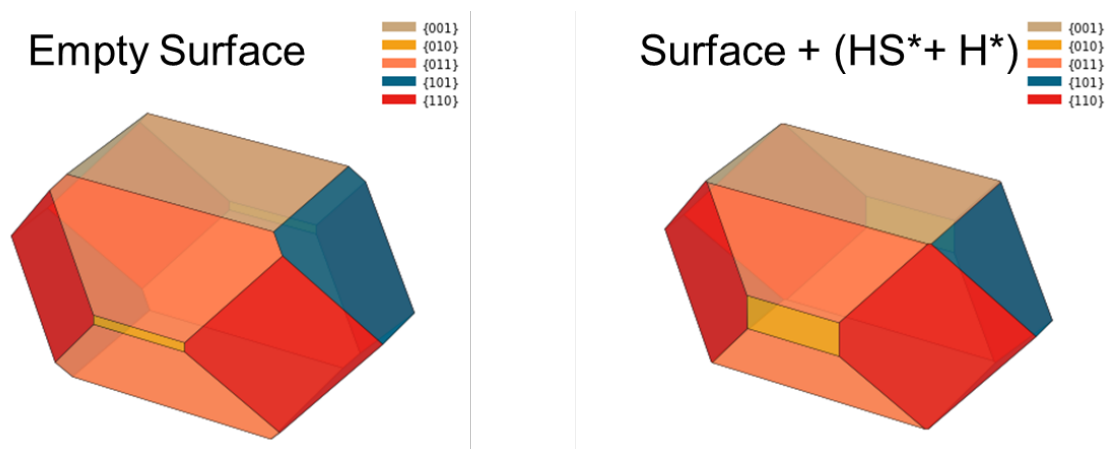


Figure D4. Wulff particle of Cs₂S without (left) and with (right) HS*+H* adsorption, corresponding to a temperature of 600 K and a H₂S pressure of 10 bar.

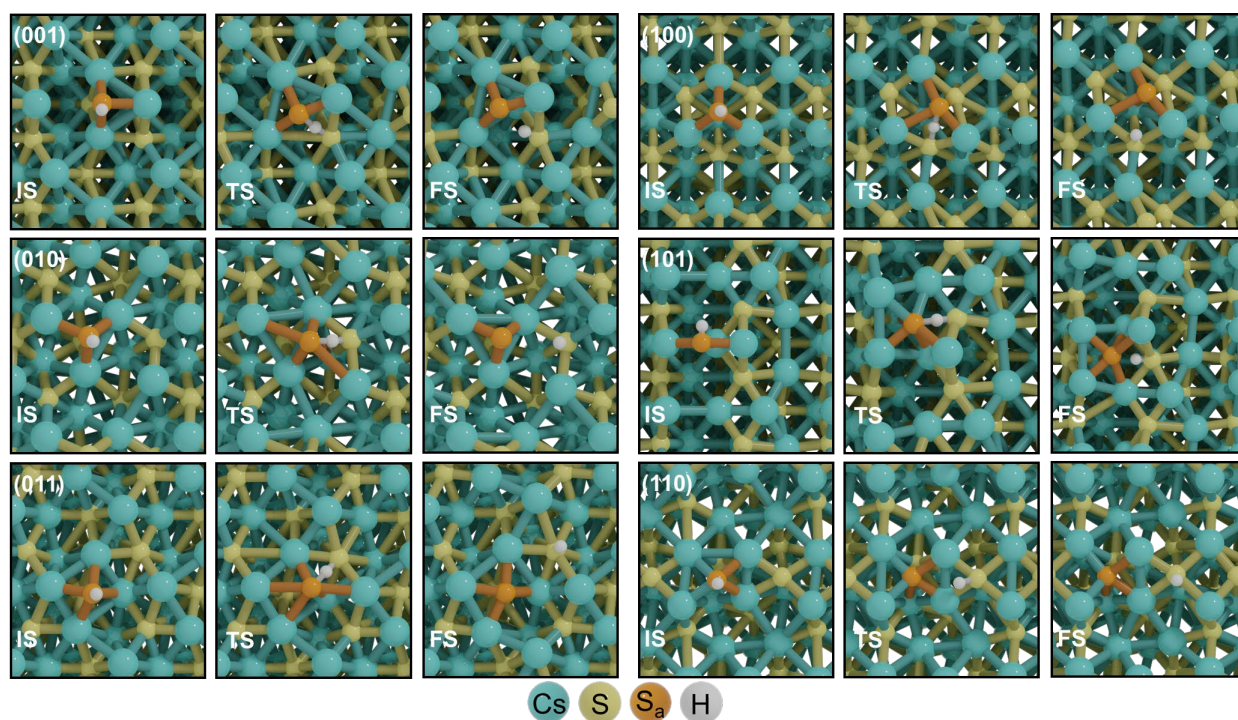


Figure D5. Configurations of IS, TS and FS for HS* dissociation on the 6 considered facets of Cs₂S.

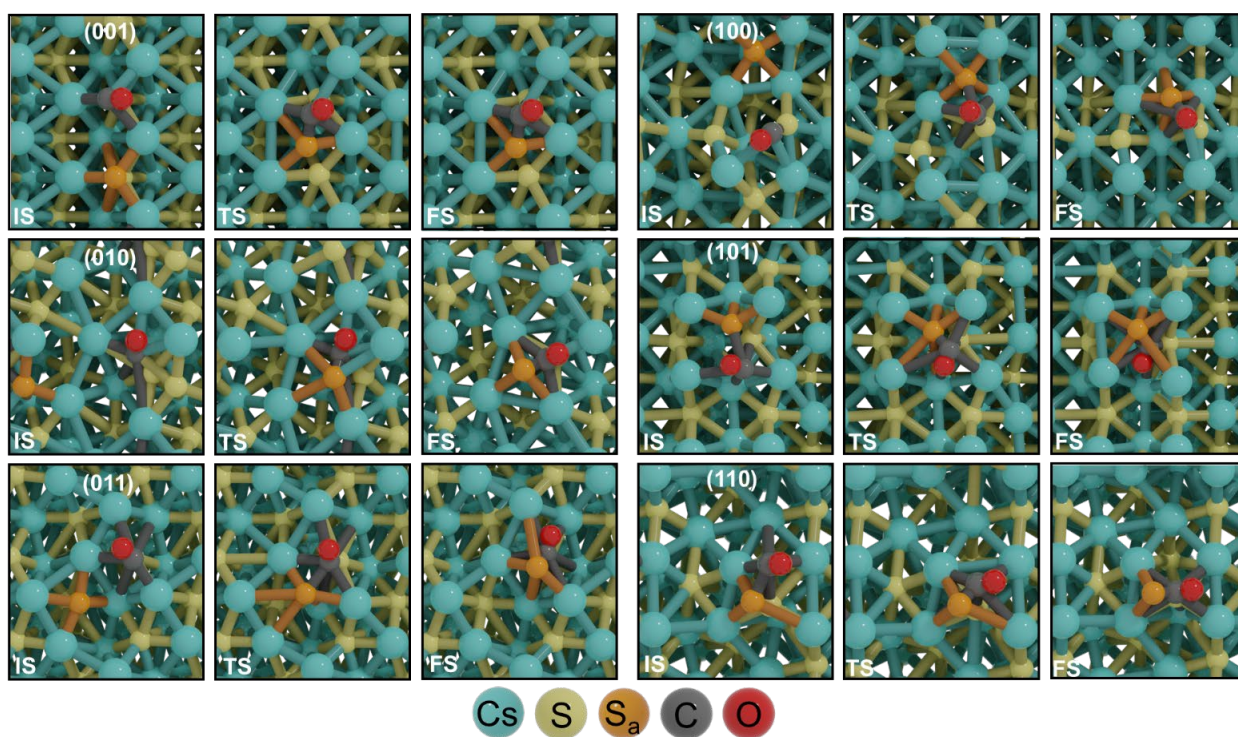


Figure D6. Configurations of IS, TS and FS for COS* formation on the 6 considered facets of Cs₂S.

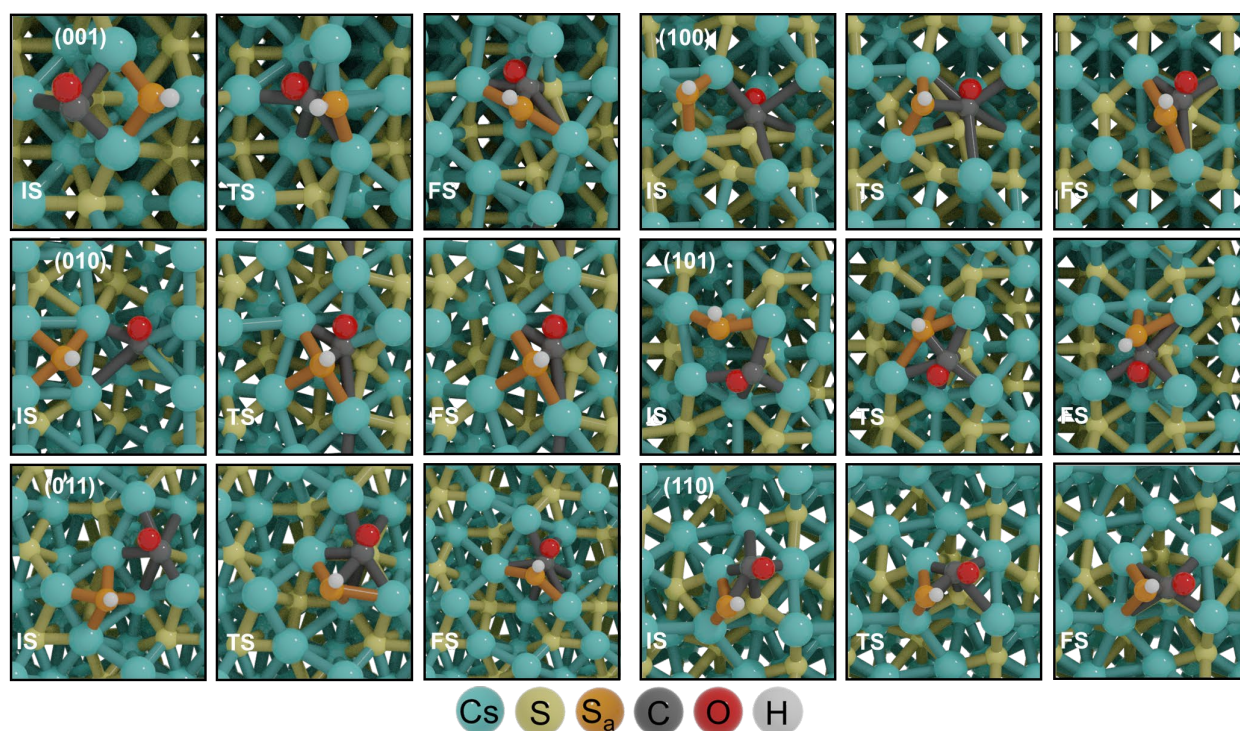


Figure D7. Configurations of IS, TS and FS for COSH* formation on the 6 considered facets of Cs₂S.

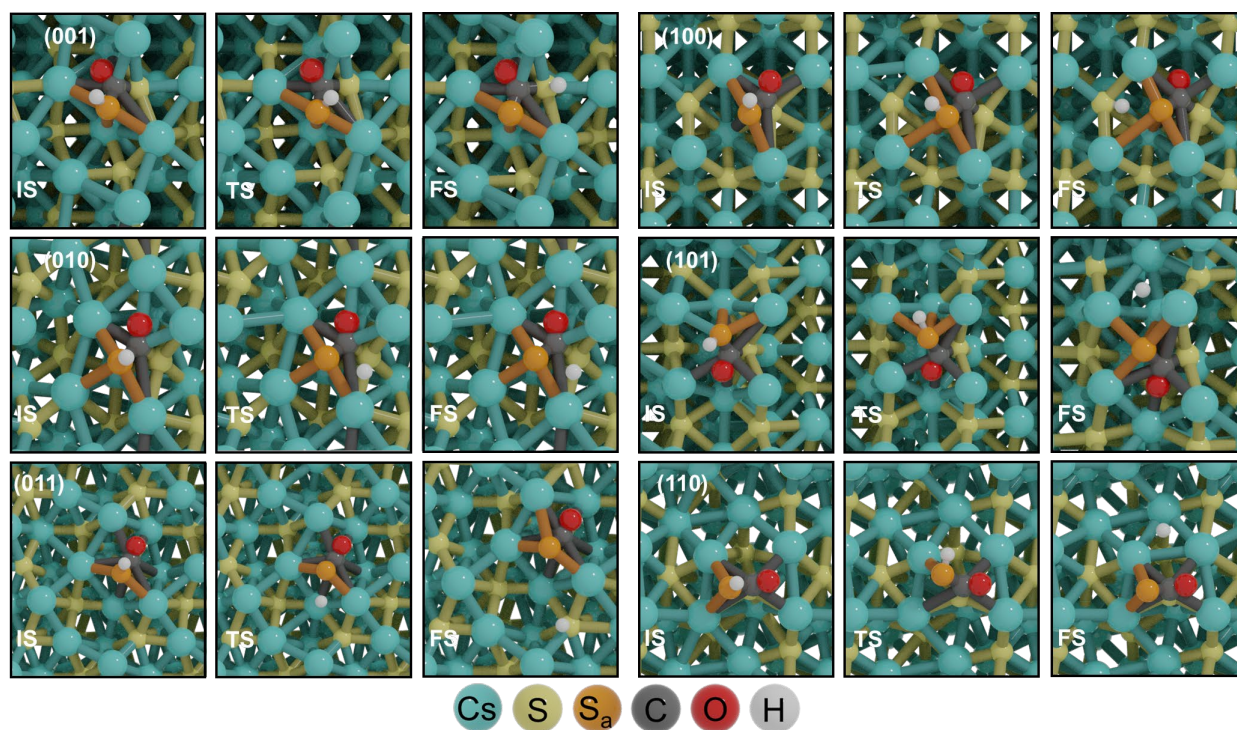


Figure D8. Configurations of IS, TS and FS for COSH* dehydrogenation on the 6 considered facets of Cs₂S.

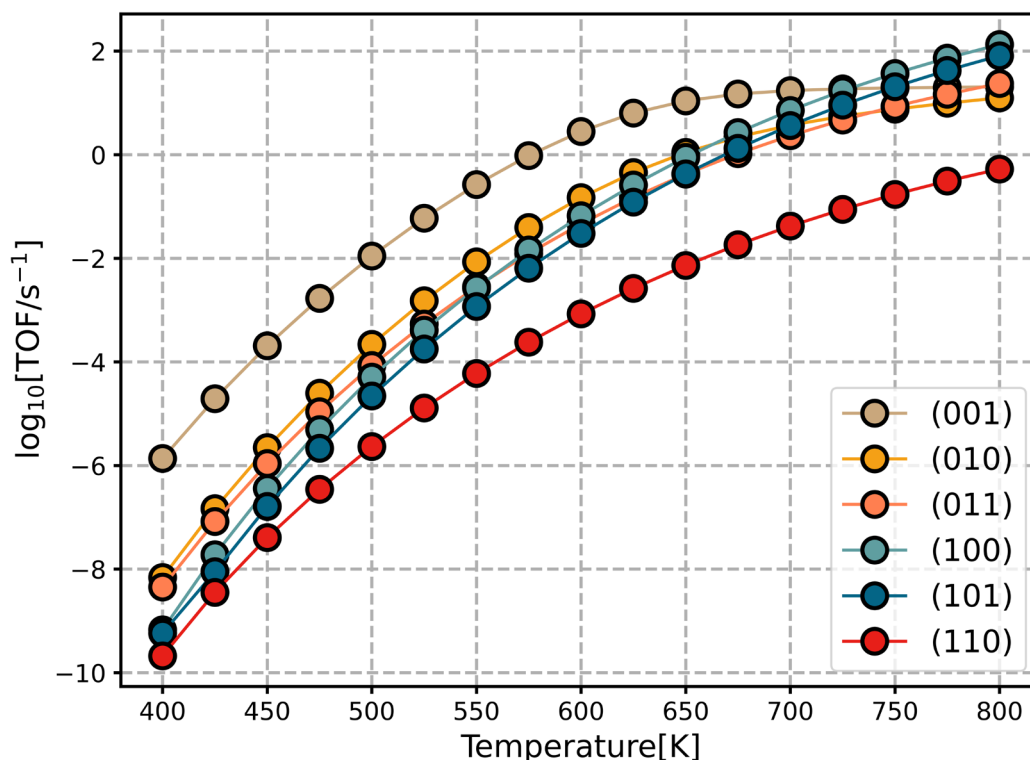


Figure D9. Microkinetics simulations of the $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$ reaction on the 6 considered Cs_2S facets: TOF as a function of the temperature ($\text{H}_2\text{S}/\text{CO}$ ratio = 1, $p = 10$ bar, $T = 400 - 800\text{K}$).

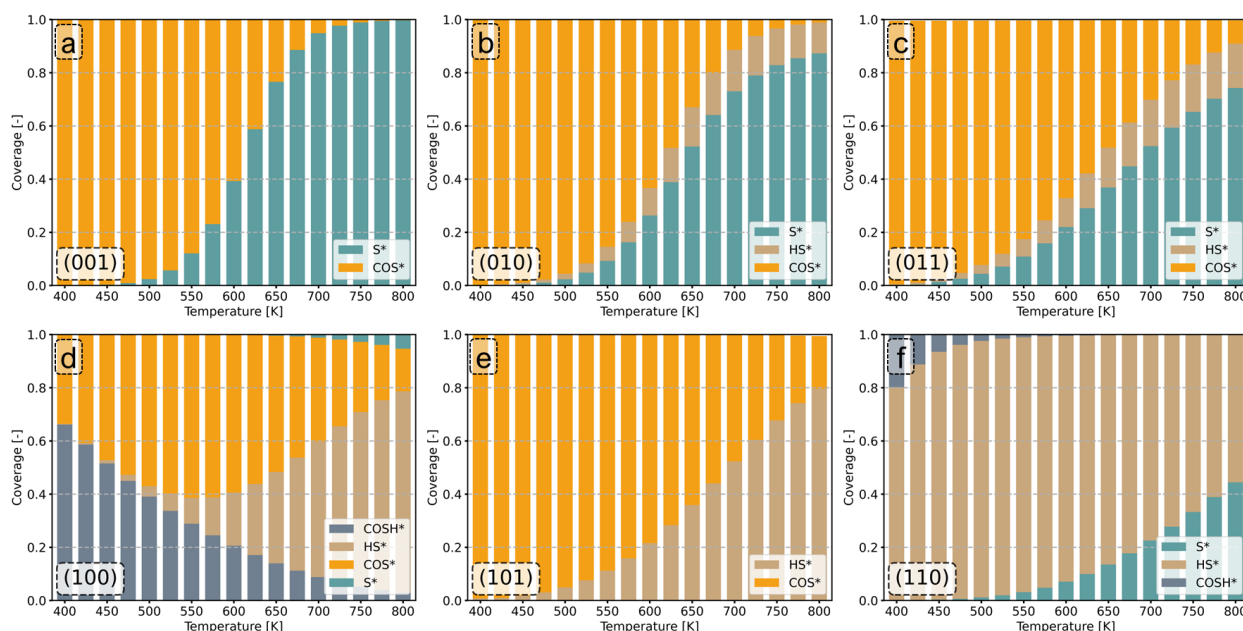


Figure D10. Steady-state surface coverages during the $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$ reaction on the 6 considered Cs_2S facets ($\text{H}_2\text{S}/\text{CO}$ ratio = 1, $p = 10$ bar, $T = 400 - 800\text{K}$).

Table D1. Forward barriers (E_f) and back-forward barriers (E_b) of elementary reaction steps considered for the $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$ reaction on the 6 considered facets of Cs_2S .

Surface termination	$\text{HS}^* \rightarrow \text{S}^* + \text{H}^*$		$\text{CO}^* + \text{S}^* \rightarrow \text{COS}^*$		$\text{CO}^* + \text{SH}^* \rightarrow \text{COSH}^*$		$\text{COSH}^* \rightarrow \text{COS}^* + \text{H}^*$	
	E_f (kJ/mol)	E_b (kJ/mol)	E_f (kJ/mol)	E_b (kJ/mol)	E_f (kJ/mol)	E_b (kJ/mol)	E_f (kJ/mol)	E_b (kJ/mol)
(001)	71	122	87	186	29	42	63	200
(010)	100	112	140	309	42	49	82	255
(011)	107	131	130	262	60	66	86	237
(100)	98	67	92	214	72	162	88	89
(101)	115	63	134	297	83	38	56	212
(110)	135	175	182	277	90	91	71	204

Table D2. Forward and back-forward pre-exponential factors of elementary reaction steps considered for the $\text{CO} + \text{H}_2\text{S} \rightarrow \text{COS} + \text{H}_2$ reaction on the 6 considered facets of Cs_2S .

Surface termination	$\text{HS}^* \rightarrow \text{S}^* + \text{H}^*$		$\text{CO}^* + \text{S}^* \rightarrow \text{COS}^*$		$\text{CO}^* + \text{SH}^* \rightarrow \text{COSH}^*$		$\text{COSH}^* \rightarrow \text{COS}^* + \text{H}^*$	
	ν_f (s ⁻¹)	ν_b (s ⁻¹)	ν_f (s ⁻¹)	ν_b (s ⁻¹)	ν_f (s ⁻¹)	ν_b (s ⁻¹)	ν_f (s ⁻¹)	ν_b (s ⁻¹)
(001)	3.1×10^{12}	1.3×10^{12}	1.7×10^{12}	7.6×10^{13}	2.9×10^{13}	2.6×10^{12}	9.3×10^{13}	1.3×10^{13}
(010)	7.4×10^{13}	1.4×10^{13}	2.6×10^{13}	1.3×10^{12}	2.3×10^{13}	7.5×10^{12}	4.8×10^{13}	6.7×10^{12}
(011)	2.5×10^{12}	6.8×10^{12}	1.5×10^{13}	2.7×10^{13}	7.9×10^{13}	1.5×10^{13}	2.3×10^{12}	8.1×10^{13}
(100)	1.5×10^{13}	1.7×10^{13}	3.6×10^{12}	2.1×10^{13}	9.7×10^{13}	1.1×10^{13}	2.8×10^{13}	5.6×10^{13}
(101)	3.3×10^{13}	2.5×10^{13}	9.3×10^{13}	1.5×10^{13}	4.2×10^{13}	1.7×10^{13}	3.7×10^{13}	2.0×10^{13}
(110)	9.3×10^{11}	4.2×10^{12}	4.5×10^{13}	2.4×10^{13}	1.3×10^{13}	1.4×10^{12}	3.2×10^{13}	1.3×10^{13}

Chapter 7. Summary and Outlook

Unraveling the Mechanistic Role of Promoters in Fe-Carbide-Catalyzed Fischer-Tropsch Synthesis

Summary

Fischer-Tropsch (FT) synthesis is a promising catalytic process for converting syngas, produced from natural gas, biomass, and coal by gasification or reforming, to high-value-added chemical compounds such as paraffins, olefins and oxygenates. Fe and Co are widely used in industrial catalyst formulations for FT synthesis. Compared to Co, Fe is cheap and provides a relatively high selectivity to light olefins. Moreover, Fe-based catalysts can be used in a wider range of process conditions. Their flexibility is especially important in processing syngas feeds from less clean carbon sources such as coal and biomass, accommodating broad variations in temperature, pressure and low H₂/CO ratios. Under practical FT synthesis conditions, Fe-based catalysts undergo inevitable carburization into a mixture of carbide phases, including ϵ -Fe₂C, ϵ' -Fe_{2.2}C, χ -Fe₅C₂, θ -Fe₃C, and Fe₇C₃. Among them, Hägg iron carbide (χ -Fe₅C₂) has been identified as the main active phase for CO activation and chain growth in FT synthesis. The incorporation of promoters can enhance the performance of Fe-based catalysts, such as increasing the CO conversion or altering the product distribution to the desired long-chain hydrocarbons. Notably, alkali promoters are widely used to improve the catalytic performance of Fe-based catalysts by increasing the catalytic activity and the selectivity to lower olefins. However, the nature of alkali promoter phases under FT synthesis conditions and their mechanistic role in promoting chain-growth remains unclear.

This thesis investigates the mechanistic role of alkali promoters, with a focus on potassium (K), in Fe-catalyzed CO/CO₂-Fischer-Tropsch (FT) synthesis by employing density functional theory in conjunction with microkinetic simulations. The study provides a systematic investigation of the nature of K species and their mechanistic role in key processes in FT synthesis, such as CO dissociation, and CH₄ formation, O removal as CO₂ and H₂, and chain growth to longer hydrocarbons on the most active Hägg carbide phase. The combined quantum-chemical and kinetic approach offers a comprehensive understanding of the promotional effects of K on Fe catalysts, elucidating its role in enhancing reaction efficiency and selectivity. In addition to K, the thesis also discussed the role of cesium (Cs) sulfide as an active phase in H₂S-containing syngas

conversion. Collectively, these studies offer valuable insights into the fundamental mechanisms of alkali promotion in FT synthesis, paving the way for the development of more efficient and selective catalytic systems.

Chapter 2 outlines the computational methodologies employed in this study, focusing on Density Functional Theory (DFT) for electronic structure calculations. These calculations yield critical thermodynamic and kinetic parameters, such as adsorption energies, activation barriers, and pre-exponential factors. These parameters are then incorporated into a microkinetic model to enable a detailed examination of the reaction mechanisms.

In **Chapter 3**, we provided an atom-level understanding of K promotion on CO dissociation by applying density functional theory (DFT) to 5 representative facets of χ -Fe₅C₂. It was first established that K₂O is the most stable form of K promoter on these surface facets of χ -Fe₅C₂. Based on the resulting surface models, CO activation was investigated via direct and H-assisted dissociation pathways. K₂O reduces the dissociation barriers of CO, HCO and COH. Electronic structure analysis provided deeper insight into the promoter role: electron transfer from K₂O to the Fe-carbide surface leads to an increased electron occupation in anti-bonding CO orbitals and electron-electron repulsion between the bonding orbitals and surface. This weakens the C-O bond strength. Effective promotion of C-O bond dissociation requires K to be adjacent to the active sites for CO dissociation on the χ -Fe₅C₂ surface. When the promoter is placed on the active sites or at a larger distance, it can also inhibit the reaction.

Chapter 4 investigated the mechanistic role of K promoter in the chemokinetic network of CO hydrogenation to methane and longer hydrocarbons using density functional theory (DFT) and microkinetics simulations. The effect of K on the main reaction pathways and intermediates involved in the conversion of CO and hydrogen to these products and those of O removal were studied. K₂O enhances the adsorption strength of surface CO, H, C and CH species. Electronic analyses were conducted to compare the electron density at the surface with and without K₂O. The results revealed that K₂O leads to a higher electron density on nearby Fe atoms, which destabilizes the C-O bond, resulting in a decreased barrier of CO dissociation, confirming the result in **Chapter 3**. For O removal, H₂O is the main product with OH* disproportionation acting as the main pathway. CO₂ formation proceeds through much higher barriers, irrespective of the presence of K₂O. K₂O suppresses CH₄ formation by increasing the hydrogenation barrier of lattice C and adsorbed C due to the stabilization of C* and H*. Likewise, the formation barrier of C₂ and C₃ are typically higher in the presence of K₂O due to the stabilization of C* and CH*, while the dominant pathway for chain growth remains unaffected. Microkinetics simulations show that K₂O addition

enhances the chain-growth probability, leading to an increased C₅⁺ selectivity at the expense of the CH₄ selectivity. This shift in product distribution is driven by the increased availability of CH chain-growth monomers due to the enhanced CO conversion and suppressed chain-termination via inhibition of the hydrogenation of C_n intermediates. Notably, the dominant pathways for chain growth, which include chain-growth and depolymerization steps during FT synthesis, remain unaffected by K₂O.

In **Chapter 5**, the influence of K on CO₂-FT synthesis was investigated for two χ -Fe₅C₂ surfaces, i.e., (510) and (010), using DFT in conjunction with microkinetic simulations. It was verified that K also preferentially resides on these surfaces as K₂O under CO₂-FT synthesis conditions. DFT calculations show that the adsorption and dissociation of CO₂ and CO are enhanced by K₂O. A comprehensive electronic structure analysis, including density of states (DOS), crystal orbital Hamilton population (COHP), and charge density analyses, revealed that K₂O promotes C-O bond scission in CO₂ by electron transfer to the surface, which increases electron-electron repulsion in low-lying bonding orbitals while enhancing the occupation of high-lying anti-bonding orbitals. Overall, this weakens bonding and strengthens anti-bonding interactions of C-O bonds in adsorbed CO₂. The effect of K on CO₂ and CO activation are very similar. Microkinetics simulations showed that K₂O increases the CO₂ conversion. At low temperatures, CH₄ is the main reaction product, with K₂O promoting its formation. With increasing temperatures, the product shifts to CO due to the increased rate of CO desorption. O removal via H₂O formation is identified as the rate-controlling step on all surfaces, irrespective of the presence of K. These findings highlight the role of K₂O in steering product selectivity and reaction kinetics in the rWGS reaction and subsequent hydrocarbon formation in the CO₂-FT synthesis process.

Chapter 6 expands the scope of this work by exploring the catalytic role of alkali in the conversion of H₂S-containing syngas. Specifically, we studied Cs₂S as the most active alkali sulfide for the CO + H₂S → COS + H₂ reaction, by identifying the active sites and reaction mechanism on the 6 low-index Miller planes of Cs₂S, employing DFT in conjunction with microkinetics simulations. The adsorption behavior of CO and H₂S are systematically examined, revealing that CO weakly adsorbs on the exposed S atoms of these surfaces, whereas H₂S strongly adsorbs in a dissociative manner, producing HS* and H*. This strong dissociative adsorption stabilizes the surface thermodynamically with minimal structural reconstructions by lowering the free energy of all surfaces at typical reaction temperatures. This study demonstrated that the reaction predominantly follows a Langmuir-Hinshelwood (LH) mechanism, where CO* reacts with HS* and S* to form COSH* and COS*, with COSH* formation and its subsequent dehydrogenation being critical

steps. The alternative Mars-van Krevelen (MvK) mechanism is not favored due to the high barrier for CO reacting with lattice sulfur. Among the investigated Cs_2S facets, the (001) surface exhibits the lowest activation barrier, making it the primary contributor to COS formation. Microkinetic simulations further showed that the overall reaction rate is dominated by the (001) facet, with minor contributions from the (010), (011), and (100) facets. Key steps such as COSH^* formation, dehydrogenation, and COS^* desorption act as rate-controlling steps. The findings provided detailed atomistic insights into the mechanism and active sites for COS formation, suggesting that similar LH mechanisms may operate in other alkali metal sulfides due to stronger metal-sulfur bonds.

Outlook

The rapid advancements in computational methods, particularly in multi-scale simulations, have significantly deepened our understanding of complex catalytic reactions. These methods find increasing utility in interpreting complex processes such as the Fischer-Tropsch (FT) synthesis. While we can already describe complete reaction mechanisms and predict catalytic performance, the rapid developments in computational power and methods drive research into predictive design. A substantial societal aspect is the replacement of fossil carbon feedstock by renewable carbon feedstock. Biomass can play an immediate role in replacing fossil carbon, while captured CO_2 is relevant in long-term solutions. It is likely that especially Fe-based FT catalysts will play a significant role in processing such alternative carbon feedstocks. Fe-based FT catalysts can cope with a wider range of pollutants in synthesis gas with a relatively low H_2/CO ratio as obtained by the gasification of biomass. Besides, these catalysts can directly convert CO_2/H_2 mixtures to hydrocarbons, whereas Co-based catalysts typically produce CH_4 from such mixtures. This intrinsic benefit of Fe-carbide catalysts is the higher rate of C-O bond dissociation reactions, which is evident from CO activation not being rate-controlling for the overall FT reaction unlike the Co case. Besides, typical Fe-based catalysts display good activity in the reverse water-gas shift (rWGS) reaction, relevant to converting CO_2 to CO. An interesting question is then how phase-pure Fe-carbides behave in CO_2 hydrogenation compared to typical mixtures of Fe-carbides and oxides. Utilizing such alternative carbon sources is critical for mitigating the global climate crisis and reducing the dependency on fossil fuels through the sustainable production of liquid fuels, for which there will remain demand, and chemicals. Continued research into FT synthesis technology, therefore, not only contributes to advancing fundamental chemistry but also contributes to addressing global energy and environmental challenges.

The theoretical work mainly employed DFT in conjunction with microkinetic modeling to investigate the promotional effect of potassium (K) on Hägg carbide (χ -Fe₅C₂) in FT reactions. Further studies can evaluate whether these insights also apply to other Fe-carbide phases, such as epsilon (ϵ) and theta (θ) Fe-carbides. Experimental studies have demonstrated the high intrinsic activity of these Fe-carbide phases, making them promising candidates for FT catalysis in particular temperature windows. For instance, Wang et al developed a pure ϵ -Fe_{2.2}C catalyst with high durability and high carbon selectivity to desirable olefinic products.¹ θ -Fe₃C is stable at high FT temperatures with a relatively high chain-growth probability.^{2, 3} Such work could provide a generic understanding of the promoting role of K on Fe-carbides.

Most industrial catalysts contain various promoters to promote the reactions (chemical promoters) or to stabilize the active phase or the support (structural promoters). Typically, these promoters and their optimum content were determined by trial-and-error experimentation. It is often unknown how chemical promoters function at the molecular level. This thesis provides deeper insight into the impact of K on the kinetics of the FT reaction. Other common promoters for Fe-based FT catalysts are other alkali metals such as Na and Li, Cu, Mn, Zn, and S. Similar approaches as employed for K can be followed to understand their behavior. Such research should be combined with experimental studies for validation. As an example, the modification of χ -Fe₅C₂ with Mn results in a remarkable improvement of the catalytic performance.⁴ An important topic will also be to understand how these promoters affect each other.

A major assumption in most of the present computational studies is that the surface is static. In practice, the surface structure and composition will strongly depend on the interactions with the reactants and products. Current ab initio thermodynamics approaches can already probe what surface structures are relevant at a given chemical potential of the reactant-product system. Yet, this is also an approximation as the reaction and thus the surface evolves far away from thermodynamic equilibrium. Recent developments in multiscale simulation techniques, such as those employing machine learning, offer opportunities to simulate the reaction a powerful approach to studying these dynamic processes. Machine-learning models can be integrated with DFT and microkinetic simulations to offer better predictive power for larger and more complex systems, including the treatment of catalytic surfaces in a non-static manner. An example of such an approach by Liu et al. shows the potential of studying the evolution of the surface of Fe-carbide during the ongoing FT reaction, identifying a new type of active site with a low barrier for CO dissociation.^{5, 6} Their simulations employ machine-learned potentials to treat larger systems. Other

aspects to study with such methods are studying the role of Fe-oxide phases co-existing with Fe-carbides in practical catalysts and the carburization process itself.

Such large-scale simulations combined with microkinetic modeling are promising to describe complex reactions such as FT synthesis. Preferably, such studies are also integrated with reactor-scale simulations directly or via lumped microkinetic models to study in detail the effect of the conversion on the catalytic performance. This also will help to understand deactivation phenomena better, for instance, due to oxidation of the active phase due to product water. Such modeling efforts will also facilitate the design of improved reactors to maximize the performance in FT synthesis.

Finally, the advancement of computational techniques and computational power will need to go hand in hand with experiments to provide a robust framework for advancing catalyst research with an increasing focus on predictive design. By systematically exploring the active phases, their interaction with support materials, promoters, and including the dynamic behavior of catalysts with time and in response to the changing gas composition, such studies will pave the way for the development of more effective, durable, and sustainable catalysts. These advancements will not only deepen our fundamental understanding of catalytic science but also contribute to realizing carbon-neutral technologies that address pressing energy and environmental challenges.

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List of Publications

Publications within the scope of this thesis:

1. Xianxuan Ren, Rozemarijn D.E. Krösschell, Zhuowu Men, Peng Wang, Ivo A. W. Filot and Emiel J. M. Hensen *. A Computational Study of K Promotion of CO Dissociation on Hägg carbide. Catalysis Science & Technology. (Final review)
2. Xianxuan Ren, Zhuowu Men, Peng Wang, Ivo A. W. Filot and Emiel J. M. Hensen *. The nature of K promotion of χ -Fe₅C₂ for high chain-growth probability in the Fischer-Tropsch reaction. (Submitted)
3. Xianxuan Ren, Rozemarijn D.E. Krösschell, 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. Chinese Journal of Catalysis. (Accepted)
4. Xianxuan Ren, Ivo A.W. Filot, Emiel J.M. Hensen.* A density functional theory study of the formation of COS from CO and H₂S on cesium sulfide. Journal of Catalysis 2024, 438, 115731.

Publications outside the scope of this thesis:

1. Shaojie Li, Xianxuan Ren, Brahim Mezari, Yujie Liu, Peerapol Pornsetmetakul, Anna Liutkova, Nikolay Kosinov, Emiel J.M. Hensen. Direct synthesis of Al-rich ZSM-5 nanocrystals with improved catalytic performance in aromatics formation from methane and methanol. 2023, Microporous and Mesoporous Materials.112485(351): 1387-1811. DOI:10.1016/j.micromeso. 2023.112485.
2. Jiachun Chai, Xianxuan Ren, Robert Pestman, Zhuowu Men, Peng Wang, Emiel J. M. Hensen.* Comparison of ϵ (')- and χ -carbide in the Fischer-Tropsch Reaction. (In preparation)

Conference Contributions

1. Xianxuan Ren, Ivo Filot, Peng Wang, Emiel J.M. Hensen. “Elucidation of the role of potassium in CO activation on Hägg carbide (χ -Fe₅C₂)”, 24th The Netherlands’ Catalysis and Chemistry conference. March 4-6, 2024, Leiden, Netherlands. **(poster)**
2. Xianxuan Ren, Ivo Filot, Peng Wang, Emiel J.M. Hensen. “The nature of K promotion of χ -Fe₅C₂ for high chain-growth probability in the Fischer-Tropsch reaction.”, IUPAC|CHAINS. August 20-25, 2023, The Hague, Netherlands. **(oral presentation)**
3. Xianxuan Ren, Ivo Filot, Emiel J.M. Hensen. “The nature of potassium promotion of χ -Fe₅C₂ for high C₂-C₄ olefins selectivity in the Fischer-Tropsch reaction”, Syngas Convention 4. April 2-5, 2023, Cape Town, South Africa. **(oral presentation)**
4. Xianxuan Ren, Ivo Filot, Emiel J.M. Hensen. “Understanding the promotion of potassium to χ -Fe₅C₂ catalyst in the Fischer-Tropsch reaction”, Winter school 2022. November 28th to December 2nd, 2023, Han-sue-lessee, Belgium. **(oral presentation)**.
5. Xianxuan Ren, Ivo Filot, Emiel J.M. Hensen. “The nature of potassium promotion of χ -Fe₅C₂ for high C₂-C₄ olefins selectivity in the Fischer-Tropsch reaction”, 23rd The Netherlands’ Catalysis and Chemistry conference. March 6-8, 2023, Leiden, Netherlands. **(oral presentation)**.
6. Xianxuan Ren, Ivo Filot, Emiel J.M. Hensen. “Computational investigation of CO Hydrogenation on Potassium-Promoted χ -Fe₅C₂ Hägg carbide”, KNCV-CTC-PhD+ symposium 2022. September 14th, 2022, Amsterdam, Netherlands. **(oral presentation)**.
7. Xianxuan Ren, Ivo Filot, Emiel J.M. Hensen. “Computational investigation of Fischer-Tropsch (FT) synthesis on K-promoted iron-carbide”, 22nd The Netherlands’ Catalysis and Chemistry conference. May 9-11, 2022, Leiden, Netherlands. **(poster)**.

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Eindhoven

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Xianxuan Ren

Curriculum Vitae

Xianxuan was born in Hebei province, China, on 7th November 1992. He pursued his bachelor's degree in Chemical engineering and Technology at the University of Science and Technology Liaoning from 2013 to 2017. During his undergraduate studies, He started his academic research on a Coumarin-based Colorimetric and Fluorescent Chemosensor in 2015 under the supervision of Prof. Qingtao Meng. After obtaining his bachelor's degree in 2017, he enrolled in the master's program at State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, Dalian University of Technology in Dalian. Under the supervision of Associate Professor Xiaowa Nie, he continued his research journey on the Computational identification of the strong synergy of the Fe/ZnO catalyst. In 2020, he obtained his master's degree in Chemical Engineering. In the same year, He received financial support from the China Scholarship Council to further his academic research at Eindhoven University of Technology. Under the supervision of prof.dr.ir. E.J.M. Hensen and dr.ir. I.A.W. Filot, he started his PhD project in the Inorganic Materials and Catalysis group, focusing on the computational investigation of the mechanistic role of promoters in iron-carbide catalyzed Fischer-Tropsch Synthesis. Throughout his PhD studies, he presented the research results at several national and international conferences. The main results of his research are summarised in the dissertation.



