Structure Sensitivity in the Fischer-Tropsch Synthesis

Sharan Shetty* and Rutger A. van Santen
Schuit Institute of Catalysis, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands
**Corresponding author's email: s.g.shetty@tue.nl*

Abstract

Fischer-Tropsch (F-T) synthesis to produce synthetic fuel from syn-gas is one of the most important reactions in the field of heterogeneous catalysis. Hence, investigating the molecular steps underlying this process from the experimental and theoretical point of view is of utmost importance. Here, we present a brief review on the recent analysis of the molecular reactions involved in the F-T synthesis such as CO dissociation, CH_x formation and C-C coupling reactions on the transition metal surfaces. Our review will mainly focus on the influence of the surface structures on the reaction mechanisms involved in the F-T reactions.

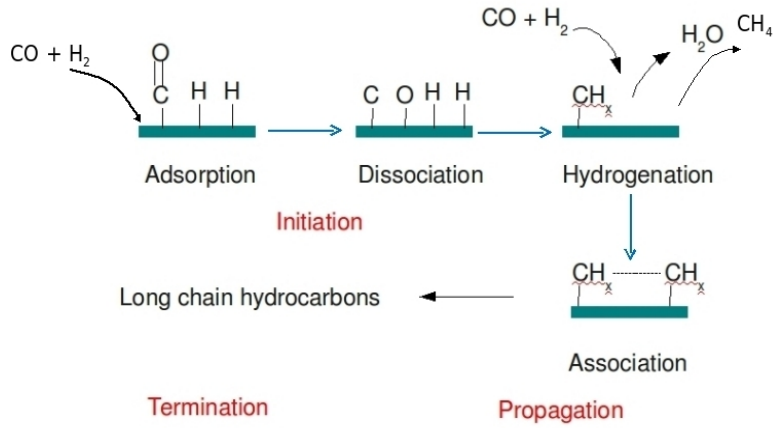
Keywords : Fischer-Tropsch, DFT, hydrocarbons, surface reactions, catalysis

1. Introduction

The discovery of F-T synthesis dates back to the early 20th century when F. Fischer and H. Tropsch working at Kaiser Wilhelm Institute, Germany, produced hydrocarbon molecules using syn-gas (CO + H_2) derived from the gasification of coal.[1] This discovery led to the first synthesis of synthetic fuel which avoids the drilling of conventional crude oil. Hence, F-T synthesis is considered to be one of the alternative routes to produce liquid fuel. The F-T process was popular in the countries where there were no oil fields but had coal reserves. After the WWII this process was efficiently commercialized by companies such as Shell (The Netherlands) and Sasol (South Africa) to produce fuel.[2] There are two major steps to produce synthetic fuel via the F-T process (1) to obtain the syn-gas from the feedstocks such as coal, natural gas or biomass and (2) to convert the syn-gas into the liquid hydrocarbons on transition metal surfaces.[2, 3] In the present short review, we will discuss the issues concerning the molecular mechanisms involved in the later step of the F-T synthesis on the metal surfaces.

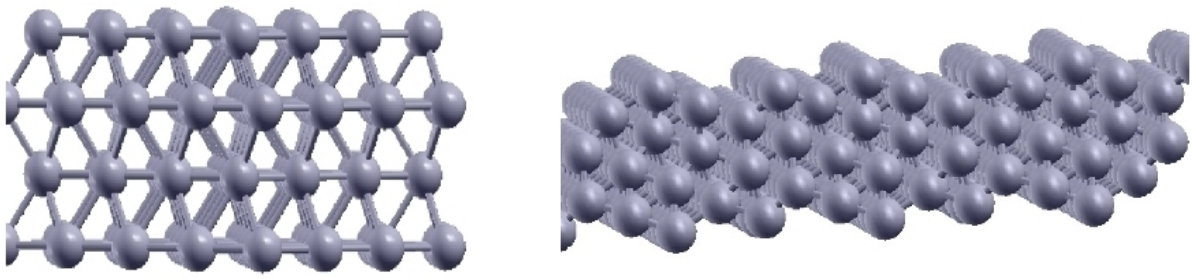
The molecular mechanism in the syn-gas conversion via the F-T synthesis on transition metal surfaces can be categorized in three basic steps as shown in Scheme 1 i.e. (a) CO dissociation (b) C hydrogenation to form CH_x ad-species followed by CH_x- CH_x coupling (association) and finally (c) chain termination of the hydrocarbons.[4] CO dissociation is a critical step in the F-T synthesis because it is the initiation step and is also considered to be the rate-determining step in the F-T reaction sequence.[3, 4] Hence, to dissociate CO at a low barrier is a primary condition. This is followed by the hydrogenation of the C ad-species to form the CH_x building blocks for the polymerization of the C-C coupling reactions. If the hydrogenation of the C is faster than the C-C coupling reactions, the selectivity towards methane is high. According to Sabatier's principle a proper balance between the CO

dissociation and C-C coupling reactions in the F-T synthesis is very a important factor to control the selectivity towards the formation of hydrocarbons.[5,6] A low barrier dissociation of CO will adsorb C and O atoms so strongly that the propagation steps will be hindered. On the other hand a very high CO dissociation barrier will not initiate the F-T reaction. Considering this balance Ru and Co based catalysts have been proposed to be active for the F-T synthesis.[7] The surface structure of these transition metals also plays a critical role in the activity of the products obtained in the syn-gas conversion. The low index planes such as flat surfaces can have different reactivity compared to that of the high index planes such as stepped or corrugated surfaces (Figure 1).[8, 9] The reaction kinetics which depend on the surface structures are known as structure-sensitive reactions otherwise structure-insensitive reactions.[10] In the F-T synthesis, CO dissociation i.e. initial step has been considered to be extremely structure-sensitive. The barrier required for CO dissociation on the flat Ru and Co surfaces is higher than the desorption energy of CO.[11, 12] This implies that before dissociation, CO will desorb from the surface. Hence, the initiation of the FT synthesis on flat Ru and Co surfaces is a difficult process. Contrary to this, the CO dissociation barrier is much lower than the desorption energy of CO on the stepped or corrugated surfaces.[11, 13-15] This difference is due to the active sites present on the stepped and corrugated surfaces which pre-activate the CO bond. This is not the case on the flat surfaces where there are no such active sites. The fundamental controversy is about the initial step in the F-T synthesis. There are three possible reactions through which the CO can dissociate to create the CH_x species.[12, 14, 16, 17] The C or O of the adsorbed CO molecule can be hydrogenated to form HCO (formyl) or COH intermediates respectively.[16, 17] The other route is to dissociate CO directly to form C and O which is known as the carbide mechanism.[14] Fisher and Tropsch proposed that the later i.e. carbide mechanism is the initial step when they observed C ad-species on the surface during the F-T synthesis.[1] However, recent studies have suggested a hydrogen-mediated CO dissociation. In the present short review, we will discuss the recent developments on the F-T synthesis on the active transition metal surfaces.



Scheme 1

Scheme 1: The molecular steps in the F-T synthesis on metal surface.



(a) **(b)**

Figure 1. (a) Low index plane of flat Ru(0001) surface. (b) High index plane of Ru stepped surface.

2. Methodology

Briefly we will present the theoretical methods used to study the reactions on surface, cluster and nanoparticle. Density functional theory (DFT) based on the periodic boundary conditions have made possible to study the surface and bulk calculations under realistic conditions. A surface slab of particular thickness with well defined (hkil) for hcp or (hkl) for fcc parameters is cut from the bulk. One should note that the thickness of the slab should be chosen appropriately because that can vary with respect to whether the surface corresponds to a high or low index plane. The molecules or atoms (ad-species) are adsorbed on both the sides of the surface slab considering the center of inversion. The coverage of the ad-species is maintained from 11 to 100 %. For eg. if there is one ad-species in a 2×2 unit cell then the coverage is denoted as 25 %. The codes applied for these reactions use the plane wave basis set for the valence electrons in conjunction with the projector augmented-wave (PAW) potentials or ultra-soft pseudo potentials (USPP) for the core. This combination significantly decreases the computational time and not ignoring the chemical characteristics of the system. The kinetic energy cut-off for the plane wave basis set is chosen after optimization. The k-point sampling is necessary for the metallic surfaces. For a detailed explanation we refer to our earlier work presented in the references 13 and 14 (and references therein).

3. Discussion

3.1 CO dissociation

CO dissociation is not only the initial step in the F-T synthesis but is also considered to be the rate-limiting step. In the initial step CO and H_2 adsorb on the surface and dissociate (Scheme 1). The adsorbed H_2 molecule dissociates without any barrier. However, the critical issue is to break the CO triple bond.[5] The CO molecule adsorbs with the C end on the surface. The CO bond weakens due to the transfer of electrons from the metal to the π^* anti-bonding orbitals of CO which is termed as back-

bonding as proposed by Blyholder.[18] There have been other proposals for the weakning of the CO bond independently by Bagus et al and Föhlisch et al who suggested internal mixing of the bonding and anti-bonding orbitals of the CO molecule.[19, 20] On the flat Ru surface the adsorbed CO molecule bends and the C and O atom share the metal atom in the transition state (TS).[11] In the final state the C and O atoms move in their respective stable states. Ciobica and van Santen in a theoretical work reported a barrier of 227 kJ/mol on a flat Ru(0001) surface (Figure 2).[11] This is around 51 kJ/mol higher than the desorption energy of CO. This indicates that the CO molecule will desorb before dissociation. Hence, the F-T reaction would be very difficult to initiate. Furthermore, they showed that if the CO dissociation is carried out on the stepped Ru surface, the barrier reduces to 89 kJ/mol (Figure 2).[11] This barrier is 91 kJ/mol lower than the desorption energy of CO. This clearly suggests that the F-T reaction will easily initiate at the stepped surface. The CO dissociation at the stepped surface proceeds with the CO adsorbed at the bottom of the step. In the TS, the C and O adspecies do not share the metal atoms. This configuration reduces the repulsive interaction between the C and O atoms with the metal d-orbitals. In the FS, the O atom moves over the step. In this reaction the C and O atoms are attached to three-fold (3F) hollow and bridge sites respectively. This configuration is termed as a B_5 site.[21, 22] In another work, we have shown that the barrier for CO dissociation on the open Ru(1121) surface is 24 kJ/mol lower than that on the stepped surface (Figure 2).[13] We proposed a different active site which was more reactive than that on the stepped surface. Very recently, we demonstrated that instead of a B_5 site if the Ru surface consists of six-fold (F_6) sites which are present on Ru(1010)B surface.[23] The CO dissociation barrier is only 47 kJ/mol with respect to the adsorbed state. Such a low barrier for CO dissociation is attributed to the geometry of the unique F_6 site where the CO molecule is pre-activated. This clearly demonstrates that the CO dissociation is extremely structure-sensitive reaction. These kind of sites are also available on the nanoparticles (Figure 3). Hence, the next question is, what is the reactivity of these sites on the nanoparticle ? de Jong and coworkers have shown that the maximum for the TOF in the F-T synthesis on supported Co nanoparticles exist around 6 nm.[24] They proposed that the selectivity towards methane formation is more when the particles are smaller than 6 nm.

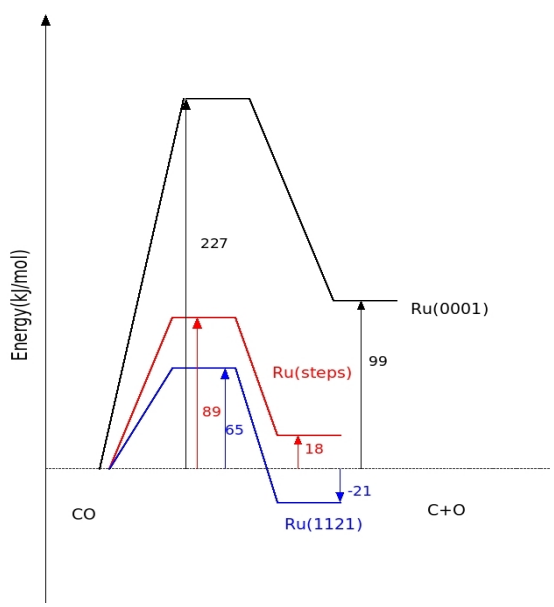


Figure 2: The CO dissociation barriers and reaction energies on flat Ru(0001) (black line) Ru(steps) (red line) and Ru(1121) (blue line) surfaces. The values have been taken from references 11 and 13

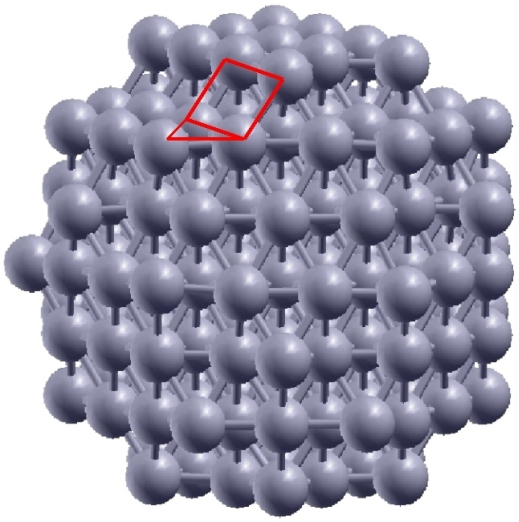


Figure 3. An incomplete cuboctaheron of 1.5 nm particle with the active B_5 sites for CO dissociation shown in red colour.

The other fundamental issue concerning the initial step in the F-T synthesis is whether the CO dissociation is direct (carbide mechanism) or hydrogen assisted. Fischer and Tropsch in their experiments observed carbide formation on the surface and hence suggested a carbide mechanism.[1] Mitchell et al proposed from the experiments that the hydrogen assistance CO dissociation via the formyl route is the initial step.[25] However, their experiments were based on the Eley-Rideal mechanism. Contrary to this, Yates and co-workers have shown that the formyl intermediate is difficult to detect from the experiments under Langmuir-Hinshelwood mechanism.[26] They also showed that the formyl intermediate is highly endothermic. Ciobica and van Santen showed that the CO dissociation has a very high barrier on flat Ru(0001) surface and hydrogen assistance may be the route to dissociate CO.[11] However, they also concluded that the HCO is highly unstable and cannot be stabilized under normal F-T conditions. King and co-workers also proposed a hydrogen assisted CO dissociation on flat Co surface.[12, 16] Recently we resolved this fundamental issue. We showed that on Ru(1121) and Ru(1010)B surfaces which consist of active sites for low barrier CO dissociation.[14, 23] The carbide mechanism is the dominating pathway. The overall barriers via the hydrogen assisted paths are much higher than the direct CO dissociation paths. This clearly implies that on the flat Ru surface which do not consists B_5 or F_6 sites for low barrier CO dissociation the hydrogen assistance may be the route to dissociate CO. However, on the corrugated or stepped surfaces and nanoparticles the carbide mechanism is the only path to produce active carbon for the polymerization in the F-T synthesis.

3.2 CH_x formation

The formation of CH_x is also an important step in the F-T synthesis. The CH_x adspecies form the building blocks for the propagation of the chain to form hydrocarbons. One should note that the hydrogenation step in the F-T synthesis is a very critical step. If the hydrogenation is at a faster rate than the C-C coupling reaction, the product selectivity will mostly be methane. Hence, the selectivity towards the formation of methane should be negligible. In recent years, there has been debate on whether the hydrogenation process is structure-sensitive or insensitive.[27-29] Goodman and co-workers have carried out several experimental studies to investigate the adsorption of CH_x and C- CH_x species on Ru surfaces.[30,31] They showed that CH and C-CH_2 species are stable on flat Ru(0001) surface, while on more open Ru(1120) surface the C-CH_3 is also stable. Ciobica et al also proposed in a theoretical study that the stability of CH_x species is different on Ru(0001) compared to that on the Ru(1120) surface.[32] This clearly implies that the distribution of the CH_x species depends on the surface structures.

Ciobica and van Santen studied the complete path for methane decomposition on Ru(0001) surface.[33, 34] Let us consider the reverse reaction which is the methane formation on Ru(0001) surface. They showed that the CH was the most stable species on this surface. The formation of CH from the gas phase C and H corresponds to a barrier of 73 kJ/mol. Since the CH is the most stable species on this surface. We can consider CH as the building block for the formation of hydrocarbons. The overall barrier for the formation of methane from the stable CH species is around 141 kJ/mol. The rate limiting step in this reaction is the last step to form methane from co-adsorbed CH_3 and H which corresponds to a barrier of 91 kJ/mol. Bouke and Kramer have shown that the hydrogenation of C leading to methane on Rh is much more easier than that on the Ru surface.[35] This demonstrates that Rh is suitable for methanation reaction, while Ru is good for the C-C coupling reaction. Chen and Liu also proposed from the results obtained from Monte Carlo simulations that the C hydrogenation is difficult on Ru compared to that on Rh.[36] Gong et al found that the C hydrogenation on Co surfaces is a structure-insensitive reaction.[37] They suggested that the CH_2 species is the least stable species among the CH_x ad-species. Hence, this implies that the CH_2 cannot be one of the probable building blocks for the F-T synthesis on the Co surfaces.

3.3 C-C coupling

This step is the propagation step in the F-T synthesis. The CH_x species derived from the CO dissociation and subsequent hydrogenation steps couple to form hydrocarbons. Due to the complicated reaction steps along with several permutations involved in the C-C coupling reactions. Compared to the above steps there have been less studies to understand the propagation step. van Santen and co-workers and Amariglio and co-workers independently proposed a direct route to produce hydrocarbons via a two-step methane homologation.[38, 39] This route avoids the indirect route to produce hydrocarbons from steam reforming or oxidative coupling of methane to first syn-gas and then to hydrocarbons.

Goodman and co-workers have studied the C-C coupling ad-species from the decomposition of CH_4 on Ru surfaces and supported nanoparticles.[30, 31, 40] From the experimental techniques such as HREELS they observed C_2 intermediates such as ethylidyne, methylidyne and vinyledene species on the Ru(1120) and supported Ru particles. They found that the vinyledene species was stable at higher temperatures (325°C)compared to that of ethylidyne ad-species which transform to vinyledene species. Ciobica et al studied several C_xH_y species adsorption on the flat Ru(0001) surface.[33] They showed from the theoretical calculations that the most stable C_2 ad-species on Ru surfaces is the vinyledene (CCH_2) species in good agreement with the experimental results of Goodman and co-workers.[33, 34] In the adsorption state the C is attached to the three-fold hollow site of the surface while the CH_2 group is at the atop site. The C-C bond is inclined in such a state that neither it is parallel nor perpendicular to the surface. They also proposed that the the ethylene (C_2H_4) adsorption on the Ru(0001) surface is along the π bond rather than the di-σ. The interesting conclusion was that the interaction between the CH_x and CH_y coadsorbed states is repulsive due to the steric hindrances. Hence, the C-C coupling reactions between the bulkier CH_x groups is not the possible route to form the hydrocarbons. Instead they will hydrogenate to form methane. Maitlis and co-workers proposed that the alkenyl + CH_2 ad-species account for the chain growth. In this mechanism they suggested that the polymerization initiates from the vinyl (CH_2=CH) intermediate. [41]

In recent years an alternative route to produce C_2 hydrocarbons have been proposed. On flat Ru and Co surfaces it is known that the CO dissociation has high barrier as discussed above. Hence, to avoid several rate limiting steps to create the CH_x species, another route via CO insertion in the CH_x species has been suggested.[42] In the first step the CO is dissociated through the hydrogen assisted pathway and in the later stage the undissociated CO is inserted in the CH_x to form CH_x-CO intermediate. This intermediate is hydrogenated to form CH_x CH_yO which weakens the CO bond. This dissociates into CH_xCH_y ad-species with co-adsorbed oxygen. This route has also been suggested for the formation of ethanol on Rh surfaces and clusters.[43, 44]

4. Conclusions

In the present review we discuss the recent developments in the molecular mechanisms of the F-T synthesis. The surface structure plays an important role in the activity of the F-T synthesis. CO dissociation which is considered to be the rate-limiting step in the F-T synthesis depends on the local structure and coordination of the metal atoms on the surface. This path is well understood from the experimental and theoretical studies. However, the hydrogenation and the C-C coupling reactions depends on the surface structure is still a matter of debate. Moreover, there are several open questions regarding the F-T synthesis such as (a) where and how does the chain polymerization takes place ? (b) whether the F-T synthesis on nanoparticles is structure or size dependent ? (c) How to control the selectivity towards the methane formation (d) how to avoid the deactivation of the catalyst during the F-T process ?

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