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Modeling the Fischer-Tropsch reaction on Cobalt surfaces

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Abstract

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Modeling the Fischer-Tropsch reaction on Cobalt surfaces

by Bart Zijlstra

In this thesis I present an approach towards a mechanistic understanding of Fischer-Tropsch (FT) synthesis. Starting from syngas I will show an integrated study into the fundamentals of making longer hydrocarbons on the transition metal cobalt. Understanding how the FT reaction works is of great importance to a society depending on fossil (transportation) fuels. With FT synthesis, extremely clean diesel can be produced from natural gas. By using natural gas surpluses and converting them to valuable liquid fuels, we might bridge the gap towards a more sustainable energy future.

Together with my colleagues, I do Density Functional Theory (DFT) calculations to find electronic energies for all intermediate states in the FT reaction. Using these energy states and their corresponding vibrational contributions, we can build reaction energy diagrams. I contribute to this by investigating the methanation reaction on terrace (0001) and stepped (1121) cobalt surfaces. Studying the formation of methane gives us insight into the initial monomer formation during FT synthesis. The route to methane also provides knowledge about possible deactivation mechanisms and selectivity issues. From analyzing the energy barriers from DFT, we conclude that CHO and CH2O dissociation are the main C1 formation pathways on the cobalt terrace. For the stepped cobalt surface the main pathway is direct CO dissociation. For further understanding of concentration-dependent kinetics we use our DFT data in microkinetic modeling. We find that hydrogen-assisted dissociation is indeed rate limiting on the terrace cobalt surface. The stepped surface has both rate limitation in direct CO dissociation and the product termination steps.

Finally, we show some preliminary work towards molecular dynamics with reactive force fields. By creating a training set of DFT data we want to visualize metal atom migrations leading to surface reconstruction of the catalyst during FT synthesis. We expect this to confirm that direct CO dissociation on the cobalt steps is responsible for C1 formation.
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I would like to thank my parents for the invaluable support they have given me. They have been there for me during all stages of my education. I would not have made it so far without them. My parents always say I should not work hard just because of them. They have tried to encourage intrinsic motivation above else. Looking back I realize that this thesis would not have been here without that approach.

Choosing the topic for specialization in my Master was difficult. The breakthrough for that choice was provided by my supervisor – and good friend – Iva Filot. He saw value in my programming work and he proposed a theoretical project within the Inorganic Materials Chemistry group of Emiel Hensen. This project has catalyzed my interest in theoretical chemistry and I have a lot of fun researching the topic. In addition to my large gratitude to Ivo, I of course want to thank Emiel. Without his great support, this project would not have been possible. This regards both resources, helpful academic discussions and giving me the opportunity to develop myself at conferences and courses outside of Eindhoven. I would also like to thank Emiel, Ivo, Weiyu Song, Frank Peters and Sander van Bavel for being part of the graduation committee for this project. Xueqing Zhang, thank you for providing your results on molecular dynamics with ReaxFF. Wei Chen, thank you for the added insight from your SSITKA and CTKA results. I would like to acknowledge William van der Graaff and Arno van Hoof for suggesting improvements to the language throughout this thesis. Of course I want to thank Emma Eltink for being an excellent secretary, assisting me with everything I need during my activities in the IMC group.

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Chapter 1

Introduction

I like to go out for a long walk in De Meinweg National Park [1] close to my home in Limburg. There I enjoy observing the flora and fauna that nature has to offer. When I think about sustainability, that National Park is the first to cross my mind. After a few hours in the park I return to the car and drive home, burning petrol and exhausting carbon dioxide into the air. Sadly, this is not very sustainable. On a larger scale, for our current society, I think it is impossible to be fully sustainable. However, we should try to move towards a reduced dependency on fossil fuels.

Actually, our crude oil reserves should be running out already. At least that was the expectation of M. King Hubbert in 1956. That year, he presented his research before the Spring Meeting of the American Petroleum Institute in San Antonio, Texas. His message was clear: A peak oil production would occur somewhere around the year 2000 [2]. Years later, oil production is still rising after a small dip in 2009 [3]. Is this any reason to stop worrying? No. A rough estimation tells us that we have natural gas and oil for a little more than half a century. This is based on the 2013 reserves and consumption as shown in Figure 1.1.

An important hurdle towards lowering our oil dependency is our well-established energy infrastructure around oil. We would like to keep using petrol and diesel as easy transportation fuels. In addition, crude oil can be transported from off-shore reserves to refineries without much trouble. An example of underutilization of other resources is the flaring of natural gas associated with crude oil recovery. This is a waste of resources. A possible solution is transporting the gas in a liquefied form (LNG) [4]. Another utilization of natural gas is converting it chemically into liquid products. These can then be directly used as clean transport fuels or chemical feedstock. This gas-to-liquids (GTL) technology is called Fischer-Tropsch Synthesis (FTS).
1.1 Fischer-Tropsch Synthesis

Abundant and remote deposits of natural gas can be transformed to liquid fuels and chemicals via the Fischer-Tropsch (FT) process. This synthetic route provides an attractive alternative to the current crude oil-based pathways. The general FT-reaction is shown in equation 1.1. In this reaction, syngas — consisting of H₂ and CO — is consumed to form (longer) hydrocarbons and water.

\[
(2n + 1) \text{H}_2 + n \text{CO} \rightleftharpoons C_n\text{H}_{(2n+2)} + n\text{H}_2\text{O}
\]  

(1.1)

In this thesis the simplest form of this reaction will be investigated. With \( n = 1 \) the FT-reaction reduces to the methanation reaction as shown in equation 1.2.

\[
3\text{H}_2 + \text{CO} \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}
\]  

(1.2)

Common ways to make syngas are the steam reforming and partial oxidation of natural gas [5]. As such, the methanation reaction is of little industrial interest. After all, the product methane is the compound one started with. However, academically studying this reaction is very useful. Understanding the formation of methane gives us insight into the initial monomer formation during FT synthesis. The route to methane also provides knowledge about possible deactivation mechanisms and selectivity issues.
In addition to the GTL route from natural gas, also coal, CO$_2$ and biomass can be used as feedstock. A collection of the different routes towards liquid products can be seen in Figure 1.2.

1.1.1 History of the Fischer-Tropsch reaction

The initial development of the FT process took about 20 years. Early experiments of invention were carried out around the year 1925. The main development was done in Germany. Largely this was done in Franz Fischer's laboratories at the Kaiser Wilhelm Institute for Coal Research (now Max Plank Institute) at Mülheim. Commercialization of the process was done in collaboration with the Ruhchemie Company. In 1945 an annual capacity of 600,000 tonnes was reached. Reasons for realizing this capacity were mostly based on strategic arguments, rather than economic aspects. [6]

1.1.2 Process conditions

The temperature at which FT synthesis is carried out has a strong effect on the performance of the reaction and of its product distribution. Generally increasing the temperature increases reaction rates. However for FT it results in an increase of selectivity towards shorter average chain lengths and ultimately methane. Also carbon deposition and catalyst deactivation are stronger at higher temperatures. Iron in particular readily
forms carbide phases [7].

Two FT operating modes can be chosen relating to the mentioned temperature effects [8]. For iron-based catalyst a high-temperature process (HTFT) can be carried out at 300-350 °C. Mainly gasoline products and linear low molecular mass olefins will be produced. Alternatively, 200-240 °C is the range for low-temperature Fischer-Tropsch (LTFT). Using iron or cobalt catalysts, the LTFT process is used for the production of high molecular mass linear waxes. These waxes can then be used to make diesel through hydrocracking.

Pressures used during FT synthesis are mostly above 10 bar and can be as high as 60 bar. H2/CO ratios should be chosen appropriately. A consumption ratio of 3 would correspond to the methanation reaction. When producing longer hydrocarbons, the consumption ratio tends to be about 1.7 to 2.15 [8]. Higher ratios can be fed to the reactor to speed up hydrogenation reactions at the cost of selectivity. Additionally, the water-gas shift (WGS) reaction might occur on iron catalysts, forming CO2 as a byproduct. In principle the reverse WGS reaction could be used to turn CO2 into FT products.

1.1.3 Mechanistic pathways

Although many details about the Fischer-Tropsch process are known, there is an ongoing debate in the literature about the molecular mechanism by which the monomeric species is incorporated in the growing chain [9]. Basically, there are two conflicting pathways towards adding a C1 species to the hydrocarbon. These mechanisms are the carbide mechanism and the CO-insertion mechanism. Having either of the two as the dominant mechanism has important consequences for the structure sensitivity of the reaction.

According to the carbide mechanism, the C1 intermediate is formed by initial cleavage of the C-O bond of carbon monoxide. The chemisorbed carbon is then partially hydrogenated to a CHx intermediate that is inserted into the growing chain. A representation of this pathway is shown in the top part of Figure 1.3.

The CO-insertion mechanism, also called the Pichler-Schulz mechanism, can be seen in the bottom part of Figure 1.3. In this mechanism an initial CO bond breaks to form a C1 intermediate. However, further propagation of the chain growth happens by inserting chemisorbed CO molecules, rather than coupling with other dissociated C1 intermediates.

For this thesis we shall assume the carbide mechanism as the dominant pathway for Fischer-Tropsch synthesis. As such, C1 monomer formation is expected to influence both initiation as well as chain growth in the FT reaction.
1.1.4 Choosing a catalyst

From left to right in the periodic table the d-band filling of transition metals increases. Atom interactions increase until the d-band is half filled, which happens at chromium and manganese. Going to the right further increases d-band filling and causes antibonding orbitals to get filled. Atomic shells become more diffuse as one goes down the periodic table and into higher shells. As a result going down the transition metal rows also tends to give lower binding energies.

For Fischer-Tropsch synthesis an intermediate bonding with FT intermediates is needed. With a low bonding energy the dissociation of the bond between carbon and oxygen is slow. Hence monomer formation is limited. However, if the bonding energy is too high, dissociated atomic species will not take part in propagation of the chain.

We can now rationalize Figure 1.4. Palladium and platinum only produce methanol because CO-dissociation is too slow. Nickel produces methane as CO-dissociation is possible, but slower than hydrogenation. To the upper left lies iron, which has the fastest CO-dissociation. Due to the higher metal-carbon interaction, iron-based FT catalyst actually form an active carbide phase. A good alternative is cobalt, which does not show this carbide formation.

Industrially both iron- and cobalt-based catalysts are used for FT synthesis. Academically, ruthenium is interesting because it shows even higher activity than iron and cobalt.
As seen in Figure 1.5 however, the higher costs of ruthenium make it unsuitable for industrial use. A more extreme case is rhodium, which is even more expensive. Rhodium is of great academic interest for its ability to form longer oxygenates.

Figure 1.5: Prices per troy ounce of the academically interesting FT transition metal catalysts. The high prices of ruthenium and rhodium are unsuitable for industrial use. (Image by ir. I.A.W. Filot, 2014)
1.2 The Scope of this Thesis

This thesis is aimed towards a mechanistic understanding of FT synthesis. The conversion of \( \text{H}_2 \) and \( \text{CO} \) to \( \text{CH}_4 \) and \( \text{H}_2\text{O} \) will be modeled using integrated methods. I will show Density Functional Theory (DFT) calculations for the methanation reaction on terrace (0001) and stepped (1121) cobalt surfaces. For further understanding of concentration-dependent kinetics we use our DFT data in microkinetic modeling. Finally, we show some preliminary work on doing molecular dynamics with reactive forcefields.

1.2.1 Density Functional Theory

Density Functional Theory (DFT) calculations are used by academics in both physics and chemistry. We will use them to find electronic energies for all intermediate states in the methanation reaction. Using these energy states and their corresponding vibrational contributions, we can build reaction energy diagrams. Studying the formation of methane on terrace (0001) and stepped (1121) cobalt surfaces gives us insight into the initial monomer formation during FT synthesis. The route to methane also provides knowledge about possible deactivation mechanisms and selectivity issues. We will learn more about DFT theory in chapter 2.

1.2.2 Microkinetic Modeling

The Holy Grail in catalysis is rational catalyst design. To accomplish this, we need thorough understanding of intrinsic kinetics and the detailed mechanisms behind the reactions in question. Moreover, one must make an inventory of all elementary reaction steps occurring on the catalyst surface. The speed at which these steps take place should be modeled by appropriate equations dependent on e.g. temperature and surface concentrations. Also, sensible parameters should be found to correctly describe the system at hand. A common way to express concentration-independent reaction rates is by using the Arrhenius equation:

\[
    k = \nu \cdot \exp\left(\frac{-E_{\text{act}}}{RT}\right)
\]

The pre-exponential factor and the activation energy for elementary reaction steps are often calculated by Density Functional Theory (DFT). This is also the case in this thesis. With equation 1.3 known for both directions, the total rate for the reaction of ‘A’ going
to ‘B’ can be described by:

\[ r = \nu_{\text{forward}} \cdot \exp \left( \frac{-E_{\text{act}}^{\text{forward}}}{RT} \right) \cdot [A] - \nu_{\text{backward}} \cdot \exp \left( \frac{-E_{\text{act}}^{\text{backward}}}{RT} \right) \cdot [B] \]  

(1.4)

Setting up this total rate can be done for all elementary steps, after which they should be solved simultaneously, i.e. as a set of ordinary differential equations (ODE’s). In this thesis we shall refer to this as microkinetic modeling. Complex reaction mechanisms comprise of large sets of steps, and as such, require a lot of function evaluations during numerical solving. It is therefore preferred to have a quick program doing this for you. High level interpreters such as MATLAB™ [10] are slow compared to a compiled low level programming language such as C++ [11].

1.2.3 Molecular Dynamics with reactive force fields

Many quantum chemical (QC) methods exist that elaborate upon structures and energies of small molecules. To conclude anything sensible for big molecules and non-periodic systems, molecular dynamics with empirical force fields proves to be an attractive alternative to the computationally expensive ab-initio quantum chemical methods. These force fields can be used for quick evaluation of many system properties such as the energies in the conformational space. A disadvantage however is that chemical reactivity is generally not included in the force field. To describe bond-breaking and formation while still being able to model a large system (i.e. nanoparticles of 1000+ atoms), a reactive force field like ReaxFF is preferred [12]. ReaxFF uses hundreds of parameters to properly describe bond dissociation through bond distance, bond order and bond energy relationships. As such, the creation of a good ‘training set’ is mandatory for developing a potential describing a certain system. This training set is normally built from quantum chemical calculations on structures common to the system at hand. Currently we have a training set available containing the various interactions between cobalt and carbon. From this set, dr. X.Q. Zhang has optimized ReaxFF parameters [13] by using a Metropolis Monte-Carlo (MMC) algorithm with simulated annealing (SA) to find the global error minimum [14]. As this method does not rely on a good set of initial values, it is found to lead to a lower error and a tighter fit than with a simple single-parameter parabolic-search.

Using a ReaxFF force field optimized for the different interactions of cobalt with FT intermediates, we aim to visualize metal atom migrations. These would then explain surface reconstruction of the catalyst during FT synthesis. Some initial results towards building an expanded training set will be shown in chapter 4.
Chapter 2

Theory

2.1 Kinetics and Catalysis

Our current fossil fuel reserves have been formed from many dead organisms over a time period of millions of years. We would like our chemical reactors to have faster conversion rates than that. Kinetics is study of such chemical process rates. To understand the kinetics of a given system, we can investigate how macroscopic changes to the reaction conditions change the rate. Examples of such conditions are concentration, pressure and temperature. Generally mass and temperature transport limitations are avoided in order to measure intrinsic kinetics.

Catalysis is unavoidably linked to kinetics. A good catalyst is able to selectively alter intrinsic kinetics. In this way desired reactions can go faster and undesired reactions can be avoided by allowing other process conditions.

The transition metals used for Fischer-Tropsch synthesis are heterogeneous catalysts; A distinction can be made between a solid and a fluid phase. The existence of multiple phases should be included in the kinetic description. Most kinetic models therefore consider two types of events. Molecules from the fluid phase adsorb to and desorb from a solid surface. At the same time molecules and atoms on the surface react to form various intermediates. In the following sections we will briefly see important concepts regarding chemical kinetics. A more complete description can be found in the book Concepts of Modern Catalysis and Kinetics[15].

2.1.1 Adsorption and Desorption

A common way of expressing adsorption of reactants on a surface is to derive the Langmuir adsorption isotherm. Three cases of such isotherms are associative adsorption,
dissociative adsorption and competitive adsorption.

**Associative adsorption**

With only the species A in the gas phase we can write the reaction equation

\[ A + \star \underset{k_A^-}{\overset{k_A^+}{\rightleftharpoons}} A^* , \]  

(2.1)

and the rate equation

\[ \frac{d\theta_A}{dt} = P_A k_A^+ \theta_s - k_A^- \theta_A , \]  

(2.2)

with

\[ \theta_s = (1 - \theta_A) . \]  

(2.3)

The first term in equation 2.2 is due to adsorption and the second due to desorption. Under equilibrium we can write

\[ \theta_A = K_A P_A (1 - \theta_A) , \]  

(2.4)

with

\[ K_A = k_A^+ / k_A^- . \]  

(2.5)

Finally some rearrangement leads to the Langmuir adsorption isotherm for associative adsorption of a single gas:

\[ \theta_A = \frac{K_A P_A}{1 + K_A P_A} \]  

\[ \theta_s = \frac{1}{1 + K_A P_A} \]  

(2.6)

**Dissociative adsorption**

When the species A_2 directly dissociates on the surface, we can write the reaction equation

\[ A_2 + 2\star \underset{k_{A_2}^-}{\overset{k_{A_2}^+}{\rightleftharpoons}} 2A^* \]  

(2.7)

and the rate equation

\[ \frac{d\theta_A}{dt} = P_{A_2} k_{A_2}^+ \theta_s^2 - k_{A_2}^- \theta_A^2 . \]  

(2.8)
Rearrangement now leads to the Langmuir adsorption isotherm for dissociative adsorption:

\[ \theta_A = \frac{\sqrt{K_{A2}P_{A2}}}{1 + \sqrt{K_{A2}P_{A2}}} \]
\[ \theta_\ast = \frac{1}{1 + \sqrt{K_{A2}P_{A2}}} \]  

(2.9)

**Competitive adsorption**

In most reaction situations multiple species compete for the same sites. For species A and B adsorbing in an associative way

\[ A + \ast \overset{k_A^+}{\underset{k_A^-}{\rightleftharpoons}} A^\ast \]
\[ B + \ast \overset{k_B^+}{\underset{k_B^-}{\rightleftharpoons}} B^\ast \]

we find the Langmuir isotherms similar to before. With conservation of sites

\[ \theta_A + \theta_B + \theta_\ast = 1, \]  

(2.11)

we can derive:

\[ \theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \]
\[ \theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \]
\[ \theta_\ast = \frac{1}{1 + K_A P_A + K_B P_B} \]  

(2.12)

### 2.1.2 Langmuir-Hinshelwood mechanism

To exemplify a catalytic reaction with Langmuir-Hinshelwood kinetics we can expand upon the competitive adsorption case:

\[ A + \ast \overset{k_1^+}{\underset{k_1^-}{\rightleftharpoons}} A^\ast \]
\[ B + \ast \overset{k_2^+}{\underset{k_2^-}{\rightleftharpoons}} B^\ast \]
\[ A^\ast + B^\ast \overset{k_3^+}{\underset{k_3^-}{\rightleftharpoons}} AB^\ast + \ast \]
\[ AB^\ast \overset{k_4^+}{\underset{k_4^-}{\rightleftharpoons}} AB + \ast \]  

(2.13)
Similar to previous cases we obtain the following rates:

\[
\begin{align*}
    r_1 &= k_1^+ P_A \theta_* - k_1^- \theta_A \\
    r_2 &= k_2^+ P_B \theta_* - k_2^- \theta_B \\
    r_3 &= k_3^+ \theta_A \theta_B - k_3^- \theta_{AB} \theta_* \\
    r_4 &= k_4^+ \theta_{AB} - k_4^- P_{AB} \theta_*
\end{align*}
\] (2.14)

At this point the full set of differential equations can be solved numerically. Alternatively, various approximations can be made [15]. One of the approximations is the steady state approximation. In steady state the system has reached a constant output of products. As a result we can set all coverage differentials equal to zero. A further approximation can be made by assuming quasi-equilibrium. The latter sets one elementary step as rate determining, with the others at quasi-equilibrium. An even simpler reaction rate expression can be achieved by making the irreversible step approximation. This states that the rate determining step is also irreversible, and the backward rate can be neglected. All in all the system can be reduced to:

\[
r = r_3 = r^+ = \frac{k_3^+ K_1 K_2 P_A P_B}{(1 + K_1 P_A + K_2 P_B)^2}
\] (2.15)

Of course these approximations have to be taken with care. Such a model cannot be used to describe the transient behavior towards steady state. Setting one rate determining step might also be difficult for complex reactions.

Another approximation underlying the Langmuir approach is the mean-field approximation. It has two assumptions. First, all adsorbed species are distributed randomly over the surface. Secondly, there is no interaction between the adsorbed species. Although a common approximation, real systems might behave differently. In reality lateral interactions between the adsorbates can have a profound influence on reaction rates [16].

### 2.1.3 Transition state theory

Let us go back to the Arrhenius equation:

\[
k = \nu \cdot \exp \left( \frac{-E_{act}}{RT} \right)
\] (2.16)

This simple expression can be used with remarkable accuracy for describing a reaction rate. Transition state theory (TST) results in a equation bearing strong resemblance to the empirical Arrhenius equation. TST was developed independently by Henry Eyring, and by Meredith Gwynne Evans and Michael Polany. This Eyring equation [17, 18]
Chapter 2. Theory

states:
\[ k = \kappa \frac{k_B T}{h} \frac{Q\#}{Q_A Q_B} \exp \left( \frac{-\Delta E}{RT} \right) \] (2.17)

In section 2.2 about DFT, we will see how to determine both the pre-exponential factors and the \( \Delta E \). \( Q \) is a partition function and \( \kappa \) is the transmission coefficient. The latter accounts for tunneling effects that might lower the possibility of an activated complex giving rise to products. For now we will assume a value of one for the transmission coefficient.

Partition functions \( Q \) can be split into translational, vibrational and rotational contributions

\[ Q = q_{\text{trans}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \] (2.18)

where for a diatomic molecule we can state that for one degree of freedom

\[ q_{\text{trans}} = \frac{L \sqrt{2\pi m k_B T}}{h} \] (2.19)

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

\[ q_{\text{rot}} = \frac{8\pi^2 I k_B T}{h^2} \] (2.21)

where \( L \) is a length unit for translation. Note that the reaction coordinate is excluded from the TS partition function \( Q\# \).

2.1.4 Hertz-Knudsen kinetics

Alternative to using DFT to find the pre-exponential factors for adsorption and desorption, we can directly derive expressions corresponding to the work of Hertz [19] and Knudsen [20]. For adsorption we assume that the only partition function of interest is the translational partition function. This is true for loose adsorption transition states at higher temperatures. By going from three translational degrees of freedom to two we get:

\[ k_{\text{adsorption}} = S \cdot \frac{k_B T}{h} \frac{q_{\text{trans}}^2}{q_{\text{trans}}} = S \frac{k_B T}{L \sqrt{2\pi m k_B T}} \] (2.22)

Here we have introduced \( S \) as the sticking coefficient. By assuming the ideal gas law

\[ P = \frac{k_B T}{V} \] (2.23)

and using

\[ A_{\text{site}} = \frac{V}{L} \] (2.24)
where $A_{\text{site}}$ is the area of the surface site to be adsorbed upon, we get:

$$k_{\text{adsorption}} = S \cdot \frac{P \cdot A_{\text{site}}}{\sqrt{2 \pi m k_B T}} = P \cdot \nu_{\text{adsorption}} \quad (2.25)$$

with

$$\nu_{\text{adsorption}} = S \cdot \frac{A_{\text{site}}}{\sqrt{2 \pi m k_B T}} \quad (2.26)$$

For desorption we assume that the differences between transition state and initial state are the two degrees of translational freedom and the rotational partition function. We then get:

$$\nu_{\text{desorption}} = \frac{k_B T \cdot A_{\text{site}}}{\hbar} \cdot \frac{8 \pi^2 I k_B T}{\sigma \hbar^2} = k_B T^3 \cdot \frac{A_{\text{site}} \cdot 2 \pi m k_B}{\sigma \theta_{\text{rot}}} \quad (2.27)$$

with $\sigma$ as the symmetry number and

$$\theta_{\text{rot}} = \frac{\hbar^2}{2 k_B I} \quad (2.28)$$

as the characteristic temperature for rotation.

### 2.1.5 Brønsted-Evans-Polanyi relationship

Brønsted observed various relationships governing activity during acid and base catalysis. One such relationship is a proportionality between the catalytic constant and the strength constant of the acid or basic catalyst. [21]

Evans and Polanyi generalized this relation for reaction barriers. This lead to the ability to relate activation energies to the reaction energy by using the Brønsted-Evans-Polanyi (BEP) relationship

$$\delta E_{\text{act}} = \alpha \delta E_{\text{reac}} \quad (2.29)$$

where $\delta E_{\text{act}}$ is the change in activation energy corresponding to a change of the reaction energy $\delta E_{\text{reac}}$. The linear scaling is determined by the constant $\alpha$, which is based on the particular reaction type. [22]

Using the BEP relation we can explain why reaction energy barriers change for different transition metals. For dissociation reactions, the atom binding energy in the final state is higher for transition metals to the upper left of the periodic table. The resulting $\delta E_{\text{reac}}$ leads to a lower barrier. Generally the $\alpha$ value for dissociation of $\pi$ bonds is close to 1, indicating a late transition state. This late or tight transition has more resemblance to the strongly bound final state. Using BEP relations to predict barriers on different metals is only valid when the reactions have similar reactive environments. For a detailed review on BEP relations see [23].
2.2 Density Functional Theory

A valuable property to know about molecular systems is their ground state energy. From those energies, we can derive relative stabilities and reactivity. In more difficult terms this means we need to find solutions of the non-relativistic time-independent Schrödinger equation

\[ H \left| \Phi \right> = E \left| \Phi \right> \]  

(2.30)

where \( H \) is a Hermitian operator called the Hamiltonian, \( |\Phi\rangle \) is the wave function, and \( E \) is the energy. Only the simplest cases can be solved exactly. Therefore we are interested mostly in the approximate solutions.

In this section I will cover some important aspects for finding ground state energies of molecular systems. A more in-depth introduction to the matter can be found in [24].

2.2.1 The Born-Oppenheimer Approximation

The ground state energy can be split into a number of contributions. One way to split it, is to consider energy contributions from the atom nuclei and from the electrons.

\[ E_{\text{tot}} = E_{\text{elec}} + E_{\text{nucl}} \]  

(2.31)

Atom nuclei are much heavier than the electron around them. As such, the nuclei move more slowly. Therefore, a good approximation is to consider the electrons to be moving in the field of fixed nuclei. This does not mean that the energy contribution from the nuclei is negligible to that of the electrons. However, the nuclear repulsion can be added to the electronic problem as a constant.

\[ E_{\text{tot}} = E_{\text{elec}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \]  

(2.32)

Now we are left with solving the electronic Schrödinger equation.

\[ H_{\text{elec}} \Phi = E_{\text{elec}} \Phi_{\text{elec}} \]  

(2.33)

2.2.2 Hohenberg-Kohn

In this section I will closely follow the original 1964 paper of Hohenberg and Kohn [25]. Let us consider a collection of an arbitrary number of electrons. They are enclosed in a large box and are moving under the influence of an external potential \( v(r) \) and the mutual Coulomb repulsion. The (electronic) Hamiltonian has the following form:
\[
H = T + V + U
\]  
(2.34)

Here \( T \) is the kinetic part, \( V \) relates to the external potential and \( U \) holds the electron-electron interactions. In atomic units these parts are:

\[
T = \frac{1}{2} \int \nabla \psi^*(r) \nabla \psi(r) dr
\]  
(2.35)

\[
V = \int v(r) \psi^*(r) \psi(r) dr
\]  
(2.36)

\[
U = \frac{1}{2} \int \frac{1}{|r - r'|} \psi^*(r) \psi^*(r') \psi(r) \psi(r') dr dr'
\]  
(2.37)

For a nondegenerate ground state \( \Psi \) we can denote the electronic density by

\[
n(r) = (\Psi, \psi^*(r) \psi(r) \Psi),
\]  
(2.38)

which is a functional of \( v(r) \). By *reductio ad absurdum* Hohenberg and Kohn show that \( v(r) \) is (to within a constant) a unique functional of \( n(r) \). As a result \( H \) is fixed by \( v(r) \) and the ground state wave function is a unique functional of \( n(r) \).

From equation 2.34 we can combine the kinetic and interaction energy to define a universal functional, valid for any number of particles and any external potential:

\[
F[n(r)] = (\Psi, (T + U) \Psi)
\]  
(2.39)

For a given potential \( v(r) \) we can now give the energy functional

\[
E_v[n(r)] = \int v(r) n(r) dr + F[n(r)].
\]  
(2.40)

Determining the ground-state energy and density is done by minimization of this functional. This rather simple statement is an important part of Hohenberg-Kohn theory. The difficulty here is that the universal functional \( F[n(r)] \) is still unknown.

For most purposes it is convenient to separate the classical Coulomb energy from \( F[n(r)] \) and write

\[
F[n(r)] = \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr dr' + G[n(r)].
\]  
(2.41)

\( G[n(r)] \) is still unknown, but smaller than \( F[n(r)] \).
Chapter 2. Theory

2.2.3 Kohn-Sham

In this section I will closely follow the 1965 paper of Kohn and Sham [26]. Continuing from equation 2.41 we write

\[ G[n] = T_s[n] + E_{xc}[n]. \]  

(2.42)

Here \( T_s[n] \) is the kinetic energy of a system of noninteracting electrons with density \( n(r) \). Kohn and Sham define \( E_{xc} \) as the exchange and correlation energy of an interacting system with density \( n(r) \). Equation 2.40 has to be stationary when switching to the kinetic description of noninteracting electrons. Therefore we can derive from it, subject to the condition

\[ \int \delta n(r) dr = 0, \]  

(2.43)

the equation

\[ \int \delta n(r) \left\{ \phi(r) + \frac{\delta T_s[n]}{\delta n(r)} + v_{xc}(n(r)) \right\} dr = 0; \]  

(2.44)

Here we have

\[ \phi(r) = v(r) + \int \frac{n(r')}{|r - r'|} dr', \]  

(2.45)

and

\[ v_{xc}(n) = \frac{\delta E_{xc}[n]}{\delta n(r)} \]  

(2.46)

is the exact exchange and correlation contribution to the one-particle potential. For given \( \phi \) and \( v_{xc} \) we can now obtain the corresponding density by solving the one-particle Schrödinger equation

\[ \left\{ -\frac{1}{2} \nabla^2 + [\phi(r) + v_{xc}(n(r))] \right\} \psi_i(r) = \epsilon_i \psi_i(r), \]  

(2.47)

and setting

\[ n(r) = \sum_{i=1}^{N} |\psi_i(r)|^2, \]  

(2.48)

where \( N \) is the number of electrons.

Equations 2.45, 2.46, 2.47 and 2.48 have to be solved self-consistently. The procedure is as follows: An initial guess is made for density \( n(r) \). Next we find \( \phi(r) \) and \( v_{xc}(n) \) by using 2.45 and 2.46. From 2.47 and 2.48 we can then construct the new density.

In section 2.2.2 we learned that we find the real ground state when the energy is minimal. We thus continue the above procedure until a new iteration does not lead to a
The exact total energy is given by

\[ E = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{xc}[n] - \int v_{xc}(r)n(r)dr. \]  

(2.49)

The one limitation that prevents us from directly applying this method is that we do not know \(E_{xc}[n]\) and \(v_{xc}\). No DFT theory at this moment is possible to give an exact exchange correlation functional. However some very useful approximations have been developed.

### 2.2.4 Local-density approximation (LDA)

The exchange-correlation energy is no simple expression. Two limiting cases exist where an exact value for \(G[n]\) can be given.

As a first case, if the electron density is sufficiently slowly varying, Hohenberg and Kohn have shown that

\[ E_{xc}[n] = \int n(r)\epsilon_{xc}(n(r)) dr, \]  

(2.50)

where \(\epsilon_{xc}(n)\) is the exchange and correlation energy per electron of a uniform electron gas of density \(n\). This procedure gives the density correct to order \(|\nabla|^2\) inclusive. As such, an exact answer is found for the limit of slowly varying density.

The second case holds for systems with a high density. For higher electron densities the kinetic energy \(T_s[n]\) tends to overrule the exchange and correlation energy. Even with varying density, \(T_s[n]\) can be determined with no approximations.

If we now apply this theory to atoms and molecules we notice the following: Near the atomic nucleus the electronic density is high, and the second case holds. Large parts of the charge distribution are slowly varying, and there the first case holds. However, at the outer shells of atoms and at overlap regions in molecules neither case applies. This leads to the conclusion that the LDA method is suitable for systems like bulk metals, but not for surface regions or chemical bonding properties.

### 2.2.5 Local spin-density approximation (LSDA)

Although the LDA approximation can give good results for some bulk systems, it fails to properly describe magnetism. In order to include magnetic properties, Kohn and Sham extended the Hohenberg-Kohn theory. In LSDA the ground-state energy is not only a functional of the total electron density. Both charge densities of electrons with spin + and spin - are taken into account.
2.2.6 Generalized gradient approximations (GGA)

To predict binding energies with sufficient accuracy ($\sim \pm 10 \text{kJ/mol}$) the exchange correlation can be expanded to include gradient corrections like in

$$E_{xc}[n] = \int n(r)\varepsilon_{xc}(n)dr + \int |\nabla n|^2 \varepsilon_{xc}^{(2)}(n)dr + \cdots,$$  \hspace{1cm} (2.51)

where $\varepsilon_{xc}^{(2)}$ is the exchange and correlation portion of the second term in the energy expansion in powers of the gradient operator.

In the early eighties Langreth and Mehl presented their Nonlocal Exchange-Correlation Energy Functional [27, 28]. With it they found energies closer to experimentally derived values. The results gave atomic total energies to accuracies of $\pm 13 \text{kJ/mol}$.

Two GGA functionals popular in use are PW91 [29] and PBE [30–32]. PBE is meant to replace PW91 by producing similar results, but having a simpler form and derivation. To achieve this, some correct but less important features from PW91 were sacrificed. Both GGA methods produce similar numerical results for many simple properties. However, some more exotic properties like monovacancy formation energies might deviate between the two [33]. In any case, when reporting the use of DFT-GGA, one should explicitly mention which functional was used.

In this thesis all calculations were done using the PBE approximation. Furthermore, the used PBE potentials are based on the pseudopotential approximation and the projector augmented-wave method (PAW).

2.2.7 Pseudopotentials

Electronic calculations can require a large amount of computing power. Especially systems of many electrons take tremendous effort to evaluate every single electron contribution to the Hamiltonian. In 1934 Hans G. A. Hellmann developed a pseudopotential to prevent this [34, 35]. Hellmann realized that the outer few (valence) electrons contribute the most to the chemical and physical properties of atoms. Although the complicated interactions between core electrons do not provide much more information, most computational time is spent for the latter. Hellmann therefore replaced these effects by a Zusatzpotential.

The less accurate pseudopotential method appeared to simulate the results of all electron calculations surprisingly well. With it, simulation expenses of heavy atoms were substantially reduced. In the early seventies Melius and Goddard III investigated the method for ab initio molecular calculations [36, 37]. They found that the pseudopotential, or effective potential method, was a reliable tool for attempting calculations on very large molecules.
2.2.8 Projector augmented-wave (PAW) method

The wave functions representing the electronic density can take many forms. Generally the wave functions are build out of linear combinations of certain basis functions. This is called a basis set. An example of a basis set is a collection of atomic orbitals which can be combined to form molecular orbitals. For DFT most basis sets are made from a large amount of plane waves. An upper limit for the spatial resolution of a plane wave representation is set by the minimal allowed wavelength. Usually this is done by setting a maximum wave energy. The valance electron wave functions have strong fluctuations in the core region. As such the plane wave method is usually used together with methods like the pseudopotentials [38]. A generalization of that combination was shown in the 1994 article of Blöchl [39] on the projector augmented-wave (PAW) method.

In DFT it is too expensive to always use the all-electron (AE) method. Therefore we supply appropriate pseudopotentials. In the software package used in this thesis, VASP [40–43], this is done through POTCAR files. These potentials include the exchange-correlation approximations. The software then generates a trail density for the given system. Following the procedure as mentioned in section 2.2.3 it finds the pseudo (PS) wave functions to generate a new density. Unfortunately, chemical and physical properties are not correct when derived directly from the PS wave functions using the usual method. Therefore we first need to convert the PS wave functions back to AE wave functions. Obviously we do not know the exact conversion factors, as we can only get these from doing the tedious math we avoided in the first place. The PAW method provides us with augmented partial waves to use for the PS to AE conversion. The partial waves are made by using the one-center expansion. Normally integration is needed over the coordinates relative to multiple nuclei. This is computationally complex and expensive. The one-center expansion is a sum of integrations over only one center at a time. In this way spherical symmetry can be applied and many computational expenses are saved. The PS wave function $|\tilde{\Psi}\rangle$ can be converted to the AE wave function $|\Psi\rangle$ by

$$|\Psi\rangle = |\tilde{\Psi}\rangle - \sum_i |\tilde{\psi}_i\rangle c_i + \sum_i |\psi_i\rangle c_i,$$  \hspace{1cm} (2.52)

where $|\tilde{\psi}_i\rangle$ and $|\psi_i\rangle$ are the PS and AE partial waves respectively. Projector functions $|\tilde{p}_i\rangle$ are used to form a scalar product with the PS wave function to give the coefficients

$$c_i = \langle \tilde{p}_i \mid |\tilde{\Psi}\rangle.$$  \hspace{1cm} (2.53)

The projector functions are such that the one-center PS expansion, within the augmentation zone, is identical to the PS wave function itself. Summarizing we can now get the
AE wavefunction from the PS wavefunction by

$$|\Psi\rangle = |\tilde{\Psi}\rangle - \sum_i \left( |\psi_i\rangle - |\tilde{\psi}_i\rangle \right) \langle \tilde{\rho}_i | \tilde{\Psi} \rangle.$$  \hspace{1cm} (2.54)

### 2.2.9 Cancellation of error

Because not every contribution of the true exchange-correlation potential is captured, the absolute energies are subject to some error ($\sim \pm 10\text{kJ/mol}$). One of the contributions that is not incorporated well in both LDA and GGA is the van der Waals force. A part of the van der Waals force, the London dispersion force [44], is caused by correlation effects missing in both density approximations.

Still DFT is an extremely powerful tool for investigating trends. By comparing similar systems, the systematic energy errors cancel each other. The DFT calculations in this thesis were done to construct energy barriers. Therefore in all cases energies are compared to each other within the same PAW-GGA method. Some absolute error differences may be present between gaseous molecules and molecules adsorbed on the surface. We assume that cancellation of error is valid while comparing the different intermediates on the metal surfaces. In other words, we expect that adsorption energies might be less accurate. For the surface reactions we expect higher accuracy.

### 2.2.10 Conjugate gradient method

From the previous sections we know how to find the electronic ground state of a given system of ions placed within three-dimensional space. This means we can give any input geometry and get a total energy. We know that geometries of lower energy are more likely in a real system. Thus we would like to know what that geometry is. To find it, we calculate the energy and forces for an initial set of coordinates. From the forces we know the direction of the local downhill gradient. By now taking a step in this direction we get closer to the minimal energy configuration. Repeating this procedure for many times is called the *steepest descent method* [45]. Sadly this simple method, in many cases, is not very efficient. Preferably we would like to use the information of previous steps in our new search direction. By taking the new direction coupled, or *conjugate*, to the previous step(s) we get the *conjugate gradient method* [45]. Some additional computation is required for each step in the method, but generally it converges in a lot less steps.
2.2.11 Zero-point energy (ZPE) correction

The conjugate gradient method returns the configuration of (local) minimum energy. However, even in the ground state a quantum mechanical system will have vibrations. The associated energy with those vibrations is called the zero-point energy (ZPE) [46]. To obtain the ZPE in DFT we first need to find the second derivatives of the energy with respect to the atomic positions. In other words, we need to determine the Hessian matrix. To obtain this matrix ions \( i \) and \( j \) are displaced along each Cartesian coordinate. We collect the forces — which are the first derivatives of the energy — at the various perturbations and determine the curvature. The resulting matrix of second derivatives should mathematically be symmetric. Consider perturbing atom 1 in the x-direction after having perturbed atom 2 in the y-direction. This should lead to the same result as the other way around. Usually the computed matrix values turn out to be asymmetric. The matrix can be re-symmetrized easily by setting

\[
H_{i,j} = \frac{H_{i,j}^{\text{sym}} + H_{j,i}^{\text{sym}}}{2}.
\]  

(2.55)

In addition to symmetrization, the Hessian matrix should also be mass-weighted according to the masses of displaced atoms \( i \) and \( j \) so that

\[
H_{i,j}^{\text{m}} = \frac{H_{i,j}}{\sqrt{M_i \cdot M_j}}.
\]  

(2.56)

Diagonalization of \( H_{i,j}^{\text{m}} \) yields eigenvalues \( \epsilon \) from which the vibrational frequencies can be calculated with

\[
\nu_i = \frac{1}{2\pi} \sqrt{\epsilon_i}.
\]  

(2.57)

Determining the ZPE correction is now simply doing a summation over all real frequencies (i.e not the imaginary frequencies).

2.2.12 Vibrational Partition function

With equation 2.17 in section 2.1.3 we established that we need partition functions of the transition state relative to the initial and final states. With these we can determine pre-exponential factors for the reaction rates. For our surface reactions we assume that all contributions are captured by taking the relative vibrational partition functions. Considering some transition state \( AB# \) we can get the vibrational partition function by calculating

\[
q_{\text{vib}}^{AB#} = \prod_i \left[ 1 - \exp \left( -\frac{\nu_i^{\text{real}}}{k_B T} \right) \right].
\]  

(2.58)

The same can be done for the initial and final states.
2.2.13 Nudged Elastic Band (NEB) method

We now have almost all ingredients to compute energy barriers. Using the conjugate gradient algorithm we can find initial and final states of a surface reaction. We can compute zero point energy corrected values and find the vibrational partition functions. We know the reaction energy, but not the energy barriers. Nor do we know the precise geometry of the transition state.

Imagine connecting the initial and final states to each end of a rubber string. Next we try to pull this string down to its lowest energy possible. As the sting has to connect the IS and FS, somewhere it has a maximum energy. This is the position of the transitions state, a saddle point in the energy landscape. In DFT we make interpolated images between the IS and FS. These images are force-coupled by springs. After optimization the image highest in energy is most likely the TS. This procedure is called the *Nudged Elastic Band (NEB) method*. In the NEB method, a minimization of an elastic band is carried out where the perpendicular component of the spring force and the parallel component of the true force are projected out. In this way the spring force does not pull the images away from the minimal energy path and the true force does not slide the image down. [47, 48].

An improvement on the NEB method was made by the Henkelman research group. Two additions allow the more accurate determination of saddle points using NEB with fewer images than the original method. The first addition is a climbing image method [49]. This modification drives the highest energy image up to the saddle point. The spring forces of the band are relaxed for this image so it can maximize its energy along the band. The second addition is an improved way of estimating the local tangent [50]. With it, better convergence is possible for systems where forces along the reaction coordinate are strong compared to its perpendicular direction.

2.3 Microkinetic Modeling (MKM)

In section 2.1.2 we saw an example of Langmuir-Hinselwood kinetics. Section 2.1.3 shortly showed the concept of transition state theory. Then in section 2.2 the DFT method for determining energy barriers was explained. Coverages and total rates for a set of elementary reactions can be calculated by making various approximations or by numerically solving the entire set of differential equations. With microkinetic modeling (MKM) we do the latter and solve the full set of elementary reactions.
2.3.1 Ordinary Differential Equation (ODE) solving

To solve ordinary differential equations (ODEs) we first need some initial conditions. In MKM these are the component concentrations. Solving the ODEs with specific initial conditions is called solving the initial value problem. A simple way to do this numerically is to use the Euler method. Considering a system evolving over time, we choose a certain time step $\Delta t$. Finding a new value $y_i(t + \Delta t)$ from a known value $y_i(t)$ can be done by using the differential:

$$y_i(t + \Delta t) \approx y_i(t) + \Delta t \cdot y'_i(t) \tag{2.59}$$

As the step size decreases, so does the error in the method. Computation of the new value is done with known values. This means that the Euler method is explicit.

An alternative is the Backward Euler method where

$$y_i(t + \Delta t) \approx y_i(t) + \Delta t \cdot y'_i(t + \Delta t) \tag{2.60}$$

This method is implicit, because the derivative $y'_i(t + \Delta t)$ is not known and this equation has to be solved. As a result the computational costs of implicit methods are higher.

An advantage of implicit methods is that they perform better for stiff systems. Most ODEs we will be dealing with are in fact stiff.

Stiffness is a phenomenon that is difficult to define in precise mathematical terms. For chemical systems, stiffness mostly arises from the fact that reaction rates can differ for multiple orders of magnitude. The resulting range of differential values requires an unworkable small step size when using an unsuited solving algorithm.

Multiple methods exist specifically to handle stiff ODEs. In this thesis we use a linear multistep backward differentiation formula method [51–54]. Basically this is an extension of the Backward Euler method. In addition to using the information of the direct previous step, information of up to five previous steps is used.

2.3.2 Initial rate experiment

With MKM we fix the partial pressures of the gas phase components. In this way we are sure that we are simulating intrinsic kinetics corresponding to a differential operated reactor. In a real sized plug flow reactor the steady state partial pressures change as a function reactor of length. With a continuously stirred tank reactor the steady state concentrations are dependent on flow to reactor volume ratio, or space velocity. A differential reactor has a small volume and operates under low conversion. Taking the limit to zero conversion is performing an initial rate experiment.
2.3.3 Sensitivity analysis

From MKM we can find surface coverages and reaction rates, both under transient and steady-state conditions. By slightly altering input conditions, the system’s sensitivity to a certain change can be analyzed. These simulated sensitivities can be related to experimental phenomena.

Reaction orders

Without making approximations to the total microkinetic ODE set, it is difficult to analytically derive quantitative reaction orders. With numerical solutions we can. Consider the reaction $A + B \rightarrow C$. A possible parameterization of the rate is the power rate law:

$$r = k \cdot [A]^{n_A} \cdot [B]^{n_B} \cdot [C]^{n_C} \quad (2.61)$$

or

$$r = k \cdot P_A^{n_A} \cdot P_B^{n_B} \cdot P_C^{n_C} \quad (2.62)$$

where $n_X$ is the reaction order of component $X$. Now let us determine for example $n_A$. We can change the partial pressure of $A$ by small amounts and measure the rates at zero conversion. Then we plot the following derivative:

$$n_A = \frac{\partial \ln r^+}{\partial \ln [A]}$$

$$= [A] \frac{\partial \ln r^+}{\partial [A]}$$

$$= [A] \cdot \frac{\partial (\ln k + n_A \ln [A] + n_B \ln [B] + n_C \ln [C])}{\partial [A]}$$

$$= [A] \cdot \frac{n_A}{[A]} \quad (2.63)$$

Apparent activation energy

By performing sensitivity analysis on the temperature, we can get an apparent activation energy:

$$E_{\text{app}} = RT \frac{\partial \ln r^+}{\partial T} \quad (2.64)$$

The apparent activation energy can be envisioned as the energy barrier in a single Arrhenius equation describing the total reaction. With

$$r^+ = \nu \cdot \exp \left( \frac{-E_{\text{app}}}{RT} \right) \quad (2.65)$$
we get
\[ RT^2 \frac{\partial \ln r^+}{\partial T} = RT^2 \frac{\partial}{\partial T} \left( \ln \nu + \frac{E_{\text{app}}}{RT} \right) \]
\[ = RT^2 \cdot \frac{E_{\text{act}}}{RT^2} = E_{\text{app}} \]

**(Thermodynamic) Degree of Rate Control**

Often a single elementary reaction step is assumed as rate determining, with the other reactions in equilibrium. However multiple steps can be rate determining. A rigorous method for identifying the rate-determining step has long been absent. The degree of rate control method can identify these steps. In particular, rate-controlling transition states and intermediates can be identified [55].

For elementary step \( i \) the degree of rate control \( X_{RC,i} \) is defined as
\[ X_{RC,i} = \frac{k_i}{r} \left( \frac{\partial r}{\partial k_i} \right)_{k_j \neq k_i, K_i} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} \] (2.67)

where only the rate constants of step \( i \) are changed. Equilibrium constant \( K_i \) is kept constant, so forward and backward \( k_i \) are changed by equal factors. Essentially this method is changing the free energy of the transition state. A positive \( X_{RC,i} \) value implies that the overall reaction speeds up when stabilizing the transition state of step \( i \). Summation over all steps leads to conservation of the DRC:
\[ \sum_i X_{RC,i} = 1 \] (2.68)

The same method can be applied to the reaction intermediates. This gives the thermodynamic degree of rate control \( X_{TRC,n} \) of intermediate \( n \):
\[ X_{TRC,n} = \frac{1}{r} \left( \frac{\partial r}{\partial \left( -\frac{G_0}{RT} \right)} \right)_{G_{m,x,n},G_{n}^{\text{TSS}}} = \left( \frac{\partial \ln r}{\partial \left( -\frac{G_0}{RT} \right)} \right)_{G_{m,x,n},G_{n}^{\text{TSS}}} \] (2.69)

Now a negative \( X_{TRC,n} \) value implies that the overall reaction slows down when stabilizing an intermediate. Generally \( X_{TRC,n} \) can be linked to the coverage \( \theta_n \) of intermediate \( n \) by
\[ X_{TRC,n} = -\sigma \cdot \theta_n \] (2.70)

where \( \sigma \) is the average number of sites required in the rate limiting steps. Typically this value varies between 1 and 2.
Chapter 2. Theory

2.4 Molecular Dynamics

Molecular dynamics involves solving the equations of motion for a system of \( N \) atoms or molecules interacting via some potential. Considering pair-potentials, the equation of motion is

\[
\frac{d^2r_i}{dt^2} = \sum_{j \neq i} f(r_{ij})
\]

(2.71)

A very simple algorithm to integrate 2.71 is the Verlet algorithm [56]:

\[
r_i(t + h) = -r_i(t - h) + 2r_i(t) + \sum_{j \neq i} f(r_{ij}(t))h^2
\]

(2.72)

Of course the time step \( h \) should be chosen appropriately for the molecular system under investigation. Mostly this value is of the order of femtoseconds.

2.4.1 Reactive Force Fields

Roughly most molecular dynamic methods can be placed in one of two categories. Either they are accurate but computationally expensive, or fast but inaccurate for complex systems. An important requirement for modeling catalytic mechanisms like that of Fischer-Tropsch is the inclusion of bond-breaking and bond-formation. Modeling reactive events without directly resorting to ab-initio electronic structure calculations can be done using reactive force fields. ReaxFF [12] is such a force field. It divides the system energy into various partial energy contributions:

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdW}} + E_{\text{Coulomb}}
\]

(2.73)

The \( E_{\text{bond}} \) part is determined with the fundamental assumption that the bond order between a pair of atoms can be directly obtained from the interatomic distance. In this 2-body interaction the sigma, pi and double pi bonds all add to the bond order a value between zero and unity.

\( E_{\text{over}} \) and \( E_{\text{under}} \) contain the multibody atom under- and over-coordination. For example, an energy penalty is applied when the bond order of carbon atom is higher than 4. \( E_{\text{val}}, E_{\text{pen}} \) and \( E_{\text{tors}} \) hold corrections for varying 3-body valence and 4-body torsion angles. \( E_{\text{conj}} \) contains the conjugation effects which are maximum when successive bonds have bond-order values of 1.5. 2-body nonbonded van der Waals and Coulomb interactions are added in \( E_{\text{vdW}} \) and \( E_{\text{Coulomb}} \).

All of these energy contribution are parameterized using many terms. Globally a ReaxFF force field is defined by specifying general parameters, atom parameters, bond parameters, off-diagonal parameters, angle parameters and torsion parameters.
2.4.2 Force field fitting

A ReaxFF force field has to be fitted against an accurate experimental and/or theoretical dataset. This training set should contain common configurations of the system at interest. A good source for such a dataset is a collection of ab-initio electronic structure calculations. In particular the force field should be able to reproduce (relative) energies and geometries of the training set.

Parameter optimization can be done by minimizing the sum of squares:

\[
\text{sum of squares} = \sum_{i=1}^{n} \left[ \frac{(x_{i, \text{training set}} - x_{i, \text{reaxff}})}{\sigma_i} \right]^2
\]  

(2.74)

where \( x_{i, \text{training set}} \) is a property in the training set, \( x_{i, \text{reaxff}} \) is the corresponding value calculated by the force field and \( \sigma_i \) is an acceptance criterion which can change for different properties.

A simple approach for minimizing the sum of squares is using a successive one-parameter search technique [57]. Basically you iteratively go through all parameters, optimizing them one at a time with a parabolic search.

The one-parameter search technique is very dependent on initial parameter values, which generally are hard to find. With bad initial values, the search may end in a local error minimum, rather than the global minimum. The Metropolis Monte-Carlo (MMC) algorithm with simulated annealing (SA) provides a more robust way to find the global error minimum [14]. As it does not rely on a good set of initial values, it is found to lead to a lower error and a tighter fit with the training set.
Chapter 3

Computational Methods

3.1 Density Functional Theory

All quantum chemical calculations were performed using a plane-wave density functional theory approach with the projector-augmented wave (PAW) method [39], as implemented in version 4.6.38 of the Vienna ab initio simulation package (VASP) [40–43]. For exchange-correlation, the Perdew-Burke-Ernzerhof (PBE) functional [30, 31] was used. For the plane wave basis set the kinetic energy cutoff was set at 400 eV. A Monkhorst-Pack mesh [58] k-points of (21 x 21 x 21) was used for bulk HCP cobalt, and (5 x 5 x 1) for the HCP surface slabs. For calculations in the gas phase references only the Gamma-point was used. The gas phase references were calculated using 10 x 10 x 10 Å cells containing one molecule of the particular species. Adsorptions on the Co(0001) surface slab were done mirrored over the xy-plane to avoid dipole-dipole interaction between the supercells. For the Co(1121) surface slab the adsorbates were placed using an offsetted inversion. The degrees of freedom of the system were optimized using the conjugate-gradient technique. We found reaction paths with the climbing image nudged elastic band (cNEB) implementation [47–50]. The transition states (TS) were optimized using a quasi-Newton algorithm and are confirmed by the saddle points obtained from frequency calculations. The frequency calculations, which were done using the finite displacement technique were also used to compute the zero point energy (ZPE) corrections of all adsorbed species and transition states. The lattice parameters giving the lowest bulk energy for our calculations on cobalt correspond to 2.49, 2.49 and 4.03 Å for a, b and c directions respectively.
Co(0001) surface slabs

The Co(0001) slabs used, were all 3x3 supercells with 5 layers of metal, corresponding to 45 cobalt atoms. The slabs were separated using a 15 Å vacuum layer. All adsorbed species were placed only once on each side of the surface, thus corresponding to 1/9 ML. Figure 3.1 shows the transition state of CH$_2$O dissociation to illustrate the topology of the terrace surface.

![Co(0001) surface slabs](image)

Figure 3.1: Transition state of CH$_2$O dissociation on a 3x3 Co(0001) supercell.

Co(1121) surface slabs

The Co(1121) slabs used, were all 2x2 supercells with 3 layers of metal, corresponding to 48 cobalt atoms. The slabs were separated using a 15 Å vacuum layer. All adsorbed species were placed only once on each side of the surface, thus corresponding to 1/16 ML. Figure 3.2 shows the transition state of CO dissociation to illustrate the topology of the stepped surface.

![Co(1121) surface slabs](image)

Figure 3.2: Transition state of CO dissociation on a 2x2 Co(1121) supercell.
3.2 Microkinetic Modeling

The microkinetic modeling (MKM) was done using version 1.3.3 of MKMCXX [59], an in-house written C++ software suite of microkinetic modeling for heterogeneous catalysis.

Surface reactions

All elementary surface reaction rates are described using Arrhenius equations. The corresponding pre-exponential factors and activation energies in both directions are taken from DFT and given as input to the program. The temperature dependency of the pre-exponential factor is fixed at 800 K, giving pre-factors in the order of $10^{13}$. For the calculated prefactors, please refer to appendix A. It also includes an overview of all reaction barriers. We set a minimum barrier energy of 5 kJ/mol. Furthermore, CH₄ desorption is considered instantaneous.

Adsorption and Desorption

All adsorption/desorption rates are described in a way similar to the Arrhenius equation. Adsorption is assumed to happen without an energy barrier, giving a value of unity to the exponential. For desorption, the energy of adsorption is used as found with DFT. The adsorption and desorption prefactors are determined according to Hertz-Knudsen (HK) kinetics with their corresponding temperature dependence. For the HK parameters and resulting prefactors, please refer to appendix A. For comparison to experimental SSITKA results, a syngas pressure of 465 mbar was used with a H₂/CO ratio of 5.
Chapter 4

Results and discussion

4.1 Density Functional Theory

We calculated several compounds in the gas phase to act as references to the adsorbed species. The energies can be found in Table 4.1. As hydrogen and deuterium do not differ in their electronic nature, their ground state energies are the same. The ZPE-corrected energies do differ. Because a deuterium atom is one neutron heavier, the mass-weighted Hessian matrix has lower values. As a result the ZPE-contribution is smaller, and the ZPE-corrected energy is lower than that of hydrogen.

**Table 4.1**: Gas phase energy references for various species. $E_0$ is the electronic ground state energy. $E_{ZPE}^0$ is the ground state energy corrected for zero point energy.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_0$ [eV]</th>
<th>$E_{ZPE}^0$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-14.79</td>
<td>-14.65</td>
</tr>
<tr>
<td>H$_2$</td>
<td>-6.77</td>
<td>-6.48</td>
</tr>
<tr>
<td>D$_2$</td>
<td>-6.77</td>
<td>-6.57</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-9.84</td>
<td>-9.74</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-14.22</td>
<td>-13.64</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-24.02</td>
<td>-22.83</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-22.97</td>
<td>-22.66</td>
</tr>
</tbody>
</table>

**Table 4.2**: Adsorption energies for the various species on Co(0001) and Co(1121). $E_{ads}$ is derived from the electronic ground state energies. $E_{ads}^{ZPE}$ is corrected for zero point energy.

<table>
<thead>
<tr>
<th>Species</th>
<th>Co(0001) [kJ/mol]</th>
<th>Co(1121) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ads}$</td>
<td>$E_{ZPE}$</td>
<td>$E_{ads}$</td>
</tr>
<tr>
<td>CO</td>
<td>-167</td>
<td>-170</td>
</tr>
<tr>
<td>H</td>
<td>-53</td>
<td>-45</td>
</tr>
<tr>
<td>O</td>
<td>-252</td>
<td>-265</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-28</td>
<td>-57</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-2</td>
<td>-6</td>
</tr>
</tbody>
</table>
4.1.1 Co(0001) surface slabs

With the gas phase energies from Table 4.1 as a reference, the adsorption energies in Table 4.2 were calculated. CO adsorbs strongly onto the empty Co(0001) surface, similar to findings in the literature [60].

Table 4.3 shows zero point energy corrected barriers for the methanation reaction on Co(0001). All values are migration corrected; i.e. all intermediate energies are taken with a single adsorbate in a separate unit cell. In other words, the adsorbates are considered at infinite distance so that lateral interactions are absent. The advantage of this methodology is that we find the same total reaction energy for all paths. The potential energy diagram in Figure 4.1 shows this is the case. In some low barrier reactions, the transition state might be lower in energy than the migration and ZPE corrected initial or final state. From table 4.3 we can see that this is the case for the dehydrogenation of CHOH to COH. This does not undermine the validity of the transition state, as it still has exactly one imaginary frequency in its converged state.

As this frequency is real for the initial and final states, the ZPE contribution of those states tends to be a little higher. Without the ZPE correction, the barrier would be positive. We use a minimum barrier energy of 5 kJ/mol for the kinetic modeling later in this thesis.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{act}^{forw}$ [kJ/mol]</th>
<th>$E_{act}^{back}$ [kJ/mol]</th>
<th>$\Delta E_{react}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + H $\rightarrow$ COH</td>
<td>175</td>
<td>77</td>
<td>98</td>
</tr>
<tr>
<td>CO + H $\rightarrow$ CHO</td>
<td>127</td>
<td>10</td>
<td>119</td>
</tr>
<tr>
<td>CHO + H $\rightarrow$ CH$_3$O</td>
<td>43</td>
<td>10</td>
<td>33</td>
</tr>
<tr>
<td>CHO + H $\rightarrow$ CHOH</td>
<td>102</td>
<td>51</td>
<td>51</td>
</tr>
<tr>
<td>COH + H $\rightarrow$ COH</td>
<td>68</td>
<td>-5</td>
<td>72</td>
</tr>
<tr>
<td>CH$_2$OH + H $\rightarrow$ CH$_2$OH</td>
<td>65</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>CH$_2$O + H $\rightarrow$ CH$_2$OH</td>
<td>96</td>
<td>38</td>
<td>58</td>
</tr>
<tr>
<td>C + H $\rightarrow$ CH</td>
<td>71</td>
<td>90</td>
<td>-19</td>
</tr>
<tr>
<td>CH + H $\rightarrow$ CH$_2$</td>
<td>52</td>
<td>14</td>
<td>38</td>
</tr>
<tr>
<td>CH$_2$ + H $\rightarrow$ CH$_3$</td>
<td>51</td>
<td>52</td>
<td>-1</td>
</tr>
<tr>
<td>CH$_3$ + H $\rightarrow$ CH$_4$</td>
<td>106</td>
<td>88</td>
<td>18</td>
</tr>
<tr>
<td>CO $\rightarrow$ C + O</td>
<td>225</td>
<td>158</td>
<td>66</td>
</tr>
<tr>
<td>COH $\rightarrow$ C + OH</td>
<td>149</td>
<td>145</td>
<td>5</td>
</tr>
<tr>
<td>CHO $\rightarrow$ CH + O</td>
<td>63</td>
<td>135</td>
<td>-72</td>
</tr>
<tr>
<td>CH$_2$O $\rightarrow$ CH$_2$ + O</td>
<td>59</td>
<td>126</td>
<td>-67</td>
</tr>
<tr>
<td>CHOH $\rightarrow$ CH + OH</td>
<td>62</td>
<td>149</td>
<td>-86</td>
</tr>
<tr>
<td>CH$_2$OH $\rightarrow$ CH$_2$ + OH</td>
<td>45</td>
<td>134</td>
<td>-89</td>
</tr>
<tr>
<td>O + H $\rightarrow$ OH</td>
<td>121</td>
<td>85</td>
<td>36</td>
</tr>
<tr>
<td>OH + H $\rightarrow$ H$_2$O</td>
<td>139</td>
<td>72</td>
<td>67</td>
</tr>
<tr>
<td>OH + OH $\rightarrow$ H$_2$O + O</td>
<td>47</td>
<td>17</td>
<td>30</td>
</tr>
</tbody>
</table>
For the terrace Co(0001) surface, direct CO dissociation is difficult. Although the direct dissociation is less endothermic than the CO hydrogenation reactions, the barriers for the latter are lower. The migration corrected overall barrier for CHO dissociation is 182 kJ/mol. This is lower than the overall barriers for CH₂O dissociation (212 kJ/mol), direct CO dissociation (225 kJ/mol), CHOH dissociation (233 kJ/mol), COH dissociation (247 kJ/mol), and CH₂OH dissociation (256 kJ/mol).

**Figure 4.1:** Potential energy diagram of the methanation reaction on Co(0001). Energy levels are based on DFT barriers from Tables 4.2 and 4.3. Note that the barrier for CHOH formation from COH has been raised by 10 kJ/mol.

### 4.1.2 Co(1121) surface slabs

The adsorption energies on the stepped Co(1121) surface are mostly similar to the adsorption energies on the Co(0001) terrace. Though due to the more open geometry, different orientations for adsorption are possible. Especially for H₂O this seems to lead to a stronger binding energy, as seen in Table 4.2.

For the stepped Co(1121) surface, direct CO dissociation is much more favorable compared to the terrace. Also direct dissociation is more or less thermo-neutral. The barrier for CO dissociation is 106 kJ/mol. This is lower than the overall barriers for CHO dissociation (161 kJ/mol), CH₂O dissociation (187 kJ/mol), CH₂OH dissociation (204 kJ/mol), COH dissociation (207 kJ/mol) and CHOH dissociation (207 kJ/mol).
TABLE 4.4: ZPE corrected forward ($E_{act}^{forw}$) and backward ($E_{act}^{back}$) reaction barriers for the methanation reaction on the stepped Co(1121) surface. All reaction barriers are given with reference to the most stable state found for each species, i.e. migration corrections are taken into account.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_{act}^{forw}$ [kJ/mol]</th>
<th>$E_{act}^{back}$ [kJ/mol]</th>
<th>$\Delta E_{react}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + H ⇌ COH</td>
<td>207</td>
<td>105</td>
<td>102</td>
</tr>
<tr>
<td>CO + H ⇌ CHO</td>
<td>97</td>
<td>18</td>
<td>78</td>
</tr>
<tr>
<td>CHO + H ⇌ CH$_2$O</td>
<td>75</td>
<td>32</td>
<td>42</td>
</tr>
<tr>
<td>CH$_2$O + H ⇌ CHOH</td>
<td>147</td>
<td>77</td>
<td>71</td>
</tr>
<tr>
<td>COH + H ⇌ CHOH</td>
<td>74</td>
<td>28</td>
<td>47</td>
</tr>
<tr>
<td>CHO + H ⇌ CH$_2$OH</td>
<td>63</td>
<td>40</td>
<td>56</td>
</tr>
<tr>
<td>CH$_2$O + H ⇌ CH$_3$OH</td>
<td>81</td>
<td>40</td>
<td>51</td>
</tr>
<tr>
<td>C + H ⇌ CH</td>
<td>60</td>
<td>37</td>
<td>23</td>
</tr>
<tr>
<td>CH + H ⇌ CH$_2$</td>
<td>77</td>
<td>37</td>
<td>27</td>
</tr>
<tr>
<td>CH$_2$ + H ⇌ CH$_3$</td>
<td>81</td>
<td>78</td>
<td>63</td>
</tr>
<tr>
<td>CH$_3$ + H ⇌ CH$_4$</td>
<td>78</td>
<td>68</td>
<td>10</td>
</tr>
<tr>
<td>CO ⇌ C + O</td>
<td>106</td>
<td>108</td>
<td>-2</td>
</tr>
<tr>
<td>COH ⇌ C + OH</td>
<td>28</td>
<td>68</td>
<td>-88</td>
</tr>
<tr>
<td>CHO ⇌ CH + O</td>
<td>83</td>
<td>140</td>
<td>-58</td>
</tr>
<tr>
<td>CH$_2$O ⇌ CH$_2$ + O</td>
<td>66</td>
<td>150</td>
<td>-84</td>
</tr>
<tr>
<td>CHO + H ⇌ CH + OH</td>
<td>47</td>
<td>159</td>
<td>-112</td>
</tr>
<tr>
<td>CH$_2$OH ⇌ CH$_2$ + OH</td>
<td>43</td>
<td>151</td>
<td>-108</td>
</tr>
<tr>
<td>O + H ⇌ OH</td>
<td>102</td>
<td>159</td>
<td>-112</td>
</tr>
<tr>
<td>OH + H ⇌ H$_2$O</td>
<td>153</td>
<td>159</td>
<td>-112</td>
</tr>
<tr>
<td>OH + OH ⇌ H$_2$O + O</td>
<td>53</td>
<td>68</td>
<td>63</td>
</tr>
</tbody>
</table>

**Figure 4.2:** Potential energy diagram of the methanation reaction on Co(1121). Energy levels are based on DFT barriers from Tables 4.2 and 4.4.
Chapter 4. Results and discussion

4.1.3 Including lateral interactions

All calculations in the above sections are under low coverage conditions. This provides us with well defined model reactions for good comparison of the different pathways. Unfortunately, coverage effects are quite pronounced in real systems. A way to get a closer resemblance to the ‘real’ surface is to include spectator molecules or atoms in the unit cells of your calculation. Several questions remain: Which spectators should we include? How many spectators should we include? Is it actually worth the additional computational cost?

Ojeda et al. have answered the latter question with ‘Yes’. In their 2010 paper they include 0.5 ML CO spectator molecules into their Co(0001) calculations [61]. We want to understand how the added lateral interactions influence the potential energy paths. Therefore we calculate the differences in absolute intermediate energies between our data and that of Ojeda et al. Do note that this exercise, although very interesting, can only be used for investigating trends. Ojeda et al. have used another DFT code (DACAPO) with various settings different from ours. Also, we use the differences in the Co(0001) datasets to add lateral interactions to both our terrace and stepped surface.

Figure 4.3: Close-ups of the C₁ monomer formation parts of the potential energy diagrams in Figures 4.1, 4.2, 4.4 and 4.5.
Chapter 4. Results and discussion

Table 4.5: Energies of Co(0001) species without lateral interactions, compared to energies with 0.5 ML CO spectator. Data from Ojeda et al. [61]

<table>
<thead>
<tr>
<th>Species</th>
<th>Energy of Adsorption [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clean 0.5 ML CO ΔE</td>
</tr>
<tr>
<td>C</td>
<td>-647 -541 106</td>
</tr>
<tr>
<td>O</td>
<td>-524 -419 105</td>
</tr>
<tr>
<td>H</td>
<td>-278 -221 57</td>
</tr>
<tr>
<td>OH</td>
<td>-310 -255 55</td>
</tr>
<tr>
<td>H2O</td>
<td>-28 -50 -22</td>
</tr>
<tr>
<td>CO</td>
<td>-181 -75 106</td>
</tr>
<tr>
<td>CH</td>
<td>-609 -529 80</td>
</tr>
<tr>
<td>CH2</td>
<td>-372 -263 109</td>
</tr>
<tr>
<td>CH3</td>
<td>n.a. n.a. 138*</td>
</tr>
<tr>
<td>CH4</td>
<td>n.a. n.a. 167**</td>
</tr>
<tr>
<td>COH</td>
<td>-423 -360 63</td>
</tr>
<tr>
<td>CHO</td>
<td>-216 -36 180</td>
</tr>
<tr>
<td>CH2O</td>
<td>-85 -28 57</td>
</tr>
<tr>
<td>CHOH</td>
<td>-289 -185 104</td>
</tr>
<tr>
<td>CH2OH</td>
<td>n.a. n.a. 80.5***</td>
</tr>
</tbody>
</table>

* Value extrapolated by 2 · CH2 – CH
** Value extrapolated by 2 · CH3 – CH3
*** Value averaged from CHOH and CH2O

Table 4.6: ZPE and migration corrected forward (E_{forw}^{act}) and backward (E_{back}^{act}) reaction barriers for methanation with lateral interactions included.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>α BEP</th>
<th>Co(0001) [kJ/mol]</th>
<th>Co(1121) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_{forw}^{act}$</td>
<td>$E_{back}^{act}$</td>
</tr>
<tr>
<td>CO + H ⇌ COH</td>
<td>0.5</td>
<td>150 102 48</td>
<td>182 130 52</td>
</tr>
<tr>
<td>CO + H ⇌ CHO</td>
<td>0.5</td>
<td>131 13 128</td>
<td>101 14 87</td>
</tr>
<tr>
<td>CHO + H ⇌ CH2O</td>
<td>0.5</td>
<td>-2 55 -57</td>
<td>30 77 -48</td>
</tr>
<tr>
<td>CHO + H ⇌ CHOH</td>
<td>0.5</td>
<td>68 84 -15</td>
<td>114 110 4</td>
</tr>
<tr>
<td>COH + H ⇌ CHOH</td>
<td>0.5</td>
<td>64 -1 64</td>
<td>70 32 39</td>
</tr>
<tr>
<td>CHOH + H ⇌ CH2OH</td>
<td>0.5</td>
<td>45 45 0</td>
<td>42 70 -28</td>
</tr>
<tr>
<td>CH3O + H ⇌ CH2OH</td>
<td>0.5</td>
<td>88 46 42</td>
<td>73 49 24</td>
</tr>
<tr>
<td>C + H ⇌ CH</td>
<td>0.08</td>
<td>33 93 -60</td>
<td>22 40 -18</td>
</tr>
<tr>
<td>CH + H ⇌ CH2</td>
<td>0.08</td>
<td>39 15 24</td>
<td>65 62 2</td>
</tr>
<tr>
<td>CH2 + H ⇌ CH3</td>
<td>0.08</td>
<td>38 53 -15</td>
<td>68 69 -1</td>
</tr>
<tr>
<td>CH3 + H ⇌ CH4</td>
<td>0.08</td>
<td>93 89 4</td>
<td>66 69 -4</td>
</tr>
<tr>
<td>CO ⇌ C + O</td>
<td>0.9</td>
<td>230 111 119</td>
<td>111 61 50</td>
</tr>
<tr>
<td>COH ⇌ C + OH</td>
<td>0.9</td>
<td>154 101 54</td>
<td>33 72 -39</td>
</tr>
<tr>
<td>CHO ⇌ CH + O</td>
<td>0.9</td>
<td>63 132 -69</td>
<td>83 138 -55</td>
</tr>
<tr>
<td>CH2O ⇌ CH2 + O</td>
<td>0.9</td>
<td>67 56 12</td>
<td>74 79 -5</td>
</tr>
<tr>
<td>CHOH ⇌ CH + OH</td>
<td>0.9</td>
<td>64 135 -71</td>
<td>49 145 -97</td>
</tr>
<tr>
<td>CH2OH ⇌ CH2 + OH</td>
<td>0.9</td>
<td>49 96 -47</td>
<td>47 114 -67</td>
</tr>
<tr>
<td>O + H ⇌ OH</td>
<td>0.08</td>
<td>121 138 -17</td>
<td>102 139 -38</td>
</tr>
<tr>
<td>OH + H ⇌ H2O</td>
<td>0.08</td>
<td>77 78 0</td>
<td>91 95 -4</td>
</tr>
<tr>
<td>OH + OH ⇌ H2O + O</td>
<td>0.08</td>
<td>35 18 17</td>
<td>40 6 34</td>
</tr>
</tbody>
</table>
Using the energy differences from Table 4.5 we can easily adjust the levels of all intermediate states in Figures 4.1 and 4.2. By employing the BEP relationships as shown in section 2.1.5, we can also correct the transition states. Ojeda et al. have shown that 0.5 ML of spectator CO already has a large influence on the intermediate energies. For example the adsorption energy of CO is more than halved. We are interested in trends going from low coverage to intermediate coverage. Therefore we will only use 50% of the energy differences in Table 4.5. The corrected energy barriers and used BEP parameters are shown in Table 4.6. The BEP values for hydrogenation of CH$_x$ and OH$_x$ are small [62]. The C-O dissociations have a value close to one [23]. Hydrogenation of CH$_x$OH$_x$ is not the same as that of CH$_x$ and OH$_x$. For example, in the literature a BEP of 0.3 was found for CO hydrogenation [63]. To not wrongfully bias these states, we will apply a BEP of 0.5.

In Figure 4.3c, the methanation reaction on the Co(0001) surface is shown with lateral interactions. From this figure, we can see that hydrogen-assisted CO dissociation is still the most plausible pathway towards C$_1$ species. However, the CH$_2$O species is less destabilized than the other species. In relative sense, it has been stabilized. As a result, not CHO but CH$_2$O dissociation is the lowest path for C$_1$ formation.

**Methanation on Co(0001) - with lateral interactions**

![Potential energy diagram](image)

**Figure 4.4**: Potential energy diagram of the methanation reaction on Co(0001) with lateral interactions included. Note that some transition states have been adjusted to have a minimum energy barrier of 5 kJ/mol.
Figures 4.5 and 4.3d show the result of adding lateral interactions to the stepped Co(1121) surface. Again the CH2O pathway has become more favorable compared to the other hydrogen-assisted CO dissociations. For this surface however, the direct CO dissociation is still competing as a low-energy pathway. From this lateral corrected dataset the dominant path cannot be predicted with full certainty. This can be done with microkinetic modeling, as it uses the intermediate surface coverages. These modeling results are shown in section 4.2. For now we can hypothesize that for low hydrogen coverage, the direct CO dissociation will be the dominant pathway on Co(1121).

![Methanation on Co(11-21) - with lateral interactions](image)

**Figure 4.5:** Potential energy diagram of the methanation reaction on Co(1121) with lateral interactions included.

### 4.1.4 Isotope effect from zero point energies

In Table 4.1 it is shown that there is a difference in zero point energy between hydrogen and deuterium. To obtain the ZPE energies of all our intermediates with deuterium substituted for hydrogen we can recompute the Hessian with a deuterium potential. However, as the mass is the only thing different, we do not have to run the calculation again. By adjusting the mass in the Hessian (equation 2.56 from section 2.2.11) we can directly convert hydrogen vibrations to deuterium.

Here we will show the energy differences on Co(0001) for three main reactions in which
hydrogen is involved. Figure 4.6a shows hydrogen versus deuterium adsorption. Figures 4.6b and 4.6c show hydrogenation of CO and termination of CH$_3$/CD$_3$. For all energy barriers with deuterium, please refer to appendix A.

The influence of deuterium does not give differences larger than 5 kJ/mol. Compared to lateral interactions this is not very significant. It seems that the hydrogenation reactions with deuterium become slightly less endothermic. This shows that the ZPE contribution of hydrogen bonds is bigger when bonded to carbon or oxygen, rather than to the metal.

![Diagram](image)

(A) Hydrogen adsorption. (B) CO hydrogenation. (C) Methane formation.

**Figure 4.6**: Effect of exchanging hydrogen for deuterium on Co(0001).

Appendix A also shows the differences in pre-exponential factors and Hertz-Knudsen parameters between hydrogen and deuterium. From these parameters we can expect an isotope effect. The equilibrium constant for deuterium adsorption is about 3.6 times lower at 533 K. This will result in lower hydrogen surface coverages, which can be related to lower rates for positive reaction orders of hydrogen. The pre-exponential factors for hydrogenation reactions are also lower. This will further lower the rate in case of hydrogenation limitation.
4.2 Microkinetic Modeling of the methanation reaction on cobalt surfaces

Microkinetic modeling was done using the calculated energy barriers as shown in sections 4.1.1 and 4.1.2. We investigated the lateral interaction trends by using the barriers as shown in 4.1.3. Prefactors for the Arrhenius equations were determined as explained in section 2.2.12. For comparison to experimental results from our group, the input condition are chosen different from actual FT operational conditions. There is another important reason for this. As the chain growth reactions have yet to be calculated in future work, the phase space of the model is limited. By using low partial pressures and a high hydrogen to CO ratio, we ensure that we are simulating the correct part of phase space. Using these conditions experimentally will lead to methane as the major product.

4.2.1 Surface coverages and production rates

Surface coverages and production rates are the main properties that we can acquire by doing microkinetic modeling on a system. The temperature range used for the simulations is 400 K up to 1200 K. The high end was chosen solely to verify trends. In a real setup, sintering effects will reduce the catalytic activity well below 1200 K. For reference, 473-513 K is a typical LTFT range and 573-623 K a typical HTFT range. To compare values, we will use the results at a temperature of 533 K, or 260 °C.

Co(0001) surface

For the terrace surface, the surface coverages are shown in Figure 4.7a. We can see that up to 650 K the microkinetic simulation gives a full coverage of CO. Between 650 K and 900 K the amount of chemisorbed hydrogen increases. From 700 K onwards the amount of empty sites increases. The Fischer-Tropsch range is within the part dominated by CO coverage.

For dissociation of the C-O bond we need a combination of CO and free sites. Because the latter is lacking at low temperatures, we expect the turnover to be low. Figure 4.8a shows this. At 533 K the production is only $9.5 \times 10^{-12}$ mol/s.
Co(1121) surface

Figure 4.7b shows that the high coverages of CO at low temperatures are also present on the Co(1121) surface. Different from the terrace, a minor coverage of carbon atoms is present at higher temperatures. This is an interesting observation, as it suggests a fast dissociation of CO in that range. Even a minor oxygen amount can be seen. We can conclude from this that for the stepped surface, CO dissociation rates and subsequent hydrogenation rates are similar in magnitude. The production shown in Figure 4.8b is 4 orders of magnitude higher than on the terrace surface. At 533 K the production is $2.1 \times 10^{-7}$ mol/s.

Including lateral interactions

The addition of lateral interactions has a major influence on the equilibrium coverages. Figures 4.7c and 4.7d show that free sites are now being created starting at 500 K. As this is 200 K lower than without lateral effects, free sites are now available within the
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FT temperature range.

We expect the temperature for maximum production to lower similarly. Figures 4.8c and 4.8d show this is indeed the case. Furthermore, the maximum production is 2 and 3 orders of magnitude lower for lateral corrected Co(0001) and Co(1121) respectively. At 533 K however, the production is $1.4 \times 10^{-5}$ mol/s for the terrace, and $4.2 \times 10^{-3}$ mol/s for the stepped surface. This is much higher than without the lateral correction, about 6 and 4 orders of magnitude respectively.

Analytical reaction rates

We derived Langmuir-Hinshelwood mechanisms according to section 2.1.2 to analytically describe our reaction rates under steady state. The microkinetic method is better, but this can verify our results under specific limitation assumptions. These can be: hydrogenation prior to dissociation, dissociation itself, and hydrogenation after dissociation. Table 4.7 shows the different expressions. These expressions are mostly similar to those found by Yang et al. [64]. However, for hydrogenation limitation after dissociation Yang
et al. use a water equilibrium. This is not suitable to describe initial-rate FT experiments for which it tends to give an over estimated reaction order in hydrogen. Yang et al. exclude termination limitation based on this. In the next section we will show that termination limitation is in fact a possibility.

Table 4.7: Langmuir-Hinshelwood rates derived according to the reactions equations shown in Table B.1 in appendix B. All cases with hydrogenation limitation after dissociation have OH + H as limitation for water formation.

<table>
<thead>
<tr>
<th>Rate expression</th>
<th>( \frac{r}{\theta_r^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO} \rightarrow \text{C} + \text{O} )</td>
<td>( k_{d1}^+ K_{CO} \cdot P_{CO} )</td>
</tr>
<tr>
<td>( \text{C} + \text{H} \rightarrow \text{CH} )</td>
<td>( \sqrt{K_{d1} k_{h1}^+ K_{o1} k_{o2}^+ K_{CO} K_{H2}^{0.75} P_{CO}^{0.5} P_{H2}^{0.75}} )</td>
</tr>
<tr>
<td>( \text{CH} + \text{H} \rightarrow \text{CH}_2 )</td>
<td>( \sqrt{K_{d1} K_{h1} k_{h2}^+ K_{o1} k_{o2}^+ K_{CO} K_{H2}^{0.5} P_{CO}^{0.5} P_{H2}^{1}} )</td>
</tr>
<tr>
<td>( \text{CH}_2 + \text{H} \rightarrow \text{CH}_3 )</td>
<td>( \sqrt{K_{d1} K_{h1} k_{h2}^+ k_{h3}^+ K_{r1} k_{o2}^+ K_{CO} K_{H2}^{1.25} P_{CO}^{0.5} P_{H2}^{1.25}} )</td>
</tr>
<tr>
<td>( \text{CH}_3 + \text{H} \rightarrow \text{CH}_4 )</td>
<td>( \sqrt{K_{d1} K_{h1} K_{h2} K_{h3} k_{h4}^+ K_{r1} k_{o2}^+ K_{CO} K_{H2}^{1.5} P_{CO}^{0.5} P_{H2}^{1.5}} )</td>
</tr>
<tr>
<td>( \text{CHO} \rightarrow \text{CH} + \text{O} )</td>
<td>( k_{a2}^+ K_{CO} \sqrt{K_{H2}^{1.5} P_{CO}^{0.5} P_{H2}^{0.5}} )</td>
</tr>
<tr>
<td>( \text{CHO} \rightarrow \text{CH} + \text{O} )</td>
<td>( K_{a2} k_{d3}^+ K_{CO} \sqrt{K_{H2}^{1.5} P_{CO}^{0.5} P_{H2}^{0.5}} )</td>
</tr>
<tr>
<td>( \text{CH}_3 + \text{H} \rightarrow \text{CH}_4 )</td>
<td>( \sqrt{K_{a2} K_{d3} K_{h2} K_{h3} k_{h4}^+ K_{r1} k_{o2}^+ K_{CO} K_{H2}^{1.5} P_{CO}^{0.5} P_{H2}^{1.5}} )</td>
</tr>
<tr>
<td>( \text{CH}_2 \text{O} \rightarrow \text{CH}_2 + \text{O} )</td>
<td>( k_{a2} k_{d3}^+ K_{CO} K_{H2} \cdot P_{CO} P_{H2} )</td>
</tr>
<tr>
<td>( \text{CH}_2 \text{O} \rightarrow \text{CH}_2 + \text{O} )</td>
<td>( K_{a2} k_{d4}^+ K_{CO} K_{H2} \cdot P_{CO} P_{H2} )</td>
</tr>
<tr>
<td>( \text{CH}_3 + \text{H} \rightarrow \text{CH}_4 )</td>
<td>( \sqrt{K_{a2} K_{d3} K_{d4} K_{h3} k_{h4}^+ K_{r1} k_{o2}^+ K_{CO} K_{H2}^{1.5} P_{CO}^{0.5} P_{H2}^{1.5}} )</td>
</tr>
</tbody>
</table>

4.2.2 Reaction orders

Reaction orders are powerful indicators of sensitivity to reactant concentrations going into the reactor. A positive reaction order tells us that turnover should increase with increasing partial pressure of the corresponding reactant. In our case we have two reactants, CO and hydrogen. We expect hydrogen to have a positive order. During methanation, CO dissociates and hydrogen removes dissociated products from the surface. From our zero-conversion limit MKM simulations we have shown that CO is the major species on the surface at low temperatures. Dissociation of CO is only possible.
when free sites are available. Termination reactions by hydrogen make these free sites. Therefore we expect hydrogen to have a positive reaction order and CO a negative order.

Co(0001) surface

Corresponding to our hypotheses hydrogen has a positive reaction order over the whole temperature range. CO is negative by unity for the Fischer-Tropsch temperature range and positive by unity for higher temperatures. Figure 4.9a shows that at 533 K the hydrogen order is 0.67 and slowly decreasing. So increasing hydrogen partial pressures will increase methanation rates. But is it solely due to faster termination? Imaginably, a higher hydrogen coverage on a terrace surface may increase rates of hydrogen-assisted CO dissociation. To confirm this we carry out Degree of Rate Control in section 4.2.4.

Figure 4.9: Reaction orders during the methanation reaction at 465 mbar pressure with a H₂/CO ratio of 5, with and without lateral interactions.
Co(1121) surface

Figure 4.9b shows the reaction orders for the stepped surface. The reaction order of CO is similar to the terrace, however the hydrogen order is not. For the stepped surface the hydrogen order is zero over the whole FT range. This suggests that hydrogen-assisted CO dissociation is not a major contribution to the rate.

Including lateral interactions

After adding lateral interactions we see two changes in the reaction orders. Figures 4.9c and 4.9d show that the order in CO now goes from negative to positive much lower in temperature. This effect is directly correlated with the lower coverage of CO by introducing lateral interactions. The second change is that the hydrogen order is now around unity over the whole FT range. For the stepped surface this indicates a termination limitation.

Analytical reaction orders

From the analytical rates in Table 4.7 we can predict corresponding analytical reaction orders. An upper value for the CO and hydrogen orders is found by letting $\theta_*$ approach a value of unity. We will assume that CO and H$_2$ will be the main surface intermediates. All rate expressions contain $\theta^2$. Correspondingly, with high CO coverage the lower bound for CO is a value of 2 lower than the upper value. For high H$_2$ coverage the minimum H$_2$ order is the upper bound minus 1. Basically this leaves us with the ranges of reaction orders as shown in Table 4.8. We can now look up the expected values for our limitation hypotheses. From the DFT data we proposed assisted dissociation for the terrace. Under high CO coverage this should give a CO order of -1 and a H$_2$ order between 0.5 and 1. Direct dissociation on the steps under high CO coverage should give a CO order of -1 and a H$_2$ order of 0. From Figure 4.9 we see that this is indeed the case. The lateral corrected stepped surface indeed shows orders corresponding to termination limitation.

4.2.3 Apparent activation energy

Sensitivity analysis of the rate towards minor temperature differences yields an apparent activation energy. This energy should be positive below the temperature optimum of the reaction and negative above the temperature optimum.
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TABLE 4.8: Langmuir-Hinshelwood derived reaction orders according to the rate equations shown in Table 4.7. All cases with hydrogenation limitation after dissociation have OH + H as limitation for water formation.

<table>
<thead>
<tr>
<th>Reaction order</th>
<th>Limitation \ Mechanism</th>
<th>( n_{CO}^{Min} )</th>
<th>( n_{CO}^{Max} )</th>
<th>( n_{H_2}^{Min} )</th>
<th>( n_{H_2}^{Max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CO \rightarrow C + O )</td>
<td>( CO \rightarrow C + O )</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>( C + H \rightarrow CH )</td>
<td>( CO \rightarrow C + O )</td>
<td>-1.5</td>
<td>0.5</td>
<td>-0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>( CH + H \rightarrow CH_2 )</td>
<td>( CO \rightarrow C + O )</td>
<td>-1.5</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( CH_2 + H \rightarrow CH_3 )</td>
<td>( CO \rightarrow C + O )</td>
<td>-1.5</td>
<td>0.5</td>
<td>0.25</td>
<td>1.25</td>
</tr>
<tr>
<td>( CH_3 + H \rightarrow CH_4 )</td>
<td>( CO \rightarrow C + O )</td>
<td>-1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>( CHO \rightarrow CH + O )</td>
<td>( CHO \rightarrow CH + O )</td>
<td>-1</td>
<td>1</td>
<td>-0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>( CH_3 + H \rightarrow CH_4 )</td>
<td>( CH_3 + H \rightarrow CH_4 )</td>
<td>-1</td>
<td>1</td>
<td>-0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>( CH_2O \rightarrow CH_2 + O )</td>
<td>( CH_2O \rightarrow CH_2 + O )</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( CHO + H \rightarrow CH_2O )</td>
<td>( CHO + H \rightarrow CH_2O )</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( CH_2O \rightarrow CH_2 + O )</td>
<td>( CH_2O \rightarrow CH_2 + O )</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( CH_3 + H \rightarrow CH_4 )</td>
<td>( CH_3 + H \rightarrow CH_4 )</td>
<td>-1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Co(0001) surface

As shown in Figure 4.10a the transition from a positive to a negative apparent activation energy happens between 900 and 950 K. This corresponds well with the production plot shown early in Figure 4.8a. At 533 K the apparent activation energy is 298 kJ/mol.

Co(1121) surface

The stepped surface, for which the apparent activation energy is shown in Figure 4.10b, behaves similar to the terrace. At 533 K the value of 287 kJ/mol is slightly lower than for the terrace. Furthermore, the temperature optimum is exactly at 900 K.

Including lateral interactions

Figures 4.10c and 4.10d support the lowering of the temperature optimum. Both apparent activation energies go through zero at 200 K lower temperature. At 533 K the value
becomes 199 kJ/mol for the Co(0001) surface and 237 kJ/mol for the Co(1121) surface.

Analytical correlation with reaction orders

The apparent activation energies found at low temperatures may seem higher than expected. The potential energy diagrams do not show barriers above 250 kJ/mol, even when combining steps. Yet we find higher values in the computed apparent activation energies. This is because we need to take into account the enthalpy of adsorption. At low temperatures the CO coverage is so high that no free sites are available for dissociation. For the reaction to proceed we first need to invest energy to desorb CO. The apparent activation energy can be related to the reaction orders in the following way:

\[ E_{\text{act}}^{\text{app}} = E_{\text{act}}^{\text{ads}} + n_{\text{CO}} \left( \Delta H_{\text{ads}}^{\text{CO}} - 3RT \right) + n_{\text{H}_2} \left( \Delta H_{\text{ads}}^{\text{H}_2} - 3RT \right) \] (4.1)

Note that the correction with \(-3RT\) is a consequence of the \(T^3\) dependence in the Hertz-Knudsen desorption kinetics. Also \(E_{\text{act}}^{\text{ads}}\) is lumped in the case of hydrogen assisted CO dissociation. This means that if we know the adsorption enthalpies, we can determine
the lumped limiting barrier by experimentally measuring or computing the apparent activation energy and reaction orders. This is shown in Figure 4.10. The CO and H₂ contributions are subtracted from the total apparent activation energy, resulting in the contribution of the surface reactions. We see that although the apparent barriers change sign, the surface reaction contributions remains much more constant. When the surface contribution does differ, this indicates a change in rate limitation.

For the terrace surface without lateral interactions the surface barrier is 193 kJ/mol at 533 K. The lumped barriers for CHO and CH₂O dissociation correspond to 182 kJ/mol and 212 kJ/mol respectively on that surface. With the calculated barrier somewhere in between, we can expect both pathways to share rate limitation. With lateral interactions the Co(0001) surface barrier is 137 kJ/mol. With 191 kJ/mol and 138 kJ/mol as lumped CHO and CH₂O barriers, we now expect CH₂O dissociation to be the main pathway.

For the Co(1120) surface at 533 K we have surface barriers of 106 kJ/mol and 104 kJ/mol without and with lateral interaction respectively. The CO dissociation barriers are 106 kJ/mol and 111 kJ/mol without and with lateral interaction. From this we can expect that the interaction-free surface is purely CO dissociation limited. For the laterally corrected steps we expect sharing with another (non-dissociative) rate limitation.

4.2.4 (Thermodynamic) Degree of Rate Control

The most value of MKM comes from its Degree of Rate Control. With it we can establish which elementary reaction steps are controlling the rate in the methanation reaction. The results should be consistent with the expectations in earlier sections. Positive DRC values correspond to an increase of reaction rate when lowering or stabilizing the energy of the specific transition state.

Alternatively, the energies of specific surface species can be stabilized. As the transition states are kept at the same level, barriers from these species increase. Generally this leads to a lower rate and thus negative TDRC values.

Co(0001) surface

Controlling the rate on the terrace Co(0001) surface appear to be the hydrogen-assisted CO dissociation reactions. Figure 4.11a shows that in particular the CHO dissociation reaction is limiting for the high temperature range. At temperatures below the FT range the CH₂O dissociation is limiting. A minor contribution in the FT range is CHOH dissociation.

The TDRC values, shown in Figure 4.13a, are all zero except for hydrogen and CO. This corresponds to the fact that these two species determine the majority of the surface
coverage. We already established that the CO coverage is too high at low temperatures for fast CO dissociation. Stabilizing CO even more will slow it down further.

![Graph showing adsorption/desorption and reaction pathways](image)

**Figure 4.11**: Degree of rate control during the methanation reaction on Co(0001) at 465 mbar pressure with a H₂/CO ratio of 5, with and without lateral interactions.

Co(1121) surface

In contrast to the terrace surface, Figure 4.12a shows direct CO-dissociation as rate limiting for the whole FT range. Only at very high temperatures the termination reactions start to compete in rate control.

In Figure 4.13b the major TDRC contributions are again from hydrogen and CO. However, in the FT range the contribution of hydrogen has disappeared. This is in line with
FIGURE 4.12: Degree of rate control during the methanation reaction on Co(1121) at 465 mbar pressure with a H₂/CO ratio of 5, with and without lateral interactions.

After adding lateral interactions, the rate control plots are totally different. This is very interesting, and explains all our previous results.

Including lateral interactions

After adding lateral interactions, the rate control plots are totally different. This is very interesting, and explains all our previous results.

For the terrace surface with lateral interactions, we can see in Figure 4.11b that not CHO, but CH₂O dissociation is the main limiting step. A minor rate limitation is present in the hydrogenation step towards CH₂O. At higher FT temperatures CHOH
dissociation is a minor contribution to the C\textsubscript{1} formation.

For the stepped surface, Figure 4.12b shows that multiple reaction steps are competing. The main C\textsubscript{1} formation step is still direct CO dissociation. However, water formation and CH\textsubscript{2}/CH\textsubscript{3} hydrogenation are sharing the rate limitation. Interesting as well is the negative DRC in proton migration during the water formation. This negative value is an indication that oxygen atoms can go through multiple hydrogenation/migration cycles before leaving as water.

Figures 4.13c and 4.12b again show only major contributions from CO and hydrogen. As expected the CO TDRC value again correlates with its coverage. The hydrogen TDRC value is now somewhat more negative for the terrace surface. For the stepped surface the value has dropped even more. For the Co(0001) the cause can be found in the change from CHO to CH\textsubscript{2}O dissociation as rate limiting. CH\textsubscript{2}O is hydrogenated twice, and thus favors a lower thermodynamic stability of free hydrogen. For the Co(1121) surface multiple hydrogenation limitations have appeared. Thus the forward barriers are sensitive to free hydrogen stability.
4.2.5 Transient Kinetic Analysis

Steady State Isotopic Transient Kinetic Analysis (SSITKA) and Chemical Transient Kinetic Analysis (CTKA) were simulated using the MKMCXX software. Qualitatively these simulations show similarities to experimental results. However the time scales for the transient MKM results do not correspond well to experiments. Due to this the transient nature of the actual experiments is difficult to capture. Figure 4.14 shows a qualitative impression on the combined SSITKA and CTKA results found on the laterally corrected Co(1121) surface. The results are similar in form for the other surfaces.

\[ ^{13}\text{CO} \rightarrow ^{12}\text{CO}/\text{H}_2 \]  Labeled methane production spikes before normal methane rises. The time scale for this process is much shorter than the time it takes to fully regain isotopic steady state. We also see that normal methane peaks. We expect this to be an effect of the dissociation equilibrium before the switch. Under this condition the atomic carbon and oxygen coverages will be higher than under syngas. After introduction of hydrogen these atoms are quickly hydrogenated. A higher than steady state amount of free sites is created temporarily. This speeds up dissociation of the newly adsorbed CO.

\[ ^{12}\text{CO}/\text{H}_2 \rightarrow ^{13}\text{CO}/\text{H}_2 \]  Normal methane quickly switches with labeled methane. Compared to experimental timescales, the simulation shows an almost instantaneous switch.
\[ ^{13}\text{CO}/\text{H}_2 \rightarrow \text{H}_2 \] During the desorption of CO the surface regains free sites. Due to this the methane production greatly spikes. Actually the simulated spikes are multiple orders of multitude higher than the steady state turnover. Again this is an effect of the different timescales between experimental and simulated switches.
4.3 Towards Molecular Dynamics of cobalt nanoparticles

We are able to compute reaction barriers on surfaces with DFT and calculate reaction rates with microkinetics. But we need to do something else to know which surfaces are actually present on a nanoparticle during FT. With a reactive molecular dynamics force field we wish to see how the surface morphology changes under adsorption of atoms and molecules. First we need to have a correctly parameterized force field.

An example of what happens with an incorrectly parameterized force field can be seen in Figure 4.15a. For a periodic cobalt lattice the HCP structure should be favorable. However, the incorrect force field distorts the structure to a combination of HCP and BCC packing. The re-optimized force field retains the original HCP packing. For more simulations with this force field, please refer to [65].

![Incorrect force field vs. Re-optimized force field](image)

**Figure 4.15:** Molecular dynamics simulation results starting from a periodic cobalt HCP crystal packing. The incorrect force field distorts the structure to a combination of HCP and BCC packing. The re-optimized force field retains the original HCP packing.

### 4.3.1 Generation of a DFT training set

The re-optimized force field is build out of a training set containing cobalt clusters and slabs. Also calculations on carbon are included. If we want to go further in modeling FT intermediates, we have to expand the training set. We might encounter many different bonding configurations of adsorbates on a structure. Therefore we would like to procedurally generate a representative set of those configurations. To do this we decided to write a C++ program called *Aequor*. 
Why choose C++ as a programming language?

It seems fitting to use a language capable of procedural programming to handle procedural generation of structures. In this way we can reuse certain procedures or routines to create the many subtly different structures. Actually we do not use the procedural paradigm, but we like to use a similar paradigm called object-oriented programming. For example we make an atom object and a structure object. The structure object is then build from atom objects. C++ is a language specifically for object-oriented programming.

The second reason to use C++ is speed. As a compiled program, execution is much faster compared to interpreted scripts. This is important as the amount of possible adsorbate configurations is huge. Making a selection out of all possible configurations is not something we could manually do in a lifetime. As a matter of fact, let us consider the Co(O001) surface. In our DFT calculations we used a 3x3 unit cell. Every unit cell has an atop adsorption site. A bridge mode is available in all three directions. Finally two threefold sites are available. By taking 9 unit cells we therefore have $9 \times 6 = 54$ possible adsorption sites. As each site can have one or zero adsorbates, this gives $2^{54} \approx 1.8 \times 10^{16}$ possible combinations. Obviously the majority of these combinations has atoms overlapping or is just a translation or rotation of a previous combination. With the speed of C++ we can use smart tricks to discard redundant combinations and greatly reduce this number.

Finding surface atoms of a metal structure

_Aequor_ reads in _POSCAR_ and _POTCAR_ files as used in VASP. Figure 4.16 shows a periodic metal slab and a small cluster that can be read. The atom properties and coordinates of a metal structure are loaded into memory. The first step is to determine which atoms are part of the surface. This can be done in two ways. One way is based on coordination numbers, selecting all atoms with less then 12 neighbors. This is especially useful for placing adsorbates around a nanoparticle. For slabs we use a somewhat other method. Slabs are commonly oriented to be periodic in the xy-plane, with vacuum positioned above and below in the z-direction. To get the upper surface atoms we imagine looking down on the structure. We then select those atoms which are not blocked off by atoms above them.

Finding adsorption sites from surface atoms

Atop sites are the easiest to find. Each surface atom gives one atop site. We select a surface atom and center on it. Using the locations of the nearest neighbors we
can determine the direction of least steric repulsion. For a terrace surface this will generally be the z-direction. We then move a given distance in this direction. This is the location of the atop site. We can see this in Figure 4.17a.

**Bridge sites** can be found from the unique pairs of surface atoms. We look for pairs that are less than a given distance apart. For such a pair we put ourself in between and look at the nearest neighbors of the atom pair to find the orientation. Again we move in the direction of this orientation and we have the location of a bridge site. This is shown in Figure 4.17b.

**Threefold sites** are found similar to bridge sites, but now we need to look at unique groups of three surface atoms. The condition is now that all three atoms are close enough to each other. Figure 4.17c shows such a site.

**Fourfold sites** are found from unique groups of four atoms. Not all groups of four connected surface atoms are valid for a fourfold site; we also make sure that the diagonal distances are not too large. Figure 4.17d shows CO adsorbed on a fourfold site.

**Generating possible combinations**

The amount of combinations exponentially increases with the amount of available sites. Therefore we reduce the amount of different structures in several ways:

- A minimum amount of adsorbates can be defined.
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(A) Atop site.  (B) Bridge site.  (C) Threefold site.  (D) Fourfold site.

FIGURE 4.17: Aequor was used to place a CO adsorbate on various sites on a small metal cluster.

- A maximum amount of adsorbates can be defined.
- Combinations with adsorbate atoms too close to each other are discarded.
- Combinations that are translations of a previous combination are discarded.

Placing adsorbates

Adsorbates can be added either by choosing a specific element like carbon, or defining a custom group like CH₃ in an XYZ file. Atomic adsorbates are placed directly at the coordinates defined by the sites. For multi-atomic adsorbates we need to give it the correct orientation. The origin of the coordinates in the XYZ file is placed in the
site. The z-axis of the adsorbate’s coordinate system is then rotated towards the site orientation. This is done with a quaternion rotation matrix. A good example of this can be seen in Figure 4.18b, where all atop sides are loaded with CO. We can see that all adsorbates are correctly rotated by the quaternion operations.

![Figure 4.18: A screenshot of the Aequor visualizer. The user can browse through the different structures.](image)

**(A) Empty.**  
**(B) CO on atop sites.**

Exporting structures

All different adsorbate configurations can be directly exported to be used as VASP input files themselves. We integrated a visualizer written by Ivo Filot to show the different structures on screen. Figure 4.18 shows this visualizer. While browsing through the structures in the visualizer, the user can separately export structures of interest. This is particularly helpful when preparing structures with only one or two adsorbates, like those earlier in this thesis.
Chapter 5

General Discussion

Using the integrated approach of Density Functional Theory and Microkinetic Modeling we have tried to elaborate upon the catalytic mechanism behind Fischer-Tropsch synthesis. Comparing the terrace Co(0001) surface to the stepped Co(1121) surface we found different possible mechanisms. Furthermore, we have found the effects of lateral interactions and the deuterium isotope switch to be substantial.

We must realize the difficulty when relating real experiments to the calculations done in this project. A crystal may express different surfaces during reaction conditions, with varying surface coverages. In our calculations we established the most favorable adsorption modes under low coverage. Probably the surface topology differs enough under high CO coverage for these favorable adsorption modes to change.

Just using a lateral interaction correction will not be enough. Also it is difficult to establish how much lateral interaction is actually present. This is one of the major drawbacks in the current MKM method; each dataset is valid only for a specific amount of lateral interactions. Previous attempts at incorporating a dynamic lateral interaction correction have been only partially successful. The additional degrees of freedom in the differential equations result in an impractical increase of computational time.

Although the actual lateral interactions are unknown, we have shown in this work how the surface reactions might change under the influence of those interactions. For the terrace surface the dissociation of the C-O bond takes place assisted by hydrogen. For the stepped surface the dominant mechanism is direct CO dissociation. These observations do not change when adding lateral interactions.

The question however remains whether the stepped or the terrace surface contributes most to the methanation and FT rates. We have seen that in the FT temperature range the production of methane is much higher on the stepped surface. Although carbon coverage only appears on high temperatures on the stepped surface, this is an indication that FT rates will also be high on that surface.
Chapter 5. General Discussion

Let us consider a cobalt nanoparticle larger than 10 nm. Under non-reactive environments we expect terrace surfaces to be much more represented than stepped surfaces. As such, the majority of terraces may be able to produce more product than the minority of steps. Of course under reactive conditions the steps might be formed in-situ. We do not know the magnitude of this morphology change and its effect on the terrace versus steps ratio.

Another interesting consideration is a cooperation between the two surfaces. Relatively, the terrace surface is better at water removal, whereas the stepped surface has a lower barrier for termination of methane. If $\text{CH}_x$ and $\text{OH}_x$ species can migrate from the steps to the terrace, the water removal rate can be enhanced while methane production is suppressed. Correspondingly chain growth should increase. Unfortunately we do not know the energy landscape of the C-C coupling reactions yet.

We might hypothesize that indeed C$_1$ fragments are formed on the active steps and grow on the terrace. As atomic adsorption energies are higher on the steps the migration to the terrace will be endothermic. As a result carbon species might build up in the active sites. This would explain catalyst deactivation through excessive carbon deposition. At the same time the hydrogenation of this carbon could explain extra methane production. Alternatively we could consider extra methane production to be from the terrace. C$_1$ fragments formed from the active steps will have a higher probability to meet than those produced on the larger less active terraces. The separated C$_1$ fragments on the terrace could then be more prone to form methane.

Doing reactive molecular dynamics on cobalt nanoparticles or slabs could give us insight in surface reconstructions and C$_1$ mobility. We have seen though that an incomplete parameterization can give unrealistic reconstructions. An example being the introduction of a BCC phase in a large cobalt slab.

We are developing the C++ program Aequor to generate an appropriate training set. At the moment the program is already useful as a tool to help make DFT input structures. Some of the adsorbate structures calculated in this project were made with earlier versions of Aequor. The program still has a bottleneck we need to tackle before it can be used for training set generation. A huge amount of redundant adsorbate combinations are discarded during structure generation. However still too many structures are possible, much more than feasible to be calculated with DFT. We think that this can be fixed. First, we should also remove rotationally equivalent structures. Secondly, we could skip structures where adsorbates are grouped close together. In this way we would only calculate high entropic configurations that we are more likely to observe in MD.
Chapter 6

Conclusions

With our DFT calculations we have shown that CO strongly adsorbs on the catalyst surface. The dissociation and subsequent hydrogenation of the CO is a mostly an endothermic pathway. As such we expect CO to be a major contributor to the surface coverage. MKM simulations have shown this to be the case under FT temperatures. Adding lateral interactions destabilizes the adsorbed H₂ and CO. As a result, the temperature at which most of the surface is empty can drop several hundred degrees. TOF’s at methanation conditions are in the order of 10⁻⁵ s⁻¹ and 10⁻³ s⁻¹. This is for the terrace Co(0001) and stepped Co(1121) surfaces respectively, and includes lateral interaction. Without this lateral interaction the TOF’s are 6 and 4 orders of magnitude lower, which is unrealistically low.

The main pathway for monomer formation on the terrace is hydrogen assisted CO dissociation. In particular via CHO and CH₂O dissociation. With increasing lateral interactions the CH₂O pathways becomes more favorable.

For the stepped surface the main pathway is direct CO dissociation. Dissociation is fast enough to be competing with termination and water removal. Adding lateral interactions speeds up this dissociation, causing a stronger limitation in termination and water removal.

The reaction orders found in the MKM simulations agree with the analytical expressions corresponding to the found rate limitations. In the FT temperature range the CO order is negative. The hydrogen order is zero for the CO dissociation limited steps without lateral interaction. For the other surfaces the hydrogen order is positive.

Using the reaction orders, we can find the contributions to the apparent activation energy. By subtraction the adsorption contributions, we find the surface reaction contribution. This contribution corresponds to the lumped rate limiting barrier.

SSITKA and CTKA results can be reproduced qualitatively, though not on the same
timescale. Extra methane is produced for an extremely short time and in amounts several orders of magnitude higher than under steady state.

By alteration of the Hessian matrix the isotope effect of switching hydrogen for deuterium was calculated. The changes in the energy landscape are not larger than 5 kJ/mol, which is small compared to the lateral interactions. However, the corrections to the Hertz-Knudsen kinetics will result in a decreased hydrogen coverage. The latter can be correlated to a lower rate via the reaction order. Due to lower prefactors for hydrogenation reactions, the rate will further drop in conditions of hydrogenation limitation.

Molecular dynamics with a fitted ReaxFF forcefield show that wrong parameters can easily result in unrealistic results. An earlier version of the forcefield caused transitions to a BCC crystal packing in cobalt particles. Further improvements of the force field removed this behavior, retaining the correct HCP structure. Our C++ program Aequor shows promising development towards creating a training set for an even better force field.

Without the molecular dynamics approach we cannot fully exclude either terrace or steps as major source of FT monomer species. From this work we do hypothesize in favor of the direct CO dissociation on the cobalt steps.
Chapter 7

Outlook

We have found that it is important to include lateral interactions. Therefore we should do additional DFT calculations with a varying amount of spectator CO. Then we can do a quantitative comparison with our current dataset. These calculations also serve a dual purpose as we can use them to train the ReaxFF force field.

With a quantitative measure of lateral interactions, we can try again to incorporate this effect in the MKM code. Increasing ODE solving time is inevitable, but the lateral interactions are too important to neglect.

Obviously we are interested in the exact barriers of C-C bond formations on cobalt terraces versus the steps. By investigating these reactions we can proceed towards microkinetic modeling of chain formation on cobalt. Combining multiple surfaces and sites into one microkinetic simulation will then show us the true origin of C1 species.

Another important addition to the MKM method is a reactor model. Re-adsorption effects may cause isomerised or branched chains to be formed. By introduction of a variable (not infinite) space velocity we might be able to better capture the experimental SSITKA and CTKA effects. In addition to concentration effects a plug flow reactor model can also provide information on temperature gradients.

Excellent work on making a reactor model has already been done by Samantha Basalo Vazquez during her bachelor. Her wrapper program is currently being used for workshops during master courses and to complement our experimental FT research.

The other branch of our integrated method will be that of reactive molecular dynamics. We have discussed that morphology changes under reactive conditions will change the expression of terrace and stepped surfaces. Earlier projects involving Wulff constructions have shown this to be a major effect. Molecular dynamics will eventually make this quantitative.

Development of the C++ program Aequor has shown great progress. Nevertheless, for use as a training set system generator it is not yet complete. First, we should remove
rotationally equivalent structures during procedural generation. Secondly, we should skip low entropic configurations. With the amount of structures limited to a viable number, we can start building the actual training set.

Here great preliminary work has been done by Joost van der Meijs during his bachelor. Combining this work with our own Markov chain Monte Carlo fitting code we hope to make a reactive force field for all C\textsubscript{1} intermediates. First we will look at the effects of CO.
Appendix A

Elementary reactions for methanation

TABLE A.1: Parameter set for adsorption and desorption. The prefactors $\nu$ are calculated by using these parameters in the Hertz-Knudsen kinetics.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>area/site $\sigma$ mass $\theta_{\text{rot}}$</th>
<th>$S$</th>
<th>$\nu_{\text{ads}}^{333K}$</th>
<th>$\nu_{\text{des}}^{333K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + * ⇌ CO*</td>
<td>$1 \times 10^{-19}$ 28 2.8 1 1</td>
<td>6.82 $\times 10^{8}$</td>
<td>1.04 $\times 10^{17}$</td>
<td></td>
</tr>
<tr>
<td>H$_2$ + 2* ⇌ 2H*</td>
<td>$1 \times 10^{-19}$ 2 88 2 1</td>
<td>2.55 $\times 10^{8}$</td>
<td>1.18 $\times 10^{14}$</td>
<td></td>
</tr>
<tr>
<td>D$_2$ + 2* ⇌ 2D*</td>
<td>$1 \times 10^{-19}$ 4 44 2 1</td>
<td>1.80 $\times 10^{8}$</td>
<td>4.71 $\times 10^{14}$</td>
<td></td>
</tr>
<tr>
<td>O$_2$ + 2* ⇌ 2O*</td>
<td>$1 \times 10^{-19}$ 32 2.1 2 1</td>
<td>6.38 $\times 10^{8}$</td>
<td>7.89 $\times 10^{12}$</td>
<td></td>
</tr>
<tr>
<td>H$_2$O + * ⇌ H$_2$O*</td>
<td>$1 \times 10^{-19}$ 18 22 2 1</td>
<td>8.51 $\times 10^{8}$</td>
<td>4.23 $\times 10^{15}$</td>
<td></td>
</tr>
<tr>
<td>D$_2$O + * ⇌ D$_2$O*</td>
<td>$1 \times 10^{-19}$ 18 22 2 1</td>
<td>8.07 $\times 10^{8}$</td>
<td>8.63 $\times 10^{15}$</td>
<td></td>
</tr>
<tr>
<td>CH$_4$ + * ⇌ CH$_4$</td>
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<td>9.02 $\times 10^{8}$</td>
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</tr>
<tr>
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TABLE A.2: Zero point energy corrected desorption energies in kJ/mol.

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<tr>
<th>Reaction</th>
<th>Co(0001)</th>
<th>Co(0001)</th>
<th>Co(1121)</th>
<th>Co(1121)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + * ⇌ CO*</td>
<td>164</td>
<td>111</td>
<td>166</td>
<td>113</td>
</tr>
<tr>
<td>H$_2$ + 2* ⇌ 2H*</td>
<td>99</td>
<td>42</td>
<td>86</td>
<td>29</td>
</tr>
<tr>
<td>D$_2$ + 2* ⇌ 2D*</td>
<td>101</td>
<td>44</td>
<td>88</td>
<td>31</td>
</tr>
<tr>
<td>O$_2$ + 2* ⇌ 2O*</td>
<td>498</td>
<td>393</td>
<td>529</td>
<td>424</td>
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<tr>
<td>H$_2$O + * ⇌ H$_2$O*</td>
<td>25</td>
<td>35</td>
<td>51</td>
<td>62</td>
</tr>
<tr>
<td>D$_2$O + * ⇌ D$_2$O*</td>
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<td>35</td>
<td>52</td>
<td>63</td>
</tr>
<tr>
<td>CH$_4$ + * ⇌ CH$_4$</td>
<td>2</td>
<td>-81</td>
<td>6</td>
<td>-77</td>
</tr>
<tr>
<td>CD$_4$ + * ⇌ CD$_4$</td>
<td>2</td>
<td>-81</td>
<td>6</td>
<td>-77</td>
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</table>
Table A.3: Parameter set for surface reactions on Co(O001). $v_{\text{forw}}$ and $v_{\text{back}}$ are the forward and backward pre-exponential factors as calculated via the Hessian. $E_{\text{act}}^\text{forw}$ and $E_{\text{act}}^\text{back}$ are the ZPE corrected forward and backward reaction barriers. All reaction barriers are given with reference to the most stable state found for each species, i.e. migration corrections are taken into account.

<table>
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<tr>
<th>Reaction</th>
<th>$v_{\text{forw}}$</th>
<th>$v_{\text{back}}$</th>
<th>$E_{\text{act}}^\text{forw}$</th>
<th>$E_{\text{act}}^\text{back}$</th>
<th>$\Delta E_{\text{rec}}$</th>
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<td>119</td>
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<td>CHO + H ⇌ CH₂O</td>
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<td>33</td>
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<tr>
<td>CHO + H ⇌ CHOH</td>
<td>7.66 x 10^{13}</td>
<td>7.40 x 10^{12}</td>
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<td>51</td>
<td>51</td>
</tr>
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<td>72</td>
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<td>CHO + H ⇌ CH₂OH</td>
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<td>40</td>
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<td>CH₂O + H ⇌ CH₂OH</td>
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<td>1.40 x 10^{12}</td>
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<td>58</td>
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<tr>
<td>C + H ⇌ CH</td>
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<td>-19</td>
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<tr>
<td>CO + C + O</td>
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<td>1.64 x 10^{13}</td>
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Lateral corrections

<table>
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<th>$v_{\text{back}}$</th>
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<th>$E_{\text{act}}^\text{back}$</th>
<th>$\Delta E_{\text{rec}}$</th>
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<td>8.70 x 10^{12}</td>
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<td>-5</td>
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<tr>
<td>CH₃ + H ⇌ CH₄</td>
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<td>1.51 x 10^{11}</td>
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<td>92</td>
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<td>CO + C + O</td>
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<td>1.64 x 10^{13}</td>
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<td>158</td>
<td>66</td>
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<tr>
<td>COH + C + OH</td>
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<td>2.07 x 10^{13}</td>
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<td>145</td>
<td>5</td>
</tr>
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<td>CHO + CH + O</td>
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Lateral corrections
Table A.4: Parameter set for surface reactions on Co(1121). $\mu_{\text{forw}}$ and $\mu_{\text{back}}$ are the forward and backward pre-exponential factors as calculated via the Hessian. $E_{\text{act}}^{\text{forw}}$ and $E_{\text{act}}^{\text{back}}$ are the ZPE corrected forward and backward reaction barriers. All reaction barriers are given with reference to the most stable state found for each species, i.e. migration corrections are taken into account.

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<th>$E_{\text{act}}^{\text{forw}}$</th>
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<th>Lateral corrections</th>
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<td>102</td>
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<td>18</td>
<td>78</td>
<td>182</td>
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<td>CHO + H ⇌ CH$_2$O</td>
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<td>2.26 x 10^{13}</td>
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<td>32</td>
<td>42</td>
<td>101</td>
</tr>
<tr>
<td>CHO + H ⇌ CHOH</td>
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<td>6.46 x 10^{12}</td>
<td>4.13 x 10^{12}</td>
<td>147</td>
<td>77</td>
<td>71</td>
<td>114</td>
</tr>
<tr>
<td>COH + H ⇌ CHOH</td>
<td></td>
<td>4.73 x 10^{12}</td>
<td>2.21 x 10^{13}</td>
<td>74</td>
<td>28</td>
<td>47</td>
<td>70</td>
</tr>
<tr>
<td>CHOH + H ⇌ CH$_2$OH</td>
<td></td>
<td>2.44 x 10^{12}</td>
<td>5.63 x 10^{11}</td>
<td>63</td>
<td>50</td>
<td>13</td>
<td>42</td>
</tr>
<tr>
<td>CH$_2$O + H ⇌ CH$_2$OH</td>
<td></td>
<td>1.20 x 10^{14}</td>
<td>1.74 x 10^{13}</td>
<td>81</td>
<td>40</td>
<td>41</td>
<td>42</td>
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<tr>
<td>C + H ⇌ CH</td>
<td></td>
<td>7.99 x 10^{12}</td>
<td>5.19 x 10^{12}</td>
<td>60</td>
<td>37</td>
<td>23</td>
<td>73</td>
</tr>
<tr>
<td>CH + H ⇌ CH$_2$</td>
<td></td>
<td>2.12 x 10^{13}</td>
<td>1.22 x 10^{13}</td>
<td>77</td>
<td>61</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>CH$_2$ + H ⇌ CH$_3$</td>
<td></td>
<td>3.39 x 10^{13}</td>
<td>1.57 x 10^{12}</td>
<td>81</td>
<td>68</td>
<td>13</td>
<td>20</td>
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<tr>
<td>CH$_3$ + H ⇌ CH$_4$</td>
<td></td>
<td>5.60 x 10^{12}</td>
<td>5.91 x 10^{12}</td>
<td>78</td>
<td>68</td>
<td>10</td>
<td>10</td>
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<tr>
<td>CO ⇌ C + O</td>
<td></td>
<td>4.96 x 10^{10}</td>
<td>1.15 x 10^{12}</td>
<td>106</td>
<td>108</td>
<td>-2</td>
<td>111</td>
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<tr>
<td>COH ⇌ C + OH</td>
<td></td>
<td>2.43 x 10^{12}</td>
<td>6.50 x 10^{12}</td>
<td>28</td>
<td>116</td>
<td>-88</td>
<td>33</td>
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<tr>
<td>CHO ⇌ CH + O</td>
<td></td>
<td>2.12 x 10^{12}</td>
<td>2.14 x 10^{12}</td>
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<td>140</td>
<td>-58</td>
<td>83</td>
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<tr>
<td>CH$_2$O ⇌ CH$_2$ + O</td>
<td></td>
<td>5.52 x 10^{12}</td>
<td>1.53 x 10^{12}</td>
<td>66</td>
<td>150</td>
<td>-84</td>
<td>47</td>
</tr>
<tr>
<td>CHOH ⇌ CH + OH</td>
<td></td>
<td>1.40 x 10^{13}</td>
<td>5.19 x 10^{12}</td>
<td>47</td>
<td>159</td>
<td>-112</td>
<td>49</td>
</tr>
<tr>
<td>CH$_2$OH ⇌ CH$_2$ + OH</td>
<td></td>
<td>1.79 x 10^{13}</td>
<td>1.66 x 10^{13}</td>
<td>43</td>
<td>151</td>
<td>-108</td>
<td>47</td>
</tr>
<tr>
<td>O + H ⇌ OH</td>
<td></td>
<td>3.54 x 10^{13}</td>
<td>8.37 x 10^{12}</td>
<td>102</td>
<td>86</td>
<td>16</td>
<td>102</td>
</tr>
<tr>
<td>OH + H ⇌ H$_2$O</td>
<td></td>
<td>8.30 x 10^{12}</td>
<td>6.83 x 10^{9}</td>
<td>153</td>
<td>90</td>
<td>63</td>
<td>91</td>
</tr>
<tr>
<td>OH + OH ⇌ H$_2$O + O</td>
<td></td>
<td>1.39 x 10^{12}</td>
<td>4.85 x 10^{9}</td>
<td>53</td>
<td>5</td>
<td>47</td>
<td>40</td>
</tr>
</tbody>
</table>
Appendix B

Langmuir-Hinshelwood Kinetics

Following section 2.1.2 we can set up Langmuir-Hinshelwood mechanisms to analytically describe our reaction rates under steady state. We will do this for the various possible mechanisms and corresponding rate limiting steps. The mechanisms can be differentiated according to the dominant dissociation reaction (d1-d6 in Table B.1). For each mechanism we can have multiple rate limiting steps. These can be: hydrogenation prior to dissociation, dissociation itself, and hydrogenation after dissociation. We will now work out some of those mechanisms.

Table B.1: Langmuir-Hinshelwood reaction reference.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + * ⇌ CO*</td>
<td>(C0)</td>
</tr>
<tr>
<td>H2 + 2* ⇌ 2H*</td>
<td>(H2)</td>
</tr>
<tr>
<td>CO* + H* ⇌ COH* + *</td>
<td>(a1)</td>
</tr>
<tr>
<td>CO* + H* ⇌ CHO* + *</td>
<td>(a2)</td>
</tr>
<tr>
<td>CHO* + H* ⇌ CH2O* + *</td>
<td>(a3)</td>
</tr>
<tr>
<td>CHO* + H* ⇌ CHOH* + *</td>
<td>(a4)</td>
</tr>
<tr>
<td>COH* + H* ⇌ CHOH* + *</td>
<td>(a5)</td>
</tr>
<tr>
<td>CHOH* + H* ⇌ CH2OH* + *</td>
<td>(a6)</td>
</tr>
<tr>
<td>CH2O* + H* ⇌ CH2OH* + *</td>
<td>(a7)</td>
</tr>
<tr>
<td>C* + O* ⇌ C* + OH*</td>
<td>(d1)</td>
</tr>
<tr>
<td>CHO* ⇌ CH* + O*</td>
<td>(d2)</td>
</tr>
<tr>
<td>CH2O* ⇌ CH2* + O*</td>
<td>(d3)</td>
</tr>
<tr>
<td>CHO* ⇌ CH* + OH*</td>
<td>(d4)</td>
</tr>
<tr>
<td>CH2OH* ⇌ CH2* + OH*</td>
<td>(d5)</td>
</tr>
<tr>
<td>C* + H* ⇌ CH* + *</td>
<td>(h1)</td>
</tr>
<tr>
<td>CH* + H* ⇌ CH2* + *</td>
<td>(h2)</td>
</tr>
<tr>
<td>CH2* + H* ⇌ CH3* + *</td>
<td>(h3)</td>
</tr>
<tr>
<td>CH3* + H* ⇌ CH4 + 2*</td>
<td>(h4)</td>
</tr>
<tr>
<td>O* + H* ⇌ OH* + *</td>
<td>(o1)</td>
</tr>
<tr>
<td>OH* + H* ⇌ H2O + 2*</td>
<td>(o2)</td>
</tr>
</tbody>
</table>
Direct CO dissociation limitation

The most simple case is the direct CO dissociation mechanism (d1) with its limiting reaction the dissociation itself. In the zero-conversion limit, the reaction rate can be given as

\[ r = k_{d1}^{+} \theta_{CO} \theta_{*}, \quad (B.1) \]

with

\[ \theta_{CO} = K_{CO} P_{CO} \theta_{*}. \quad (B.2) \]

Conservation of sites gives

\[ \theta_{*} = 1 - \theta_{CO} - \theta_{H}, \quad (B.3) \]

with

\[ \theta_{H} = \sqrt{K_{H_{2}} P_{H_{2}} \theta_{*}}. \quad (B.4) \]

from which follows that

\[ \theta_{*} = \frac{1}{1 + K_{CO} P_{CO} + \sqrt{K_{H_{2}} P_{H_{2}}}}, \quad (B.5) \]

and the rate equals

\[ r = \frac{k_{d1}^{+} K_{CO} P_{CO}}{(1 + K_{CO} P_{CO} + \sqrt{K_{H_{2}} P_{H_{2}}})^2}. \quad (B.6) \]

Direct CO dissociation with hydrogenation limitation

Now lets see what happens if we want the rate for the direct CO dissociation mechanism (d1), but with CH₃ hydrogenation (h4) as rate limiting. We can do this in two different ways. Oxygen can be removed from the surface in an equilibrium with gas phase water. Alternatively, we can take both CH₃ hydrogenation and the water removal path as irreversible.

First we will consider a water equilibrium:

\[ \theta_{O} = \frac{P_{H_{2}O} \theta_{*}}{K_{o1} K_{o2} \theta_{H}^{2}} = \frac{P_{H_{2}O}}{K_{o1} K_{o2} K_{H_{2}} P_{H_{2}} \theta_{*}} \quad (B.7) \]

\[ \theta_{CO} = \frac{K_{d1} \theta_{CO} \theta_{*}}{\theta_{O}} = \frac{K_{d1} K_{o1} K_{o2} K_{H_{2}} P_{H_{2}} K_{CO} P_{CO} \theta_{*}}{P_{H_{2}O}} \quad (B.8) \]

\[ \theta_{CH_{3}} = \frac{K_{h1} K_{h2} K_{h3} \theta_{CH_{3}}^{3} \theta_{H}^{2}}{\theta_{*}^{2}} = \frac{K_{d1} K_{h1} K_{h2} K_{h3} K_{o1} K_{o2} (K_{H_{2}} P_{H_{2}})^{2.5} K_{CO} P_{CO} \theta_{*}}{P_{H_{2}O}} \quad (B.9) \]

\[ r = k_{h1}^{+} K_{d1} K_{h1} K_{h2} K_{h3} K_{o1} K_{o2} (K_{H_{2}} P_{H_{2}})^{2.5} K_{CO} P_{CO} \theta_{*}^{2}. \quad (B.10) \]
with conservation of sites

\[ \theta_* = 1 - \theta_{CO} - \theta_{H} - \theta_{C} - \theta_{CH} - \theta_{CH_2} - \theta_{OH} \]  \hspace{1cm} (B.11)

and usage of the abc-formula (to include \( \theta_{O} \) and \( \theta_{OH} \)), we get:

\[ \theta_* = \frac{1}{2} \theta_{*-O-OH} + \frac{1}{2} \sqrt{\theta_{*-O-OH}^2 - 4 \left( \frac{K_{CO}P_{H_2O}}{P_{H_2}} + \frac{K_{OH}P_{H_2O}}{\sqrt{P_{H_2}}} \right)} \]  \hspace{1cm} (B.12)

with

\[ \theta_{*-O-OH} = 1 - K_{CO}P_{CO} - \sqrt{K_{H_2}P_{H_2}} \]

\[ \frac{K_{CH}P_{H_2}P_{CO}}{P_{H_2O}} - \frac{K_{CH_2}P_{H_2}^2P_{CO}}{P_{H_2O}} - \frac{K_{CH_3}P_{H_2}^3P_{CO}}{P_{H_2O}} \]  \hspace{1cm} (B.13)

\[ K_C = K_{d1}K_{o1}K_{o2}K_{H_2}K_{CO} \]  \hspace{1cm} (B.14)

\[ K_{CH} = K_{d1}K_{h1}K_{o1}K_{o2}K_{H_2}^{1/2}K_{CO} \]  \hspace{1cm} (B.15)

\[ K_{CH_2} = K_{d1}K_{h1}K_{h2}K_{o1}K_{o2}K_{H_2}^2K_{CO} \]  \hspace{1cm} (B.16)

\[ K_{CH_3} = K_{d1}K_{h1}K_{h2}K_{h3}K_{o1}K_{o2}K_{H_2}^{2.5}K_{CO} \]  \hspace{1cm} (B.17)

\[ K_{O} = \frac{1}{K_{o1}K_{o2}K_{H_2}} \]  \hspace{1cm} (B.18)

\[ K_{OH} = \frac{1}{K_{o2}\sqrt{K_{H_2}}} \]  \hspace{1cm} (B.19)

In our microkinetic calculations we set the partial pressures of the products to zero to have an initial rate experiment. Equation B.10 goes to infinite at zero water pressure, so it is not appropriate to our system. Therefore it is better to set water formation as irreversible. Doing this with \( CH_3 + H (h4) \) and \( OH + H (o2) \) as limiting gives us the following equality:

\[ r = k_{h4}^+\theta_{CH_3}\theta_H = k_{o2}^+\theta_{OH}\theta_H \]  \hspace{1cm} (B.20)

The oxygen coverage can now be found as follows:

\[ \theta_{CH_3} = \frac{K_{h1}K_{h2}K_{h3}\theta_C\theta_H^3}{\theta_*^3} \]  \hspace{1cm} (B.21)

\[ \theta_{OH} = \frac{K_{o1}\theta_O\theta_H}{\theta_*} \]  \hspace{1cm} (B.22)

\[ \frac{\theta_{CH_3}^+}{\theta_{CH_3}} = \frac{k_{h4}^+}{k_{h4}} = \frac{K_{h1}K_{h2}K_{h3}\theta_C\theta_H^2}{K_{o1}\theta_O\theta_H^2} \]  \hspace{1cm} (B.23)
\[ \theta_c = \frac{K_{o1}k_{o2}^+}{K_{h1}K_{h2}K_{h3}k_{h4}^+} \theta_0 \theta_*^2 \frac{\theta_0^2}{\theta_*^2} \]  
\[ \theta_o = \frac{K_{d1}\theta_{CO}\theta_*}{\theta_c} = \frac{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+}{K_{o1}k_{o2}^+} \theta_{CO}\theta_*^2 \frac{\theta_0^2}{\theta_*^2} = \sqrt{\frac{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+}{K_{o1}k_{o2}^+}} \theta_{CO}\theta_*^2 \frac{\theta_0^2}{\theta_*^2} \]  
Which makes:
\[ \theta_C = \sqrt{\frac{K_{d1}K_{o1}k_{o2}^+}{K_{h1}K_{h2}K_{h3}k_{h4}^+}} \theta_{CO}\theta_*^2 \frac{\theta_0^2}{\theta_*^2} \]  
\[ \theta_{CH_3} = \sqrt{\frac{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+}{k_{h4}^+}} \theta_{CO}\theta_*^2 \frac{\theta_0^2}{\theta_*^2} \]  
\[ r = k_{h4}^+\theta_{CH_3}\theta_H = \sqrt{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+} K_{o1}k_{o2}^+ \theta_{CO}\theta_*^2 \frac{\theta_0^2}{\theta_*^2} \]  
Finally resulting in:
\[ r = \sqrt{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+} K_{o1}k_{o2}^+ \theta_{CO}P_{CO} (K_{H_2}P_{H_2})^{1.5} \theta_*^2 \]  
with
\[ \theta_* = 1 - K_{CO}P_{CO} - \sqrt{K_{H_2}P_{H_2}} - \frac{K_{CO}P_{CO}}{\sqrt{P_{H_2}}} - K_{CH}P_{CO} - K_{CH_3}P_{H_2}P_{CO} - K_{CH_3}P_{H_2}P_{CO} \]  
\[ - K_{O}\sqrt{P_{H_2}P_{CO} - K_{OH}P_{H_2}\sqrt{P_{CO}}} \]  
\[ K_C = \sqrt{\frac{K_{d1}K_{o1}k_{o2}^+K_{CO}}{K_{h1}K_{h2}K_{h3}k_{h4}^+K_{H_2}}} \]  
\[ K_{CH} = \sqrt{\frac{K_{d1}K_{h1}K_{o1}k_{o2}^+K_{CO}}{K_{h2}K_{h3}k_{h4}^+}} \]  
\[ K_{CH_2} = \sqrt{\frac{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+K_{CO}K_{H_2}}{K_{h3}k_{h4}^+}} \]  
\[ K_{CH_3} = \sqrt{\frac{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+K_{CO}K_{H_2}}{k_{h4}^+}} \]  
\[ K_O = \sqrt{\frac{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+K_{CO}K_{H_2}}{K_{o1}k_{o2}^+}} \]  
\[ K_{OH} = \sqrt{\frac{K_{d1}K_{h1}K_{h2}K_{h3}k_{h4}^+K_{o1}K_{CO}}{K_{H_2}}} \]
**CH$_2$O dissociation limitation**

With a hydrogen-assisted dissociation mechanism we expect greater hydrogen orders than with direct CO dissociation limitation. Using CH$_2$O dissociation (d4) as limiting gives us multiple possible hydrogenation pathways. In the derivation there is no real difference between CHO and COH or CH$_2$O and CHOH. Here we will follow a2, a3 and finally d4:

$$r = k_{d4}^+ \theta_{CH_2O} \theta_*,$$

with

$$\theta_{CH_2O} = K_{a2} K_{a3} \frac{\theta_{CO} \theta_H^2}{\theta_*^2}.$$  \hspace{1cm} (B.38)

Conservation of sites gives

$$\theta_* = 1 - \theta_{CO} - \theta_H - \theta_{CHO} - \theta_{CH_2O},$$  \hspace{1cm} (B.39)

with

$$\theta_{CHO} = K_{a2} \frac{\theta_{CO} \theta_H}{\theta_*}.$$  \hspace{1cm} (B.40)

from which follows that

$$\theta_* = \frac{1}{1 + K_{CHO} P_{CO} + \sqrt{K_{H_2} P_{H_2} + K_{CHO} P_{CO} \sqrt{P_{H_2}} + K_{CH_2O} P_{CO} P_{H_2}}},$$  \hspace{1cm} (B.41)

with

$$K_{CHO} = K_{a2} K_{CO} \sqrt{K_{H_2}}$$  \hspace{1cm} (B.42)

$$K_{CH_2O} = K_{a2} K_{a3} K_{CO} K_{H_2}$$  \hspace{1cm} (B.43)

and the rate equals

$$r = \frac{k_{d4}^+ K_{CH_2O} P_{CO} P_{H_2}}{(1 + K_{CHO} P_{CO} + \sqrt{K_{H_2} P_{H_2} + K_{CHO} P_{CO} \sqrt{P_{H_2}} + K_{CH_2O} P_{CO} P_{H_2}})^2}. $$  \hspace{1cm} (B.44)

Similar derivations are possible for the other rate limitation cases.
Bibliography


Bibliography


