Doctoral Thesis

Methanation of biomass-derived synthesis gas – in situ DRIFTS studies over an alumina supported nickel catalyst

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Methanation of biomass-derived synthesis gas – *in situ* DRIFTS studies over an alumina supported nickel catalyst

A thesis submitted to attain the degree of

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presented by

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ABSTRACT

In central Europe, wood represents a sustainable energy resource due to the high availability of forests. The conversion of wood biomass to Synthetic Natural Gas (SNG) contributes to the development of the upcoming renewable energies. The production of SNG can be achieved in the course of four process steps and the produced gas can be provided to the public gas distribution infrastructure. Heterogeneous catalysis plays a key role in the conversion of the producer gas (H₂, CO, CH₄, CO₂ and CₓHᵧ) over a Ni/γ-Al₂O₃ catalyst in a methanation reactor. In particular, unsaturated hydrocarbons (C₂H₄, C₂H₂) cause carbon deposition and detachment of nickel particles from the support [1], if the methanation is conducted in a fixed-bed reactor. In contrast, fluidized-bed methanation facilitates the regeneration of the nickel catalyst because surface carbon can be converted to CH₄ in areas of the fluidized-bed that still reveal a high concentration of hydrogen [2].

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) offers an important advantage of in situ investigations of adsorbed and gas phase species, while the methanation is carried out. DRIFTS combined with concentration modulation and isotope-labeling shines a light on the reaction pathway of an industrial relevant nickel catalyst. Phase sensitive detection enables to identify reactive adsorption sites on nickel. CO concentration modulation experiments revealed that the dissociation of sub-carbonyls and linear-CO species occurs on low coordination sites, such as steps and edges. On the contrary, undissociated CO is accumulated on less active crystalline nickel sites. The stepwise hydrogenation of adsorbed C-species on nickel accounts for the formation of methane.
In this work, it is aimed to explore the methanation over nickel that is in reaction conditions comparable to industrial applications. After focusing on the CO methanation itself, each saturated and unsaturated C₂-hydrocarbons were added separately to the synthesis gas feed. In that way, the composition of biomass-derived producer gas could be approached. It was observed that surface reactions on Ni are dependent of the reaction conditions. At high temperature (300°C), the commercial nickel catalyst breaks C-C bonds and unreactive carbon is deposited on nickel. On the contrary, reactive surface carbon species are hydrogenated to methane or are oxidized to carbon dioxide. A second reaction pathway for the formation of CO₂ was observed. However, CO₂ is mainly produced via the water-gas-shift reaction at 300°C. Lower reaction temperature, such as 200°C, affected the reaction pathway of C₂-hydrocarbons. For instance, the addition of acetylene to the synthesis gas feed resulted in the formation of adsorbed methylene species (CH₂) that were precursors of methane. In addition, the accumulation of methylene species on the catalyst surface may account for a deactivation of the Ni-catalyst. Lower temperatures (200°C) also induced direct hydrogenation of unsaturated hydrocarbons. Hydrogenation and decomposition of C₂-hydrocarbons can be considered as parallel reactions of the CO methanation. As a consequence, adsorbed C-species that originate from CO dissociation or C₂-hydrocarbon decomposition compete for hydrogen or adsorption sites. The obtained insights from this work can be used to improve a fluidized-bed methanation model.
KURZFASSUNG


Hydrierung von adsorbierten C-Spezies ist für die Bildung von Methan verantwortlich.

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1 INTRODUCTION

The world energy consumption is constantly growing, and according to predictions of the U.S. Energy Information Administration, the energy consumption will increase by 56% till 2040 [3]. The Asian continent contributes most to the huge energy demand. Fossil fuels are still dominating the energy market, and until 2040 around 80% of the world energy use will be provided by fossil fuels. Nevertheless, renewable energy is an energy source of great importance and its contribution to the worldwide energy supply is growing very fast lowering in parallel the CO$_2$ emissions. In particular, the use of biomass as energy carrier is CO$_2$ neutral because CO$_2$ that is produced during combustion of biomass has been absorbed during the growth of plants.

1.1 METHANE FROM WOOD

Large areas of land are covered by forests in Europe and each year the size of the forests is increased [4]. The conversion of wood to Synthetic Natural Gas (SNG) is a sustainable application of wood as biofuel. There exist different opportunities how to use the energy that is stored in wood. One opportunity is to gasify wood and to convert the obtained gases into synthetic natural gas. The process chain of the production of SNG comprises four steps that are summarized in Figure 1.1. In the first step, solid dry wood is gasified with the help of steam. The generated producer gas needs to be cleaned to remove ash and impurities like tars and sulfur-containing
compounds. The third step represents the methanation process that is carried out in a fluidised bed reactor. The final step in the process chain is the upgrading of the gas. Mainly water and CO$_2$ are removed in order to fulfill quality requirements, because SNG can also be transported through the existing gas distribution grid.

1.1.1 GASIFICATION OF WOOD

Gasification is carried out either in a fixed-bed reactor or in a fluidized-bed reactor that allows varying the flow rate. The principle of gasification is explained with regard to an allothermal dual fluidised-bed reactor and it is depicted in Figure 1.2. The idea of this gasifier considers a combustion and a gasification area [5]. In the gasification area, biomass (e.g. wood chips) is gasified with steam in an endothermic reaction. Bed material (e.g. olivine) and charcoal flow to the combustion area where oxidation of charcoal takes place with the help of air. Thermal energy is released and it is used for the endothermic gasification that is carried out at temperatures above 800°C. The
Introduction

Producer gas consists mainly of H₂, CO, CO₂, CH₄, C₂H₆, and H₂O, and the flue gas is composed of CO₂, H₂O and N₂.

![Diagram of gasification process](image)

**Figure 1.2: Schematic presentation of gasification of wood, modified from [5]**

### 1.1.2 Gas Cleaning and Conditioning

The producer gas usually contains impurities like ash, tars, sulfur- and chlorine-containing compounds, etc. that either deactivate the nickel catalyst [6, 7] in the subsequent methanation step or induce plugging or corrosion of the tubing. In order to clean the producer gas, particles are filtered out and water is condensed by a gas cooler. Sulfur-containing compounds can be removed by gas scrubbing that is performed at low temperatures. In contrast, hot gas cleaning with a catalytically active filter enables to obtain a producer gas free of particles and tar without lowering the gas temperature [8, 9].

Biomass-derived producer gas usually has a H₂ : CO ratio that is lower than three but for the methanation step (3 H₂ + CO ↔ CH₄ + H₂O) additional hydrogen is required. Therefore, by means of the water-gas-shift reaction (CO + H₂O ↔ CO₂ + H₂) hydrogen can be formed when water is added to the feed.
1.1.3 Methanation Process

After the gas cleaning step, the biomass-derived producer gas that is obtained for example from the Fast Internally Circulating Fluidized Bed (FICFB) gasifier in Güssing/Austria [10] reveals the composition listed in Table 1.1. The exothermic methanation step \(3 \text{H}_2 + \text{CO} \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}\) is catalyzed by a methanation catalyst (e.g. \(\text{Ni}/\gamma-\text{Al}_2\text{O}_3\)) and it usually is performed either in a series of adiabatic fixed-bed reactors or in an isothermal fluidized-bed reactor between 250°C and 450°C [2]. In principle, a chemical efficiency of up to 65% can be achieved for the methane from wood process [11]. The use of fluidized-bed reactors for methanation is more advantageous as the mixing of the solids enables almost isothermal reaction conditions [12]. In addition, heat and mass transfer is enhanced in comparison to fixed-bed reactors.

Table 1.1: Composition of cleaned producer gas after biomass gasification in the FICFB gasifier in Güssing/Austria [10].

<table>
<thead>
<tr>
<th>Producer Gas</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2) [mol.%]</td>
<td>35-45</td>
</tr>
<tr>
<td>(\text{CO}) [mol.%]</td>
<td>22-25</td>
</tr>
<tr>
<td>(\text{CH}_4) [mol.%]</td>
<td>~10</td>
</tr>
<tr>
<td>(\text{CO}_2) [mol.%]</td>
<td>20-25</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_4) [mol.%]</td>
<td>2-3</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_6) [mol.%]</td>
<td>~0.5</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_2) [mol.%]</td>
<td>~0.4</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_6) [g/m(^3)]</td>
<td>~8</td>
</tr>
<tr>
<td>TARS [mg/m(^3)]</td>
<td>20-30</td>
</tr>
</tbody>
</table>

The complex composition of the biomass-derived producer gas leads to variety of possible reactions occurring on the surface of the methanation catalyst (see Theoretical Background). Hydrogenation reactions, such as CO methanation, result in the formation of methane whereas unsaturated hydrocarbons (e.g. \(\text{C}_2\text{H}_4\), \(\text{C}_2\text{H}_2\)) can be hydrogenated to ethane or ethylene. On the other hand, hydrocarbons can be decomposed into different types of surface carbon that either might be hydrogenated to methane or form carbonaceous deposits. In addition, the possible formation of oligomers due to the presence of CO or hydrocarbons also needs to be taken into
account. The variety of possible reactions on the catalyst requires a detailed investigation of the surface reactions, in order to obtain detailed mechanistic insights.

1.1.4 GAS UPGRADING

After the methanation step of the process chain, gas upgrading of the produced synthetic natural gas is conducted in order to fulfill gas quality requirements for the public gas grid. Therefore, H₂, CO₂ and H₂O need to be removed from the gas feed. H₂ is recycled internally for methanation. H₂O is stripped off by condensation and drying. CO₂ is removed by amine scrubbing [9] and geologic sequestration might be applied afterwards for underground storage of CO₂.

Research objectives and methods

The focus of this dissertation is directed to the mechanistic investigation of surface reactions of a commercial Ni/γ-Al₂O₃ catalyst that is used in industrial fluidized-bed methanation. The application of DRIFTS in combination with mass spectrometry offers the opportunity of in situ investigations while the methanation catalyst is working.

Inside the fluidized-bed, catalyst particles are moving through the reactor and experience varying gas compositions. The application of DRIFTS demands for conducting experiments in a fixed-bed reactor set-up. In order to simulate fluidized-bed conditions, the catalyst is periodically exposed to changing gas compositions. The used fixed-bed reactor of the DRIFTS setup enables applying isothermal reactions conditions due to water-cooled reactor walls and dedicated temperature control of the catalyst bed. In addition, the Ni catalyst used for the experiments reveals a similar particle size as the Ni catalyst used in fluidized-bed methanation. Applying all those measures, the industrial reaction conditions of fluidized-bed methanation can be approached to a relatively good extent during the DRIFTS experiments.
In the first part of the experimental investigations, a simple gas mixture, namely CO and H₂, was applied over a commercial Ni/γ-Al₂O₃ catalyst, in order to obtain insights about the mechanism of CO methanation which is still under discussion (see chapter 2.1.1). TPD and TPR measurements revealed the coordination mode and the different reactivities of adsorbed CO species. The application of Modulation Excitation Spectroscopy tremendously enhanced the sensitivity of DRIFTS towards variations of IR signals that were caused by CO modulation. This procedure enabled e.g. identifying adsorption sites for CO dissociation. Further mechanistic insights about the CO methanation were obtained by use of isotope-labeled ¹³CO.

In the second part of the thesis, the more complex composition of the biomass-derived producer gas is approached by adding either ethane, or ethylene or acetylene to the CO/H₂ feedstock to investigate separately each influence on the reactions over the nickel catalyst. The modulation of the different hydrocarbons under CO methanation conditions simulates the changing gas composition around the catalyst particle during its travel through the fluidized-bed. A variety of surface reactions can occur on the surface of the catalyst. As the concentration of CO/H₂ remained constant while the concentration of the hydrocarbons was changed, it is possible to distinguish reactions induced by the addition of hydrocarbons from the CO methanation with the help of the modulation excitation technique. Additionally, isotope-labelling allows the identification of reaction pathways and enables determining possible competitive reactions between carbon species on the catalyst surface.

The experiments should contribute for better understanding of surface reactions of a working catalyst that is used for industrial methanation. In particular, the findings of the investigation should help interpreting kinetic data used to develop mathematical models that would allow predictions regarding the performance of a methanation plant.
2 THEORETICAL BACKGROUND

The following chapter provides an overview about fundamental reactions regarding the topic of this thesis. It should illustrate the various reactions that might occur over the commercial Ni-catalyst under methanation conditions. Consequently, this chapter contributes for better interpretation and comprehension of the results of the conducted experiments in this thesis.

2.1 CO METHANATION

Nickel catalyzed CO methanation plays a central role in industrially relevant processes such as CO removal from hydrogen-rich gases or conversion of gasification producer gas to synthetic natural gas (SNG). Beside nickel, other transition metals (e.g. Ru, Rh, Pd, Fe, Co; etc.) are also catalytically active towards methanation [12, 13]. Generally, nickel can be considered as an efficient methanation catalyst due to its low cost and high activity. Basically, the methanation as a heterogeneously catalyzed process comprises three exothermic reactions that are listed below:

Methanation: \[ \text{CO} + 3 \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_r^0 = -206.28 \text{kJ/mol}[11] \] (2.1)

Water-gas-shift: \[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_r^0 = -41.16 \text{kJ/mol}[11] \] (2.2)
Boudouard: \[ 2 \text{CO} \leftrightarrow \text{C} + \text{CO}_2 \quad \Delta H^\circ_{R} = -172.54 \text{ kJ/mol} \] (2.3)

The water-gas-shift (WGS) and the Boudouard reactions produce a considerable amount of CO\(_2\) that theoretically can be converted to methane. However, the adsorption strength of CO is larger than that of CO\(_2\) [14, 15]; therefore, CO blocks catalytically active nickel sites and prevents the hydrogenation of CO\(_2\). In addition, the WGS reaction has a positive effect on the H\(_2\) : CO ratio because additional hydrogen is generated that is required in the methanation reaction. The Boudouard reaction also leads to carbon deposition on nickel. On one side, deposited carbon can deactivate the catalyst [6] and on the other side, surface carbon can be hydrogenated to methane.

Due to the highly exothermic methanation and Boudouard reaction, overheating must be avoided. Therefore, a temperature control of the reactor needs to be applied, in order to prevent deactivation of the catalyst and limitation of the methane production as a consequence of the chemical equilibrium [11, 13]. Figure 2.1 illustrates that the equilibrium constant of methanation and WGS reaction decreases with increasing temperature, resulting in lower methane yield. On the contrary, the reaction enthalpies are not extremely affected by the temperature.

![Figure 2.1: Equilibrium constant of methanation and WGS reaction, adapted from [11]](image)
Theoretical Background

2.1.1 MECHANISM OF CO METHANATION

Despite numerous investigations [13, 16-35], the elementary steps of the catalytic reaction, \( \text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \), are still not fully understood.

Araki et al. [17] showed dissociative chemisorption of CO on nickel films at around 300°C and low pressures. Several studies of the methanation reaction over Ni/Al\(_2\)O\(_3\), Ni/SiO\(_2\) or unsupported nickel catalysts came to the same conclusion [17, 21, 25, 27, 30-34, 36, 37]. Surface carbides on nickel are widely accepted reaction intermediates; therefore, the following mechanism A is proposed in Figure 2.2 [17, 21, 25, 27, 30-34, 36, 37]:

![Figure 2.2: Mechanism A of CO methanation, modified from [38]. * indicates an empty surface site, or an adsorbed species (e.g. CO*).](image)

After dissociative chemisorption of CO, adsorbed carbon and oxygen are hydrogenated. The stepwise hydrogenation of surface carbon results in the formation of methane. The existence of adsorbed CH\(_x\) species on Ni/\(\gamma\)-Al\(_2\)O\(_3\) at 100°C was proved using infrared spectroscopy [21]. Adsorbed CH* species were considered to take part in the methanation, whereas CH\(_2^*\) or CH\(_3^*\) species might also be involved in the formation of higher hydrocarbons. There is no consensus with respect to the rate-determining-step (RDS). Zagli et al. [34] assumes C-O bond breaking to be the RDS, whereas other authors [27, 31, 33, 36, 38] propose the hydrogenation of CH\(_x\) species as rate-limiting. Regarding the hydrogenation of surface carbon, two
different types of hydrogen atoms are relevant. One type is hydrogen adsorbed on the surface that was generated by dissociative chemisorption of H$_2$. The other type is bulk hydrogen that occupies octahedral sites below the surface on Ni(111) [39]. It was shown that for the hydrogenation of CH$_3$ adsorbed on Ni(111) bulk H atoms were the reactive species whereas H atoms adsorbed on the surface were unreactive [40].

Scanning tunneling microscopy (STM) revealed that CO dissociation preferably takes place on steps on Ni(111) [16]. The STM image in Figure 2.3 shows atomic steps on Ni(111) after addition of CO at 227°C. Carbon formation in terms of carbidic islands was observed along the steps but on the terraces no carbon was identified. However, the structure sensitivity of the reaction remains debated. CO methanation was also considered to occur irrespective of exposed Ni plane as a result of Ni particle smoothing by CO [41]. Agnelli et al. [41] proposed that CO methanation occurs on CO-free Ni atoms adjacent to the adsorbed CO layer and hydrogen can dissociate on Ni atoms free from adsorbed CO. The presence of nickel carbide was recognized that is continuously covered by an ad-layer of adsorbed CO species of Ni$_2$CO stoichiometry. The carbon atom of the carbidic layer near the CO-free Ni atoms is hydrogenated and it is replaced by decomposition of a multi-bonded CO species. Carbon deposits on nickel can also be responsible for deactivation of the catalyst by fouling [6]. Consequently, the H$_2$:CO ratio is typically maintained higher than three, in order to prevent carbon deposition [2].
Theoretical Background

A second mechanism of CO methanation over Ni/SiO\(_2\) or unsupported nickel that is under discussion in literature [16, 20, 23, 42], supports COH-reaction intermediates. Coenen et al. [20] carried out the methanation with an equimolar mixture of \(^{13}\)C\(^{16}\)O and \(^{12}\)C\(^{18}\)O but no isotopic scrambling was observed. Due to this key observation, dissociative adsorption was assumed to be invalid. On the contrary, Coenen et al. stated a mechanism B that is presented in Figure 2.4:

\[
\begin{align*}
H_2 + 2^* & \rightleftharpoons 2 H^* \\
CO + ^* & \rightleftharpoons CO^* \\
CO^* + H^* & \rightleftharpoons COH^* + ^* \\
COH^* + H^* & \rightleftharpoons C^* + H_2O + ^* \\
C^* + H^* & \rightleftharpoons CH^* + ^* \\
CH^* + H^* & \rightleftharpoons CH_2^* + ^* \\
CH_2^* + H^* & \rightleftharpoons CH_3^* + ^* \\
CH_3^* + H^* & \rightleftharpoons CH_4 + 2^*
\end{align*}
\]

**Figure 2.4**: Mechanism B of CO methanation, modified from [20]

DFT studies [16] also showed that hydrogen lowers the barrier for CO dissociation and that COH\(^*\) intermediates could appear as formyl (HC-O) or as carbon-hydroxyl (C-OH) species on nickel. So far, these surface species were not identified experimentally as intermediates for CO methanation on nickel. On the other hand, adsorbed formyl species were detected as intermediates on Ru/Al\(_2\)O\(_3\) during CO methanation at 190°C in a DRIFTS study [43]. After hydrogen induced dissociation of CO, surface carbon is stepwise hydrogenated to methane alike mechanism A. It was assumed that the dissociation of the COH-complex is the rate-determining-step.

A third mechanism of CO methanation over Ni/Al\(_2\)O\(_3\) was suggested in an IR-study which gives rise to the assumption that surface methoxy and formate groups are intermediates [44, 45] in the formation of methane. The mechanism C is depicted in Figure 2.5.
It was assumed that the reaction takes place over an oxide surface [44, 45]. Adsorbed CO interacts with surface OH-groups of Al₂O₃ and forms surface formate species. Then, formates are hydrogenated to methoxy species, which on their turn are hydrogenolyzed to form methane selectively. It was also speculated that on Ni/Al₂O₃ catalysts with lower nickel loading (< 1wt.% Ni) most of the adsorbed CO spills over to the Al₂O₃ surface where methoxy species can be formed [45].
2.2 THE WATER-GAS-SHIFT (WGS) REACTION

The WGS reaction (CO + H$_2$O $\leftrightarrow$ CO$_2$ + H$_2$) is an important reaction in industry for hydrogen production [46] but it is also part of the nickel catalyzed methanation process. The addition of water to the CO/H$_2$ reaction feed generates additional hydrogen but it also affects the chemical equilibrium of the methanation [47]. Beside the production of hydrogen, more CO$_2$ is formed because the CO conversion is enhanced in the WGS reaction. As a consequence, the selectivity towards CH$_4$ and the chemical efficiency are lowered. Commercial catalysts that are used for the WGS reaction are usually mixtures of Fe–Cu, Fe–Cr or Cu–Zn oxides [48].

2.2.1 REACTION MECHANISM OF THE WGS REACTION

In general, two mechanistic concepts for the water-gas-shift are widely discussed [46, 48-52]. Experimental studies (DRIFTS, ambient pressure XPS) and DFT investigations support a redox-type mechanism for Cu-based catalysts [46, 48, 49, 53] that is outlined in Figure 2.6. In the Redox-mechanism, the reactants induce a cyclic change in the oxidation state of the catalytic material [54].

![Figure 2.6: Redox-mechanism of water-gas-shift, modified from [49]](image)

After CO and H$_2$O adsorption on the catalyst surface and H$_2$O dissociation into H* and OH* species, further dissociation of OH* species results in O* and H*. Alternatively, O* can be formed via disproportionation of two OH* species. Adsorbed
CO is oxidized by atomic O* and CO₂ is formed. Two H* species recombine to H₂ and H₂ and CO₂ desorb from the surface. H₂O activation and CO oxidation are considered as rate-limiting-steps [53]. Ni/Al₂O₃ is also active towards the WGS reaction with a redox-type mechanism and the activity increases with the temperature and the nickel loading [52, 55], whereas the activity is related to the availability of an optimal Ni²⁺/Ni³⁺ ratio. Another mechanistic concept of the WGS reaction considers an associative mechanism [48, 53, 56] that was also observed on Cu- and Pt-based catalysts. The suggested reaction steps are depicted in Figure 2.7.

Adsorbed CO* and OH* forms HCOₓ* intermediates [48] whose structure can be assimilated to surface formate species [56-58], carbonate species [59] or carboxylate species [49] (Figure 2.8). In contrast, another study [49] suggests that formate species are probably spectator species during WGS reaction that originate from the reaction of CO₂ with atomic H. Moreover, formates are assumed to block active sites on the catalyst. The decomposition of the HCOₓ* species results in the formation and desorption of CO₂. Mechanistic studies of the WGS reaction are still controversial. It is also discussed that both the Redox-type and the associative mechanism are probable over a Cu/ZnO/Al₂O₃ catalyst. The two different pathways might be influenced by the experimental conditions [54].
2.3 HYDROGENATION OF CO$_2$

The hydrogenation of CO$_2$ enables to form a variety of different products, such as oxygenates or hydrocarbons [60]. In general, catalysts that are active in CO methanation also catalyze the CO$_2$ methanation [13]. As long as CO is present in the gas feed, CO$_2$ is not converted to methane via equation 2.4. On the other side, CO$_2$ can react with H$_2$ to form CO and H$_2$O in the reverse water-gas-shift (RWGS) reaction (see equation 2.5). Methane is generated in the subsequent hydrogenation of CO. In this case, CO can be considered as reaction intermediate in the formation of methane [55]. The RWGS reaction is observed during CO methanation over Ni/Al$_2$O$_3$ when CO$_2$ is added to the CO/H$_2$ gas feedstock [12].

$$\text{CO}_2 + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad \Delta H_r^0 = -165.12 \text{ kJ/mol}^{[55]} \quad (2.4)$$

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_r^0 = +41.16 \text{ kJ/mol}^{[55]} \quad (2.5)$$

2.3.1 MECHANISM OF CO$_2$ METHANATION

In the past, controversial discussions about CO$_2$ methanation led to a variety of different mechanistic assumptions. In 1923, Medsforth [61] considered oxygenated reaction intermediates for CO$_2$ hydrogenation over nickel. This mechanism takes into account the reaction of adsorbed CO$_2$ with adsorbed atomic hydrogen (Figure 2.9). CH$_3$OH was observed as intermediate, whereas CH$_2$O and C(OH)$_2$ (bis-hydroxycarbene) could not be identified.

![Figure 2.9: Mechanism of CO$_2$ methanation suggested by Medsforth/Pichler, adapted from [62]](image-url)
Later, Vlasenko and Yuzefovich [42] proposed a mechanism where only hydrogen is dissociated on the nickel surface whereas the reaction with CO$_2$, producing CH$_4$, takes place in the gas phase. This mechanism was concluded after realizing that the weight of the catalyst during CO$_2$ methanation did not change. Solymosi [63] presents a mechanism that is in contrast to the work of Vlasenko and Yuzefovich. In an IR-study, Solymosi investigated CO$_2$ methanation over a Rh/Al$_2$O$_3$ catalyst at 250°C and proposed adsorbed CO as reaction intermediate. Also formate species were found which were not considered as relevant for the formation of methane. The mechanism suggested by Solymosi is depicted in Figure 2.10.

![Figure 2.10: Mechanism of CO$_2$ methanation suggested by Solymosi, (a) denotes adsorbed species, (g) gaseous species and C$_s$ surface carbon, adapted from [63]](image)

Upon introduction of a CO$_2$/H$_2$ mixture over the Rh catalyst, adsorbed CO is present on the surface [62]. In principle, it reflects the reverse-water-gas shift. A hydrogen transfer from the support to the metal center is assumed and the C-O bond is weakened due to an electron-donating H atom [63]. Consequently, CO is more easily dissociated. On the other side, CO$_2$ methanation over Rh occurs faster than CO methanation. This observation was explained that a certain fraction of adsorbed CO during CO methanation forms less reactive carbon species that require higher activation energy. Weatherbee et al. [64] also proposes a mechanism over nickel that considers a dissociative adsorption of CO$_2$ to CO that is followed by CO hydrogenation. The dissociation of adsorbed CO was assumed to be the rate-determining-step.
Theoretical Background

Recently, Pan et al. [65] studied CO\(_2\) methanation over Ni/\(\gamma\)-Al\(_2\)O\(_3\) with FTIR and presented the mechanism shown in Figure 2.11. Activation of CO\(_2\) takes place on the \(\gamma\)-Al\(_2\)O\(_3\) support. Hydrogen carbonates and bidentate formates were assumed as intermediates on \(\gamma\)-Al\(_2\)O\(_3\). CO\(_2\)-TPD measurements revealed weak and strong basic sites on the catalyst which were ascribed to surface hydroxyls and surface oxygen, respectively.

\[
\text{Ni} \quad \xrightarrow{\text{OH}} \quad \text{Ni} \quad \xrightarrow{\text{H}_2} \quad \text{Ni} \quad \xrightarrow{\text{H}_2} \quad \text{Ni} \quad \xrightarrow{\text{H}_2} \quad \text{Ni} \\
\gamma-\text{Al}_2\text{O}_3 \quad \xrightarrow{\text{CO}_2} \quad \gamma-\text{Al}_2\text{O}_3 \quad \xrightarrow{\text{H}_2} \quad \gamma-\text{Al}_2\text{O}_3 \quad \xrightarrow{\text{H}_2} \quad \gamma-\text{Al}_2\text{O}_3
\]

**Figure 2.11: Mechanism of CO\(_2\) methanation suggested by Pan, adapted from [65]**

Hydrogenation of the formate species to methane was concluded as probable reaction route. A similar mechanism was presented for Ni/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\), whereas Ni/Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) reveals a higher activity towards CO\(_2\) methanation than Ni/\(\gamma\)-Al\(_2\)O\(_3\). This effect was explained in terms of a weaker basicity of Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\), in comparison to the \(\gamma\)-Al\(_2\)O\(_3\) support. It was assumed that weak basic sites of the support are prerequisite for the activation of CO\(_2\) [66] and that CO\(_2\) adsorbed on strong basic sites is not involved in the reaction [65].
2.4 **Carbon Deposition in Methanation**

Carbon deposits on nickel provoked by dissociation or decomposition of CO or hydrocarbons can deactivate the catalyst through poisoning or fouling [6]. When active sites are blocked for catalytic reactions, the catalyst is considered to be poisoned. Fouling is related to encapsulation of catalyst particles or to plugging of the porous structure and can be considered as deactivation by mechanical destruction of the catalyst. On the other side, it was reported [1] that carbon deposits on nickel display a loose structure enabling the reactant gases to diffuse to active nickel sites. Consequently, only a slight effect on the methane yield was observed.

Besides mechanical and chemical deactivation, thermal deactivation needs to be considered as well. Sintering of the catalyst can be observed above 500° which involves two processes [6]. On one hand, the metal crystallite is growing and the catalytically active surface area is decreased. On the other hand, disruption of pores takes place and the support collapses. High temperature and oxygen can enhance sintering whereas hydrogen decreases the rate of sintering. Generally, sintering damages the catalyst and should be avoided by choosing the proper temperature and atmosphere during a reaction.

The nature of the $\gamma$-Al$_2$O$_3$ support enables the catalyst to resist harsh conditions inside the methanation reactor. Apart from $\gamma$-Al$_2$O$_3$, also TiO$_2$ or SiO$_2$ would be qualified as support for nickel [47]. According to Bartholomew et al. [67], the catalyst support has an effect on carbon deposition during CO methanation. It was found that the carbon deposition rate on nickel at 325-450°C depends on the catalyst support and the rate is increasing as follows: SiO$_2 < \gamma$-Al$_2$O$_3 <$ TiO$_2$.

In particular, unsaturated hydrocarbons enhance the deposition of carbon on nickel that is demonstrated in faster kinetics for acetylene and olefin decomposition in Figure 2.12 [68]. It was reported that surface carbon can form carbon whiskers that detach nickel particles from the surface [1, 6, 69], whereas methane formation is not greatly disturbed.
Theoretical Background

Figure 2.12: Formation of carbon species from (A) acetylene, (B) olefin and (C) paraffin on a Ni foil at 450°C, adapted from [68]

Figure 2.13: HRTEM image of carbon whiskers and nickel clusters after fixed-bed methanation (400°C, 1.5 bar) under influence of unsaturated hydrocarbons, adapted from [1]

In Figure 2.13, a HRTEM (high resolution transmission electron microscopy) image of carbon whiskers and nickel clusters is depicted. A commercial nickel catalyst (50 mass% Ni on γ-Al₂O₃) that was also used for the following DRIFTS studies of this thesis was exposed to synthetic producer gas simulating the Güssing gasifier [10] in a fixed-bed set-up. This led to a massive formation of C-whiskers and a detachment of Ni clusters from the alumina support [1].
It was concluded that a lattice mismatch between Ni\(^0\) and \(\gamma\)-Al\(_2\)O\(_3\) resulted in the formation of an interface (Ni-NiC\(_x\) or Ni\(_3\)C). As a consequence, the bonding between nickel and \(\gamma\)-Al\(_2\)O\(_3\) is weakened [1]. It facilitates the detachment of nickel clusters when C-whiskers are formed.

Shen et al. [70] reported that Ni/Al\(_2\)O\(_3\) is deactivated during CO methanation due to the formation of Ni(CO)\(_4\) at high partial pressures of CO (>20kPa) and temperatures below 425°C. An increase of the Ni particle size is ascribed to the deactivation. The growth of the nickel particle size is related to the generation of Ni(CO)\(_4\) and its diffusion over the catalyst surface where Ni(CO)\(_4\) is decomposed. In addition, a loss of Ni via the gas phase also needs to be taken into account (see Figure 2.14). However, a high Ni content of the catalyst, a low Ni dispersion and a lower CO partial pressure may prevent the formation of Ni(CO)\(_4\) [71]. Recently, it was demonstrated that the particle size affects the stability of a Ni catalyst [72]. In particular, small particles (3-4 nm) tend to form larger particles due to the formation of Ni(CO)\(_4\) which destabilize the catalyst. On the other hand, medium sized particles (8nm) showed an enhanced stability and higher activity. As a result, catalysts exhibiting small Ni particles are deactivated more quickly.

Under adiabatic fixed-bed methanation conditions, the formation of adsorbed atomic surface carbon, bulk Ni\(_3\)C, amorphous carbon and carbon whiskers takes place on the nickel catalyst if the H\(_2\) : CO ratio is lower than three [7]. In Table 2.1, it is demonstrated that the different surface carbon species on nickel reveal various reactivities as can be seen from the different peak temperatures for the reaction with H\(_2\) in a TPR experiment.
### Theoretical Background

**Table 2.1: Carbon species after dissociation of CO on nickel, adapted from [6, 7]**

<table>
<thead>
<tr>
<th>Structural type</th>
<th>Designation</th>
<th>Temperature of formation (°C)</th>
<th>Peak temperature (°C) for reaction with H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed, atomic (surface carbide)</td>
<td>Cᵣ</td>
<td>200-400</td>
<td>200</td>
</tr>
<tr>
<td>Polymeric, amorphous films or filaments</td>
<td>Cₚ</td>
<td>250-500</td>
<td>400</td>
</tr>
<tr>
<td>Vermicular filaments, fibers, and/or whiskers</td>
<td>Cᵥ</td>
<td>300-1000</td>
<td>400-600</td>
</tr>
<tr>
<td>Nickel carbide (bulk)</td>
<td>Cᵥ</td>
<td>150-250</td>
<td>275</td>
</tr>
<tr>
<td>Graphitic (crystalline) platelets or films</td>
<td>Cᵣ</td>
<td>500-550</td>
<td>550-850</td>
</tr>
</tbody>
</table>

Adsorbed atomic carbon (Cᵣ) seems to be the relatively most reactive species and is already hydrogenated at 200°C. If the temperature is increased, adsorbed atomic carbon can be converted to less reactive amorphous (Cᵥ) and graphitic surface (Cᵣ) carbon that deactivate the nickel catalyst [7]. Hydrocarbons in the synthesis gas feed for methanation result in accumulation of surface carbon on nickel. According to Bartholomew [6, 7], hydrocarbons (CₙHₘ) decompose to adsorbed atomic carbon (Cᵣ), adsorbed CHₓ and CₙHₗₘ species. As a consequence, adsorbed Cᵣ and CHₓ species might be hydrogenated to form methane if sufficient hydrogen is provided. On the other hand, the transformation of Cᵣ and CHₓ species to less reactive carbon species like amorphous or graphitic carbon needs be taken into account. These processes are summarized in Figure 2.15.

![Figure 2.15: Scheme of formation and hydrogenation of carbon species on nickel (a = adsorbed, g = gaseous, s = solid), adapted from [6, 7]](image-url)

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**Figure 2.15:** Scheme of formation and hydrogenation of carbon species on nickel (a = adsorbed, g = gaseous, s = solid), adapted from [6, 7]
In contrast to fixed-bed methanation, the catalyst is in motion under fluidized-bed conditions. Figure 2.16 shows the axial gas concentration profile in the fluidized-bed methanation reactor at 320°C. In principle, in the fluidized-bed a distinction is made between the bubble phase where the solid concentration is low and the dense phase which reveals a high solid density [12, 47].

The gas concentrations of Figure 2.16 are ascribed to the dense phase [73]. In the first 5 mm of the fluidized-bed, 75% of CO was reacting to CH\textsubscript{4} and CO\textsubscript{2} but also carbon deposition on the nickel catalyst and a temperature increase of 40°C was observed [2]. The decreasing CO\textsubscript{2} concentration is related to the reverse water-gas-shift reaction. In the region above 5 mm, the hydrogenation of adsorbed carbon species (C\textsubscript{α} and C\textsubscript{β}) was assumed as the CH\textsubscript{4} concentration was increasing and the amount of H\textsubscript{2} was decreasing. In addition, surface carbon is oxidized, resulting in the formation of CO\textsubscript{2}. At around 20 mm, CH\textsubscript{4} reaches its maximum concentration. The upper part of the fluidized-bed still features a high amount of hydrogen (see Figure 2.16). Bartholomew [7] stated that if enough hydrogen is available during CO methanation, carbon deposition can be avoided on nickel. This environment regenerates the nickel catalyst when reactive surface carbon reacts with hydrogen to form CH\textsubscript{4} [2, 73].
2.5 **Methanation Catalysts**

Group VIII transition metals reveal a high activity towards CO methanation. Vannice compared alumina supported metals for their activity and selectivity to methane [47, 74]. High catalytic activity results in lowered selectivity.

Activity: Ru>Fe>Ni>Co>Rh>Pd>Pt>Ir

Selectivity: Pd>Pt>Ir>Ni>Rh>Co>Fe>Ru

Nickel is the material of choice for CO methanation due to its high catalytic activity and low price [75]. However, nickel catalysts are deactivated at low temperatures due to the formation of mobile nickel subcarbonyls [76]. Highly loaded Ru/Al$_2$O$_3$ (15 wt%) exhibits a reaction rate that is ten times higher than that of nickel catalysts but the use of Ru catalysts is not economical for large-scale production [75].

Metal nanoparticles are dispersed on the surface of a metal oxide support which can affect the activity of the metal catalyst [77, 78]. The higher activity of Ni/TiO$_2$ and Ni/Al$_2$O$_3$ for CO hydrogenation compared to Ni/SiO$_2$ was explained by the strong metal-support interactions that increase the activity of available nickel sites for CO methanation [79]. Originally, the strong metal-support interaction (SMSI) described changes in the chemisorption properties of group VIII metals on metal oxides [78]. An electron transfer from the support to the active metal caused the modification of the adsorption properties. The SMSI concept involves also different aspects, such as formation of interphases, encapsulation of metal particles by the support and effect of the support on the shape of metal particles.

The shape of metal particles of a supported catalyst is determined by the strength of the interaction with the support [78] but other factors can influence the particle shape as well. In a TEM study [80], it was shown that the drop-like shape of Cu nanoparticles supported on ZnO changes into a disc-like structure when the CO/H$_2$ ratio of the gas composition is increased at 220°C. Adsorbate-induced changes in surface energies might be the reason for the shape change of the particles. In general, a shape change of metal particles can also be associated with an activity change of catalysts for chemical reactions.
Theoretical Background

Metal particles can also form an interphase with the metal oxide support when high temperature reduction, calcination or annealing is applied to the supported catalyst [78]. For example, $\text{Al}^{3+}$ ions of the $\text{Al}_2\text{O}_3$ support may migrate to the interior of nickel particles and a nickel aluminate (NiAl$_2$O$_4$) interphase is formed [1]. If the formed interphases are catalytically active, the new phases can improve the catalyst performance.

Another issue that needs to be addressed is related to the metal particle size of supported catalysts. Van Meerten et al. [81] studied the influence of the Ni-particle (0.5–13 nm) size of Ni/SiO$_2$ catalysts on the catalytic performance and stated that larger Ni particles are more active in CO methanation than smaller ones. The catalytic activity of alumina supported methanation catalysts was studied with respect to the effect of Ni particle size (5–10, 10–20, and 20–35 nm) [82]. Ni particles of 10-20 nm exhibited the highest CH$_4$ yield and lowest carbon deposition. In other reactions, such as partial oxidation of CH$_4$, nickel particles of 6 nm feature the best catalytic activity [83]. The low activity of small metal particles towards CO hydrogenation is related to a stronger CO adsorption. As a consequence, strongly bonded carbon and oxygen surface species may block active sites [84, 85], which would explain the lower catalytic activity. Ni/Al$_2$O$_3$ catalysts that are used for methanation often exhibit a higher Ni loading (up to 50% wt%) but small Ni particles aggregate to form larger particles (up to 40 nm) when the methanation is carried out at higher temperatures (300-600°C) [82]. The increase of the particle size (sintering process) also leads to a lower surface area; hence the activity per unit surface area is decreased and less active sites are available [86]. In summary, it can be stated that both very small and very large metal particles of supported catalysts have a negative effect on the catalytic methanation performance.

The properties of a catalyst also can be modified by addition of a promoter. For example, the addition of alkali metals such as potassium to Ni/SiO$_2$ shifts the selectivity of the CO hydrogenation towards heavier hydrocarbons [87] and a larger amount of carbon deposits was observed [88]. Potassium as an electron donor transfers electrons to the metal phase and increases the carbon-metal bond. As a result, the carbon built-up on the surface is enhanced. Another study [89] also notes that alkali promotion of Ni/SiO$_2$ inhibits nickel sintering. On the other side, the addition of cerium oxide to a Ni/Al$_2$O$_3$ catalyst results in an increased methanation
activity and in an enhanced nickel dispersion [90]. In addition, the reaction temperature for CO methanation is lowered. Ni/Al\textsubscript{2}O\textsubscript{3} that is promoted with manganese (1-3 wt.\%) exhibits an increased surface area and average pore volume. The CO conversion and CH\textsubscript{4} yield is also higher compared to Mn-free nickel catalysts [91]. The Ni-dispersion that is also a crucial factor of the methanation activity can be improved by zirconia doping [92].

2.5.1 Methanation over Metal Hydride Surfaces

An alternative to conventional supported metal methanation catalysts might be hydrogen storage alloys, such as LaNi\textsubscript{5}, Mg\textsubscript{2}Ni and FeTi [93]. For example, Mg\textsubscript{2}Ni reacts with hydrogen to form the hydride Mg\textsubscript{2}NiH\textsubscript{4} which exhibits a hydrogen storage capacity of 98 kg H\textsubscript{2}/m\textsuperscript{3}. Mg\textsuperscript{2+} cations are surrounded by (NiH\textsubscript{4})\textsuperscript{4-} anions [94]. During CO\textsubscript{2} methanation, dissociative adsorption of CO\textsubscript{2} on the hydride surface is the rate determining step [93]. While hydrogen desorbs in CO\textsubscript{2} atmosphere, Mg is oxidized and the formed Mg oxides segregate (Figure 2.17). Nickel particles are formed during decomposition of Mg\textsubscript{2}NiH\textsubscript{4} and the surface becomes more active towards CO\textsubscript{2} methanation. The oxide layer also hampers the decomposition of the hydride.

![Figure 2.17: Decomposition of Mg\textsubscript{2}NiH\textsubscript{4} during CO\textsubscript{2} methanation, adapted from [93]](image)

In particular, intermetallic compounds that consist of rare earth metals and transition metals, such as LaNi\textsubscript{5}, are considered as effective hydrogen storage alloys [95]. LaNi\textsubscript{5} can store hydrogen as metal hydride and it catalyzes methanation reactions [95-98] and the hydrogenation of ethylene [99]. During the hydrogenation of CO\textsubscript{2}, the
catalytic activity of LaNi\textsubscript{5} that was pretreated with hydrogen increases gradually over
the time at 250°C and 50 bar, reaching maximum conversion after 5 hours on-stream [95]. During the reaction, the structure of LaNi\textsubscript{5} is decomposed into metallic nickel and La\textsuperscript{3+}. Therefore, LaNi\textsubscript{5} can be seen as precursor of an efficient methanation catalyst. Another study [97] associated the increase in methanation activity with the increase of metallic nickel. The interaction between Ni and La in an amorphous alloy seems to be significant for the formation of active sites [100].

Soga et al. [99] reported that LaNi\textsubscript{5} alloys also catalyze the hydrogenation of C\textsubscript{2}H\textsubscript{4}. The hydrogenation was studied both over LaNi\textsubscript{5} and LaNi\textsubscript{5}H\textsubscript{n}. For the preparation of LaNi\textsubscript{5}H\textsubscript{n}, LaNi\textsubscript{5} was exposed to a hydrogen atmosphere at 450°C and 100 bar. It was revealed that LaNi\textsubscript{5}H\textsubscript{n} features a higher hydrogenation rate than LaNi\textsubscript{5}. In particular, hydrides from the bulk contribute to the increased hydrogenation rate for LaNi\textsubscript{5}H\textsubscript{n}. Hydrogenation of ethylene was even observed when no gaseous hydrogen was admitted over LaNi\textsubscript{5}H\textsubscript{n}. The migration of hydrides from the bulk to the surface was assumed as rate-determining-step.

Endo et al. [101, 102] studied CO methanation and C\textsubscript{2}H\textsubscript{4} hydrogenation over both CeNi\textsubscript{2} and amorphous CeNi\textsubscript{2}H\textsubscript{x} in a fixed-bed reactor. It was shown that intermetallic compounds, such as CeNi\textsubscript{2}, can be transformed from the crystalline state into an amorphous state with the help of hydrogen absorption [102]. This treatment was termed as hydrogen-induced amorphization (HIA) and creates a structure change through hydrogen absorption. CO methanation was carried out with a H\textsubscript{2}/CO ratio of 2 at 1 bar in the temperature range between 200°C and 300°C. Amorphous CeNi\textsubscript{2}H\textsubscript{x} exhibited the highest activity towards CO methanation. The high activity of CeNi\textsubscript{2}H\textsubscript{x} was ascribed to its amorphous surface structure that includes defect sites. Both catalysts (CeNi\textsubscript{2} and CeNi\textsubscript{2}H\textsubscript{x}) showed almost the same methane selectivity at higher temperatures (280°C). C\textsubscript{4} hydrocarbons were only observed for the CeNi\textsubscript{2}H\textsubscript{x} catalyst.

C\textsubscript{2}H\textsubscript{4} hydrogenation was conducted at different temperatures up to 160°C at 1 bar [102]. A gas mixture with a ratio of H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} = 14 was applied over intermetallic CeNi\textsubscript{2} and amorphous CeNi\textsubscript{2}H\textsubscript{x} that is much more efficient towards C\textsubscript{2}H\textsubscript{4} hydrogenation than CeNi\textsubscript{2}. The high activity of CeNi\textsubscript{2}H\textsubscript{x} was only indicated under H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} gas flow conditions but under He/C\textsubscript{2}H\textsubscript{4} conditions no hydrogenation activity was observed. It was assumed that absorbed hydrogen evolves the amorphous
structure of CeNi₂Hₓ and forms active sites for the hydrogenation. On the other hand, the hydrogenation of C₂H₄ probably proceeds via adsorbed hydrogen atoms and absorbed hydrogen is less relevant for hydrogenation. This finding was in contrast to C₂H₄ hydrogenation over LaNi₅Hₓ where absorbed hydrogen migrated from the bulk to the surface and was used for C₂H₄ hydrogenation [99].

Swalus et al. [103] presented another approach to increase the catalytic activity of the methanation. This approach considers an in-situ supply of hydrogen by use of Ni/activated carbon. A catalyst (Rh/γ-Al₂O₃) that is active towards CO₂ hydrogenation was mixed with Ni/activated carbon that activates hydrogen and a synergy between the two catalysts was observed. Ni/activated carbon can also store hydrogen [104]. Hydrogen that is dissociated on the nickel phase migrates onto the carbon support where it is incorporated. During CO₂ hydrogenation, CO₂ adsorbs on the Rh catalyst and is dissociated into adsorbed CO and O species but little CO₂ adsorption takes place on Ni/activated carbon at reaction conditions of 125 °C and 2 bar [103] (see Figure 2.18). CO₂ is preferably adsorbed on rhodium and competes with hydrogen for adsorption sites; hence low hydrogen coverage is assumed. It was proposed that activated hydrogen species migrate from Ni/activated carbon to Rh/γ-Al₂O₃ by means of a spill-over mechanism and enhance the methanation rate. In addition, hydrogen keeps the rhodium particles in a reduced state which is advantageous for CO₂ hydrogenation.

![Figure 2.18: Supply of hydrogen by Ni/activated carbon during CO2 methanation over Rh/γ-Al₂O₃, adapted from [103]](image-url)
Theoretical Background

2.6 HYDROGENATION OF C\textsubscript{2}H\textsubscript{4}

In the 19\textsuperscript{th} century, Sabatier and Senderens discovered the hydrogenation of ethylene over platinum [105]. Since that time, the hydrogenation of olefins has become an important step in petroleum hydrotreating as well as in the food industry where saturated oil is hydrogenated [106]. As the hydrogenation of olefins is also relevant during the methanation step of biomass-derived synthesis gas, further insights of C\textsubscript{2}H\textsubscript{4} hydrogenation are provided in this section.

The C\textsubscript{2}H\textsubscript{4} hydrogenation belongs to very fast heterogeneous catalytic reactions with turnover rates in the range of 10 molecules/s site on platinum surfaces at ambient temperature and shows a heat of formation of about -136 kJ/mol [105]. C\textsubscript{2}H\textsubscript{4} hydrogenation is a structure insensitive reaction on platinum surfaces, whereas C\textsubscript{2}H\textsubscript{4} decomposition is structure sensitive.

2.6.1 MECHANISM OF C\textsubscript{2}H\textsubscript{4} HYDROGENATION

The mechanism for C\textsubscript{2}H\textsubscript{4} hydrogenation on transition metal surfaces was first proposed by Horiuti and Polanyi in 1934 [107]. The Horiuti-Polanyi mechanism is described using the example of Pd(111) surface. Firstly, the interaction of hydrogen with palladium needs to be considered. Molecular hydrogen is σ-bonded to a palladium atom (Figure 2.19). After dissociation of hydrogen on the Pd surface, hydrogen atoms also migrate into the interior of Pd and hydride species are formed. In particular, the small size of the H atom enhances its solubility in solids [108]. In Figure 2.19, H-atoms are located in octahedral holes of the Pd(111) surface, whereas H-atoms can move from one hole to another hole [109].

![Figure 2.19: Hydrogen on Pd(111)](image)

Figure 2.19: Hydrogen on Pd(111), (a) σ-bonded hydrogen (green), (b) H-H bond cleavage, (c) H-atoms in octahedral holes within Pd, adapted from [109]
The Horiuti-Polanyi mechanism is schematically depicted in Figure 2.20. The use of deuterium instead of hydrogen enables a clearer insight into the mechanistic procedure over Pd(111). Deuterium atoms are illustrated in red and already cover the surface. In the first step, ethylene is adsorbed on the surface. Subsequently, one of the C-C double bonds is cleaved and two $\sigma$-bonds with two adjacent Pd atoms are formed [105]. In addition, a donation of a $\pi$-electron to a Pd atom needs to be considered as well [109, 110].

In a further step, atomic deuterium forms a $\sigma$-bond with one carbon atom of ethylene, while the other carbon atom is $\sigma$-bonded to Palladium [109]. The steps from (a) to (c) are reversible; hence a manifold hydrogen-deuterium exchange needs to be taken into account. The stepwise hydrogenation of the di-$\sigma$-bonded species results in an ethyl intermediate on the surface. In the last step, a reductive elimination with a deuterium atom occurs and ethane is desorbed from the surface.

Cremer et al. [111] investigated $\text{C}_2\text{H}_4$ hydrogenation on platinum (111) using IR-visible sum frequency generation (SFG) at a temperature of 22°C and a total pressure of 1 bar. In the course of the reaction (133 mbar $\text{H}_2$ + 47 mbar $\text{C}_2\text{H}_4$ in He), ethylidyne ($\text{C}_2\text{H}_3$), di-$\sigma$-bonded ethylene, and $\pi$-bonded ethylene were observed on the surface (Figure 2.21). On the other hand, adsorbed ethyl groups ($\text{C}_2\text{H}_5$) were just visible in the SFG spectra at high hydrogen partial pressures (970 mbar) at ambient temperature. Adsorbed ethylidyne ($\text{C}_2\text{H}_3$) seems to have an inactive role as $\text{C}_2\text{H}_4$ hydrogenation on clean and $\text{C}_2\text{H}_3$ precovered Pt(111) revealed almost the same turnover rate towards $\text{C}_2\text{H}_6$ [105]. By the presence of adsorbed ethylidyne, the surface concentration of di-$\sigma$-bonded ethylene can be lowered due to competition reactions with ethylidyne. On the other hand, the reaction rate towards ethane
formation was not affected, hence di-\(\sigma\)-bonded \(\text{C}_2\text{H}_4\) is not considered as reaction intermediate.

Figure 2.21: SFG spectrum of \(\text{C}_2\text{H}_4\) hydrogenation on Pt(111) with 133 mbar \(\text{H}_2\) and 47 mbar \(\text{C}_2\text{H}_4\) at 22°C, adapted from [111]

Probable reaction intermediates for \(\text{C}_2\text{H}_4\) hydrogenation are \(\pi\)-bonded ethylene and surface ethyl species (\(\text{C}_2\text{H}_5\)), whereas surface ethelyldyne is considered as spectator species [111] (Figure 2.22). IR-studies of \(\text{C}_2\text{H}_4\) hydrogenation over Pt/Al\(_2\)O\(_3\) in the temperature range between 50-200°C and a pressure of 1 bar proposed that the hydrogenation of surface ethyl species is the rate-determining-step. It was found that the decay time of surface ethyl (\(\text{C}_2\text{H}_5\)) concentration is consistent with the rise time of ethane concentration [112].

Figure 2.22: Mechanism of \(\text{C}_2\text{H}_4\) hydrogenation on Pt(111) proposed by Cremer et al. [111]
Theoretical Background

Ethylidyne and di-σ-bonded ethylene are strongly adsorbed to the surface but are very mobile on Pt surfaces [105]. However, these species do not directly take part in the hydrogenation process. The weakly adsorbed species, such as π-bonded ethylene and surface ethyl species, participate in the hydrogenation. The high mobility of strongly adsorbed species enables that active sites on the surface become available for weakly adsorbed species that are catalytically more active. As defect sites less likely become available (due to high adsorption energies), the major part of weakly bonded species is most probably hydrogenated on terrace sites.

Another reaction path was suggested by Zaera et al. [113]. It was assumed that on Pt(111) ethylidyne (≡CCH₃) transfers hydrogen to ethylene that is weakly adsorbed on top of a carbonaceous layer. Adsorbed hydrogen incorporates into adsorbed ethylidyne and ethylidene (=CHCH₃) species are formed which transfers hydrogen to the weakly adsorbed ethylene. Later, this assumption was ruled out by Beebe et al. [114] and the role of ethylidyne as spectator was accepted. After adsorption of ethylene on Pt(111), adsorbed ethylidyne (CCH₃) was readily formed [115]. But if C₂H₄ encounters nickel, no formation of adsorbed ethylidyne is observed [39]. Therefore, large barriers to the production of CCH₃ on Ni are assumed.

Daley et al. [116] studied C₂H₄ hydrogenation on Ni(111) and it was realized that surface hydrogen atoms were not active for hydrogenation of ethylene. However, bulk H atoms were active towards C₂H₄ hydrogenation and produced gaseous ethane. Bulk H atoms are more energetic than surface H atoms [39]. When a bulk H atom interacts with an adsorbate, the energy of the bulk atom can activate a reaction with the adsorbate. Gas phase H atoms are even more energetic than bulk H atoms. Bürgi et al. [39] investigated in an electron energy loss spectroscopy (EELS) study the reactions of gas phase H atoms with ethylene, acetylene and ethane that were adsorbed on Ni(111). It was found that all of the three hydrocarbons formed adsorbed ethylidyne (CCH₃), concluding that ethylidyne is the most stable C₂ species.
2.6.2 REACTIONS OF C₂H₄ DURING CO HYDROGENATION

As ethylene and CO appear simultaneously over the catalyst during the methanation process, a more detailed description of possible interactions of CO and ethylene is presented in this passage. Chuang et al. [117] examined the reaction of ethylene with syngas (CO+H₂) on Ni/SiO₂ (14.4 wt.% Ni) in an IR-study at 240°C and varying pressure. A strong CO insertion activity was identified [118-120]; hence the formation of methane, ethane, C₃-hydrocarbons, propionaldehyde and 1-propanol as reaction products were observed under steady-state conditions when the pressure was increased to 10 bar [117]. This finding is in accordance with the possible reactions (see Figure 2.23) that might occur due to addition of ethylene during CO hydrogenation [120]. Ethylene can decompose on the catalyst to surface carbon that is then hydrogenated to methane. Adsorbed ethylene also can be hydrogenated to ethane. Moreover, chain growth to higher hydrocarbons or CO insertion to form hydrocarbon oxygenates are also relevant reactions.

Figure 2.23: Reactions due to C₂H₄ addition during CO hydrogenation, adapted from [120]

In the reaction of syngas with ethylene, carbonylation of Ni/SiO₂ occurred that was indicated by the formation of Ni(CO)₄ [117]. As a consequence, about 50% of the nickel content was removed from Ni/SiO₂, leading to an inhibition of CO methanation. On the contrary, the catalyst demonstrated increasing selectivity to
Theoretical Background

propionaldehyde with rising pressure [118]. In another in-situ IR-study [121], the reaction of adsorbed CO with C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} over reduced/oxidized Rh/SiO\textsubscript{2} was investigated at 100°C and 240°C at 1 bar. Linearly adsorbed CO both on Rh\textsuperscript{0} (reduced catalyst) and on Rh\textsuperscript{+} (oxidized catalyst) was involved in the CO insertion step that resulted in the formation of propionaldehyde from H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}. Nevertheless, linear CO adsorbed on Rh\textsuperscript{+} seemed to be more active towards CO insertion; hence oxidized Rh/SiO\textsubscript{2} showed higher selectivities and rates for the formation of propionaldehyde than the reduced catalyst. The differences between the reduced and the oxidized catalyst can be related to a different electronic state and the different geometric structure of the Rh surface atoms. CO insertion was observed for all group VIII metal carbonyls. The proposed reaction pathway [121, 122] for ethylene hydroformylation is depicted in Figure 2.24. In the first step, adsorbed C\textsubscript{2}H\textsubscript{4} is hydrogenated to form surface ethyl species (C\textsubscript{2}H\textsubscript{5}). Subsequently, adsorbed CO is inserted into adsorbed ethyl and an adsorbed acyl intermediate is generated. In the last step, hydrogenation of the adsorbed acyl species results in the formation of propionaldehyde.

![Reaction pathway for C\textsubscript{2}H\textsubscript{4} hydroformylation](image)

Figure 2.24: Reaction pathway for C\textsubscript{2}H\textsubscript{4} hydroformylation, * denotes adsorbed species, (HC)= hydrocarbon, adapted from [121]

Jordan et al. [123] studied the influence of C\textsubscript{2}H\textsubscript{4} on CO hydrogenation over a Ru/SiO\textsubscript{2} catalyst. The reaction of ethylene with hydrogen without addition of CO results in the hydrogenation of ethylene to ethane. In addition, hydrogenolysis of C\textsubscript{2}H\textsubscript{4} occurred that was indicated by the formation of methane and small amounts of C\textsubscript{3}-hydrocarbons were observed. When CO was added to the C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} gas feed, hydrogenation of C\textsubscript{2}H\textsubscript{4} to C\textsubscript{2}H\textsubscript{6} was suppressed but the concentration of C\textsubscript{3}-hydrocarbons formed through a chain growth mechanism was increased. It was suggested that the chain growth mechanism probably proceeds via addition of methylene species (CH\textsubscript{2}) to alkyl or alkylidene species [124, 125]. Increasing of the C\textsubscript{2}H\textsubscript{4} concentration resulted in suppression of CO hydrogenation but the formation of propionaldehyde (hydroformylation of C\textsubscript{2}H\textsubscript{4}) was enhanced.
Theoretical Background

2.7 HYDROGENATION OF $\text{C}_2\text{H}_2$

The producer gas of the wood gasification process also contains about 0.5 mol.% acetylene. During CO methanation over Ni/Al$_2$O$_3$, acetylene can be hydrogenated to ethylene and ethane at a temperature of 200°C. In the olefin industry, the selective hydrogenation of acetylene to ethylene plays an important role, in order to remove acetylene from ethylene feeds [126]. Palladium based catalysts are well established due to their high selectivity and high activity towards partial hydrogenation of alkynes to alkenes. Beside palladium, also nickel and copper catalysts exhibit a good performance for partial hydrogenation of alkynes. Recently, it was shown that CeO$_2$ catalyzes the selective hydrogenation of alkynes to olefins [127].

The catalytic performance of a catalyst is also governed by the particle size [105]. A change of the particle size alters the atomic surface structure; hence the particle size has an impact on the specific activity and selectivity of a catalyst [128]. It was revealed that the turn-over-frequency of Pd-particles is enhanced with increasing particle size whereas above a particle size of 11 nm, the specific activity does not depend on the size [129].

Another issue that influences the selectivity of hydrogenation catalysts is the presence of subsurface hydride or carbide phases [130-135]. In an *in situ* XPS study [134], it was demonstrated that a subsurface carbide phase can drive the selectivity in Pd-catalyzed alkyne hydrogenation towards alkenes. The catalyst must enable a strong bonding of acetylene and a weak bonding of ethylene, in order to enhance the selectivity towards the formation of ethylene [136]. Palladium can also form Pd-hydrides even at low hydrogen pressures but subsurface hydrides enhance the formation of alkanes [126]. On the other hand, the addition of Ag to the Pd-catalyst results in the same effect of subsurface carbon [136]. Khan et al. [137] showed in temperature programmed desorption experiments over alumina supported Pd-Ag catalysts that subsurface hydrogen favors the full hydrogenation of acetylene. On the contrary, surface hydrogen enhances the selectivity towards the formation of ethylene. The effect of subsurface hydrides and carbides on alkyne hydrogenation is schematically depicted in Figure 2.25.
Also nickel exhibits the ability to form subsurface hydrides and carbides [40, 138]. Palladium and nickel have a low barrier for hydrogen dissociation [132] which favors the formation of hydrides. Surface carbon species can be formed through dissociation of hydrocarbons on Ni or Pd but subsurface carbon in octahedral absorption geometry seems to be energetically favoured in Pd [132].

Subsurface carbon can also affect the adsorption behaviour of adsorbates, such as adsorbed CO, [139] because the binding energy of CO to palladium is weakened in the presence of subsurface carbon [134]. Also the adsorption of hydrogen on Pd is weakened and the Pd/C phase hampers the transport of hydrogen to the subsurface [135]. Moreover, the migration of bulk hydrogen to the surface is hindered as well. As a consequence, the hydrogenation of alkynes occurs selectively towards alkenes via surface hydrogen. On the contrary, the initial presence of a Pd/H phase hinders the formation of a carbide phase [131].

2.7.1 MECHANISM OF \( \text{C}_2\text{H}_2 \) HYDROGENATION

The formation of ethylene and ethane via hydrogenation of acetylene follows a Horiuti-Polanyi mechanism over Palladium based catalysts [107, 131]. After adsorption of acetylene and dissociation of hydrogen, the sequential addition of hydrogen to adsorbed acetylene gives an adsorbed vinyl species (HCCH₂) (see Figure 2.26). Further hydrogenation of adsorbed vinyl species results in the formation of adsorbed ethylidene (HCCH₃) or ethylene (\( \text{H}_2\text{CCH}_2 \)). Ethylene can
desorb from the surface or it is further hydrogenated [131]. Hydrogenation of adsorbed ethylidene and ethylene leads to an adsorbed ethyl species (H₂CCH₃). The last hydrogenation step forms ethane. The rate determining step of alkyne hydrogenation is proposed to be the first hydrogen addition step [134].

![Figure 2.26: Reaction pathway for C₂H₂ hydrogenation, adapted from [131]](image)

### 2.7.2 FORMATION OF OLIGOMERS DURING C₂H₂ HYDROGENATION

Alkynes, especially acetylene, can also form oligomers during C₂H₂ hydrogenation [130] whereas gas phase oligomers (C₄-C₈) or green oil (C₉+) are probable products. Also nickel is active towards oligomerization of acetylene [140]. Oligomers that are adsorbed on the catalyst surface can be related to coke. By choosing proper reaction conditions, surface oligomers can be removed from the surface due to hydrogenation treatment at increased temperatures. The H₂:C₂H₂ ratio and the temperature are important factors that affect the selectivity of oligomers but also the presence of CO can lead to the formation of oligomers when considering CO insertion to acetylene in the form HC=CH-CHO [131]. Usually, higher C₂H₂ concentrations enhance the formation of oligomers and in the absence of hydrogen, oligomers are unlikely to be formed [141]. In the case of the mechanism of oligomer formation, it was originally suggested that di-adsorbed C₂H₂ is hydrogenated to form surface vinyl species in the radical form (see Figure 2.27). The combination of the radical with di-adsorbed C₂H₂ results in a C₄ radical [140, 142]. On the other hand, the existence of free radicals on metals is still under debate [130, 140, 143].
Theoretical Background

\[
\text{HC}^* = \text{C}^* \text{H} + \text{H}^* \rightarrow \text{H}_2\text{C} = \text{C}^* \text{H} \rightarrow \text{H}_2\text{C}^* - \text{C}^* \text{H}
\]

\[
\text{H}_2\text{C}^* - \text{C}^* \text{H} + \text{HC}^* = \text{C}^* \text{H} \rightarrow \text{H}_2\text{C}^* - \text{C}^* \text{H} - \text{C}^* \text{H} = \text{C}^* \text{H}, \quad \text{etc.}
\]

Figure 2.27: Formation of oligomers during \( \text{C}_2\text{H}_2 \) hydrogenation, \(^* \) denotes adsorbed species, adapted from [140]

The cyclotrimerization of acetylene over Ni/SiO\(_2\) or Pd-based catalysts gives aromatic compounds, such as benzene [144]. On the nickel catalyst, benzene was already formed at lower temperatures (< 150°C). Benzene can be formed on Pd(111) via reaction of acetylene and an intermediate metallocyclic \( \text{C}_4\text{H}_4 \) species [145, 146]. Under high pressure conditions, acetylene and vinylidene were combined to form a \( \text{C}_4\text{H}_4 \) intermediate that produced benzene.

2.7.3 Role of CO during \( \text{C}_2\text{H}_2 \) Hydrogenation

CO is described as selectivity enhancer during acetylene hydrogenation over palladium catalysts that enhance the alkene selectivity [130, 132, 147, 148]. A similar behaviour of CO was observed during selective acetylene hydrogenation over Ni/SiO\(_2\) below 100°C [149]. The addition of CO decreased the formation of ethane. However, the nickel catalyst was slowly deactivated during repeated experiments and oligomers were formed to a greater extent. The deactivation was ascribed to a carbonaceous deposit on the catalyst. It was reported that CO was not directly involved in acetylene oligomerization; hence no CO insertion to acetylene occurred [150]. Moreover, CO improved the conversion of acetylene towards oligomers and the formation of oligomers from \( \text{C}_4 \) to \( \text{C}_{10} \) was increased at 200°C. Longer chains above \( \text{C}_{10} \) were not observed as the dense CO layer on nickel might hamper the growth of longer chains. It was also mentioned that an enhanced unsaturation of surface species due to lowered hydrogen availability on nickel might increase the reactivity between long-chain molecules. Therefore, condensation reactions of unsaturated hydrocarbons might lead to carbonaceous deposits on nickel. This could also be a reason for the absence of oligomers longer than \( \text{C}_{10} \).
Theoretical Background

CO develops dense layers on Pd(111); hence less surface sites are available for hydrogen and the adsorption energies of alkynes, alkenes and hydrogen (surface and subsurface) are lowered [131, 132]. As a consequence, the formation of a hydride phase is hindered, resulting in enhanced alkene selectivity. Regarding to oligomerization, it can be stated that the formation of oligomers is energetically favored in the presence of CO on Pd(111) [131]. On the other hand, also geometric effects need to be taken into account. The dense CO layer on Pd prevents the formation of oligomers because there are less neighboring surface sites that are needed for C-C coupling [147]. The direct alkyne-alkyne coupling becomes less probable and alkyne diffusion is blocked.
2.8 DECOMPOSITION OF ALKANES, ALKENES AND ALKYNES

Beside CO methanation and the hydrogenation of unsaturated hydrocarbons, such as ethylene and acetylene, the decomposition of hydrocarbons plays a significant role during the conversion of biomass-derived producer gas to synthetic natural gas.

Otsuka et al. [151] showed that the life of a Ni/SiO$_2$ catalyst (5 wt.% Ni) was determined by the types of hydrocarbons that were decomposed on the catalyst. The catalytic life increased in the following order: alkanes > alkenes > alkynes. On the other hand, decomposed alkanes revealed a higher degree of graphitization on nickel than alkenes and alkynes below 500°C. In addition, the deposited hydrocarbons were different in shape. Deposited carbon species from methane exhibit zig-zag fiber structures whereas carbon species from ethylene and acetylene show rolled fibers and entwined clusters of fibers (see Figure 2.28).

![Figure 2.28: SEM images of deposited carbon on Ni/SiO$_2$ (5 wt.% Ni) from (A) methane (500°C), (B) ethylene (400°C) and acetylene (400°C), adapted from [151]](image)

When the reactivities of surface carbon species deposited from different hydrocarbons were compared by the use of hydrogen, it was demonstrated that carbon species from methane and ethylene revealed a higher reactivity than carbon species from acetylene at a temperature of 500°C [151]. Summarizing, different mechanisms for the decomposition of alkanes, alkenes and alkynes were derived.
2.8.1 Decomposition of Methane

Methane decomposes on silica-supported nickel catalysts into carbon and hydrogen at temperatures higher than 175°C [152]. The first C-H bond breaking of methane is considered as the rate-determining step in the decomposition reaction [153]. During decomposition of CH$_4$ over Ni/SiO$_2$, an aggregation of Ni particles was observed on the catalyst at 530°C [154]. The catalytic performance of Ni/SiO$_2$ towards methane decomposition is increased with higher amounts of Ni in the range from 1 to 40 wt.% [155]. On the contrary, above a Ni loading of 50 wt.% the rate of methane decomposition was lowered. Thus, the nickel particle size could be associated with the catalytic performance for methane decomposition.

The deposited carbon reacts with hydrogen to form methane between 100°C and 300°C. On the other hand, carbon species from CO disproportionation may react to higher hydrocarbons below 200°C [30]. Kuijpers et al. [156] determined an increased activity of silica-supported nickel catalysts towards decomposition of CH$_4$ after several carburizing-decarburizing cycles of the catalyst. Carburization was carried out by decomposition of CH$_4$ or CO and decarburization by H$_2$. It was assumed that deposition of carbon caused surface reconstruction; hence more H$_2$ could be adsorbed after decarburization due to an increased surface area leading to higher activity for decomposition. Mechanistic information regarding methane-nickel interaction was provided by CH$_4$/D$_2$ exchange reactions over silica-supported nickel catalysts. Leach et al. [157] fed methane and deuterium over the catalyst and identified CH$_3$D and CD$_4$ as main products, whereas the concentration of CD$_4$ was decreased when the reaction temperature was lowered. For CH$_3$D the opposite behaviour was observed. The formation of CH$_3$D was proposed to proceed via an associative mechanism where a single-atom was exchanged. CD$_4$ was suggested to be generated via a dissociative adsorption mechanism with the occurrence of carbon species [157, 158].

Few infrared studies [159-161] exist about chemisorption and decomposition of methane over supported nickel catalysts. In a DRIFTS study Guo et al. [159] found CH$_x$ species on a Ni/SiO$_2$ catalyst after adsorption of CH$_4$ at 500°C. However, no CH$_x$ species were visible at lower temperature.
Ethane hydrogenolysis is the most probable reaction if ethane interacts with nickel in the presence of hydrogen. Hydrogenolysis stands for breaking of C-C bonds and further hydrogenation of the adsorbed carbon fragments. A generally accepted mechanism of hydrogenolysis on nickel suggests adsorption of \( \text{C}_2\text{H}_6 \) with cleavage of C-H bonds [162, 163].

Subsequently, the C-C bond of the hydrogen-deficient species is cleaved and the corresponding carbon species are hydrogenated. Leach et al. [157] reported the formation of \( \text{CD}_4 \) after applying \( \text{C}_2\text{H}_6 \) and \( \text{D}_2 \) over silica-supported nickel catalyst. In addition, Tanaka et al. [163] reported that any type of carbon on Ni/\( \gamma \)-Al\(_2\)O\(_3\) might decelerate hydrogenolysis of ethane. Studies on single crystals [164] showed that hydrogenolysis of ethane is a structure sensitive reaction. Ni(111) exhibited less activity towards ethane hydrogenolysis than Ni(100) surface. The activation energy for Ni(100) was determined to 100 kJ/mole, which is very similar to the value of CO methanation (105 kJ/mole).

Goodman [164, 165] proposed that CO methanation and ethane hydrogenolysis follow the same reaction pathway on Ni(100). As a consequence, the reaction pathway must include carbon species and hydrogenation of surface carbon because it already has been demonstrated for CO methanation [166]. Ni(111) showed an activation energy of 193 kJ/mole for ethane hydrogenolysis; hence a different mechanism was supposed for that surface [165]. The lower activity of Ni(111) surface can be explained in terms of different electronic structure or different distance between high coordination bonding sites. Ni(111) enables the formation of stable adsorbed C-C species with a bond length of around 1.3 Å - 1.5 Å [164]. In contrast, on Ni(100) the spacing between the sites is about 2.5 Å, which makes the C-C bond unstable, thus enabling ethane dissociation [164, 165].
2.8.3 DECOMPOSITION OF ETHYLENE

Low temperature gasification producer gas contains about 2-3 mol.% ethylene [10]. In comparison to ethane and acetylene, ethylene is represented in higher concentrations in the producer gas and is therefore of major interest during CO methanation. Several studies describe the interaction and decomposition of ethylene on nickel single crystals [167-169]. Zhu et al. [168] show in a SSIMS (Static Secondary Ion Mass Spectrometry) study that ethylene is di-σ bonded to Ni(111) between -150 and -110°C, after dosing 2 L of ethylene. After heating up to -60°C, di-σ bonded ethylene is converted to surface acetylene and hydrogen. At around 10°C, Ni(111) is covered by acetylide (CCH) and methylidyne (CH) species that decompose to surface carbon during heating up to 330°C. STM studies [138, 170] on Ni (111) clearly demonstrate that step-edges are more reactive towards decomposition of ethylene than highly coordinated terrace sites at room temperature (Figure 2.29). On step edges, C-C bond scission is more favored than C-H bond scission, what implies that free step edges are required.

Figure 2.29: STM images of Ni(111) in color scaling before (a) and after (b) addition of 1 L C₂H₄ for 100 s at ambient temperature and 1*10⁻⁸ mbar, adapted from [170]

Lapinski et al. [171, 172] report in an IR-study the formation of ethylidyne species (CCH₃) on Ni/Al₂O₃ after dosing of ethylene at around -20°C. Ethylidyne decomposes to surface carbon at around 30°C but also adsorbed C₄-species that indicate polymerization are observed on the surface. Several studies [173-175] already demonstrated that on nickel surface carbon deriving from ethylene decomposition can be partly hydrogenated to form methane.
2.8.4 DECOMPOSITION OF ACETYLENE

When \( \text{C}_2\text{H}_2 \) is brought into contact with a nickel surface at elevated temperature, decomposition of \( \text{C}_2\text{H}_2 \) is observed. Both decomposition of \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) is structure sensitive. On Ni(100) twice as much surface carbon was created by \( \text{C}_2\text{H}_2 \) decomposition than by \( \text{C}_2\text{H}_4 \) decomposition [176, 177]. In contrast, on Ni(111) a similar amount of carbon is generated both from \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \) decomposition [176, 178]. Molecular adsorption of \( \text{C}_2\text{H}_2 \) with rehybridization (sp\(^3\)) on Ni(110), (100) and (111) was observed at -193 °C, -183 °C and -153 °C [168, 179, 180]. On Ni(100), \( \text{C}_2\text{H}_2 \) starts to decompose to form acetylide (CCH) and methylidyne (CH) species at around -53 °C. Further heating above 127 °C results in the formation of surface carbon [176, 179]. Zhu et al. [168] report that \( \text{C}_2\text{H}_2 \) partially decomposes to form ethylidyne (CCH\(_3\)), acetylide (CCH) and surface hydrogen on Ni(111) above -43 °C when the surface coverage of \( \text{C}_2\text{H}_2 \) is about 0.33 monolayer (ML). Above 57 °C, residual \( \text{C}_2\text{H}_2 \) on the surface reacts to form acetylide (CCH) and methylidyne (CH) that is both decomposed to surface carbon upon further heating above 177 °C. For lower coverages of \( \text{C}_2\text{H}_2 \), (< 0.24 ML) on Ni(111), the same decomposition pathway is suggested as described for Ni(100) [168]. Lehwald et al. [181] demonstrated that step atoms on Ni(111) rupture C-H bonds at -123 °C and C-C bonds break at higher temperatures. Terrace atoms on Ni(111) show an opposite behaviour as C-C bonds decompose at around 127 °C but C-H bonds break at elevated temperatures.

Summarizing, step atoms exhibit a higher activity towards decomposition/dehydrogenation than terrace atoms and preadsorption of \( \text{H}_2 \) enables lowering the amount of surface carbon due to hydrogenation of \( \text{C}_2\text{H}_2 \). Sheppard et al. [182] investigated \( \text{C}_2\text{H}_2 \) hydrogenation on a silica-supported nickel catalyst by means of Infrared Spectroscopy. It was figured out that hydrogenation of \( \text{C}_2\text{H}_2 \) only takes place upon preadsorption of \( \text{H}_2 \). If \( \text{C}_2\text{H}_2 \) is first introduced to nickel, carbon species are deposited on the surface and the hydrogenation becomes very slow. IR spectra revealed that alkyl groups were formed on nickel by self-hydrogenation and by polymerization [182].
3 **Fundamentals of IR-spectroscopy and MS-spectrometry**

This chapter of the thesis gives an overview about infrared (IR) spectroscopy and the Diffuse Reflectance sample technique that is mainly used for subsequent experiments. This technique has a particular relevance in catalysis because it allows identifying adsorbed species on the catalyst what is required for the elucidation of the reaction pathway. Fundamentals of IR-spectroscopy are discussed and developments for sensitivity enhancement and noise reduction are described.

Gaseous molecules that are formed during CO methanation and during the conversion of hydrocarbons are detected by means of mass (MS) spectrometry. In particular, it enables identifying isotope-labeled compounds that assist in the investigation of reaction mechanisms. This chapter also explains the fundamentals of mass spectrometry and provides a brief overview of the instrumentation.
### 3.1 IR-SPECTROSCOPY

Infrared radiation can be classified into three different regions, namely far-, mid- and near-IR that is overviewed in Table 3.1. Mid-IR is of particular interest as molecular vibrations are detected in that region [183]. The parameter wavenumber is commonly used in IR-spectroscopy and it is expressed as the reciprocal of the wavelength in cm. The wavenumber is directly proportional to the frequency of IR-radiation.

**Table 3.1: Different regions of infrared radiation, modified from [183]**

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength [µm]</th>
<th>Energy [meV]</th>
<th>Wavenumber [cm⁻¹]</th>
<th>Detection of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared</td>
<td>1000 - 1</td>
<td>1.2 - 1240</td>
<td>10 – 10 000</td>
<td></td>
</tr>
<tr>
<td>Far</td>
<td>1000 - 50</td>
<td>1.2 - 25</td>
<td>10 - 200</td>
<td>Lattice vibrations</td>
</tr>
<tr>
<td>Mid</td>
<td>50 - 2.5</td>
<td>25 - 496</td>
<td>200 - 4000</td>
<td>Molecular vibrations</td>
</tr>
<tr>
<td>Near</td>
<td>2.5 - 1</td>
<td>496 - 1240</td>
<td>4000 - 10 000</td>
<td>Overtones</td>
</tr>
</tbody>
</table>

Molecules that absorb IR-radiation can be excited to vibrate and rotate. Electrons jump to an excited energy level, that has a specific quantized energy content [184]. The energy difference \( E_1 - E_2 \) between the excited and the low energy level matches with the frequency of the IR-light according to equation 3.1. The frequency is represented by \( \nu \) [s⁻¹] and \( h \) stands for the Planck constant (= \( 6.626 \times 10^{-34} \) Js).

\[
E_1 - E_2 = h \times \nu
\]  

(3.1)

When electrons go back to the ground state energy level, radiation is emitted or energy is released according to equation 3.1 [184]. Nevertheless, IR-radiation is only being absorbed if the dipole moment of the molecule is changed during molecular vibration. Molecules with a permanent or transition dipole moment are IR-active. Molecules like \( N_2 \) or \( O_2 \) are not IR-active because they do not show any dipole moment [184].
3.1.1 MOLECULAR VIBRATIONS

The number of vibrations (normal modes of vibration) can be calculated for non-linear molecules according to equation 3.2 and for linear molecules according to equation 3.3. \( N \) denotes the number of atoms.

\[
Z = 3N - 6 \quad (3.2)
\]

\[
Z = 3N - 5 \quad (3.3)
\]

These equations consider the fact that a single atom can move to three directions in space, whereas each three translational and rotational degrees of freedom are subtracted for non-linear molecules because the translational and rotational movements do not affect the distance and the angle between atoms [185]. In contrast, only two rotational degrees of freedom are subtracted with regard to linear-molecules because the rotation around the main axis does not change the energy [183, 184].

In principle, there exist two main categories of molecular vibrations, namely bending and stretching vibrations. Stretching vibrations are associated with a change of the bond length but the bond angle is not affected. Bending vibrations are related to a change of the bond angle, whereas the bond length remains unchanged. Stretching and bending vibrations exhibit sub-categories that are depicted in Figure 3.1, Figure 3.2 and Figure 3.3. The motions of the atom of non-linear molecules during the vibration are indicated with an arrow.

![Symmetric and asymmetric stretching vibrations.](image)

**Figure 3.1: Symmetric and asymmetric stretching vibrations.**
3.1.2 ASSIGNMENTS OF IR-ABSORPTION BANDS

The group frequency concept facilitates the interpretation of IR-spectra as functional groups of a molecule are discussed independently. The vibrational frequency of functional groups that can be approximated by Hooke’s law is related to the bond strength and the atomic mass. The corresponding equation is presented in equation 3.4, where $\mu$ is the reduced mass and $k$ denotes the force constant.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

(3.4)

The force constants of relevant carbon-carbon bonds are increasing in the following order: single bond $<$ double bond $<$ triple bond [184]. For that reason, IR-frequencies are increasing in the same sequence; hence the highest frequency is expected for C≡C triple bonds. With regard to the mass of substituents, an increasing mass results in a lowered frequency in the IR-spectrum. For example, the C-H stretching
vibration is usually observed at around 3000 cm$^{-1}$ and the substitution of hydrogen by chlorine decreases the IR-signal to 700 cm$^{-1}$ [184].

3.2 **FOURIER-TRANSFORM INFRARED (FT-IR) SPECTROMETER**

Generally speaking, in the FT-IR spectrometer the light source emits IR-radiation that is directed to the beamsplitter of the interferometer. The modulated IR-radiation is shining on the sample and it is monitored by the IR-detector. After signal amplification and analog-to-digital conversion, the IR-spectrum is obtained by use of Fourier Transformation [186]. Figure 3.4 shows schematically the structure of a FT-IR spectrometer.

![Figure 3.4: Schematic structure of a FT-IR spectrometer, modified from [186]](image)

### 3.2.1 **MICHelson INTERFEROMETER**

The interferometer that consists of a beamsplitter, a fixed mirror and a moving mirror is the central part of the IR-spectrometer (Figure 3.5).

![Figure 3.5: Schematic illustration of a Michelson interferometer including (A) IR-light source, (B) beamsplitter, (C) fixed mirror and (D) moving mirror.](image)
IR-radiation reaches the beamsplitter which divides the beam into two equal parts. One part of the IR-beam is directed to a fixed mirror, whereas the other part of the beam shines on a moving mirror. Both partial beams are reflected back to the beamsplitter where they are recombined. The moving mirror induces an optical path difference between the two partial IR-beams and constructive or destructive interference can occur for various frequencies depending on the position of the moving mirror [187].

The modulated IR-beam shines on the sample that absorbs specific frequencies of the IR-radiation. The remaining IR-light is focused on the detector and an interferogram is acquired that can be considered as interference of all relevant frequencies of the IR-beam. The interferogram is represented as electrical signal from the IR-detector versus the optical path difference [184, 188]. An example of an interferogram is shown in Figure 3.6.

![Interferogram](image)

**Figure 3.6: Example of an interferogram for a polychromatic IR-radiation source.**

The interferogram contains all the spectroscopic information; hence the interferogram that can be considered as a spectrum in the time-domain is converted to a frequency-domain spectrum by application of Fourier Transformation [187]. The obtained spectrum is called single beam spectrum but it includes spectroscopic contributions of the spectrometer like signals of contaminations. After division of the single beam spectrum by the reference spectrum, the final IR-spectrum is obtained that enables an assignment of absorption bands to specific wavenumbers of gaseous or adsorbed species.
3.3 Diffuse Reflectance

In heterogeneous catalysis, where significant reactions take place on the surface of a catalyst, a surface sensitive IR sample technique is required, in order to elucidate reaction pathways. Diffuse Reflectance enables in situ investigations of surface reactions and it is applicable to powder samples [189]. In addition, gas can flow through the sample without additional sample preparation. When IR-radiation impinges on the rough surface of a catalyst, one part of the radiation is mirror-like (specular) reflected. The other part penetrates the sample and it is either partially absorbed and refracted or scattered inside the porous structure of the catalyst [184]. Backscattered radiation contributes to the diffusely reflected IR-light that is collected by a mirror and directed to the detector.

![Figure 3.7: Rough and porous surface of a catalyst where IR-radiation is either specularly (arrows in blue) or diffusely (arrows in red) reflected](image)

3.3.1 Limitations of Diffuse Reflectance Infrared FT-spectroscopy (DRIFTS)

In practice, samples like catalysts with a high metal loading absorb a large part of the incident IR-radiation. As a consequence, approximately 5% of the initial IR-beam arrive at the detector [190]. The detector signal needs to be amplified but the signal-to-noise ratio is rather low afterwards [191]. Adsorbates on surfaces are in the focus of catalysis research but adsorbed species exhibit weak bands in the DRIFTS
spectrum. That is why signals of adsorbed species interfere with noise in the spectrum and interpretation of the signals becomes more complicated.

Figure 3.8: Three situations of \textit{in situ} DRIFT spectroscopy: (a) signals of a common method; (b) a more sensitive method; (c) a very sensitive method. “A” stands for active species and “B” for spectator species, modified from [192]

Figure 3.8a illustrates such a realistic case when DRIFTS spectra are acquired with limited time-resolution, large contributions of noise and low sensitivity. Basically, a blurry picture is exhibited that does not allow analyzing the situation. When the sensitivity is increased and the noise is lowered, the picture shown in Figure 3.8b is obtained. On one hand, it could be achieved by the use of synchrotron infrared light that is characterized by its enhanced brightness compared to ordinary IR-light sources. On the other hand, if there is no synchrotron IR-light available, dilution of the sample with an IR-transparent and inert matrix can enhance the signal-to-noise ratio so that the picture seen in Figure 3.8b is approached. It is still difficult to interpret the picture because unwanted spectator species interfere with active species. The aim is the separation of active and spectator species. When you realize which species are taking part in a reaction, it can contribute to the understanding of a surface reaction. The final step to reach the picture in Figure 3.8c can be reached by the application of Modulation Excitation Spectroscopy [193] that can be considered as a transient response technique. This method is used for the experiments in this thesis and it is explained in chapter 4.6.1.
In mass spectrometry, gaseous molecules or atoms are ionized, the produced ions are separated according to their mass-to-charge ratios and the sorted ions are detected [194-196]. A mass spectrometer consists of a sample inlet system, an ion source that produces ions, a mass analyzer that is responsible for the separation of the ionic species, a detector that determines the ion current of the separated ions and a computer that controls the spectrometer and records the acquired data. The ion source, the mass analyzer and the detector are placed into a central vacuum system, in order to avoid the impingement of neutral gas molecules with ions. The components of a mass spectrometer are schematically depicted in Figure 3.9.

![Figure 3.9: Basic components of a mass spectrometer.](image)

### 3.4.1 Ionization

There exists a variety of different ionization methods that are explained elsewhere [197, 198]. Nevertheless, electron ionization that is widely used [195] is described here. A heated filament produces energetic electrons (70 eV) at vacuum conditions and the generated electrons collide with gaseous molecules. During the electron bombardment, the sample molecule loses one electron and becomes positively charged [197]. In addition, the high energy impact causes breaking of chemical bonds and fragments of the sample molecule are obtained. In that way, fingerprint fragments of organic compounds can be acquired. If the electron energy is increased up to 150 eV, multiply charged ions are produced that is shown in Figure 3.10. After reaching a maximum, the amount of generated ions is decreased with increasing electron energy [199].
3.4.2 Mass Analysis

The functional principle of a quadrupole analyzer is described in the following part, whereas other types of mass analyzers are characterized elsewhere [198, 200]. Generally, a mass analyzer is selected in relation to metrological needs like time-resolution or accuracy. A quadrupole analyzer is comprised of four metal rods of the same size that are placed symmetrically. Direct current (dc) and radio-frequency (rf) potentials are applied at the rods; hence an electric field is generated [198, 200]. Ions are passing the electric field and start to oscillate. The separation of ions with different mass-to-charge (m/z) ratios takes place in the electric field because only those ions of a certain m/z ratio exhibit stable trajectories and reach the detector at the end of the pairs of rods. Ions with unstable trajectories can be removed by an electric pre-filter. As a consequence, the quadrupole analyzer can be considered as mass filter for ions with a specific m/z ratio. While varying the direct current and radio-frequency potentials with a constant ratio, mass spectra with different m/z values are acquired.

Figure 3.10: Ionization of Argon due to electron impact as a function of the electron energy, adapted from [199]
3.4.3 **ION DETECTION**

Upon separation of ions in the mass analyzer, the ion flux is converted into electric current at the detector. The secondary electron multiplier is a widely used detector that is based on the emission of secondary electrons [198, 200]. There exist different types of electron multipliers, namely the discrete and continuous dynode electron multiplier and the multichannel plate detector. All of them feature the same working principle that is explained by reference to the continuous dynode electron multiplier that is shown in Figure 3.11.

![Figure 3.11: Schematic depiction of a continuous dynode electron multiplier or channel electron multiplier, adapted from [200]](image)

The continuous dynode electron multiplier has the shape of a horn and it is made of leaded glass. The inside wall is covered with a semi-conductive material [198, 200]. High voltage is applied at the multiplier and the incoming ions impact on the inside wall. Electrons are released that strike in turn the inner surface. In this manner, a cascade of electrons is generated that is amplified.
4 EXPERIMENTAL SETUP AND APPROACH

In this chapter, the experimental setup and the instruments that were used for carrying out the experiments are described. The used materials, the sample preparation and experimental techniques are discussed and background information about the experiments is provided.

4.1 GAS DOSING SYSTEM

The gas dosing system (Figure 4.1) that was established for carrying out the experiments comprises seven mass flow controllers (Bronkhorst Hi-Tec) that were calibrated for Argon. The working principle of a mass flow controller is related to the thermal properties of gases. In order to feed different gas mixtures with Argon, a gas correction factor that considers changing gas density and the specific heat value needs to be applied to the flow rate. The procedure for the calculation of the conversion factor is described elsewhere [201]. After the mass flow controllers, a backpressure regulator was installed that is needed for upstream pressure control.
Experimental setup and approach

An evaporation system that can be bypassed enables evaporation of liquids with low pulsation and fast dynamics. Premature evaporation is always leading to fluctuations that must be prevented. Hence, phase transition needs to occur instantly, in order to obtain low pulsations. In the current case, liquid can be dosed by syringe pump in a fused silica capillary to the T-piece (Figure 4.2) that is heated by heating tape. The upper end of the capillary penetrates the T-piece but shouldn’t touch its inner wall.

Heated gas passing through the T-piece evaporates the micro liquid drop at the outlet of the capillary. Due to permanent heating of the tubing, condensation effects can be avoided. The heating of the tubing was provided by heating tapes (Hillesheim GmbH) and the inner diameter of the tubing is 3 mm, in order to lower the dead volume and to improve the dynamic properties needed for transient techniques. All components, including tubing, valves and fittings (Swagelok), were made of stainless steel.

Figure 4.1: Flow chart of the gas dosing system used for the experiments.
Experimental setup and approach

A two-position switching valve (VICI) allows feeding the gas-mixture into the reaction cell of the IR-spectrometer. If the position of the switching valve is changed, the reaction cell is back flushed with the carrier gas Argon and the reaction gases are directly analyzed by mass spectrometry. At the end of the pipes, pressure controllers (Bronkhorst Hi-Tec) maintain a constant pressure during experiments and a condenser keeps condensable gases away from the pressure controller. Mass flow controllers, pressure controllers, temperature regulators (Eurotherm GmbH) and the switching valve are operated by LabView and the graphical user interface is shown in Figure 4.3.

Preliminary to the experiment, the gas composition, the temperature, the pressure and the position of the switching valve are defined with a relevant dwell time as experimental sequence in an Excel-chart that is uploaded to LabView. This procedure allows applying periodic variations of the gas concentration because reaction conditions can be determined in every line of the chart (Figure 4.4).
Experimental setup and approach

Figure 4.3: Graphical user interface of LabView controlled devices.

Figure 4.4: Example of an experimental sequence with varying flow rates of Ar and N₂ at 1.1 bar absolute and ambient temperature.
4.2 DRIFTS REACTOR AND OPTICAL ACCESSORIES

All experiments were carried out in an environmental chamber (Graseby-Specac, HT-HP EC 19933) that can withstand temperatures up to 500°C and pressures up to 33 bar. The top section of the reaction chamber is equipped with a ZnSe window that is infrared-transparent between 500 and 20'000 cm\(^{-1}\) [202]. The sample holder is heated by a heating cartridge and the temperature is measured at the bottom of the sample holder with a thermocouple (Type K, \(\varnothing\) 1.5 mm). The sample holder has a holding capacity of 0.12 cm\(^3\) and the catalyst sample is placed on top of a stainless steel frit (ERC GmbH) with a porosity of 5 \(\mu\)m that uniformly distributes the gas stream.

The original design of the DRIFTS reactor was altered and the new configuration enables to feed the gas flow top-down through the catalyst fixed-bed. An additional stainless steel capillary was mounted on the base plate of the reactor by means of a temperature-resistant adhesive sealing material (Gomastit 405), in order to bring the gas outlet closer to the catalyst bed. The new configuration is depicted in Figure 4.5. A demountable conus made of stainless steel reduces the dead volume inside the reaction chamber; hence the dynamic properties are enhanced.

![Figure 4.5: Modified DRIFTS reactor with new gas outlet nearby the sample holder.](image)

In Figure 4.6, the disassembled environmental chamber is demonstrated. On the left side, the base plate including the heated sample holder is shown. The water jacket that is mounted on the reactor base-plate provides the cooling of the reactor outside and preserves the gaskets (Viton) from high temperature. The upper section holding the ZnSe window is placed on top of the reactor.
Experimental setup and approach

Figure 4.6: Disassembled environmental chamber.

The assembled environmental chamber is installed together with the Selector Diffuse Reflectance Accessory (Graseby-Specac) on the base-plate in the sample compartment of the IR-spectrometer (see Figure 4.7). The off-axis design of the accessory lowers the contribution of specular reflected IR-radiation and promotes diffusely reflected IR-light [190].

Figure 4.7: DRIFTS reactor in combination with the Diffuse Reflectance Accessory.

In order to maximize the IR-light throughput in the IR-spectrometer, the diffuse reflectance accessory needs to be aligned. KBr powder was used as reference material that was placed into the sample holder. For the alignment, the output ellipsoidal mirror and the output plane mirror were adjusted for rotation and tilt; hence the energy signal was optimized in that way. More details about the alignment procedure are found elsewhere [190].
Experimental setup and approach

4.3 **FOURIER-TRANSFORM INFRARED SPECTROMETER**

A Bomem DA8 spectrometer was used for the acquisition of DRIFTS spectra. The spectrometer can be operated under vacuum so that the reproducibility of measurements is ensured. Infrared radiation from 100 to around 7500 cm\(^{-1}\) is emitted by a SiC-globar and the IR-source compartment is cooled by water. The beamsplitter is made of Ge-coated KBr with an optical range from 450 to 4000 cm\(^{-1}\). The spectrometer is equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector that is sensitive between 800 and 5000 cm\(^{-1}\) [190, 203].

![Gas dosing system](image1)

![Sample compartment](image2)

Figure 4.8: Sample compartment of the DA8 spectrometer with the connected gas dosing system.
The DA8 spectrometer is controlled by the PCDA data acquisition software. The sample compartment (see Figure 4.8) that contains the environmental chamber and the optical accessory needs to be connected to the gas dosing system, the water cooling (Lauda RE104), the electricity and the temperature control.

For that purpose, vacuum feedthroughs for electricity (DN40 KF, MDC Vacuum Ltd.) and gas (DN40 KF, Baruvac) were established on the DA8 spectrometer that is depicted in Figure 4.9. The feedthrough for thermocouples was homemade and is based on LEMO push-pull plug connections that are soldered on a blank flange.

Figure 4.9: Klein-Flange (KF) feedthroughs on the DA8 spectrometer.
Experimental setup and approach

4.4 MASS SPECTROMETER

Gaseous samples were recorded with a Pfeiffer Prisma QME200 quadrupole mass spectrometer that has a Prisma ion source with a wolfram filament. Ion detection is carried out with a channel electron multiplier and a voltage of 1400 - 1840 V is applied. The transfer of the gaseous sample into the vacuum chamber is conducted by means of a Pfeiffer GES 010 gas inlet system [204]. The design of the inlet system (Figure 4.10) enables a gas transfer from a high pressure regime (ambient pressure) to ultra-high vacuum without changing the gas composition. The pressure reduction is achieved in two steps. The gas sample is laminarily pumped via a stainless steel capillary that has an inner diameter of 0.18 mm to the heatable valve body. In this manner, a pressure of about 1 mbar is attained in the valve body that connects the capillary with the vacuum chamber. When the valve is opened, a small proportion of the gas sample is molecularly flowing into the ion source of the mass spectrometer and the partial pressure of the different components is not changed. Quadstar software was used for data acquisition. Further details about the instrument and the software are mentioned elsewhere [199, 205].

Figure 4.10: Principle of operation of a GES 010 gas inlet system, modified from [204]
4.4.1 **DETERMINATION OF MASS FRAGMENTS OF RELEVANT GASES**

Mass spectral data of the following calibration gases (Messer AG) were acquired at a pressure of $5 \times 10^{-6}$ mbar: Ar (5.0), O$_2$ (4.8), CO (4.7), CO$_2$ (4.8), CH$_4$ (4.5), C$_2$H$_4$ (3.5), C$_2$H$_6$ (3.5), C$_3$H$_6$ (2.5), C$_3$H$_8$ (3.5). Data are normalized through dividing the ion current by the maximum value of each gas species. In this way, the distribution of the mass fragments is obtained that is represented in comparison to reference data of the Quadstar software in Figure 4.11. Eventual deviations from the reference data are ascribed to the material and state of the filament and to different settings of the ion source. The obtained data of the mass fragments help to identify gaseous species formed during experiments.

![Figure 4.11: Characteristic mass fragments of hydrocarbons are marked in yellow, relevant fragments of CO, CO$_2$ and H$_2$O are marked in blue.](image-url)
4.5 THE CATALYST AND GAS COMPOUNDS

A commercial nickel catalyst (50 wt% Ni on $\gamma$-Al$_2$O$_3$ and 3-4% graphite) with a particle size of 125-160 $\mu$m was used for the experiments. The catalyst was provided by Dr. Tilman Schildhauer. The BET specific surface area of the catalyst is 183 $m^2/g$ and was determined by N$_2$ adsorption. X-ray diffraction (XRD) measurements reveal a bimodal cluster size distribution of 1.8 and 4.2 nm [1]. The composition of the catalyst was determined by X-ray photoelectron spectroscopy (XPS) and the results are shown in Table 4.1.

<table>
<thead>
<tr>
<th>XPS atomic percentage [%]</th>
<th>Ni</th>
<th>Al</th>
<th>Na</th>
<th>O</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.0</td>
<td>28.4</td>
<td>0.6</td>
<td>54.3</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

The commercial nickel catalyst was synthesized by co-precipitation that enables a high metal loading. This technique can be understood as simultaneous precipitation of components from the same solution, resulting in the generation of mixed crystals. The detailed synthesis procedure is confidential. Co-precipitation develops a mixed-oxide consisting of NiO and the spinel-type NiAl$_2$O$_4$ [206]. Upon reduction of the oxide, highly defective nickel crystallites are formed that are desired in catalysis. Impregnated catalysts are usually easier to reduce than co-precipitated ones.

Ni/Al$_2$O$_3$ that is produced by co-precipitation has a very good sintering stability and it is therefore suited for the methanation reaction or steam reforming. The fresh Ni/Al$_2$O$_3$ catalyst that is used for the experiments of this thesis exhibits oxidized and hydratized NiO$_x$H$_z$ particles [1]. After reduction of the catalyst in H$_2$ atmosphere, Ni$^0$ sites are generated that are active in the methanation reaction. On the other side, nickel aluminate, NiAl$_2$O$_4$, is very stable and it is hard to reduce Ni$^{2+}$ of this compound to Ni$^0$. 
Experimental setup and approach

As far as the gas compounds are concerned, Argon 6.0, diluted carbon monoxide 4.7, ethane 3.5, ethylene 3.5, acetylene 2.6 and deuterium 2.7 were supplied from Messer AG, hydrogen 6.0 was provided by Air Liquide and carbon monoxide ($^{13}\text{C}$, 99%) by Cambridge Isotope Laboratories. All gases were applied without further purification and Argon was used as carrier gas for the entire experiments.

4.5.1 Upgrading of the sample preparation

Around 5% of an open IR-beam reach the MCT-detector of an IR-spectrometer; hence the signal-to-noise ratio is rather low [190]. As a result of the high metal loading of the used nickel catalyst, the energy throughput is additionally lowered because a large part of the incident IR-light is absorbed by the catalyst. Dilution of the catalyst with a non-absorbing matrix would increase the energy signal at the detector again, what means no further amplification of the signal by means of the PCDA-software must be applied anymore. A suitable matrix material has to be chemically inert during methanation, temperature stable up to 400°C and IR-transparent between 800 and 4000 cm$^{-1}$. Three materials have been considered for use as diluent matrices. Silicon [207], barium fluoride and silicon carbide provided by Alfa Aesar were chosen for further investigation. Both silicon and barium fluoride would fulfill all the requirements, whereas silicon carbide is not IR-transparent over the full range of interest. Figure 4.12 shows DRIFTS spectra of Si, SiC and BaF$_2$ when CO and H$_2$ are admitted to the reactor at 300°C and 1.1 bar after 10 minutes. The relative reflectance is plotted versus the wavenumber and downwards directed signals imply an increasing concentration of the observed species. Chemical interaction on the surface of BaF$_2$ is indicated in the region 1300-1500 cm$^{-1}$ and the signal-to-noise ratio for SiC is lower than for Si and BaF$_2$. On the other hand, pure silicon (99.999%, Alfa Aesar) demonstrates rather inert behaviour as just the gas phase signal of CO at 2143 cm$^{-1}$ and a very weak signal at 2349 cm$^{-1}$ assigned to gaseous CO$_2$ are revealed [208]. The small signal at 1240 cm$^{-1}$ may be neglected. Long-term observation of CO and H$_2$ over pure silicon did not show any alterations of the spectrum. Pure silicon was chosen as ideal diluent matrix for CO hydrogenation over Ni/$\gamma$-Al$_2$O$_3$ catalyst. In the next step, a proper dilution ratio must be figured out.
In the next step, a proper dilution ratio must be figured out. After several test runs, the results suggested that nickel catalyst should be diluted with pure silicon with a ratio of 5:1 (5 parts of silicon and 1 part of the catalyst), in order to achieve an enhanced signal-to-noise ratio and well resolved IR-bands in the spectra. When carrying out experiments, diluted nickel catalyst is placed on top of a pure silicon layer; as a result diffuse reflectance might be further improved. As DRIFTS spectra are influenced by packing density, the catalyst powder is compressed with a pressure of 100 N cm\(^{-2}\) for the purpose of reproducible measurements [184].

4.5.2 REDUCTION OF THE CATALYST

The commercial nickel catalyst sample was diluted 5:1 with Si and 50 mg of this mixture were placed on top of a 50 mg Si layer in the sample cup of the DRIFTS reactor cell. Prior to each measurement, the catalyst was heated to 400°C in an Argon flow while the H\(_2\) concentration was increased in 10 mol.% steps to 80 mol.%.

Due to high thermal conductivity of H\(_2\) and the dead volume of the reactor, the temperature of the sample holder slowly dropped to 220°C. At this temperature the catalyst was reduced in 80 mol.% H\(_2\) (10 Nml/min) for 1 h. The background single beam spectrum of the reduced catalyst was recorded in Ar at 200°C and 300°C, respectively. An identical experiment was performed with 100 mg \(\gamma\)-Al\(_2\)O\(_3\). For reference experiments in the absence of Ni, \(\gamma\)-Al\(_2\)O\(_3\) (Alfa Aesar, 50 m\(^2\)/g) was used.
4.6 EXPERIMENTAL TECHNIQUES

4.6.1 MODULATED EXCITATION DRIFTS/MS

Time-resolved DRIFTS spectra often do not allow to unambiguously distinguishing between species that participate in the catalytic reaction and species that are not involved in the reaction. The latter species can be static, or as dynamic as the active species. The presence of static spectator species causes difficulties in the interpretation of IR spectra because their signals are typically overwhelming and strongly overlap with those of the dynamic species, therefore of active species as well. Transient response techniques enable a better discrimination between dynamic and static species thus are ideally suited to identify active species. Modulated excitation spectroscopy (MES) [193] involves a periodic step change of an external parameter (e.g. concentration) while the spectroscopic acquisition is performed and the system response is recorded with MS at the reactor outlet. Species that are affected by the periodic stimulation exhibit a response that contains information on the process kinetics. Time-resolved DRIFTS spectra acquired during the modulation experiment can be averaged into a single modulation period, thus already increasing the signal to noise ratio. The time-domain response \( A(t) \), i.e. the averaged DRIFT spectra) can be further transformed into the phase-domain response, \( A_k(\phi_k^{\text{PSD}}) \), by applying phase sensitive detection (PSD) according to equation (4.1) [193]:

\[
A_k(\phi_k^{\text{PSD}}) = \frac{2}{T} \int_0^T A(t) \sin(\omega t + \phi_k^{\text{PSD}}) \, dt \tag{4.1}
\]

where, \( T \) is the modulation period length, \( k \) the demodulation index, \( \phi_k^{\text{PSD}} \) the phase angle and \( \omega \) the stimulation frequency. The fundamental frequency (\( k=1 \)) is used for the modulation experiments of this study. The practical result of equation (4.1) is the enhanced spectral sensitivity because static signals that are not affected by the periodic concentration change are canceled out. Importantly, the noise that exhibits
Experimental setup and approach

higher frequency than the stimulation frequency (ω) is strongly diminished in the phase-resolved spectra compared to difference spectra [192].

A requirement for the application of the modulation technique is that at some stage of the experiment the system response is completely reversible upon periodic stimulation [193]. The advantage of PSD has been now demonstrated for various spectroscopic and diffraction methods [209-218].

4.6.1.1 CO AND CH₄ MODULATION EXPERIMENTS

Concentration modulation experiments consisting in the variation of the CO concentration between 1.2 and 1 mol.% at constant H₂ concentration (6 mol.%) were performed at 200°C and 300°C (Figure 4.13a). A modulation experiment consisted of 14 consecutive periods. In addition, the CH₄ content was varied between 0.474 and 0.075 mol.% at constant ¹³CO and D₂ concentration at the ¹³CO:D₂ ratio of 1:5 (Figure 4.13b). In this case, 10 modulation periods were used. Before starting the modulation experiment, the reduced catalyst was equilibrated with the CO/H₂ gas feed for 10 min at 40 Nml/min and 1.1 bar. During a modulation period (T= 20 min), 220 sequential time-resolved spectra were acquired at a resolution of 4 cm⁻¹, each spectrum consisting of 8 co-added interferograms. After recording 110 spectra, a time delay of 1 min was considered, in order to set the rapid scan mode of the data acquisition software and to ensure synchronized measurements. Time synchronization between the gas supply system and the DA8 spectrometer was achieved by means of homemade relay connected to the IR spectrometer. The LabView controlled relay short-circuited the center part of the BNC connector at DA8 and started the measurement [219].

The resulting interferograms were Fourier transformed, divided by the background spectrum and averaged into one period. The time-resolved spectra were transformed into phase-resolved spectra using eq. 4.1. All spectra are presented in relative reflectance (R/R₀), where R₀ denotes the reflectance of the reduced nickel catalyst in Argon and R the reflectance of the catalyst under reaction conditions.
Experimental setup and approach

![Schematic of feedstock concentration changes in (a) CO and (b) CH₄ modulation experiments.]

**4.6.1.2 C₂H₆, C₂H₄ AND C₂H₂ MODULATION EXPERIMENTS**

Modulation excitation experiments were applied at 300°C and 200°C, while the concentration of the relevant C₂-hydrocarbons was varied over the nickel catalyst and the concentrations of CO/¹³CO and H₂/D₂ remained constant according to the scheme in Table 4.2. The total flow was 40 Nml min⁻¹ and the absolute pressure was 1.1 bar.

*Table 4.2: Modulation scheme; C₂-species were added one at a time while maintaining the matrix constant.*

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Temperature [°C]</th>
<th>Ethane [mol.%]</th>
<th>Ethylene [mol.%]</th>
<th>Acetylene [mol.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mol.% H₂</td>
<td>300</td>
<td>-</td>
<td>0.2 - 0</td>
<td>-</td>
</tr>
<tr>
<td>2 mol.% CO</td>
<td>200</td>
<td>-</td>
<td>0.2 - 0</td>
<td>0.2 - 0</td>
</tr>
<tr>
<td>10 mol.% D₂</td>
<td>300</td>
<td>0.2 - 0</td>
<td>0.2 - 0</td>
<td>0.05 - 0</td>
</tr>
<tr>
<td>2 mol.% CO</td>
<td>200</td>
<td>0.2 - 0</td>
<td>0.2 - 0</td>
<td>0.2 - 0</td>
</tr>
<tr>
<td>10 mol.% H₂</td>
<td>300</td>
<td>0.2 - 0</td>
<td>0.2 - 0</td>
<td>0.05 - 0</td>
</tr>
<tr>
<td>2 mol.% ¹³CO</td>
<td></td>
<td>0.2 - 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 mol.% D₂</td>
<td>200</td>
<td>-</td>
<td>0.2 - 0</td>
<td>0.2 - 0</td>
</tr>
<tr>
<td>2 mol.% ¹³CO</td>
<td></td>
<td></td>
<td>0.2 - 0</td>
<td></td>
</tr>
</tbody>
</table>
Prior to the measurement, 2 mol.% CO or $^{13}$CO and 10 mol.% D$_2$ or H$_2$ were admitted to the reduced catalyst for half a period, in order to equilibrate the catalyst. During a modulation period (T=20 min), 220 time-resolved spectra were recorded sequentially with a resolution of 4 cm$^{-1}$ and for each spectrum 8 interferograms were coadded. The procedure of the concentration modulation experiment is depicted schematically in Figure 4.14. After acquiring of 110 interferograms, a time delay of 1 min was taken into account for the purpose of setting the rapid scan mode of the data acquisition software. In total, 5-26 modulation periods were carried out for each experiment. Regarding the data treatment, the same procedure was applied as for the CO modulation experiments.

![Figure 4.14: Schematic depiction of modulated excitation experiment. The experiment is initiated by addition of C$_2$-hydrocarbons over the nickel catalyst and 220 spectra are recorded sequentially.](image)

### 4.6.2 Temperature-Programmed Desorption & Surface Reaction

For temperature programmed desorption (TPD) and temperature programmed surface reaction (TPSR) experiments, the reduced Ni/$\gamma$-Al$_2$O$_3$ was exposed to 5 mol.% CO at 25°C and 1.1 bar for 30 min. After flushing with Ar (30 Nml/min), the sample was heated from room temperature in Ar or in 1 mol.% H$_2$/Ar at 5°C/min (1.1. bar, 30 Nml/min) for TPD and TPSR, respectively. DRIFTS spectra were collected every 5°C. All spectra are the result of averaging 64 scans at a resolution of 4 cm$^{-1}$. 

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4.6.3 X-RAY DIFFRACTION

In situ high energy X-ray diffraction data (86.8 keV, $\lambda=0.143$ Å) were collected at beamline ID15B of ESRF (Grenoble, France) using a digital flat 2D panel detector (Pixium 4700) mounted at 900 mm from the sample position. The sample was firmly fixed between two quartz wool plugs in a homemade cell equipped with two graphite windows through which the X-rays were passed. The temperature of the sample was recorded using a thermocouple inserted at the entrance of the catalyst bed. Also in this case, a temperature decrease was observed upon introduction of H$_2$. XRD data were collected over 0.5 s at 400°C in flowing He prior to exposure to H$_2$ (100 ml/min), after 30 min exposure to 80 mol.% H$_2$/He (10 ml/min) and at 200°C in 6 mol.% H$_2$/He (10 ml/min). XRD measurements were carried out by Dr. Davide Ferri.
5 DRIFTS STUDY OF A COMMERCIAL Ni METHANATION CATALYST

ABSTRACT

CO methanation on a commercial alumina supported nickel catalyst is studied using temperature-programmed diffuse reflectance infrared spectroscopy (DRIFTS), mass spectrometry (MS) and a concentration modulation approach with the aim to provide insights into the reaction mechanism on an industrially relevant catalyst. Phase sensitive detection (PSD) greatly improves the sensitivity of DRIFTS under reaction conditions. Beside resident adsorbed CO species populating the surface of the catalyst during reaction at 200 and 300°C, carbonyl species are identified at 200°C that seem to indicate the sites where CO dissociation takes place. Such species are associated with sub-carbonyls or CO adsorbed on low coordinated Ni atoms. The product distribution observed during modulation of $^{12}\text{CH}_4$ concentration in a $^{13}\text{CO}/\text{D}_2$ feed at 300°C suggests that atomic C and H produced by CO and H$_2$ dissociation on Ni during methanation and C-H species may recombine to afford the methane product.

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5.1 INTRODUCTION

In chapter 2.1.1, different mechanisms of CO methanation were discussed, resulting that there exists no consensus in the literature. However, the stepwise hydrogenation of surface carbon on nickel to form methane is widely accepted [22, 25, 27, 30-33, 38]. DRIFTS studies over supported and unsupported nickel catalysts [36, 41, 220] also proposed dissociative chemisorption of CO with subsequent hydrogenation of surface carbon species. It was also shown that the dissociation of CO preferably takes place on steps on Ni(111) [16]. Another mechanism suggested H₂-induced CO dissociation on nickel surfaces via adsorbed C-OH or HC-O intermediates [16, 20, 23] but these surface species were not identified so far. A third mechanism was presented in an IR-study over Ni/Al₂O₃ that considered surface methoxy and formate groups as reaction intermediates [44]. Summarizing, based on the variety of proposed mechanisms for CO methanation, further mechanistic investigation is required.

Steady-state CO methanation does not allow indicating adsorption sites on Ni where CO dissociation takes place. However, modulated excitation DRIFTS as a transient response technique is suited well to provide both insights about reactive adsorption sites and about the mechanism of CO methanation. In this chapter, the nature of reactive sites during CO methanation is studied on a commercial alumina supported nickel catalyst used at industrial scale. Temperature programmed desorption (TPD) coupled with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to determine the coordination mode and speciation of the adsorbate layer following CO adsorption at room temperature and thermal desorption. Temperature programmed surface reaction (TPSR) enables studying the reactivity of adsorbed CO in the H₂ atmosphere. Modulated excitation DRIFTS combined with mass spectrometry (MS) is also applied, in order to identify relevant reactive species on nickel and to obtain insights into the elementary steps of CO methanation.
5.2 RESULTS AND DISCUSSIONS

5.2.1 XRD RESULTS

The state of the Ni component of the commercial Ni/\(\gamma\)-Al\(_2\)O\(_3\) catalyst was verified using in situ high energy X-ray diffraction (XRD, Figure 5.1). The measurement was performed similarly to the DRIFT experiments by heating the sample to 400°C in He followed by admission of 80 mol.% H\(_2\)/He to reduce Ni. The XRD pattern recorded at 400°C in He displays the characteristic reflections of NiO at 2\(\theta\) = 37° (111), 42° (200) and 63° (220). The reflections at 2\(\theta\) = 44° and 52° do not belong to \(\gamma\)-Al\(_2\)O\(_3\) but to metallic Ni indicating that part of Ni is already reduced in agreement with the passivation of Ni particles. This pattern is identical to that of the freshly received catalyst at room temperature (not shown). After admittance of H\(_2\), Ni is predominantly in the metallic state (reflections at 2\(\theta\) = 44.5° (111), 51.5° (200) and 76° (220)). This state is maintained after cooling to 200°C and changing to the H\(_2\) concentration needed for the modulation experiments. Therefore, the reduced Ni/\(\gamma\)-Al\(_2\)O\(_3\) catalyst exhibits mixed Ni/NiO state prior to the DRIFTS measurements [1]. The reflection at 2\(\theta\) = 26.5° corresponds to the graphite component of the catalyst. The reflection is clearly shifted to lower 2\(\theta\) values at 400°C as a result of thermal expansion.

![In situ high energy XRD data of Ni/\(\gamma\)-Al\(_2\)O\(_3\): (─) at 400°C in He before H\(_2\) exposure, (—) after 30 min exposure to 80 mol.% H\(_2\)/He and (--) at 200°C in 6 mol.% H\(_2\)/He. Symbols: (o) NiO, (+) Ni, (*) graphite.](image-url)
5.2.2 TEMPERATURE-PROGRAMMED METHODS

Figure 5.2: DRIFTS spectra obtained during (a) CO-TPD and (b) TPSR over reduced Ni/γ-Al₂O₃ following CO adsorption at room temperature. Spectra are offset for clarity.

Figure 5.2a shows the room temperature spectrum recorded after exposure of the in situ reduced commercial Ni/γ-Al₂O₃ catalyst to 5 mol.% CO/Ar for 30 min. The spectrum exhibits two broad signals at 2080 and 1960 cm⁻¹ suggesting a distribution of adsorption sites [19]. The signal at 2080 cm⁻¹ likely corresponds to sub-carbonyl Ni(CO)ₓ (x = 2 or 3) species [41]. Older assignments [221, 222] attributed high energy signals to weakly bonded CO to nickel sites featuring a highly disordered structure compared to crystalline structures with a different number of nearest neighbour atoms, which were denominated amorphous Ni sites. The signal at 1960 cm⁻¹ can be assigned to CO₅ species coordinated to semi-crystalline nickel [221, 222].

The broad signal at 2080 cm⁻¹ probably entails linear CO species (CO₅) as well that are reported to exhibit signals at ca. 2010 cm⁻¹ [41] or at 2060-2050 cm⁻¹ [223]. Ni(CO)₄ is characterized by a sharp signal at ca. 2045 cm⁻¹ [71] that however is clearly not a major species in the spectra of Figure 5.2.
Figure 5.2a also shows a selection of DRIFTS spectra that were acquired during TPD of CO between 25 and 400°C when flowing Ar. Spectra are shown only up to 340°C. The linear CO signal shifts from 2080 cm\(^{-1}\) to 2003 cm\(^{-1}\) upon temperature increase, which is likely the result of the destabilization of sub-carbonyl species making CO\(_L\) species visible. The CO\(_B\) signal moves from 1960 cm\(^{-1}\) to 1820 cm\(^{-1}\) when the temperature is varied between 115°C and 315°C and the only one clearly discernible above 315°C. The faster attenuation of CO\(_L\) compared to CO\(_B\) suggests that CO\(_B\) species are more strongly coordinated [41]. Signals appearing at 2057 and 2035 cm\(^{-1}\) upon temperature being raised were ascribed to CO\(_L\) adsorbed on semi-crystalline and crystalline nickel sites of Ni/γ-Al\(_2\)O\(_3\), respectively [221].

Figure 5.2a shows a signal at 2060 cm\(^{-1}\) at ca. 50°C that well compares with the signal of adsorbed CO on sites with less ordered structure and edge atoms, defined as semi-crystalline Ni [221]. Between 80°C and 145°C the CO\(_L\) signal shifts to 2040 and 2030 cm\(^{-1}\), which are associated with CO\(_L\) on crystalline nickel sites. The CO\(_B\) signal at ca. 1908 cm\(^{-1}\) is also generally ascribed to CO\(_B\) on crystalline nickel sites.

The overall red shift of the CO signals is caused by the temperature dependent decrease of CO coverage (weakening of dipole-dipole interactions) but is also partly the result of CO desorption from more labile adsorption Ni sites. Desorption of adsorbed CO reduces the CO coverage of the surface what implies that more d electrons of the substrate can be shared between nickel and the adsorbate [224]. As a consequence the C-O bond strength is lowered and a lower \(\nu\) (CO) frequency is induced. On one hand with increasing surface coverage of CO an upward frequency shift of adsorbed CO to higher wavenumbers considering the Blyholder model [225, 226] needs to be taken into account. Blyholder assumes lowered back-donation into the 2\(\pi^*\) anti-bonding CO orbital being responsible for the frequency shift because surface atoms compete for electrons. The CO-TPD data indicate that CO adsorbed on amorphous Ni sites are less stable and desorb more easily. At the temperatures at which modulation experiments are carried out in the following (200 and 300°C), the spectra show predominantly CO adsorbed on crystalline Ni domains.

In the spectral region below 1700 cm\(^{-1}\), signals appear at 1650 and 1440 cm\(^{-1}\) in the room temperature spectrum that are assigned to vibrational modes of adsorbed carbonate species [227] likely formed through interaction of CO with Al\(_2\)O\(_3\) or
residual NiO [228]. These species completely vanish in the spectrum recorded at ca. 140°C. The online mass spectrometric (MS) data of the TPD experiment show desorption of CO up to 100°C (Figure 5.3). CO₂ evolution below 250°C is also observed likely due to desorption of carbonate species in agreement with the DRIFTS spectra. The two desorption peaks at 87°C and 100°C are likely related to the oscillations of the temperature ramp program.

Figure 5.3 also displays the normalized MS signals corresponding to m/z 15 (CH₄), 18 (H₂O), 28 (CO) and 44 (CO₂) while feeding 1 mol. % H₂ on reduced Ni/γ-Al₂O₃ after CO adsorption at room temperature and increasing the temperature to 400°C at 5°C/min. At low temperature, weakly bonded CO desorbs from the surface similarly to the TPD experiment. The signal of CO₂ presents a similar behavior to that observed during TPD but the desorption maximum at 160°C is absent. In correspondence of this temperature, the maximum CH₄ evolution is observed indicating that beside CO hydrogenation also hydrogenation of adsorbed carbonate species could occur.
The observation that CO$_2$ is evolved faster than CH$_4$ may indicate that methane is formed by hydrogenation of surface carbon originating from disproportionation of CO [29]. Water evolution also begins at ca. 160°C indicating that water from CO hydrogenation may have re-adsorbed on the support [28, 229].

The room temperature DRIFTS spectrum in H$_2$ flow prior to TPSR (Figure 5.2b) matches that of Figure 5.2a and presents similar signals of sub-carbonyls, CO$_B$ and carbonate species. The carbonate signals at 1650 and 1440 cm$^{-1}$ demonstrate a similar desorption behaviour to the above TPD experiment in agreement with the similar CO$_2$ desorption profile of the MS data. The temperature increase in H$_2$ flow causes a shift of the CO$_L$ signal to lower frequency as well as intensity attenuation (Figure 5.2b). In contrast to the behavior of the TPD experiment, the CO$_B$ signal intensifies with increasing temperature and a shoulder develops at ca. 1850 cm$^{-1}$ between 140 and 170°C, suggesting that reorganization of the adsorbate layer or adsorbate-induced restructuring occurs [230]. In this temperature range, CH$_4$ is produced by reaction of adsorbed CO and hydrogen and it seems to correspond to the removal of CO$_L$. Therefore, the DRIFTS spectra of Figure 5.2b suggest that CO$_L$ is more susceptible than CO$_B$ towards CO hydrogenation. After the maximum of CH$_4$ formation, CO$_B$ species characterized by the signal at 1908 cm$^{-1}$ are left on the surface and further react with hydrogen up to 190°C, the conclusion of the CH$_4$ evolution peak. At 190-200°C, CO$_B$ has been completely reacted to form methane in agreement with the MS signal. Because of reaction, all adsorbed species vanish at lower temperature in the TPSR experiment compared to the TPD experiment.

5.2.3 CO + H$_2$ MIXTURE OVER γ-Al$_2$O$_3$ SUPPORT AT 300°C

Before discussing the DRIFTS spectra obtained under reaction conditions on the commercial catalyst, we present the data of the γ-Al$_2$O$_3$ support exposed to the CO:H$_2$= 1:5 feed at 300°C in Figure 5.4. Beside the gas phase signals of CO (2143 cm$^{-1}$) and CO$_2$ (2349 cm$^{-1}$), the signals at 1377 and 1593 cm$^{-1}$ can be assigned to the symmetric and asymmetric stretching O-C-O modes of formate groups, respectively adsorbed on Al$_2$O$_3$ [231]. The signals at 2910 and 1392 cm$^{-1}$ are the
corresponding C-H stretching and bending modes, respectively. Fermi resonance is observed between $\nu$ (CH) vibration and the combination of $\nu_{as}$ (CO$_2$) and $\delta$ (CH) vibrations, resulting in the band centered at 3000 cm$^{-1}$. Signals at 3535 and 3730 cm$^{-1}$ indicate perturbation of the OH groups of alumina upon formation of the formate species.

![DRIFTS spectra of γ-Al$_2$O$_3$ at 300°C in 6.5 mol.% CO-32.5 mol.% H$_2$-balanced with Ar.](image)

**5.2.4 Modulation of CO during CO/H$_2$ Methanation at 300°C**

The reversibility of the processes and of the structural changes stimulated by the variation of the external parameter (i.e. CO concentration) is a prerequisite for modulated excitation experiments. As it can be seen in Figure 5.5a, the reversible reaction conditions requirement is fulfilled. After stimulation of the CO methanation reaction by periodic variation of the CO concentration in the feedstock, a periodic reversible MS response is observed at the reactor outlet at 300°C. All signals, including Ar, display a slight but steady intensity decrease over time.
In detail, the MS data of the CO modulation experiment at 300°C (Figure 5.5b) reveal that the raise of the gas phase CO$_2$ is systematically slower than the response of H$_2$O and CH$_4$ species. This observation suggests that CO$_2$ is formed by a different
reaction path, e.g. the water-gas-shift reaction, and that this reaction is secondary. Also H₂O evolution seems slightly retarded compared to that of CH₄. Adsorption effects are probably responsible for this behavior that reflects the retarded evolution of water in the temperature programmed reaction experiment of Figure 5.3.

The averaged time-resolved DRIFTS spectra obtained during the modulation experiment at 300°C where the CO concentration was periodically changed between 1.2 and 1 mol.% are shown in Figure 5.6a. Several gas phase species can be recognized in the time-resolved spectra that can be easily assigned based on the available literature [208, 232]. The characteristic C-H stretch and bending modes of gaseous CH₄ are observed at 3017 and 1305 cm⁻¹, respectively. The peak centered at 2143 cm⁻¹ belongs to gaseous CO, whereas that at 2349 cm⁻¹ corresponds to gas phase CO₂. Roto-vibrational modes of gas phase H₂O formed during methanation can be observed in the region of 3950-3500 cm⁻¹. At lower frequency, the roto-vibrational fine structure is between 1770 and 1370 cm⁻¹.

Beside gas phase species, also adsorbates can be observed. Adsorbed CO on nickel generates three different species in the 2100-1800 cm⁻¹ spectral region. The COₗ signal is recognized at 2010 cm⁻¹, whereas two CO₃ contributions are found at 1890 and 1845 cm⁻¹ [221, 222, 233], indicating coordination of CO₃ species on distinct nickel sites. The position and number of the signals of adsorbed CO species in the time-resolved spectra are clearly different from the ones obtained from CO adsorption at room temperature and from the TPSR experiment. In the modulation experiment at 300°C, COₗ is slightly shifted to higher frequency compared to the spectrum obtained at 300°C during CO-TPD. The CO₃ species observed at 1960 cm⁻¹ in the TPSR experiment is absent at 300°C and is replaced by two species exhibiting lower frequency. Therefore, the TPSR experiment does not fully reproduce the situation under reaction conditions. The difference is most likely due to surface rearrangement under the reaction conditions, because we observed possible structural changes with increasing temperature in the TPSR experiment, and due to surface coverage effects, since under reaction conditions unreacted CO is replenished on the Ni surface thus providing DRIFTS spectra with COₗ and CO₃ signals at higher frequency.
Except for the signal of CO$_2$, variation of intensity of signals in response to the variation of CO concentration cannot be easily recognized in the time-domain. The situation is greatly improved in the corresponding phase-resolved spectra (Figure 5.6b). Small spectral changes are emphasized that are provoked by the repeated variation of CO concentration and by the filtration of the static signals of Figure 5.6a after phase sensitive detection (PSD). The difference of scale bar (one order of magnitude) between the two sets of data should be noticed. As a result, the PSD data are also strongly less noisy than difference time-resolved spectra. The phase-resolved data evidence changes around the CH$_4$, CO$_2$, adsorbed CO and H$_2$O signals. The signal at 3755 cm$^{-1}$ becomes clearly visible only in the PSD data and is associated with the stretch mode of OH groups of Al$_2$O$_3$ [234].

The phase angular dependence of the phase-resolved spectra shows that CH$_4$ and H$_2$O are formed in the CO rich half-period because their signals possess the same sign of that of gas phase CO. Besides, CO$_2$ is also produced by the water gas shift reaction (CO+H$_2$O→H$_2$+CO$_2$) as well. The synchronous in-phase growth of the signal of gas phase CO shows the fraction of unreacted CO and allows the assignment of the increased production of CH$_4$ to the portion of the experiment where CO concentration is increased from 1 to 1.2 mol.%. 

The phase-resolved spectra also hold precious information on adsorbed species that are really challenging to detect in the time-resolved spectra. A broad signal ranging from 2920 cm$^{-1}$ to 2800 cm$^{-1}$ suggests the formation of CH$_x$-species on nickel [235] whose surface population is lowered due to further reaction to methane or due to displacement by CO. In comparison to all other signals, the phase response of CH$_x$-species shows zero amplitude at ca. \( \phi_{PSD} \approx 95^\circ \) in contrast to \( \phi_{PSD} \approx 80^\circ \) of adsorbed species thus indicating that such species form after CO adsorption and thus originate from dissociation of adsorbed CO.

Simultaneously to the increased CO concentration, a signal is clearly observed at 2023 cm$^{-1}$ that is not obvious in the time-resolved spectra and needs to be assigned to a CO$_L$ species. As discussed above, signals between 2035 and 2000 cm$^{-1}$ originate from CO$_L$ species coordinated to crystalline nickel sites [221, 222]. EELS studies on Ni(111), Ni(100) and Ni(110) surfaces at ambient temperature support this attribution [236]. The presence of the CO$_L$ signal at 2023 cm$^{-1}$ simultaneous to the
presence of gas phase species, including CO, suggests that CO does not dissociate but is rather accumulated on ordered crystalline nickel sites when gas phase CO concentration is increased at 300°C. This observation is in agreement with the existence of active sites on nickel that enable dissociation of CO and less active sites where CO is adsorbed as spectator species [237]. Dissociation of adsorbed CO is expected to proceed on step sites [16] because of their lower activation barrier [238]. CO adsorbed on amorphous nickel domains where defect sites (e.g. step sites) are present is characterized by CO\textsubscript{L} signals at higher energy than 2060 cm\textsuperscript{-1} [221, 222]. Therefore, the CO\textsubscript{L} signal clearly isolated only in the phase-resolved spectra is a sign of increased CO coverage and is not probing active sites for the CO hydrogenation. This well agrees with the same sign of the gas phase species in the PSD data indicating that it does not contribute to form such species. At 300°C, CO adsorption and dissociation on possibly amorphous Ni sites is not detected under these experimental conditions. These species are likely reacting fast and are difficult to capture at this temperature also as a result of the time resolution of the experiment.

In the spectral region of CO\textsubscript{B} species, a dispersive-like signal is observed that is composed of a positive pole at 1902 cm\textsuperscript{-1} and a negative pole at 1847 cm\textsuperscript{-1}. The dispersive shape suggests the interconversion of adsorption sites that accompanies the increasing surface CO coverage on Ni(111) that can be followed with the CO\textsubscript{L} signal at 2023 cm\textsuperscript{-1} [239]. The increase of the CO\textsubscript{L} signal at the expense of a portion of CO\textsubscript{B} species and the reorganization of the CO\textsubscript{B} layer could also be indirectly related to the formation of adsorbed carbon from CO dissociation in analogy with similar observations on Pd/Al\textsubscript{2}O\textsubscript{3} during alternate CO and NO pulses [240]. The formation and accumulation of CH\textsubscript{x} species at this temperature, tentatively identified by the signal at 2900 cm\textsuperscript{-1}, could be the reason for the observed slow decay of all MS signals on time (Figure 5.5).
Figure 5.6: Selected (a) averaged time-resolved DRIFT spectra and (b) phase-resolved spectra of reduced Ni/γ-Al₂O₃ obtained during a CO modulation experiment at 300°C. Spectra are offset for clarity.
5.2.5 MODULATION OF CO DURING CO/H₂ METHANATION AT 200°C

The same CO modulation experiment was repeated at 200°C in order to lower the reaction rate and to have access to information on adsorbed species possibly involved in the CO methanation. The MS signal m/z= 15 (CH₄) decreases over the course of the modulation experiment, which suggests a gradual catalyst deactivation at 200°C. The MS data of Figure 5.7 show that CO methanation and water gas shift reactions occurred at this temperature as well but at lower levels than at 300°C. In contrast to the experiment at 300°C, the periodic increase of CO concentration (m/z= 28) causes a periodic reduction of CH₄ (m/z= 15), H₂O (m/z= 18) and CO₂ (m/z= 44) concentration in the gas phase, hence less hydrogen (m/z= 2) is dissociated on the catalyst. Similarly to the experiment at 300°C, adsorption effects on the high surface area catalyst may be responsible for the delayed evolution of water. A mass fragment m/z= 26 is additionally detected when the CO concentration is increased and is attributed to C₂- or C₃-species. This fragment is indicative of desorption of C-containing species probably originating from recombination of adsorbed C and H atoms.

Figure 5.7: Online MS data of gas phase components observed in a single modulation period at 200°C.
Figure 5.8: Selected (a) averaged time-resolved DRIFT spectra and (b) phase-resolved spectra of reduced Ni/γ-Al₂O₃ obtained during a CO modulation experiment at 200°C. Spectra are offset for clarity.

Figure 5.8a shows selected, averaged time-resolved spectra obtained during the modulation experiment at 200°C. At this temperature, the weak signal of gas phase CO₂ and the stronger signals of gas phase CO confirm the MS results showing that the CO methanation and water gas shift reactions are less favored. Adsorbed CO species display signals at 2060 cm⁻¹ (COₐ) and 1934 cm⁻¹ (COₖ) that are more
intense and shifted to higher energy compared to the species observed at 300°C. This reflects the higher CO surface coverage at lower temperature. CO_L species exhibit also larger signals than CO_B species and no low frequency species (1845 cm\(^{-1}\) at 300°C) is observed. Also at 200°C, the energy of the observed CO signals does not correspond to the TPD and TPSR results indicating that owing to reaction different adsorption sites are occupied compared to thermal and reactive desorption.

Further features of adsorbed species appear at 1593 and 1377 cm\(^{-1}\). These signals match well the symmetric and asymmetric stretching modes of formates coordinated to Al\(_2\)O\(_3\) that were observed when exposing γ-Al\(_2\)O\(_3\) to methanation conditions (see Figure 5.4). The signal at 1392 cm\(^{-1}\) is the corresponding C-H bending mode, whereas the C-H stretch modes are somewhat covered by the rotational fine structure of methane. On the contrary, at a reaction temperature of 300°C no formate species are visible because the concentration of hydroxyl groups on the γ-Al\(_2\)O\(_3\) surface determines the temperature required to form formates. For lower degree of dehydroxylation, formates are already produced at lower temperatures [241].

The phase-resolved spectra (Figure 5.8b) exhibit a sharp signal at 2070 cm\(^{-1}\) that is the region of sub-carbonyl and CO_L species. The signal has the same sign of gas phase CO but opposite sign to the gas phase methane product (3017 and 1305 cm\(^{-1}\)). Therefore, the observed gaseous product may arise from a transformation of the CO species giving rise to this signal. The high frequency of CO species coordinated to metallic Ni is generally associated with the presence of sub-carbonyls, Ni(CO)\(_x\) (\(x\) = 2, 3) [41, 71], which have been proposed to be precursors of CH\(_4\) on CeO\(_2\) supported Ni catalysts [242].

According to earlier assignments of CO species on Ni [221-223], the high energy value may also indicate that the signal belongs to CO coordinated to amorphous nickel sites, i.e. low coordination sites such as steps and edges. Both interpretations are consistent with the presence of isolated Ni atoms within a layer of adsorbed CO on well-defined crystal planes. The association of CO species adsorbed on low coordinated Ni atoms with the occurrence of the relevant CO dissociation step on the same sites agrees well with a recent work demonstrating that CO methanation takes place on step sites that are not poisoned by sulfur [243] and with DFT calculations.
Therefore, we assign the signal at 2070 cm\(^{-1}\) to a CO species responsible for CO adsorption and dissociation. The species appears when the CO concentration is increased, hence when the H\(_2\):CO is decreased, a condition favoring formation of the carbidic layer. This conclusion needs to be confirmed by experiments on well characterized catalysts.

Finally, alike the experiment at 300°C, the weak CO\(_b\) signal at 1944 cm\(^{-1}\) shows opposite sign to the CO\(_l\) signal, which could be interpreted with the same site interconversion with increasing CO coverage [239]. The phase-resolved spectra show also changes around the signals of adsorbed formate species. Two weak signals appear at 1593 and 1392 cm\(^{-1}\) that are clearly shifted compared to the evolution of CO\(_l\) (2070 cm\(^{-1}\)). The signals display zero amplitude at \(\varphi_{PSD}= 30^\circ\), whereas all other signals vanish at \(\varphi_{PSD}= 80^\circ\). In analogy to experiment performed on \(\gamma\)-Al\(_2\)O\(_3\) and with the observation of gas phase CO\(_2\), the formate species may form as a consequence of the water gas shift reaction and accumulate on Al\(_2\)O\(_3\).

### 5.2.6 Modulation of \(^{12}\)CH\(_4\) during \(^{13}\)CO/D\(_2\) Methanation at 300°C

A crucial aspect of CO methanation is whether the mechanism proceeds via COH-intermediates or via direct CO dissociation on Ni followed by recombination with H atoms. This issue has been addressed by adding \(^{12}\)CH\(_4\) to the \(^{13}\)CO methanation feedstock of the commercial Ni/\(\gamma\)-Al\(_2\)O\(_3\) catalyst. In order to obtain mechanistic insight into the reaction network, \(^{12}\)CH\(_4\) modulation experiments were conducted in \(^{13}\)CO/D\(_2\) (Figure 5.9). This approach can allow determining the origin of gas phase C-containing species evolving during reaction, since both \(^{12}\)C and \(^{13}\)C are fed, and the fate of H and D atoms.
Figure 5.9: Selected (a) averaged time-resolved DRIFT spectra and (b) corresponding phase-resolved spectra of Ni/γ-Al₂O₃ obtained during a CH₄ modulation experiment at 300°C in ¹³CO:D₂= 1:5. Spectra are offset for clarity.
In order to interpret the corresponding DRIFTS spectra of Figure 5.9, relevant vibrational modes of observed gaseous species on reduced Ni/γ-Al₂O₃ at 300°C are listed in Table 5.1. The vibrational modes of ¹³C-labelled species were calculated from the reduced masses assuming unchanged bond strengths [244] using the following equations:

\[ \nu(¹³CH) = 0.997 \cdot \nu(CH) \]  
\[ \nu(¹³CD) = 0.994 \cdot \nu(CD) \]  
\[ \nu(¹³CO) = 0.9778 \cdot \nu(CO) \]  

Selected average time-resolved spectra of Figure 5.9a show gas phase signals of ¹²CH₄, ¹²CD₄, ¹³CD₄, ¹³CO₂, ¹³CO and D₂O and adsorbed ¹³COₓ and ¹³COₜ species while ¹²CH₄ was periodically fed to the catalyst. ¹²CH₄ is visible through the signals at 3017 and 1305 cm⁻¹, whereas sharp signals of ¹³CD₄ are observed at 2243 and 986 cm⁻¹. In contrast, ¹²CD₄ shows a weak signal at 2257 cm⁻¹ that partly overlaps with other signals. The signals at 2283 and 2096 cm⁻¹ are assigned to ¹³CO₂ and ¹³CO, respectively. The roto-vibrational fine structure of D₂O is also present in the 2950-2550 cm⁻¹ and 1550-1000 cm⁻¹ spectral regions. Adsorbates are characterized by ¹³COₓ (1970 cm⁻¹) and ¹³COₜ (1867 and 1812 cm⁻¹). The only clear effect of the modulation on the time-resolved spectra is that in the second half-period of the modulation (after 11 min) the signals of ¹²CH₄ and ¹²CD₄ clearly vanish as soon as the ¹²CH₄ feed is switched off indicating that H/D exchange is very fast.

Contrary to the CO modulation experiments, the phase-resolved spectra of Figure 5.9b contain almost exclusively spectral changes associated with gas phase species. Adsorbed species visible in the time-resolved DRIFT spectra are not affected by the periodic concentration change of ¹²CH₄. This suggests that ¹²CH₄ does not produce appreciable changes within the adsorbate layer. The signals of gas phase ¹²CH₄, ¹²CD₄, ¹³CHD₃ and ¹³CO₂ appear in the PSD spectrum at \( \phi_{PSD} = 0° \). In contrast, signals of ¹³CD₄ at 2243 and 986 cm⁻¹ show opposite sign. Signals at 2982, 2135 and 1030 cm⁻¹ that are not visible in the time-resolved spectra are assigned to ¹³CHD₃, whose carbon source is ¹³CO. The weak signal at 2283 cm⁻¹ due to ¹³CO₂ is most probably the product of the
DRIFTS study of a commercial Ni methanation catalyst

Water gas shift reaction as a result of a shift out of equilibrium due to increased consumption of $D_2$ while adding $^{12}CH_4$.

Table 5.1: Vibrational modes of relevant gaseous species observed during the $CH_4$ modulation experiment in $^{13}CO/D_2$.

<table>
<thead>
<tr>
<th>Gaseous Species</th>
<th>Vibrational Modes</th>
<th>This Work [cm$^{-1}$]</th>
<th>Literature [208, 232] [cm$^{-1}$]</th>
<th>Calculated [244] [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>$\nu$ (CH)</td>
<td>3017</td>
<td>3019</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\delta$ ($^{12}CH$)</td>
<td>1305</td>
<td>1306</td>
<td>-</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>$\nu$ (CD)</td>
<td>2257</td>
<td>2259</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (CD)</td>
<td>994</td>
<td>996</td>
<td>-</td>
</tr>
<tr>
<td>$^{13}$CD$_4$</td>
<td>$\nu$ ($^{13}$CD)</td>
<td>2243</td>
<td></td>
<td>2243</td>
</tr>
<tr>
<td></td>
<td>$\delta$ ($^{13}$CD)</td>
<td>986</td>
<td></td>
<td>988</td>
</tr>
<tr>
<td>CHD$_3$</td>
<td>$\nu$ (CH)</td>
<td>-</td>
<td>2993</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\nu_s$ (CD$_3$)</td>
<td>-</td>
<td>2142</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (CD$_3$)</td>
<td>-</td>
<td>1036</td>
<td>-</td>
</tr>
<tr>
<td>$^{13}$CHD$_3$</td>
<td>$\nu$ ($^{13}$CH)</td>
<td>2982</td>
<td></td>
<td>2984</td>
</tr>
<tr>
<td></td>
<td>$\nu_s$ ($^{13}$CD$_3$)</td>
<td>2135</td>
<td></td>
<td>2129</td>
</tr>
<tr>
<td></td>
<td>$\delta$ ($^{13}$CD$_3$)</td>
<td>1030</td>
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<td>1030</td>
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<tr>
<td>CO$_2$</td>
<td>$\nu_{as}$ (CO)</td>
<td>-</td>
<td>2349</td>
<td>-</td>
</tr>
<tr>
<td>$^{13}$CO$_2$</td>
<td>$\nu_{as}$ ($^{13}$CO)</td>
<td>2283</td>
<td>2284</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>$\nu$ (CO)</td>
<td>-</td>
<td>2143</td>
<td>-</td>
</tr>
<tr>
<td>$^{13}$CO</td>
<td>$\nu$ ($^{13}$CO)</td>
<td>2096</td>
<td></td>
<td>2095</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$\nu_{as}$ (OH)</td>
<td>-</td>
<td>3756</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\nu_s$ (OH)</td>
<td>-</td>
<td>3657</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (OH)</td>
<td>-</td>
<td>1595</td>
<td>-</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>$\nu_{as}$ (OD)</td>
<td>2785</td>
<td>2788</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\nu_s$ (OD)</td>
<td>-</td>
<td>2671</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\delta$ (OD)</td>
<td>-</td>
<td>1178</td>
<td>-</td>
</tr>
</tbody>
</table>
The DRIFTS data are supported by the corresponding online MS data (Figure 5.10). It is clearly demonstrated that H\(_2\) is released from the catalyst when \(^{12}\)CH\(_4\) is added to the feed and \(^{12}\)CD\(_4\) is also simultaneously produced. The presence of \(^{12}\)CD\(_4\) suggests that \(^{12}\)CH\(_4\) dissociates into hydrogen and surface carbon that reacts with dissociatively adsorbed deuterium. This observation is in agreement with DFT calculations showing that \(^{12}\)CH\(_4\) formation and dissociation proceed via adsorbed carbon and hydrogen atoms [245]. The amount of \(^{13}\)CD\(_4\), produced by \(^{13}\)CO methanation with D\(_2\), decreases simultaneously due to perturbation of the chemical equilibrium of the methanation reaction as deuterium reacts with \(^{12}\)C-species from \(^{12}\)CH\(_4\) on the Ni catalyst. In addition, it can be assumed that adsorbed \(^{12}\)C- and \(^{13}\)C-species compete for recombination with deuterium or adsorption sites on nickel. While the concentration of \(^{13}\)CD\(_4\) is decreased, the amount of \(^{13}\)CHD\(_3\) increases but no \(^{13}\)CO\(_L\) and \(^{13}\)CO\(_B\) signals are visible in the phase-resolved spectra. The population of adsorbed \(^{13}\)CO is not affected by the CH\(_4\) modulation indicating that at this temperature PSD is able to see only spectator \(^{13}\)CO species and cannot distinguish \(^{13}\)CO species possibly involved in the methanation reaction similarly to the case of the \(^{12}\)CO modulation experiment of Figure 5.6. The appearance of \(^{13}\)CHD\(_3\) in the gas phase suggests that surface carbon or \(^{13}\)CD\(_x\)-species are possible reaction intermediates during \(^{13}\)CO/D\(_2\) methanation. \(^{13}\)CO dissociates on nickel and the surface \(^{13}\)C-atoms are stepwise deuterated to form \(^{13}\)CD\(_4\).

**Figure 5.10:** Online MS data of gas phase components observed during the CH\(_4\) modulation experiment at 200°C. Conditions: \(^{13}\)CO:D\(_2\) = 1:5, 300°C; 10 modulation periods.
5.3 CONCLUSIONS

DRIFTS was used to analyze the surface adsorbate layer of a commercial Ni/\(\gamma\)-Al\(_2\)O\(_3\) catalyst during CO methanation at two different temperatures, in order to identify potential adsorbed species involved in the reaction. TPD and TPR measurements clearly demonstrated that CO linearly coordinated to Ni is less strongly bonded than bridge bonded CO and is also more reactive towards CO methanation. The modulation excitation approach undertaken here enhances the sensitivity of DRIFTS towards subtle variations of the IR signals induced by changes of gas phase CO concentration (CO modulation).

Based on the results, a signal of adsorbed CO that becomes visible at 2070 cm\(^{-1}\) only after phase sensitive detection of the DRIFTS data at 200°C is associated with adsorbed species actively taking part to the reaction. This species, Ni sub-carbonyl or linear CO adsorbed on defect sites, coexists with a layer of adsorbed CO species on defined Ni planes in the classic linear and bridge geometries. The signal is not detectable at 300°C likely as a consequence of the fast C-O bond dissociation at higher temperature. Therefore, the data collected on an industrial catalyst seems to support the interpretation that CO dissociation occurs on isolated low coordination Ni sites. On the contrary, CO adsorbed on crystalline sites seems to be less reactive as it is rather accumulated than dissociated.

![Figure 5.11: Proposed mechanism of CO methanation on Ni/\(\gamma\)-Al\(_2\)O\(_3\).](image)

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From a mechanistic viewpoint, it is important to note that no change of the adsorbate layer is detected when the steady state $^{13}$CO/$D_2$ feed is perturbed by $^{12}$CH$_4$ pulses at 300°C. The only tangible effect is the slight lowering of the rate of production of $^{13}$CD$_4$. However, the product distribution in the gas phase allows us to conclude that $^{12}$CH$_4$ dissociated on nickel into surface C and hydrogen and possibly CH$_x$ species (see Figure 5.11). Desorption of CD$_4$ and $^{13}$CHD$_3$ products suggests the recombination of surface carbon or CH$_x$/CD$_x$-species that are possible reaction intermediates during $^{13}$CO/$D_2$ methanation. Therefore, $^{12}$C- and $^{13}$C-species probably compete for recombination with deuterium or for adsorption sites on nickel. The possible role of hydrogenation of adsorbed CO species cannot be disclosed by the presented measurements.
6 CONVERSION OF ETHANE / ETHYLENE / ACETYLENE UNDER METHANATION CONDITIONS

ABSTRACT

The conversion of saturated and unsaturated C₂-hydrocarbons under methanation conditions over a commercial nickel catalyst is investigated by means of DRIFTS and MS. The application of the modulation excitation technique and isotope-labelling enables to differentiate the CO methanation from parallel reactions, such as decomposition and hydrogenation of C₂-hydrocarbons. The enhanced sensitivity of the DRIFTS data after phase sensitive detection makes it possible to detect IR-signals that are invisible in the time domain. Ni/γ-Al₂O₃ tends to break C-C bonds and decomposes ethane, ethylene and acetylene to reactive and unreactive carbon species at 300°C. Reactive carbon species are either hydrogenated/deuterated to form CD₄ and CHD₃ or surface carbon is oxidized to form CO₂. Lower temperatures promote the hydrogenation/deuteration of unsaturated hydrocarbons. A different reaction pathway for acetylene decomposition results in the formation of adsorbed methylene species (CH₂⁻) that are probably precursors of methane. Isotope-labeling of CO reveals competitive surface reactions between carbon species arising from CO and carbon species originating from C₂-hydrocarbons.
6.1 INTRODUCTION

In the production of Synthetic Natural Gas (SNG) from carbonaceous feedstocks, such as coal or dry biomass, gasification is the first step followed by gas cleaning, the synthesis step (i.e. methanation) and final gas up-grading. In the gasification step, besides typical synthesis gas components such as CO, H₂, CO₂ and H₂O also hydrocarbons such as methane, ethane, ethylene, acetylene and aromatic species are formed. The formation of methane in the gasification is advantageous for the cold gas efficiency of the overall process chain because less CO has to be converted by exothermic methanation in the synthesis step. Unfortunately, the gasification favors also the formation of the other hydrocarbons, especially the C₂-species [47]. The producer gas of most allothermal wood gasification processes, e.g. the commercial dual fluidized-bed gasifier in Güssing/Austria [10], contains besides around 10 mol.% methane also more than 2 mol.% of ethylene and nearly 0.5 mol.% of each, ethane and acetylene. Especially, ethylene is known to be harmful by carbon deposition on the nickel catalyst used for the methanation in the synthesis step [1], if the catalyst is used in fixed bed operation. Therefore, upstream of fixed-bed methanation reactors applying nickel catalyst, ethylene in the feed gas has to be either removed (e.g. by Rectisol® wash) or be converted (e.g. by reforming) [11]. If the nickel catalyst is used under fluidized-bed operation conditions, ethylene seems to be converted to methane [246] and long-term stability up to 1000 h could be demonstrated [11]. Inside the fluidized-bed, catalyst particles are moving through the reactor and experience varying gas compositions.

In the present work, ethane, ethylene or acetylene were added over an alumina supported nickel catalyst during CO methanation. A periodic change of the C₂-hydrocarbon concentration over the catalyst simulates fluidized-bed conditions. It enables to systematically study an industrial working catalyst with a powerful modulation excitation (ME) technique. For a detailed description of the ME technique read through chapter 4.6.1.

The aim of this study is to further elucidate the reaction pathways of the relevant C₂-species (ethane, ethylene, acetylene) on a commercial nickel catalyst under methanation reactions and to demonstrate the influence of the C₂-species on CO
methanation. The use of Modulation Excitation DRIFT spectroscopy shall improve the sensitivity with respect to trace and intermediate species, while isotope-labeling shall help to understand in more detail some of the elementary steps.
6.2 RESULTS AND DISCUSSION

6.2.1 MODULATION OF ETHANE AT 300°C

Figure 6.1 shows time- and phase-resolved DRIFTS spectra that were acquired during an ethane modulation experiment over 50 mass% Ni/γ-Al₂O₃. The concentration of ethane was varied between 0.2 and 0 mol.% under CO/D₂ methanation conditions at 300°C and 1.1 bar absolute. Twenty modulation periods employing square wave excitation were carried out. Time-resolved DRIFTS spectra in Figure 6.1a demonstrate bands of gas phase species of CD₄, CHD₃, CO₂, CO, D₂O and adsorbed species of linear- and bridge-CO during the first half-period of the C₂H₆ modulation [208]. The vibration modes for observed gaseous and adsorbed species in Figure 6.1 are listed in Table 6.1. Linear-CO can be ascribed to the signal at 2015 cm⁻¹ and bridge-CO refers to the broad peak centered at 1917 cm⁻¹ [222]. In the second half-period, the signal at 2990 cm⁻¹ that is assigned to CHD₃ disappeared. CD₄ and D₂O are products of CO/D₂ methanation. Subsequently, CO is oxidized by D₂O to form CO₂ in the water-gas-shift reaction. Time-resolved spectra show IR-signals induced by CO methanation and decomposition of ethane over the nickel catalyst. Due to low sensitivity, IR-signal changes that are provoked by ethane stimulation cannot be recognized easily in the time-domain.
Conversion of ethane / ethylene / acetylene under methanation conditions

Figure 6.1: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, C$_2$H$_6$ modulation (0.2 - 0 mol.%) over Ni/γ-Al$_2$O$_3$ under methanation conditions (10 mol.% D$_2$, 2 mol.% CO) at 300°C and 1.1 bar.
Table 6.1: Summary and mode assignment of IR peak positions of the identified gaseous and adsorbed (marked by *) species, and comparison with literature data. $^{12}$C-species, if not stated otherwise. - Not identified signals are marked as "- ni -".

<table>
<thead>
<tr>
<th>MOLECULE /OR ADSORBATE</th>
<th>ASSIGNMENT</th>
<th>WAVENUMBER [cm$^{-1}$] (THIS WORK) (CALCULATION: LIT [244])</th>
<th>LIT [182, 208, 222, 227, 232, 233, 241, 247-250]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_g$</td>
<td>$\nu$(CO)</td>
<td>2143</td>
<td>2143</td>
</tr>
<tr>
<td>$^{13}$CO$_g$</td>
<td>$\nu$(13CO)</td>
<td>2096 (calc: 2095)</td>
<td>-</td>
</tr>
<tr>
<td>CO* LINEAR</td>
<td>$\nu$(CO) LIN</td>
<td>2000 - 2067</td>
<td>2000 - 2140</td>
</tr>
<tr>
<td>$^{13}$CO* linear</td>
<td>$\nu$(13CO) LIN</td>
<td>2005 - 2018</td>
<td>-</td>
</tr>
<tr>
<td>CO* BRIDGE</td>
<td>$\nu$(CO) BR</td>
<td>1866 - 1945</td>
<td>&lt; 2000</td>
</tr>
<tr>
<td>$^{13}$CO* bridge</td>
<td>$\nu$(13CO) BR</td>
<td>1850 - 1895</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$,g</td>
<td>$\nu$(CH)</td>
<td>3017</td>
<td>3019</td>
</tr>
<tr>
<td></td>
<td>$\delta$(CH)</td>
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<td>1306</td>
</tr>
<tr>
<td>CD$_4$,g</td>
<td>$\nu$(CD)</td>
<td>2257</td>
<td>2259</td>
</tr>
<tr>
<td></td>
<td>$\delta$(CD)</td>
<td>994</td>
<td>996</td>
</tr>
<tr>
<td>$^{13}$CH$_4$,g</td>
<td>$\nu$(13CH)</td>
<td>3007</td>
<td>3009</td>
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<td>1302</td>
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<td>$^{13}$CD$_4$,g</td>
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<td></td>
<td>$\delta$(13CD)</td>
<td>994 (calc: 988)</td>
<td>-</td>
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<td>CHD$_3$,g</td>
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<td>2990</td>
<td>2993</td>
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<td>1036</td>
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<tr>
<td></td>
<td>$\delta$(CD$_3$)</td>
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<td>1003</td>
</tr>
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<td>$^{13}$CHD$_3$,g</td>
<td>$\nu$(13CH)</td>
<td>2983 (calc: 2984)</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>$\delta$(13CD$_3$)</td>
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<td></td>
<td>$\nu$(CH$_3$)</td>
<td>2893 - 2894</td>
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<tr>
<td></td>
<td>$\delta$(CH$_3$)</td>
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<td>1469</td>
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<td></td>
<td>$\delta$(CH$_3$)</td>
<td>- ni -</td>
<td>1379</td>
</tr>
<tr>
<td>C$_2$D$_6$,g</td>
<td>$\nu$(CD$_3$)</td>
<td>2237 - 2238</td>
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<td></td>
<td>$\nu$(CD$_3$)</td>
<td>2222</td>
<td>2226</td>
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<td></td>
<td>$\nu$(CD$_3$)</td>
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<td>2087</td>
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<tr>
<td></td>
<td>$\delta$(CD$_3$)</td>
<td>- ni -</td>
<td>1081</td>
</tr>
<tr>
<td>C$_2$H$_4$,g</td>
<td>$\nu$(CH$_2$)</td>
<td>3106</td>
<td>3106</td>
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<td>1444</td>
</tr>
<tr>
<td></td>
<td>$\omega$(CH$_2$)</td>
<td>950</td>
<td>949</td>
</tr>
<tr>
<td>C$_2$H$_2$,g</td>
<td>$\nu$(CH)</td>
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<td>3295</td>
</tr>
<tr>
<td></td>
<td>$\nu$(CH)</td>
<td>3282</td>
<td>3282</td>
</tr>
<tr>
<td>CH$_2$* methylene</td>
<td>$\nu$(CH$_2$)</td>
<td>2927 ± 5</td>
<td>2927 ± 5</td>
</tr>
<tr>
<td></td>
<td>$\nu$(CH$_2$)</td>
<td>2854</td>
<td>2855 ± 5</td>
</tr>
<tr>
<td></td>
<td>$\delta$(CH$_2$)</td>
<td>1465</td>
<td>1467</td>
</tr>
</tbody>
</table>
In the phase-resolved spectra in Figure 6.1b, gaseous species are shown that originate from ethane decomposition and deuteration, respectively. Bands of linear- and bridge CO were not affected by modulation and therefore disappear in the phase-resolved spectra. At a phase angle ($\phi^{PSD}$) of 0°, a broad band between 3120 and 2750 cm$^{-1}$ dominates the spectrum and the band most probably consists of several signals of different species. In the region between 3000 cm$^{-1}$ and 2800 cm$^{-1}$, adsorbed CH$_x$ species are assumed but the superimposed bands cannot be unequivocally ascribed to a certain species. The band located at 2894 cm$^{-1}$ is assigned to the $\nu_s$ (CH$_3$) vibration of C$_2$H$_6$. The signals at 2955 and 2932 cm$^{-1}$ that represent combination bands [251] can be related to C$_2$H$_6$ as well and match with the reference spectrum of gaseous ethane in Figure 6.2. The sharp peak located at 2990 cm$^{-1}$ can be attributed to the $\nu$ (CH) vibration of CHD$_3$. Further signals of CHD$_3$ are identified at 2141, 1036 and 1002 cm$^{-1}$. The roto-vibrational fine structure of D$_2$O is observed.
between 1550 cm\(^{-1}\) and 1000 cm\(^{-1}\) but it is overlapped by the \(\delta\) (CH\(_3\)) vibration (1470 cm\(^{-1}\)) of C\(_2\)H\(_6\). The band at 2349 cm\(^{-1}\) indicates the occurrence of CO\(_2\) whenever C\(_2\)H\(_6\) is fed over Ni/\(\gamma\)-Al\(_2\)O\(_3\). The weak band located at 2257 cm\(^{-1}\) is assigned to CD\(_4\) but it is not visible at a phase angle of 0°.

**Figure 6.2: Reference DRIFTS spectrum of gaseous ethane over silicon at ambient temperature.**

Deuterolysis of C\(_2\)H\(_6\) on Ni/\(\gamma\)-Al\(_2\)O\(_3\) presumably creates surface carbon fragments. Adsorbed H-atoms are present on the surface after decomposition of C\(_2\)H\(_6\) and partially desorb as H\(_2\) from the surface (see MS-results in Figure 6.3a). Adsorbed carbon and CH-intermediates react with adsorbed D-atoms to form CD\(_4\) and CHD\(_3\), respectively. C\(_2\)H\(_6\) is the only carbon source to form additional CD\(_4\) and CHD\(_3\) that was verified by the use of isotope-labeled CO. Therefore, ethane deuterolysis can be considered as parallel reaction that does not interfere with CO methanation.

In order to identify the carbon source for CO\(_2\) formation, CO is replaced by \(^{13}\)CO keeping the gas composition constant. Figure 6.3b presents MS-data of different gaseous species at the reactor outlet over the course of the C\(_2\)H\(_6\) modulation under \(^{13}\)CO/H\(_2\) methanation conditions. The shaded area indicates when C\(_2\)H\(_6\) is added to the feed. MS data in Figure 6.3b allow distinguishing between two different CO\(_2\) species that give a clear hint for various reaction pathways.
Conversion of ethane / ethylene / acetylene under methanation conditions

For hydrogenation of surface carbon, additional hydrogen is consumed which has an influence on the chemical equilibrium of the water-gas-shift reaction ($^{13}\text{CO} + \text{H}_2\text{O} \leftrightarrow ^{13}\text{CO}_2 + \text{H}_2$); hence more $^{13}\text{CO}_2$ is formed and the amount of water is lowered.

On the other hand, carbon fragments that originate from ethane decomposition are partly oxidized to form CO$_2$. C$_2$H$_6$ is not fully converted over the nickel catalyst at 300°C because unreacted ethane is identified by MS- and IR-data. No indication of deactivation of the catalyst is observed after 20 modulation periods.

Figure 6.3: MS-signals at the reactor outlet as function of time during C$_2$H$_6$ simulation under (a) CO/D$_2$ and (b) $^{13}$CO/H$_2$ methanation at 300°C and 1.1 bar. The shaded area indicates half-periods and C$_2$H$_6$ addition.
In Figure 6.4, demodulated IR-signals are plotted versus the phase angle. Signals are normalized by dividing the demodulated IR-signals by the maximum value of each species. The phase angle demodulation plot enables to differentiate species with different kinetics. Species with the identical phase angle development exhibit comparable kinetics and may pursue the same reaction pathway. In Figure 6.4, it is demonstrated that the phase response signal of CD$_4$ is delayed with regard to CHD$_3$, C$_2$H$_6$ and CO$_2$, what implies different kinetics for deuteration of surface intermediates like C or CH. The reason might be a kinetic isotope effect with slower formation of four C-D bonds for CD$_4$ when compared with three C-D bonds for CHD$_3$ as heavier isotopes usually react more slowly [252]. Atomic surface carbon quite likely represents the major surface intermediate. The observation of gaseous CHD$_3$ indicates adsorbed methylidyne species (CH) as consecutive reaction intermediates.

![Phase angle demodulation plot of C$_2$H$_6$ modulation under methanation conditions (10 mol.% D$_2$, 2 mol.% CO) at 300°C and 1.1 bar.](image)

**6.2.2 MODULATION OF ETHANE AT 200°C**

Figure 6.5 presents time- and phase-resolved DRIFTS spectra that were collected when ethane was modulated with the same procedure at 200°C. In the time-
resolved spectra in Figure 6.5a, bands of gas phase species of CD₄, CO, D₂O, C₂H₆ and adsorbates (linear- and bridge-CO) are exhibited.

Figure 6.5: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, C₂H₆ modulation (0.2 - 0 mol.%) over Ni/γ-Al₂O₃ under methanation conditions (10 mol.% D₂, 2 mol.% CO) at 200°C and 1.1 bar.
Table 6.1 summarizes the observed vibration modes of gaseous and adsorbed species in Figure 6.5. The $\delta$ (CH$_3$) vibration of gaseous C$_2$H$_6$ is slightly visible at around 1470 cm$^{-1}$ as the sensitivity is too low in time-resolved spectra. A weak signal at around 2875 cm$^{-1}$ could be derived from CH$_x$ species [247] but it might overlap with bands dedicated to C$_2$H$_6$. Linear- and bridge-CO show bands located at 2055 cm$^{-1}$ and 1925 cm$^{-1}$, respectively [222]. The bands of adsorbed CO are shifted to higher wavenumbers and are more intense compared to the species detected at 300°C. CO also reacted with deuterium to form formates on γ-Al$_2$O$_3$ at 200°C [231, 241], thus the signal at 1584 cm$^{-1}$ can be assigned to the $\nu_{as}$ (OCO) vibration and the band at 1343 cm$^{-1}$ is ascribed to the $\nu_s$ (OCO) vibration. The weak band at 1448 cm$^{-1}$ can be assigned to an antisymmetric CO$_3^{2-}$ stretching vibration of carbonates [247, 248].

In Figure 6.5b, the phase-resolved spectrum at a phase angle of 0° is dominated by the broad band of gaseous C$_2$H$_6$ that exhibits vibration modes at 2978 cm$^{-1}$ [$\nu$ (CH$_3$)], 2893 cm$^{-1}$ [$\nu_s$ (CH$_3$)] and 1470 cm$^{-1}$ [$\delta$ (CH$_3$)] [208]. The signals located at 2955 cm$^{-1}$ and 2930 cm$^{-1}$ are also assigned to combination bands of gas phase C$_2$H$_6$ [251]. A weak band at 1555 cm$^{-1}$ that is superimposed by the signal of the $\delta$ (CH$_3$) vibration of C$_2$H$_6$ can be associated with the $\nu_{as}$ (CO$_2^{δ-}$) stretching vibration of carboxylates [247, 248]. The signal of CO$_2^{δ-}$ is anti-correlated with respect to the bands of C$_2$H$_6$, what means that the surface concentration of carboxylates is slightly decreased during the course of the modulation. The signal dedicated to carbonate species (located at 1448 cm$^{-1}$) is not visible in the phase-resolved spectra due to the overlapping $\delta$ (CH$_3$) band of C$_2$H$_6$. A very weak signal centered at 2060 cm$^{-1}$ can be ascribed to linear-CO [222].

By increasing the phase angle, all of the signals become weaker and disappear simultaneously at $\phi^{PSD}= 80°$; hence identical kinetics can be assumed. Obviously, no signal at 2257 cm$^{-1}$ [$\nu$ (CD)] that is assigned to CD$_4$ is recognized in the phase-resolved spectra, showing that neither C$_2$H$_6$ is decomposed nor CO deuteration is influenced by C$_2$H$_6$ addition. CD$_4$ that is observed in the time-resolved spectra is the product of CO deuteration only. The formation of formates on the alumina support is not affected by ethane; therefore signals of formates are filtered out by demodulation.
In addition, the water-gas-shift reaction is less relevant at 200°C because only traces of gas phase CO\textsubscript{2} are formed. Generally speaking, Ni/γ-Al\textsubscript{2}O\textsubscript{3} demonstrates no activity towards C\textsubscript{2}H\textsubscript{6} decomposition at a temperature of 200°C.

6.2.3 Modulation of Ethylene at 300°C

After the admittance of 0.2 mol.% C\textsubscript{2}H\textsubscript{4} to the CO/D\textsubscript{2} feed over Ni/γ-Al\textsubscript{2}O\textsubscript{3} at 300°C, signals of gas phase species of CD\textsubscript{4}, CHD\textsubscript{3}, CO\textsubscript{2}, CO, C\textsubscript{2}H\textsubscript{4} and D\textsubscript{2}O are observed in the time-resolved spectra in Figure 6.6a. When the C\textsubscript{2}H\textsubscript{4} concentration is lowered, the ν (CH) band of CHD\textsubscript{3} at 2990 cm\textsuperscript{-1} is decreased [208]. The only signals of adsorbates seen in the time-resolved spectra are linear- and bridge-CO located at 2015 cm\textsuperscript{-1} and 1906 cm\textsuperscript{-1} [233]. The signals of adsorbed CO are less intense than those observed during ethane modulation at 300°C.

Phase-resolved spectra in Figure 6.6b reveal bands that originate from ethylene modulation as only signal changes appear in the spectra and static signals are filtered out. Ethylene over nickel under CO/D\textsubscript{2} methanation conditions induces the formation of gaseous CD\textsubscript{4}, CHD\textsubscript{3} and CO\textsubscript{2}. Major products of ethylene decomposition and subsequent deuteration of surface carbon species are CD\textsubscript{4} and CHD\textsubscript{3}. The ν\textsubscript{as} (OD) band of D\textsubscript{2}O at 2785 cm\textsuperscript{-1} is upward directed and hints at decreasing concentration of D\textsubscript{2}O during addition of ethylene. The sharp signal located at 950 cm\textsuperscript{-1} is assigned to the ω (CH\textsubscript{2}) band of C\textsubscript{2}H\textsubscript{4} and indicates incomplete conversion of ethylene.

Linear- and bridge-CO related signals located at 2015 cm\textsuperscript{-1} and 1900 cm\textsuperscript{-1} are anti-correlated with respect to the signal of gaseous CD\textsubscript{4}. That implies that the surface population of linear- and bridge-CO on nickel is decreasing when the ethylene concentration is increased. The adsorption strength of ethylene on nickel is greater than for carbon monoxide and hydrogen [149, 253-256]. Therefore, one might speculate that adsorbed linear- and bridge CO and hydrogen are displaced by ethylene because ethylene bonds more strongly to nickel.
Conversion of ethane / ethylene / acetylene under methanation conditions

Figure 6.6: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, C$_2$H$_4$ modulation (0.2 - 0 mol.%) over Ni/γ-Al$_2$O$_3$ under methanation conditions (10 mol.% D$_2$, 2 mol.% CO) at 300°C and 1.1 bar.
Conversion of ethane / ethylene / acetylene under methanation conditions

On the other side, a change of the surface reflectance as a result of carbon deposition could contribute additionally to the decreasing intensity of adsorbed linear- and bridge-CO. However, as no major baseline shift occurred during the reaction, the effect of changing surface reflectance is rather negligible. As far as kinetics is concerned, the demodulated signal of CD$_4$ exhibits a slight phase delay with regard to the signal of CHD$_3$. This effect already has been discussed for ethane.

MS data in Figure 6.7a confirm the release of hydrogen that might be displaced by strongly adsorbed ethylene. In addition, the formation of CHD$_3$ is demonstrated that possibly arised from the reaction of dissociated deuterium on nickel and adsorbed CH-intermediates or from reactions of partly deuterated carbon with adsorbed hydrogen. For the detection of CHD$_3$, the m/z ratio of 19 is considered. In Figure 6.7b, MS data of C$_2$H$_4$ modulation under CO/H$_2$ methanation are depicted. Beside conversion of surface carbon to methane, hydrogenation of ethylene to ethane is observed as parallel reaction whereas the activity towards hydrogenation is rather low as CO might inhibit the reaction [149]. Ethylene is not completely converted as the signal measured for m/z=24 can be assigned to mass fragments of ethylene present at the reactor outlet.

The application of $^{13}$CO allows distinguishing different carbon species that either originate from CO dissociation or ethylene decomposition. Therefore, $^{13}$CO methanation (10 mol.% H$_2$ and 2 mol.% $^{13}$CO) in combination with ethylene modulation is carried out and the resulting MS data are presented in Figure 6.7c. Additional methane that is formed during ethylene addition exclusively derives from ethylene because only CH$_4$ and no additional $^{13}$CH$_4$ is detected by IR (see Figure 9.1 in supplement information). Alike the modulation experiment with ethane at 300°C, the increased consumption of hydrogen due to hydrogenation of surface carbon influences the equilibrium of the water-gas-shift reaction. As a consequence, the MS-signal of $^{13}$CO$_2$ (m/z= 45) in Figure 6.7c is increased but the content of H$_2$O in the outlet gas feed is lowered during addition of ethylene. Simultaneously, the MS-signal for CO$_2$ (m/z= 44) goes up. This finding suggests a partial conversion of adsorbed ethylene-derived carbon fragments to carbon dioxide.
Conversion of ethane / ethylene / acetylene under methanation conditions

Figure 6.7: MS-signals at the reactor outlet as function of time during C₂H₄ stimulation under (a) CO/D₂, (b) CO/H₂ and (c) ¹³CO/H₂ methanation at 300°C and 1.1 bar. The shaded area indicates half-periods and C₂H₄ addition.
According to literature [167-169] ethylene is decomposed to surface carbon on nickel at 300°C and the results of the DRIFTS-study support these findings. C-C bond scission is a required step in order to form surface carbon. STM studies on Ni(111) [138, 170] showed that C-C bond rupture preferably occurs on step-edges. It gives rise to the assumption that either free sites on step-edges are available, or hydrogen and carbon atoms that occupied step-edges are displaced during dosing of ethylene. In principle, the formation of reactive and unreactive carbon species on nickel has to be taken into account. Reactive surface carbon and CH-/CHD\textsubscript{x}-intermediates are deuterated to form CD\textsubscript{4} and CHD\textsubscript{3}, respectively, while in parallel, CO/D\textsubscript{2} methanation is proceeding. No deactivation of the catalyst caused by the presence of ethylene is observed during the course of the entire modulation.

6.2.4 Modulation of Ethylene at 200°C

The impact of the temperature on surface reactions on nickel has been already discussed for ethane but more reactive ethylene reveals stronger interaction with nickel at 200°C than ethane. Therefore, ethylene concentration was switched between 0.2 and 0 mol.% over Ni/γ-Al\textsubscript{2}O\textsubscript{3} at 200°C. Simultaneously, the CO/D\textsubscript{2} ratio was maintained constant, while DRFTS spectra were recorded sequentially. In Figure 6.8a, bands of gas phase species of CD\textsubscript{4}, CO\textsubscript{2}, CO, D\textsubscript{2}O and C\textsubscript{2}H\textsubscript{4} emerge in the time-resolved DRIFTS spectra in the first half-period up to 11 minutes. In the second half-period, the ethylene concentration decreases to zero and the band centered at 950 cm\textsuperscript{-1} (C\textsubscript{2}H\textsubscript{4}) vanishes [208]. As far as adsorbed CO is concerned, linear-CO is attributed to the band located at 2060 cm\textsuperscript{-1} and bridge-CO is associated with the broad band at 1920 cm\textsuperscript{-1} [233]. Temperatures around 200°C promote the formation of formates on the γ-Al\textsubscript{2}O\textsubscript{3} support that was already demonstrated in chapter 5.2.3. That is why the signals at 1585 cm\textsuperscript{-1} and 1343 cm\textsuperscript{-1} can be assigned to the ν\textsubscript{as} (OCO) and ν\textsubscript{s} (OCO) vibration mode of formates [241]. The signal at 1449 cm\textsuperscript{-1} can be ascribed to the asymmetrical stretching vibration of chemisorbed CO\textsubscript{3}\textsuperscript{2-} [247, 248].
Figure 6.8: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, \( \text{C}_2\text{H}_4 \) modulation (0.2 - 0 mol.%) over Ni/\( \gamma \)-Al\(_2\)O\(_3\) under methanation conditions (10 mol.% \( \text{D}_2 \), 2 mol.% CO) at 200°C and 1.1 bar.
Phase-resolved DRIFTS spectra in Figure 6.8b give an insight into the surface reactions when ethylene interacts with nickel at 200°C. The formation of gaseous CHD$_3$ and C$_2$D$_6$ is observed. The signals at 2990 cm$^{-1}$ and 1036 cm$^{-1}$ match with the bands of $\nu$ (CH) and $\delta$ (CD$_3$) that are ascribed to CHD$_3$. Gaseous C$_2$D$_6$ reveals two sharp bands located at 2237 cm$^{-1}$ and 2222 cm$^{-1}$ assigned to $\nu$ (CD$_3$) stretching vibrations [208].

Gaseous CD$_4$ is assigned to the signal at 2257 cm$^{-1}$ but it is upward directed with regard to the CHD$_3$ signal and therefore signifies decreasing concentration of CD$_4$. In addition, not converted C$_2$H$_4$ gives bands at 3106 and 950 cm$^{-1}$ as these signals match with the bands observed for gaseous ethylene in the reference spectrum in Figure 6.9. Referring to adsorbed species, linear-CO features a sharp band at 2067 cm$^{-1}$ and bridge-CO displays a band at 1945 cm$^{-1}$. Bridge-CO is anticorrelated with respect to linear-CO as CO preferentially populates terminal sites on nickel and the concentration of bridge-CO is reduced. Surnev et al. [239] refers this effect to adsorption site interconversion observed for increasing surface coverages of CO on Ni(111).

![Figure 6.9: Reference DRIFTS spectrum of gaseous ethylene over silicon at ambient temperature.](image)

As the bands of linear-CO and CD$_{4,g}$ (2257 cm$^{-1}$) exhibit signals with opposite direction, it might be possible that CD$_4$ synthesis uses the carbon atom from adsorbed linear-CO. Linear-CO at 2067 cm$^{-1}$ is generally ascribed to CO bonded
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to amorphous nickel sites [221, 222] that are active for CO adsorption and dissociation. Other assignments [41], attribute signals at around 2070 cm\(^{-1}\) to sub-carbonyls, Ni(CO)\(_x\) (x = 2, 3), adsorbed on low co-ordinated Ni atoms. One might assume that linear-CO is accumulated on amorphous nickel sites and deuterium or hydrogen is partly displaced by CO and C\(_2\)H\(_4\) [149, 257]. Moreover, atoms from dissociatively adsorbed CO and C\(_2\)H\(_4\) seem to compete for deuterium atoms on the surface. In addition, carboxylate and carbonate species on the catalyst show an upward directed signal at 1555 cm\(^{-1}\) and 1440 cm\(^{-1}\) that can be ascribed to the \(\nu_{\text{as}}\) (CO\(_2\)\(^2\)-) and \(\nu_{\text{as}}\) (CO\(_3\)\(^2\)-) vibration mode, respectively [247, 248]. The addition of ethane during CO methanation already revealed decreasing surface population of carboxylates on the catalyst. Due to the use of deuterium, MS-data of the gaseous product stream at the reactor outlet contain overlapping mass fragments of different deuterated hydrocarbons. In order to simplify the interpretation of mass spectral data, deuterium is replaced by hydrogen and the reaction conditions remained the same. MS data in Figure 6.10 underline that ethane is formed to a greater extent than at 300 °C but a certain amount of ethylene did not react on the catalyst. Ethylene hydrogenation seems to play a more important role at 200 °C. There is a hint that ethylene and CO cause a slight deactivation of the catalyst over the entire twenty modulation periods as the MS-signal for methane is gradually lowered over the time (not shown).

![Figure 6.10: MS-signals at the reactor outlet as function of time during C\(_2\)H\(_4\) stimulation under CO/H\(_2\) methanation at 200°C and 1.1 bar. The shaded area indicates half-periods and C\(_2\)H\(_4\) addition.](image)

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6.2.4.1 Replacement of CO by $^{13}$CO

Two different carbon sources, namely carbon monoxide and ethylene, contribute to the surface reactions on the catalyst during ethylene modulation at 200°C. CO methanation, C$_2$H$_4$ hydrogenation and C$_2$H$_4$ decomposition arised as main parallel reactions and in addition, formates, carbonates, carboxylates and adsorbed CO are observed on the catalyst surface. In order to clarify the assignment of different bands in the DRIFTS spectra, CO is replaced by $^{13}$CO and the experiment discussed in chapter 6.2.4 is rerun while maintaining the same reaction conditions.

In the time-resolved DRIFTS spectra in Figure 6.11a, signals of $^{13}$C containing species (from $^{13}$CO) shifted accordingly to lower wavenumbers. It enables to distinguish different reaction pathways occurring on Ni/γ-Al$_2$O$_3$. Vibration modes of gaseous and adsorbed species depicted in Figure 6.11 are listed in Table 6.1. The calculation of the vibration modes was conducted according to assumptions described in literature [244].

Therefore, following equations were obtained:

$$\nu^{(13}CH) = 0.997 \cdot \nu^{(12}CH) \quad (6.1)$$

$$\nu^{(13}CD) = 0.994 \cdot \nu^{(12}CD) \quad (6.2)$$

$$\nu^{(13}CO) = 0.9778 \cdot \nu^{(12}CO) \quad (6.3)$$

Time-resolved DRIFTS spectra in Figure 6.11a exhibit bands of gaseous $^{13}$CD$_4$, $^{13}$CO and D$_2$O but no C$_2$H$_4$ and CO$_2$ appear in the spectra. The signal to noise ratio and the sensitivity are lower because just five modulation periods were applied. In comparison to adsorbed CO in Figure 6.8a, the band of linear-CO shifted from 2060 to 2005 cm$^{-1}$ and bridge-CO shifted from 1920 to 1880 cm$^{-1}$. The interaction of $^{13}$CO with the γ-Al$_2$O$_3$ support [241] resulted in the formation of $^{13}$C-labeled formates and the signal for $\nu_{as} (O^{13}CO)$ moved to 1538 cm$^{-1}$. The corresponding $\nu_s (O^{13}CO)$ vibration mode shifted to 1330 cm$^{-1}$. The signal located at 1440 cm$^{-1}$ is probably assigned to the asymmetrical stretching vibration of chemisorbed $^{13}$CO$_3^{2-}$ because the non-labeled carbonates appear around 1449 cm$^{-1}$ [247, 248].

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Figure 6.11: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, C$_2$H$_4$ modulation (0.2 - 0 mol.%) over Ni/γ-Al$_2$O$_3$ under methanation conditions (10 mol.% D$_2$, 2 mol.% $^{13}$CO) at 200°C and 1.1 bar.
Phase-resolved DRIFTS spectra in Figure 6.11b demonstrate the formation of gaseous $^{13}$CHD$_3$, CD$_4$ and C$_2$D$_6$ in the course of C$_2$H$_4$ addition. The sharp upwards directed signal centered at 2243 cm$^{-1}$ can be assigned to the $\nu$ ($^{13}$CD) vibration of $^{13}$CD$_4$, a product of $^{13}$CO methanation. Ethylene modulation leads to the band at 2018 cm$^{-1}$ that is assigned to linear-$^{13}$CO and the upwards directed signal located at 1895 cm$^{-1}$ is related to bridge-$^{13}$CO. This effect is again related to adsorption site interconversion. In comparison to Figure 6.8b, signals of carbonates and carboxylates in Figure 6.11b shifted to 1390 cm$^{-1}$ and 1510 cm$^{-1}$, respectively. Due to the shift of those species to lower wavenumbers, it becomes evident that the carbon source of carbonates and carboxylates must be $^{13}$CO.

There is a hint that $^{13}$CO/D$_2$ mixture over the catalyst generates carbonate and carboxylate species at 200°C that are displaced whenever ethylene encounters the surface. Carboxylates and carbonates are probably formed by interaction of CO with nickel metal oxides or with the Al$_2$O$_3$ support. As already shown for ethane at 200°C, the surface population of carboxylates and carbonates possibly is decreasing on the basis of competitive reactions for adsorption sites. Alike the modulation experiment of ethane at 200°C, formates are observed on the alumina support but formates seem to act as spectators as their IR-signals vanish in the phase-resolved spectra in Figure 6.11b. The isolated peak at 2108 cm$^{-1}$ cannot be assigned to any species.

Dosing of ethylene during $^{13}$CO/D$_2$ methanation resulted in the formation of C$_2$D$_6$ and CD$_4$. Ethylene influences the methanation negatively because less $^{13}$CD$_4$ was formed. After desorbing of $^{13}$CD$_4$ from nickel, vacant surface sites might be occupied by new surface species from ethylene decomposition. Remaining $^{13}$C-species on nickel are combined with surface hydrogen and deuterium atoms to form $^{13}$CHD$_3$. It is near at hand that $^{12}$C- (from C$_2$H$_4$) and $^{13}$C-species (from $^{13}$CO) adsorbed on nickel compete for deuterium or adsorption sites. Adsorbed hydrogen that is not involved in the reaction is partly released as H$_2$,g from the surface. Kinetic information is provided by the demodulation plot in Figure 6.12 where phase-resolved IR-signals of $^{13}$CD$_4$, $^{13}$CHD$_3$ and CD$_4$ are plotted versus the phase angle. Demodulated IR-data were normalized by dividing by the maximum values of each species. CD$_4$ and $^{13}$CHD$_3$ demonstrate same time constants as both species reach zero amplitude at $\varphi_{PSD} = 77^\circ$ but $^{13}$CD$_4$ shows a phase lag with regard to the blue and red curve.
suggesting a delay in the formation of $^{13}$CD$_4$. The delay of $^{13}$CD$_4$ could be related to the kinetic isotope effect that was already discussed for ethane. The blue and red curves are almost congruent suggesting comparable kinetics for the formation of CD$_4$ and $^{13}$CHD$_3$.

![Figure 6.12](image.png)

**Figure 6.12**: Phase angle demodulation plot of C$_2$H$_4$ modulation under methanation conditions (10 mol.% D$_2$, 2 mol.% $^{13}$CO) at 200°C and 1.1 bar.

### 6.2.5 Modulation of Acetylene at 300°C

In comparison to previous experiments of ethane and ethylene, the concentration of acetylene for modulation excitation was lowered as already 500 ppm of acetylene were sufficient to cause severe carbon deposition on the nickel catalyst.

When 500 ppm of C$_2$H$_2$ were applied over Ni/γ-Al$_2$O$_3$ under methanation conditions at 300°C, the IR-detector signal intensity dropped from 52% to 44.5% within the first modulation period (Figure 6.13). This observation indicates carbon deposition on nickel because the surface reflectance changed and less energy reached the IR-detector. After twenty modulation periods, the detector signal was roughly 16% and black carbon deposition on Ni/γ-Al$_2$O$_3$ was visible to the unaided eye. In order to apply phase sensitive detection, all time-resolved DRIFTS spectra need to be averaged into one period. Hence, IR-signal changes within the first period are averaged out and cannot be observed after data treatment.
Conversion of ethane / ethylene / acetylene under methanation conditions

For the purpose of identifying signal changes during the first modulation period, raw spectra must be compared among each other. Figure 6.14a depicts untreated time-resolved DRIFTS spectra of the first period. Eight scans were coadded for one spectrum, thus the signal to noise ratio is rather low. Nevertheless, the decreasing signals of linear- and bridge-CO can be followed over the time. Linear-CO is ascribed to the band at 2015 cm\(^{-1}\) and bridge-CO to the band at 1905 cm\(^{-1}\) [222].

After feeding 500 ppm of acetylene over nickel for 10 minutes, all of adsorbed CO seems to be displaced by surface carbon as the bands for linear- and bridge-CO disappear.

Due to severe carbon deposition on nickel, a baseline shift occurred and the IR-signal intensity decreased to 16%. In addition, the signal of CD\(_4\) at 2257 cm\(^{-1}\) is slightly decreased during the first half-period. Although adsorbed linear- and bridge-CO are vanished from the time-resolved DRIFTS spectra in Figure 6.14a, just a minor decrease of the CD\(_4\) concentration is detected. CO might adsorb on surface sites that are less active towards dissociation [237], thus the decreasing concentration of adsorbed CO does not affect the CO methanation to a great degree. Despite severe carbon deposition on nickel, the catalyst was still active towards CO methanation after 20 modulation periods.
Conversion of ethane / ethylene / acetylene under methanation conditions

Figure 6.14: (a) Untreated time-resolved, (b) averaged time-resolved and (c) phase-resolved DRIFTS spectra, C<sub>2</sub>H<sub>2</sub> modulation (0.05 - 0 mol.%) over Ni/γ-Al<sub>2</sub>O<sub>3</sub> under methanation conditions (10 mol.% D<sub>2</sub>, 2 mol.% CO) at 300°C and 1.1 bar.
Figure 6.14b exhibits averaged time-resolved DRIFTS spectra that reveal bands of gaseous species of CD₄, CO₂, CO and D₂O whereas the molecular frequencies are listed in Table 6.1. Adsorbed CO is averaged out and a sharp upwards pointing feature is observed between 1285 cm⁻¹ and 1000 cm⁻¹ that indicates a baseline shift according to increasing carbon deposition. A weaker upwards directed signal arises around 1720 cm⁻¹ and might be assigned to a reflection artifact that emerges due to overlapping of dispersive and absorptive line shapes [258]. The weak signal at 2875 cm⁻¹ might be associated with adsorbed CHₓ species [247].

Phase-resolved DRIFTS spectra in Figure 6.14c only contain signals of gaseous CD₄ and CO₂. No adsorbed species are detected. The downwards pointing signal between 1285 cm⁻¹ and 1000 cm⁻¹ again is related to the baseline shift due to surface carbon on nickel. Gaseous species exhibit the same phase response because all of the signals show zero amplitude at a phase angle of 100°. The phase response of the signal (1285-1000 cm⁻¹) that is provoked by carbon deposition is slightly shifted in relation to those of the gas phase bands. In comparison to ethane and ethylene, acetylene is the most reactive hydrocarbon and therefore 100% conversion is monitored. Moreover, MS data (not shown) reveal beside CD₄ a small amount of CHD₃ that is probably generated by deuteration of adsorbed CH-intermediates or hydrogenation of adsorbed CDₓ-intermediates.

Figure 6.15: MS-signals at the reactor outlet as function of time during C₂H₂ stimulation under ¹³CO/H₂ methanation at 300°C and 1.1 bar. The shaded area indicates half-periods and C₂H₂ addition.
More mechanistic insights are obtained by use of isotope-labeled CO for methanation while the acetylene partial pressure is modulated. Mass spectral data in Figure 6.15 demonstrate the formation of CO$_2$ and $^{13}$CO$_2$ during C$_2$H$_2$ excitation. The same findings were already obtained for ethane and ethylene modulation. However, no hydrogenation of acetylene was measured.

Beside investigation by mass spectrometry, phase-resolved DRIFTS spectra in Figure 6.16 are depicted presenting signals which are induced upon acetylene modulation while keeping the partial pressures of $^{13}$CO and H$_2$ constant. Interestingly, a band centered at 3007 cm$^{-1}$ can be assigned to gaseous $^{13}$CH$_4$ [259] and a weaker signal at 3017 cm$^{-1}$ is ascribed to CH$_4$ [208].

With regard to kinetics, it can be concluded that the CH$_4$ signal shows its zero-crossing at a phase angle of 80°, whereas for $^{13}$CH$_4$ the zero-crossing can be found at $\phi^{PSD}= 115°$, indicating two differently fast hydrogenation reactions. Once more, the kinetic isotope effect might explain the slower formation of isotope-labeled methane. Reactive surface carbon generated by C$_2$H$_2$ decomposition is hydrogenated to form CH$_4$, whereas unreactive carbon is deposited on nickel without reacting further. In parallel, $^{13}$CO dissociation on nickel leads to adsorbed $^{13}$C that is stepwise hydrogenated to $^{13}$CH$_4$. Again, one might speculate that adsorbed $^{13}$C-species from dissociated $^{13}$CO and adsorbed $^{12}$C-species from decomposed acetylene compete for hydrogen or adsorption sites because the concentration of...
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gas phase $^{13}\text{CH}_4$ is increased whenever acetylene encounters the surface. However, carbon deposits also might migrate into the Ni-Al$_2$O$_3$ interface as initial step towards the formation of whiskers [1]. It was described that even detached Ni clusters on carbon whiskers are still active for methanation. Comparing the heat of adsorptions of relevant reactants on nickel surfaces [149], $\text{C}_2\text{H}_2 > \text{CO} > \text{H}_2$, the partly displacement of adsorbed CO and hydrogen could be explained in terms of a greater strength of adsorption of $\text{C}_2\text{H}_2$. Trimm et al. [149, 260] concluded that in the presence of CO and $\text{C}_2\text{H}_2$ less hydrogen atoms are available on nickel, thus a decrease in hydrogenation to $\text{C}_2$ products (ethane and ethylene) takes place. But on the other hand, carbon-carbon bond cleavage to form surface carbon intermediates is promoted [260]. Nevertheless, the availability of active sites for decomposition must be taken into account, too.

6.2.6 Modulation of Acetylene at 200°C

Acetylene dosed at 200°C catalyst temperatures leads to various surface adsorbates that are not visible in the DRIFTS spectra recorded at higher catalyst temperatures. In the following modulation experiment, acetylene was varied between 0.2 and 0 mol% over Ni/γ-Al$_2$O$_3$, in order to reveal possibilities of a different surface chemistry on the catalyst. The CO:$\text{H}_2$ ratio was 1:5 and it remained constant over twenty modulation periods. Time-resolved DRIFTS spectra in Figure 6.17b exhibit bands of gas phase species of CH$_4$, CO$_2$, CO, $\text{H}_2\text{O}$ (see Table 6.1). In contrast to the acetylene modulation experiment at 300°C, the IR-detector signal intensity slightly dropped from 59% to 56% over 20 modulation periods; hence just a slight baseline shift of the DRIFTS spectra occurred.

$\text{H}_2\text{O}$ shows additional signals at 3854 cm$^{-1}$ and 1560 cm$^{-1}$ that reflect the vibrational-rotational fine structure [232]. In the CH$_x$ spectral region, a strong signal centered at 2927 cm$^{-1}$ and a weaker signal at 2854 cm$^{-1}$ are detected that can be attributed to an asymmetrical and a symmetrical CH$_2$ stretching vibration, respectively. The observed vibrations match with those found for adsorbed methylene species (CH$_2$) bonded to carbon [182, 249].
Conversion of ethane / ethylene / acetylene under methanation conditions

Figure 6.17: (a) Untreated time-resolved, (b) averaged time-resolved and (c) phase-resolved DRIFTS spectra, C$_2$H$_2$ modulation (0.2 - 0 mol.%) over Ni/γ-Al$_2$O$_3$ under methanation conditions (10 mol.% H$_2$, 2 mol.% CO) at 200°C and 1.1 bar. One modulation period corresponds to 20 min.
Untreated time-resolved DRIFTS spectra in Figure 6.17a that were not averaged into one period clearly reveal that methylene peaks are growing in intensity over the course of the modulation periods. Spectra always were acquired at the end of each first half-period. These findings hint at an increasing coverage of CH₂ species on the catalyst or at an extended chain length of alkyl groups [249]. Due to missing signals for methyl (CH₃) groups and spectroscopic hints for C-C bonds, an increasing coverage of CH₂ species on surface carbon is more likely. Bands of linear- and bridge-CO in Figure 6.17a that are ascribed to 2035 cm⁻¹ and 1880 cm⁻¹ are shifting to lower wavenumbers [233]. Acetylene as an electron donor molecule may provide electrons for nickel, thus back-donation of metal electrons into the 2π⁺ anti-bonding orbital of CO can be favored [261]. The electron transfer increases the electron density in the 2n⁺ anti-bonding orbital and the C-O bond strength is reduced. As a consequence, the ν (CO) frequency is lowered.

The electron transfer from acetylene to nickel is lowering the work function [262]. Xu et al. [263] reported that a work function decrease could induce an interconversion of linear-CO to bridge-CO, however in their case the work function was influenced by a second physisorbed CO layer. A work function change by acetylene dosing might be also the basis of the observation in Figure 6.17a, where the COₗinear/CO₉ridge intensity ratio is decreasing during the course of the modulation periods. Note, that the averaged DRIFTS spectra in Figure 6.17b do not allow identifying any frequency shift and the change of the COₗinear/CO₉ridge ratio. Formate formation on the γ-Al₂O₃ support is observed in Figure 6.17a,b that is confirmed by signals found at 1590, 1392 and 1377 cm⁻¹ [241]. An additional peak at 1456 cm⁻¹ can be ascribed to νas (CO₂⁻) [227, 248]. Untreated DRIFTS spectra in Figure 6.17a demonstrate that the surface population of carbonates and formates is increased over the time.

When comparing time-resolved with phase-resolved DRIFTS spectra in Figure 6.17c, it is figured out that the band of formate species at 1590 cm⁻¹ is partly overlapped by a band between 1562-1577 cm⁻¹ that might be assigned to the νas (CO₂⁻) vibration [227, 248]. The phase-resolved spectra also illustrate that formates on γ-Al₂O₃ are not affected by C₂H₂ modulation because the corresponding bands disappear from the spectra. In contrast, the signals of
carbonate and carboxylate species at $\varphi_{PSD} = 0^\circ$ point to an upward direction whenever acetylene encounters the surface.

The phase-resolved spectrum at $\varphi_{PSD} = 0^\circ$ exhibits rotational-vibrational signals at around 3294, 3282 and 1327 cm$^{-1}$ that match with the reference spectrum of gaseous acetylene in Figure 6.18. It points to the fact that acetylene is not fully converted over nickel at 200°C. The signal of gaseous CH$_4$ at 3017 cm$^{-1}$ is partially overlapped by a broad band of ethane that can be ascribed to 2979 cm$^{-1}$ according to the ethane reference in Figure 6.18. The signal at 2969 cm$^{-1}$ possibly belongs to the vibrational-rotational fine structure of CH$_4$. A weak signal centered at 950 cm$^{-1}$ can be assigned to gaseous ethylene that is the product of partially hydrogenated acetylene [208]. Linear-CO gives a signal at 2055 cm$^{-1}$ and bridge-CO shows a band located at 1866 cm$^{-1}$. Alike the ethylene modulation experiment at 200°C, the bridge-CO signal exhibits opposite sign to the linear-CO signal, which can be explained in terms of site interconversion with increasing CO coverage [239].

![Figure 6.18: Reference DRIFTS spectrum of gaseous acetylene and ethane over silicon at ambient temperature.](image)

The bands centered at 2927 and 2854 cm$^{-1}$ in Figure 6.17c that belong to methylene groups (CH$_2$) [182, 249] are anti-correlated with respect to the signals of methane. Untreated time-resolved spectra in Figure 6.17a show growing signals of methylene species over 20 modulation periods.
In contrast, when focusing on signal changes that are occurring during a single modulation period (Figure 6.17c) it becomes evident that the concentration of methylene species on the catalyst diminished during addition of acetylene.

Some kinetic information is provided by the phase angle demodulation plot shown in Figure 6.19 where the maximum phase-domain response is plotted versus the wavenumber. It enables to distinguish species with different kinetics, as species that feature the same phase angle, follow the same kinetic behavior. In addition, species with a various phase angle might give an insight into the reaction pathway and the reactivity of possible intermediates. Adsorbed methylene species in the CH\_x-spectral region obviously deviated from the maximum phase responses of gas phase acetylene, ethane and methane that arise in the range of $\varphi_{\text{PSD}} = 340^\circ$. Hence, surface methylene could be considered as reaction intermediate for the formation of methane as it already appeared at a phase angle of 320° and therefore seems to exhibit faster kinetics. The upwards pointing signals of methylene (2927 and 2854 cm\(^{-1}\)) in the phase-resolved spectra in Figure 6.17c indicate a lowered surface population; that is why consumption of CH\_2 adsorbates is suggested. In combination with the findings of the phase angle demodulation plot in Figure 6.19, the assumption of CH\_2 intermediates becomes more reasonable.
Adsorbed carbonate and carboxylate species between 1450 and 1570 cm\(^{-1}\) emerge at around \(\phi^{\text{PSD}} = 330^\circ\) and are different from the phase response of gaseous methane and adsorbed methylene. Displacement or a consecutive reaction of carbonate and carboxylate species due to their decreasing signals in the phase-resolved spectra in Figure 6.17c needs to be taken into account, too.

The fact, that the phase response of linear- and bridge-CO in Figure 6.19 appears at \(\phi^{\text{PSD}} = 350^\circ\) and 345° gives rise to the assumption that those species of CO are not involved in the methanation reaction as the phase response of methane already arises at a phase angle of around \(\phi^{\text{PSD}} = 340^\circ\). Unreacted CO could be related to the band of linear-CO at 2055 cm\(^{-1}\) in Figure 6.17c and it might occupy less active nickel sites. This finding coincides with the assumption of van Looij et al. [237] who assumed that CO adsorbed on less active sites might behave as spectator species.

In Figure 6.20, mass spectral data clearly reveal that the concentrations of \(\text{CH}_4\), \(\text{C}_2\text{H}_4\) and \(\text{C}_2\text{H}_6\) are increased whenever \(\text{C}_2\text{H}_2\) is added to the synthesis gas feed. Beside CO methanation, two additional reaction pathways can be assumed. Acetylene either is decomposed to surface carbon and methylene species on nickel that are hydrogenated to methane or acetylene is directly hydrogenated to ethylene and ethane, respectively. For ethylene the m/z ratio of 24 is recorded, in order to prevent interference with mass fragments of other gaseous hydrocarbons occurring.
Conversion of ethane / ethylene / acetylene under methanation conditions
during the reaction. Slight deactivation of the catalyst caused by acetylene and CO can be observed because less CH₄ is produced over the time.

6.2.6.1 REPLACEMENT OF HYDROGEN BY DEUTERIUM AT 200°C

The use of deuterium instead of hydrogen enables to follow the hydrogenation or deuteriation of carbon fragments in more detail. Therefore, hydrogen was replaced by deuterium and acetylene modulation at 200°C was rerun while maintaining the same reaction conditions. In Figure 6.21, relevant time- and phase-resolved DRIFTS spectra are presented. In consequence of the application of deuterium, carbon species on nickel are deuterated and the corresponding ν(CH₂) vibration modes shifted to lower wavenumbers in comparison to the ν(CH₂) vibration. This procedure facilitates to identify the decomposition pathway of acetylene over nickel.

In the time-resolved DRIFTS spectra in Figure 6.21a, adsorbed deuterated methylene species (CD₂) appear, thus the νas(CD₂) vibration is ascribed to the band at 2196 cm⁻¹ and the νs(CD₂) vibration is assigned to the signal at 2095 cm⁻¹. CD₂ species are partially overlapped by gas phase CO (2143 cm⁻¹) which has rotational-vibrational bands at 2180 cm⁻¹ (R-branch) and 2112 cm⁻¹ (P-branch), respectively. Vibration modes for deuterated methylene were calculated according to equation (6.4) [244] and the result is shown in Table 6.1.

\[
ν(CD) = 0.7338 \cdot ν(CH)
\]

The symmetrical CD₂ stretching vibration at 2095 cm⁻¹ matches with the calculated vibration. Time-resolved spectra also show weak bands at 2927 cm⁻¹ and 2854 cm⁻¹ that are assigned to νas(CH₂) and νs(CH₂) vibrations of methylene (CH₂). Since both methylene and deuterated methylene arise in the spectra, hydrogen-deuterium exchange reaction might take place on the catalyst surface as well. The νs(OCO) and the νas(OCO) vibrations of deuterated formate species on γ-alumina can be assigned to 1346 and 1584 cm⁻¹, respectively. Carboxylates are attributed to the band at around 1560 cm⁻¹ that is overlapped by the broad band dedicated to formates. Carbonates are ascribed to the signal at 1448 cm⁻¹.
Conversion of ethane / ethylene / acetylene under methanation conditions

Figure 6.21: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, C$_2$H$_2$ modulation (0.2 - 0 mol.%) over Ni/γ-Al$_2$O$_3$ under methanation conditions (10 mol.% D$_2$, 2 mol.% CO) at 200°C and 1.1 bar.
As far as gaseous species are concerned, signals of CD₄, CO₂, CO and D₂O appear in the time-resolved spectra.

In the phase-resolved spectrum at a phase angle of 0° (Figure 6.21b), signals at 2990 cm⁻¹ and 1036 cm⁻¹ are ascribed to ν(CH) and δ(CD₃) vibrations of gaseous CHD₃ that is probably formed due to reaction of adsorbed methylidyne intermediates (CH) with deuterium. Two very weak signals at 2914 and 2845 cm⁻¹ could be assigned to CHₓ species [247]. The band located at 2238 cm⁻¹ [208] is probably related to the ν(CD₃) vibration of deuterated ethane that is a product of acetylene deuteration. Gaseous C₂H₂ exhibits spectral features at 3294, 3282 and 1327 cm⁻¹ that match with the bands shown in the C₂H₂ reference spectrum in Figure 6.18. Signals of deuterated methylene (CD₂) and methylene species (CH₂) are upwards directed and signalize decreasing surface concentration when acetylene is fed over the catalyst. Adsorbed CO shows the same behaviour as already observed and discussed in chapter 6.2.6. The signal of CD₄ at 2257 cm⁻¹ is overlapped by the band at 2238 cm⁻¹ but it is separated at increasing phase angle. The replacement of hydrogen by deuterium did not result in the formation of gaseous CH₂D₂ but small amounts of CHD₃ and CD₄ are detected. Previous experiments that were dealing with ethane and ethylene modulation at 200°C already revealed decreasing surface population of carbonates and carboxylates as function of increasing C₂-hydrocarbon content. This effect is demonstrated again for acetylene modulation at 200°C; hence upwards directed signals at 1554 cm⁻¹ and 1440 cm⁻¹ are depicted that are related to carboxylates and carbonates in Figure 6.21b. The use of isotope-labeled ¹³CO for the methanation again illustrates that CO probably reacted with nickel oxide or Al₂O₃ to form isotope-labeled carboxylates and carbonates whose bands shift to lower wavenumbers (Figure 9.2 in supplement information). The presence of acetylene seems to displace those species from the catalyst. Isotope-labeling of CO also approves the assumption that acetylene is broken up on nickel, resulting in adsorbed methylene species. Both reactive surface carbon and methylene species probably contribute to the formation of CD₄.
6.3 Conclusions

In this chapter, the conversion of saturated and unsaturated C$_2$-hydrocarbons over a commercial nickel catalyst was investigated under methanation conditions at 300°C and 200°C. Both C$_2$-hydrocarbons and CO interact with nickel. However, CO is dissociated on nickel step sites [16] and surface carbon is stepwise hydrogenated to form methane [22, 32, 38] according to the mechanism depicted in Figure 6.22. In principle, the reactions of the C$_2$-hydrocarbons over Ni/γ-Al$_2$O$_3$ can be considered as parallel reactions of the CO methanation and the modulation excitation technique enables to separate the reaction pathways of the C$_2$-hydrocarbons from CO methanation.

![Figure 6.22: Mechanism of CO methanation observed over Ni/γ-Al$_2$O$_3$](image)

In principle, surface carbon species deposited from the C$_2$-hydrocarbons reveal different reactivities on the nickel catalyst [151]. Acetylene gives more unreactive surface carbon than ethylene or ethane. As a consequence, during the deuteration of surface carbon originating from ethane and ethylene decomposition, additional methane in the form of CHD$_3$ and CD$_4$ was produced, in comparison to the experiment with acetylene. At 300°C, similar reaction products were observed after addition of ethane, ethylene and acetylene to the CO/D$_2$ or CO/H$_2$ feedstock (see Figure 6.23). However, the concentration of the products varied due to different reactivities of the surface carbon species. A lower temperature, such as 200°C, is not only decreasing the reaction rate, the temperature also affects the selectivity and has an influence on the reaction pathway.
Conversion of ethane / ethylene / acetylene under methanation conditions

6.3.1 ETHANE DURING METHANATION AT 300°C AND 200°C

When ethane encounters nickel during the methanation at 300°C, C-C bonds of ethane break and carbon species are formed on the surface (Figure 6.23). Atomic surface carbon and possibly consecutively formed adsorbed CH-intermediates are further stepwise deuterated to CD₄ and CHD₃. Hydrogen is released from the surface and surface carbon is partly oxidized to CO₂. The first step of the formation of CHD₃ probably is ascribed to the recombination of adsorbed C and H atoms as CH bonds are formed faster than CD bonds. CO methanation is not influenced by ethane decomposition that can be considered as parallel reaction. The catalyst is not deactivated during the modulation periods.

At lower temperatures (200°C), C-C bonds of ethane seem to remain unaffected because no methane is formed via hydrogenation of surface carbon of decomposed ethane. On the other hand, formates are generated on the alumina support which can be considered as spectator species. Formates on the alumina support are also observed during ethylene and acetylene modulation experiments at 200°C. The formation of carbonates or carboxylates on the oxidic surfaces of the catalyst seems to be induced by CO at 200°C.
6.3.2 ETHYLENE DURING METHANATION AT 300°C AND 200°C

When feeding ethylene over nickel under methanation conditions at 300°C, decomposition of ethylene with subsequent hydrogenation of surface carbon is the favored reaction. However, some activity for hydrogenation of ethylene to form ethane is identified, too. Basically, the same reaction products are obtained as for ethane decomposition but ethylene is more reactive and therefore a higher degree of ethylene is converted to surface carbon that is hydrogenated / deuterated. As a consequence of the use of D₂, the CD₄ concentration is increased but the amount of CHD₃ is lowered, in comparison to the experiment with ethane. This finding could be related to the enhanced decomposition probability of ethylene, resulting in an increased surface concentration of C-species that are converted to CD₄. On the other hand, the reduced availability of adsorbed H-atoms leads to a decreased amount of CHD₃ in the gas phase, in comparison to the experiment with ethane. In addition, CO and ethylene seem to compete for certain adsorption sites as some CO is displaced from nickel during addition of ethylene. At lower temperatures (200°C), less decomposition of ethylene is observed and direct hydrogenation to ethane seems to gain in importance (see Figure 6.24).

![Figure 6.24: Surface reactions of ethylene on nickel under methanation conditions at 200°C and 1.1 bar.](image)

Nevertheless, adsorbed C-species that either originate from ethylene or CO decomposition compete for deuterium/hydrogen or adsorption sites. In the presence of ethylene, competitive reactions also seem to displace carbonate and carboxylate species that are probably adsorbed on nickel oxides or Al₂O₃. At 200°C, the catalyst becomes less active and a decreased amount of ethylene is converted. Ethylene
also affects the CO methanation and lowers the methane yield over the time. However, the methane yield remains unchanged at 300°C.

6.3.3 Acetylene during methanation at 300°C and 200°C

Acetylene in the synthesis gas feed is completely converted over Ni/γ-Al₂O₃ at 300°C. It causes carbon deposition on nickel that changes the surface reflectance of the catalyst and limits the spectroscopic investigation by DRIFTS. On the other hand, direct hydrogenation of acetylene is suppressed at 300°C. The major part of the carbon deposition consists of unreactive carbon species and few reactive carbon fragments are deuterated to CHD₃ and CD₄. However, CHD₃ also might be formed by deuteration of adsorbed carbon fragments originating from CO dissociation. Simultaneously, surface carbon is partly oxidized to form CO₂ and redundant hydrogen desorbs from the surface. Furthermore, competitive surface reactions between different carbon species take place. Despite heavy carbon deposition, the catalyst was still active towards CO methanation after 20 modulation periods.

At lower temperatures (200°C), hydrogenation of acetylene to ethylene and ethane occurs and a different reaction pathway is identified for acetylene decomposition (see Figure 6.25). After C-C bond breaking of acetylene, methylene species that are bonded to surface carbon remain on the catalyst. However, methylene species can also be formed by recombination of reactive surface carbon with adsorbed H-atoms. This assumption was approved by the use of deuterium when deuterated methylene species (CD₂⁺) were identified on the catalyst. There are indications that methylene
species could act as reaction intermediates in the formation of methane. Additionally, hydrogenation or deuteration of reactive surface carbon to form methane cannot be excluded. Alike the experiments with ethane and ethylene at 200°C, carbonate and carboxylate species seem to be displaced from the catalyst through competitive reactions. Ni/γ-Al₂O₃ is continuously deactivated in the course of the modulation periods at 200°C, resulting in a lowered methane yield.
In this thesis, a commercial Ni/γ-Al₂O₃ catalyst that is used in fluidized-bed methanation for the production of Synthetic Natural Gas was investigated with a systematic methodology. It was aimed to study a working nickel catalyst in order to obtain mechanistic insights. The conditions encountered in a fluidized-bed methanation reactor have been simulated in the DRIFTS experiments. Varying the gas compositions over the catalyst enabled to mimic the environment which catalyst particles experience during the migration through the fluidized-bed. The fixed-bed reactor of the DRIFTS setup was operated under isothermal conditions and the Ni catalyst exhibited a similar particle size as the catalyst used in fluidized-bed methanation. However, the experimental DRIFTS setup did not allow applying modulation periods that ensure a fast altering gas composition which usually surrounds a moving catalyst particle in the fluidized-bed.

**CO methanation**

In the first part of the thesis, the focus was on more fundamental investigations of adsorbed species on the nickel catalyst which should contribute to the overall understanding of the mechanism of CO methanation. Temperature-programmed DRIFTS validated that CO in linear configuration is more weakly bonded to nickel in comparison to CO in bridge configuration. Consequently, linear-CO is more reactive towards CO methanation which is in accordance with literature [221, 222, 264]. Glugla et al. [265] also showed that two distinct CO adsorption sites exist on a
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Ni/γ-Al2O3 catalyst. At ambient temperature CO is adsorbed on nickel. At elevated temperatures and when adsorbed hydrogen is present, CO can be transferred to the alumina support where adsorbed formate or methoxy species are formed [265, 266]. In temperature-programmed reaction (TPR) experiments, performed in this thesis, the formation of formate species was not observed, most likely because the transfer of CO to the support competes with CO methanation. However at 200°C, formate species coordinated to Al2O3 were observed during CO methanation over Ni/γ-Al2O3. Kester et al. [267, 268] discussed the existence of two surface sites that are active for methanation. In particular, low weight-loading Ni/γ-Al2O3 catalysts (Ni loading < 15 wt.%) revealed two distinctive methanation sites (two methane peaks in TPR). The more active methanation site is attributed to Ni0 that was formed after reduction of surface NiO. The amount of these sites is reported to increase with higher nickel loading of the catalyst. The less active methanation site is related to nickel atoms that are surrounded by oxygen atoms of the Al2O3 lattice. These nickel atoms originate from the reduction of nickel aluminate (NiAl2O4). On the other hand, high weight-loading Ni/γ-Al2O3 catalysts (Ni loading > 15 wt.%) showed only one methanation site that can be assigned to Ni0 formed after reduction of surface NiO [267]. The commercial Ni/γ-Al2O3 catalyst that was investigated in this thesis exhibits a nickel loading of 50 wt.% and our temperature-programmed reaction measurements are in agreement with the idea of solely metallic Ni as active methanation site as only one methane peak was observed (see Figure 5.3).

DRIFTS coupled with the modulation excitation technique provide additional insights about the nature of adsorption sites and adsorbates. Phase sensitive detection enhances the sensitivity of DRIFTS; hence it enables to detect weak variations of IR-signals that were induced by changing of the CO concentration over Ni/γ-Al2O3. At 300°C, CHx-species were observed on nickel that originate from dissociation of adsorbed CO. There exists a relation between CHx-species and the formation of methane as the surface concentration of CHx-species was decreased when methane was produced. This is in agreement with Galuszka et al. [21] who also proved the existence of CHx-species on Ni/γ-Al2O3 during CO methanation. It was proposed that adsorbed CH-species are intermediates in the methanation. On the other hand, no relation was found between the formation of adsorbed -CH2 or -CH3 species and the CO methanation rate [21].
Conclusions

At 300°C, the CO modulation experiment over Ni/γ-Al₂O₃ also revealed that CO that does not dissociate is rather accumulated on ordered crystalline nickel sites when the CO concentration in the gas phase is increased. Van Looij et al. [237] assumed that there exist active sites that allow for CO dissociation on nickel and less active sites where CO is stored as spectator species. According to the observations during the CO modulation experiment at 300°C in this thesis, CO adsorbed on crystalline nickel sites was found to be less active and thus, can be ascribed to spectator species. The active sites are associated with step sites on nickel where CO dissociation preferably takes place due to their lower activation barrier [16, 238]. However, adsorbed CO species that are directly involved in CO methanation could not be identified at 300°C due to fast reacting CO species and a limited time resolution of the measurement.

At 200°C, the CO modulation experiment demonstrates a lower reaction rate and therefore a higher CO coverage on nickel was observed. Under these reaction conditions, sub-carbonyls, Ni(CO)ₓ (x= 2, 3), and linearly-adsorbed CO species that are bonded to low coordination sites such as steps and edges were identified whereas these species coexist with a layer of adsorbed CO species in linear and bridge configuration on defined Ni planes. There is a clear evidence that these adsorbed CO species are dissociated on low coordination Ni sites and contribute to the formation of methane. Recently, Ang et al. [242] reported that sub-carbonyl species on a CeO₂ supported nickel catalyst can be regarded as precursors in the formation of methane. Sub-carbonyl species are also more weakly bonded to Ni than linear-CO species. As carbon deposition is more favored on sites for weakly bonded CO, sub-carbonyl species are also considered to be related to the formation of a carbonaceous layer [17, 242]. In particular, sub-carbonyl species appear when the H₂:CO ratio is decreased which was observed in the CO modulation experiment at 200°C. The carbonaceous deposition might be also associated with the observed gradual deactivation of the catalyst under these reaction conditions. On the other hand, Seemann et al. [2] showed that a Ni-catalyst can be regenerated when the CO methanation is carried out in a fluidized-bed reactor, using the same Ni catalyst as in the thesis. Especially, due to the movement of the catalyst particles in a fluidized-bed, a built-up of carbon species on the catalyst can be avoided when reactive surface carbon is hydrogenated in the CO-lean part of the reactor [73].
Conclusions

Controversial discussions in the literature [17, 20, 38, 42, 44, 45] showed that there exists no consensus about the mechanism of CO methanation. It is still not clear whether adsorbed CO reacts first with adsorbed hydrogen or adsorbed CO is directly dissociated. For that reason, a CH₄ modulation experiment over Ni/γ-Al₂O₃ was carried out in a ¹³CO/D₂ methanation feedstock at 300°C, in order to obtain insights about the reaction pathway of CH₄. CH₄ was dissociated into surface carbon and hydrogen which was released as gaseous H₂ and surface carbon was deuterated to form CD₄. DFT calculations also confirmed that the formation and dissociation of CH₄ takes place via adsorbed hydrogen and carbon atoms [245]. In addition, the methanation reaction (¹³CO + 3 D₂ ↔ ¹³CD₄ + D₂O) proceeded over Ni/γ-Al₂O₃. However, beside ¹³CD₄ also ¹³CHD₃ appeared in the gas phase. This observation indicates that surface carbon (¹³C*) or ¹³CDₓ-species are probable intermediates during ¹³CO/D₂ methanation. However, the DRIFTS data of this thesis do not allow a clear assignment to adsorbed ¹³CD, ¹³CD₂ or ¹³CD₃ species. In conclusion, the formation of ¹³CD₄ possibly proceeds via stepwise deuteration of surface ¹³C-atoms originating from dissociation of ¹³CO. The results of the presented mechanistic investigation about CO methanation are not in disagreement with mechanism A (see chapter 2.1.1) which is widely accepted [17, 21, 25, 27, 30-34, 36, 37]. This mechanism considers a dissociative chemisorption of CO on nickel. Adsorbed carbon and oxygen atoms are hydrogenated whereas the stepwise hydrogenation of surface carbon leads to the formation of methane (see Table 7.1).

On the other hand, the question arises whether a direct dissociation of CO occurs or hydrogen assists in the CO dissociation. This issue is taken into account in mechanism B (see chapter 2.1.1) which is also under discussion in literature [16, 20, 23, 42]. Mechanism B considers formyl (HC-O) or carbon-hydroxyl (C-OH) species on nickel as intermediates during CO methanation. Adsorbed CO reacts with adsorbed hydrogen which lowers the activation barrier for C-O bond dissociation [16]. The mechanistic studies over Ni/γ-Al₂O₃ performed in this thesis did not show any evidence for the involvement of formyl (HC-O) or carbon-hydroxyl (C-OH) species in the CO methanation. However, the existence of these species cannot be completely excluded. If the formyl or carbon-hydroxyl species are fast reacting on nickel, it is difficult to capture the IR-signals due to the limited time resolution of the experiment. In this case, these species cannot be detected with DRIFTS although
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they might take part in the CO methanation. Further investigation with very high time resolution would be needed, in order to clarify this issue.

Another mechanism C of CO methanation (see chapter 2.1.1) is debated [44, 45] where the hydrogenation of adsorbed formate species to surface methoxy plays a significant role. In the last step, surface methoxy adsorbed on an oxidic surface is converted to methane. Sanchez-Escribano et al. [44] also suggested that both mechanism A (via surface carbides) and mechanism C (via oxygenates) could be co-present depending on the experimental conditions. Especially, on catalysts with lower Ni-loading (< 1wt.% Ni), adsorbed CO might be transferred to the $\text{Al}_2\text{O}_3$ support where methoxy species can be evolved. Indeed, surface formate species were observed on the commercial nickel catalyst during the CO modulation experiment at 200°C which were formed on the alumina support after interaction of CO with OH-groups of $\text{Al}_2\text{O}_3$. However, no surface methoxy was revealed during CO methanation and there was no correlation between the appearance of adsorbed formate species and the formation of methane.

Table 7.1: Different mechanisms of CO methanation

<table>
<thead>
<tr>
<th>Mechanism of CO methanation suggested in literature</th>
<th>Mechanism of CO methanation suggested in this work</th>
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<tbody>
<tr>
<td>• Mechanism A (via surface carbides)</td>
<td>$\text{H}_2 + 2 \cdot \rightarrow 2 \cdot \text{H}$</td>
</tr>
<tr>
<td>• Mechanism B (via HC-O or C-OH species)</td>
<td>$\text{CO} \cdot + \cdot \rightarrow \text{C} \cdot + \cdot \text{O}$</td>
</tr>
<tr>
<td>• Mechanism C (via formate and methoxy species)</td>
<td>or $\text{H}_2$-induced CO dissociation</td>
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<td></td>
<td>$\text{C} \cdot + \cdot \text{H} \rightarrow \cdot \text{CH} + \cdot$</td>
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<td></td>
<td>Stepwise hydrogenation to CH₄</td>
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Conclusions

In particular, phase sensitive detection enabled a kinetic differentiation between IR-signals related to the formation of methane and IR-signals arising from formate species. As a consequence, a different reaction pathway can be assumed for the formation of formate. Additionally, no methane was detected when exposing $\text{Al}_2\text{O}_3$ to methanation conditions. Based on these observations, adsorbed formate species can be ruled out as intermediates of CO methanation over commercial Ni/$\gamma$-$\text{Al}_2\text{O}_3$ and thus mechanism C.

The methanation process also comprises the water-gas-shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) which was responsible for the formation of CO$_2$ during the CO modulation at 300°C. Mass spectral data (Figure 5.5) showed a retarded formation of CO$_2$ in comparison to the formation CH$_4$. This observation demonstrates that CO$_2$ was formed through a various reaction pathway. In contrast, at lower temperatures (200°C) the water-gas-shift (WGS) reaction seemed to be less favored over Ni/$\gamma$-$\text{Al}_2\text{O}_3$. Two different mechanistic concepts for the WGS reaction are under discussion [46, 48, 49, 53]. A redox type mechanism was suggested for Ni/$\gamma$-$\text{Al}_2\text{O}_3$ based catalysts which considers a cyclic change in the oxidation state of the catalyst [54]. It was also reported that the activity towards the WGS reaction was enhanced with increasing temperature and nickel loading [52], similar to what was found in the experiments in this thesis. On the contrary, an associativistic mechanism via a formate-carbonate route was observed for the WGS reaction over a Ni/CeO$_2$ catalyst [269]. However, it was also discussed that both the redox-type and the associativistic mechanism could be active over the same catalyst whereas the degree of the reaction pathway is affected by the experimental conditions [54, 55]. During the CO modulation experiment over Ni/$\gamma$-$\text{Al}_2\text{O}_3$ at 200°C in this thesis, formate was formed on the $\text{Al}_2\text{O}_3$ support. This species might be related to an intermediate of the WGS reaction due to the simultaneous observation of CO$_2$ in the product gas feed. On the contrary, it was reported that surface formates could be also ascribed to species that were formed due to methanation of CO$_2$ [49]. However, CO$_2$ methanation is inhibited in the presence of CO in the gas feed and a high surface coverage of adsorbed CO on the catalyst [15]. Consequently, formates on $\gamma$-$\text{Al}_2\text{O}_3$ described in this thesis can be ruled out as intermediates of CO$_2$ methanation.
Conclusions

CO₂ can also be converted to CO and H₂O in the reverse water-gas-shift (RWGS) reaction (CO₂ + H₂ ↔ CO + H₂O). Kopyscinski [12] investigated the CO methanation over the same Ni-catalyst that was used in this thesis. It was concluded that the addition of CO₂ to the CO/H₂ feedstock produces additional CO by means of the RWGS reaction. As a consequence, the formation of CH₄ was enhanced and additional H₂O was produced. Adsorbed CO can be considered as intermediate in the formation of CH₄ via the RWGS reaction.

The CO modulation experiment over Ni/γ-Al₂O₃ at 200°C also gives a hint that adsorbed C and H atoms recombine to form C₂- or C₃-species to a small extent when the concentration of CO is increased. This observation might be related to a chain growth as it is the case in the Fischer-Tropsch reaction. It was suggested that the chain growth can occur via two different pathways [270-272], whereas the actual pathway seems to be influenced by the composition and structure of the catalyst. The carbide mechanism considers CHₓ intermediates that originate from the dissociation of adsorbed CO. In further consequence, adsorbed CHₓ-species are incorporated into the growing hydrocarbon chain. Another possible mechanism of the chain growth proceeds via insertion of CO into the CHₓ species. After insertion of CO, the C-O bond is ruptured and a C₂Hₓ-species is produced. If this step is repeated, longer hydrocarbon chains can be created. On nickel, the hydrogenation of CHₓ-species takes place very fast; hence the formation of CH₄ is more favored than the formation of long chain hydrocarbons. On the other hand, Fischer-Tropsch catalysts, such as Fe or Co, exhibit a slow removal rate of CHₓ as gaseous methane which increases the selectivity towards long chain hydrocarbons [270].

Addition of ethane under CO methanation conditions

In the second part of the thesis, more realistic methanation conditions were approached by adding either ethane, or ethylene, or acetylene to the CO/H₂ feedstock over commercial Ni/γ-Al₂O₃. The modulation excitation technique makes it possible to differentiate the CO methanation from parallel reactions, such as decomposition and hydrogenation of C₂-hydrocarbons.
Conclusions

The ethane modulation experiment over Ni/γ-Al₂O₃ at 300°C revealed that C-H and C-C bonds of ethane are ruptured in parallel to CO methanation. Desorption of hydrogen can be related to the initial C-H bond cleavage and hydrogen recombination. It was suggested that C-H bonds of ethane are cleaved first and that in the second step the C-C bond of the hydrogen-deficient species C₂Hₓ is ruptured [162, 163]. The formed atomic surface carbon is hydrogenated to CH₄ or deuterated to CD₄. In addition, CHD₃ was observed to a greater extent in the gas phase, indicating the possibility of CH-intermediates on nickel. DRIFTS data after phase sensitive detection support the assumption of CH-species as intermediates in the formation of methane because different kinetics are demonstrated for the deuteration of reaction intermediates, such as C or CH. The formation of CHD₃ exhibits faster kinetics than the evolution of CD₄ as CH-species react faster than CD-species. However, adsorbed CH-intermediates either might be a product of incomplete decomposition of C₂-species or adjacentlly adsorbed C- and H-atoms recombine on nickel. Studies on single crystals also demonstrated that ethane hydrogenolysis is a structure sensitive reaction that is usually favored on more open surfaces, such as Ni(100) [164].

Tanaka et al. [163] concluded that any type of carbon deposits on Ni/γ-Al₂O₃ might decelerate the hydrogenolysis of ethane. During the ethane modulation experiment at 300°C, no retard of the hydrogenolysis / deuterolysis of ethane and the formation of methane were recognized. This observation suggests that neither dissociated CO nor decomposed ethane formed unreactive carbon deposits on nickel at 300°C. However, ethane was not completely decomposed over the nickel catalyst under methanation conditions. Ethane also did not affect the CO adsorbate layer; hence ethane hydrogenolysis can be seen as parallel reaction that does not interfere with CO methanation. The addition of ethane to the CO/H₂ feedstock also resulted in the formation of gas phase CO₂. Isotope-labeling of CO enabled to distinguish CO₂ originating from two various reaction pathways. On one hand, carbon fragments from decomposed ethane were partly oxidized to gas phase CO₂. On the other hand, the water-gas-shift reaction of the methanation process also contributed to the formation of CO₂. These two different CO₂ synthesis routes were also observed during ethylene and acetylene modulation at 300°C.
Conclusions

When the ethane modulation experiment was carried out over Ni/γ-Al₂O₃ at 200°C, no methane was produced due to hydrogenation / deuteration of reactive carbon fragments originating from decomposed ethane. However, decomposition of ethane cannot be completely ruled out at lower temperatures as there is still the possibility for accumulating unreactive carbon species which are not subsequently converted to methane. Further, CO methanation was not disturbed by addition of ethane at 200°C. Alike the CO modulation experiment at 200°C, formate species were formed on the alumina support which can be considered as spectator species and they were not affected by the increasing concentration of ethane. Adsorbed formates were also observed during ethylene and acetylene modulation under methanation conditions at 200°C whereas these species exclusively are ascribed to the interaction of CO with surface OH-groups of γ-Al₂O₃.

Addition of ethylene under CO methanation conditions

Ethylene modulation over Ni/γ-Al₂O₃ under methanation conditions at 300°C results in the decomposition of ethylene with subsequent hydrogenation / deuteration of the adsorbed carbon fragments to form methane. Regarding the mechanism of ethylene decomposition, it was suggested that di-σ-bonded ethylene is converted to surface acetylene and hydrogen on Ni(111) [168]. In the next step, surface acetylene is degenerated to surface acetylide (CCH) and methylidyne (CH) which both are decomposed to adsorbed carbon and hydrogen. In addition, it was shown that the C-C bond breaking is most favored on step-edges on Ni(111) whereas terrace sites reveal a lower activity towards decomposition [170].

The present DRIFTS measurements did not allow capturing adsorbed intermediates of ethylene decomposition as the different carbon fragments were decomposing very fast on nickel under methanation conditions. Based on a higher reactivity and an enhanced decomposition probability of ethylene when compared to ethane, ethylene probably is converted to surface carbon to a greater extent than ethane. Consequently, an increased concentration of surface carbon on nickel enhanced the formation of CD₄ at 300°C. On the other hand, the gas phase concentration of CHD₃
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was lowered, possibly due to a reduced availability of surface hydrogen atoms in relation to ethane modulation.

In contrast to ethane modulation at 300°C, ethylene seemed to affect the CO adsorbate layer on crystalline nickel sites because adsorbed CO in linear and bridge configuration was displaced from nickel by more strongly bonded ethylene. However, no effect on the overall methane yield of the methanation reaction was observed during the course of the entire modulation. This finding supports again the before described assumption that CO adsorbed on ordered crystalline nickel sites does not contribute to the formation of methane under the experimental conditions.

Beside decomposition of ethylene and CO methanation, hydrogenation of adsorbed ethylene to ethane takes place to a small extent on the commercial nickel catalyst at 300°C. Nevertheless, the selectivity of Ni/γ-Al₂O₃ towards C₂H₄ hydrogenation was increased by lowering the reaction temperature to 200°C. According to Horiuti-Polanyi [107], the mechanism of C₂H₄ hydrogenation proceeds via adsorption of ethylene forming di-σ-bonded C₂H₄ which is stepwise hydrogenated by use of adsorbed atomic hydrogen [105]. It should be noted that in particular, bulk H-atoms which are more energetic than surface H-atoms favor the hydrogenation of C₂H₄ [39]. Surface ethyl species are considered as relevant intermediates before ethane is desorbed from the catalyst surface. During the ethylene modulation experiment at 200°C, it was not possible to identify adsorbed ethyl species on nickel due to the fast hydrogenation reaction. In contrast to ethylene decomposition, ethylene hydrogenation is not a structure sensitive reaction [105].

The reaction of C₂H₄ with syngas (CO+H₂) may also result in CO insertion [118-120]; hence long chain hydrocarbons, aldehydes or alcohols could be formed. However, the experimental data of ethylene modulation at 200°C in the present thesis do not provide evidence for the formation of higher hydrocarbons (e.g. C₃- and C₄-species) or oxygenated products over Ni/γ-Al₂O₃. Furthermore, a small fraction of ethylene was decomposed and the resulting carbon fragments were deuterated to CD₄. In this way, the chemical equilibrium of the CO methanation was influenced as the methane yield of the methanation reaction was lowered during addition of ethylene. Additionally, different adsorbed C-species that arise from C₂H₄ decomposition or CO dissociation compete for adsorption sites or deuterium / hydrogen atoms. The idea of
Conclusions

Competitive surface reactions is also supported in the case of adsorbed carboxylate and carbonate species which were displaced from the catalyst whenever ethylene encountered the catalyst surface. Adsorbed carboxylate and carbonate species were possibly formed by interaction of CO with Al₂O₃ or residual NiO and were also observed during ethane and acetylene modulation under methanation conditions at 200°C. However, these species were not observed during the CO modulation experiment at 200°C which might be explained by superimposing IR-signals. Generally, adsorbed carboxylate and carbonate species might be associated with intermediates of the water-gas-shift reaction or CO₂ hydrogenation which however cannot be proved by the experimental data of the thesis.

The CO modulation experiment over Ni/γ-Al₂O₃ at 200°C demonstrated that at least a small amount of adsorbed C and H atoms recombine via a chain growth mechanism to form C₂- or C₃-species. It must be noted that ethane also could be formed by means of recombination of two adjacent C₄H₈-species. Nevertheless, the hydrogenation of ethylene to ethane seems to be more likely as the formation of higher hydrocarbons via a chain growth is less favored on nickel [270]. On the other hand, Jordan et al. [123] reported that the addition of CO to the C₂H₄/H₂ gas feed over Ru/SiO₂ can suppress the hydrogenation of C₂H₄ to C₂H₆ but the formation of C₃-species is enhanced.

Kopyscinski et al. [273] investigated the reactions of ethylene in a micro-fluidised bed reactor over the nickel catalyst that was used for the experiments in this thesis. It was concluded that after hydrogenation of ethylene to ethane, the C-C bond of ethane is cleaved. In a further step, adsorbed reactive carbon fragments are hydrogenated to methane. This mechanistic assumption would require a re-adsorption of ethane on nickel, in order to be hydrogenolyzed to methane. If the formation of an ethane intermediate is an essential step in the production of methane, the product distribution of the ethane and ethylene modulation experiments must be equal. This is not the case when comparing the results of ethane and ethylene modulations because ethane is not hydrogenolyzed to methane at a temperature of 200°C. It has to be noted that the reactivity and tendency of decomposition of hydrocarbons on nickel is increasing in the following order C₂H₆ < C₂H₄ < C₂H₂ [151]. As a consequence, the fraction of ethylene that is not directly hydrogenated is more likely decomposed to surface carbon than ethane. Our
Conclusions

results suggest adsorbed carbon species as intermediates in the formation of methane. The hydrogenation of ethylene is considered as parallel reaction with respect to the stepwise hydrogenation of surface carbon from ethylene.

Addition of acetylene under CO methanation conditions

Acetylene in the synthesis gas feed was fully converted to surface carbon on the nickel catalyst at 300°C; hence the surface reflectance of the nickel catalyst was changed and the spectroscopic investigation by DRIFTS was limited. The amount of the fed acetylene was reduced to 500 ppm, in order to lower the amount of deposited carbon which mainly consists of unreactive carbon species. Otsuka et al. [151] demonstrated that deposited carbon species from acetylene show rolled fibers on nickel, which is different to deposited carbon from saturated hydrocarbons. In addition, the reactivity of surface carbon generated from acetylene is lower than the reactivity of carbon species deriving from ethylene [151] which is consistent with our findings.

As far as the mechanism of ethylene decomposition is concerned, it was reported that in the first step, C\textsubscript{2}H\textsubscript{2} adsorbed on Ni(111) is partially decomposed to ethyliydne (CCH\textsubscript{3}), acetylide (CCH) and surface hydrogen [168]. Residual C\textsubscript{2}H\textsubscript{2} and adsorbed ethyliydne react to form adsorbed acetylide (CCH) and methylidyne species (CH). In the final step, both surface species are decomposed to surface carbon while hydrogen is desorbed from the surface. Both decomposition of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} are structure sensitive and decomposition reactions most probably proceed on step sites due to their higher reactivity in relation to terrace sites [181]. The acetylene modulation experiment at 300°C revealed that a small part of the deposited surface carbon from acetylene was deuterated to CD\textsubscript{4} and CHD\textsubscript{3} whereas CHD\textsubscript{3} exhibited a minority share of the product distribution. Retrospectively, it can be noted that with increasing reactivity of the added hydrocarbons (C\textsubscript{2}H\textsubscript{6} < C\textsubscript{2}H\textsubscript{4} < C\textsubscript{2}H\textsubscript{2}), the CD\textsubscript{4} : CHD\textsubscript{3} ratio of the product gas was increased at 300°C. The lowered amount of CHD\textsubscript{3} might be explained by the fact that less hydrogen atoms were introduced into the catalytic system as compared to addition of ethane and ethylene.
Alike the ethylene modulation experiment at 300°C, adsorbed CO species were displaced by adsorbed carbon species originating from acetylene. The displacement of adsorbed CO can be explained in terms of a greater strength of adsorption of acetylene on nickel [149]. In addition, adsorbed C-species that arose from CO dissociation competed with reactive surface carbon species from acetylene for adsorption sites and deuterium/hydrogen. This observation supports the assumption that both CO dissociation and C₂H₂ decomposition takes place on similar surface sites, namely step sites on nickel.

Despite strong carbon deposition on Ni/γ-Al₂O₃, the catalyst still exhibited activity towards CO methanation after 20 modulation periods at 300°C. It was demonstrated [1] that carbon deposits on the same commercial nickel catalyst reveal a loose structure enabling the reactant gases to diffuse to active nickel sites. As a consequence, only a slight effect on the methane yield was observed which is in agreement with our results. *In situ* XPS studies [1] on the nickel catalyst of this thesis also showed that during the methanation reaction the addition of unsaturated C₂-hydrocarbons to the synthesis gas feed caused carbon deposition on nickel but also on alumina. In the meanwhile, nickel clusters grew in size and might spread out over the alumina support. Nickel carbide species in the form of Ni₃C and/or Ni₇Cₓ were formed during the methanation which seem to exist near or at the Ni-Al₂O₃ interface. After long methanation runs (up to 5 hours) in the presence of unsaturated hydrocarbons, massive formation of C-whiskers and a detachment of Ni clusters from the alumina support were observed [1]. However, even detached Ni clusters were active towards CO methanation.

At a reaction temperature of 300°C, Ni/γ-Al₂O₃ did not favor the hydrogenation of acetylene as the tendency of acetylene decomposition was more dominant. By lowering of the temperature to 200°C, a fraction of acetylene was hydrogenated to ethylene and ethane. It was suggested that adsorbed hydrogen atoms are transferred to adsorbed acetylene [107, 131]. In this way, adsorbed vinyl species (HCCH₂) are formed which are further hydrogenated to adsorbed ethylidene (HCCH₃) or ethylene species (H₂CCH₂). Both species can be hydrogenated to ethane via adsorbed ethyl species (H₂CCH₃). Another pathway considers desorption of ethylene from the surface. However, DRIFTS measurements in this thesis did not
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allow identifying adsorbed intermediates of the hydrogenation reaction due to limited
time resolution of the IR-spectrometer.

The selectivity of the hydrogenation of acetylene is considerably determined by the
presence of subsurface hydride or carbide phases [130-135]. Subsurface hydrides
favor the formation of ethane [126] and subsurface carbides enhance the selectivity
towards ethylene formation [134]. The decomposition of CO and hydrocarbons can
lead to the formation of subsurface carbides in nickel. It was reported that the
presence of CO which forms subsurface carbides lowers the formation of ethane
during acetylene hydrogenation over Ni/SiO$_2$ [149]. Subsurface carbides seem to
hinder the diffusion of bulk H-atoms to the surface; hence the hydrogenation of
acetylene proceeds selectively towards ethylene via surface hydrogen [131, 135]. In
this thesis, Ni/$\gamma$-Al$_2$O$_3$ was exposed to CO/H$_2$ before acetylene was added at 200°C.
The CO/H$_2$ gas feed most probably created subsurface carbide phases in nickel that
account for the formation of ethylene when acetylene was hydrogenated. On the
other hand, also the formation of ethane was observed which can be ascribed to the
existence of subsurface hydrides. Consequently, the transport of bulk H-atoms to the
surface is presumably not fully prevented by subsurface carbon.

It was shown that Ni-based catalysts are active towards oligomerization of acetylene
[140] whereas the H$_2$:C$_2$H$_2$ ratio and the temperature determine the selectivity of
oligomers. In the presence of CO, an insertion of CO to acetylene might be a
possible reaction [131]. However, the formation of longer chains above C$_{10}$ is unlikely
because the dense CO layer on nickel makes it difficult for the growth of longer
carbon chains [150]. Moreover, cyclotrimerization of acetylene forming aromatic
compounds could take place on nickel as well [144]. Despite the variety of possible
reactions in the presence of CO and C$_2$H$_2$, acetylene modulation experiments over
Ni/$\gamma$-Al$_2$O$_3$ performed in this thesis did not reveal any hints for the formation of
oxygenated oligomers or aromatic compounds.

At 200°C, a different pathway of acetylene decomposition was observed because
adsorbed methylene species (CH$_2$) appeared after C-C bond cleavage of acetylene
on the catalyst. However, methylene species also might be evolved by
recombination of surface carbon with adsorbed H-atoms. An adsorption study of
acetylene on Ni(111) demonstrated that adsorbed CH$_2$-species might be evolved by
Conclusions

self-hydrogenation of CH-species at temperatures higher than 180°C [274]. Generally, CH₂-species are assumed to take part in the formation of higher hydrocarbons [21]. In particular, a chain growth mechanism considers the addition of methylene species to alkyl groups [125]. On the other hand, in the framework of this thesis, acetylene modulation experiments at 200°C do not provide any evidence for chain growth reactions, resulting in the formation of higher hydrocarbons (>C₂). Nevertheless, adsorbed methylene species seem to be hydrogenated to methane under methanation conditions. In particular, DRIFTS data after phase sensitive detection allow ascribing adsorbed methylene species to intermediates in the formation of methane. The hydrogenation of methylene species seems to be a slow process as the adsorbed CH₂-species are accumulated on the catalyst before being hydrogenated (see Figure 6.17a). The accumulation of adsorbed methylene also could account for the continuous deactivation of the Ni-catalyst due to a lowered methane yield in the course of the modulation at 200°C. The addition of acetylene to the synthesis gas feed also affected the adsorption properties of nickel as the C-O bond strength of adsorbed CO species was reduced.

Difficulties of DRIFTS

DRIFTS investigations of a methanation catalyst with a nickel loading of 50 wt.% are challenging with regard to the analysis of adsorbed and gas phase species. As a consequence, a lot of effort was put into the method development that also includes the design and construction of an experimental setup. Based on the high metal loading, a large fraction of the incident IR-light is absorbed by the catalyst. Consequently, the signal-to-noise ratio is rather low which makes it very complicated to identify weak IR-signals of adsorbates. In our experimental approach, the nickel powder catalyst was diluted with a non-absorbing and inert matrix (silicon) which lowered the contribution of noise to a certain extent. Another issue that complicates the interpretation of DRIFTS spectra is the simultaneous presence of active and spectator species of a chemical reaction. In particular, IR-signals of spectator species often overlap with those of active species. In order to overcome this problem, modulated excitation spectroscopy was applied that enables a differentiation between species that take part in the reaction and species that are not
involved in the reaction. In this way, IR-signals that are not accessible with conventional DRIFTS were detected with enhanced sensitivity.

The methanation reaction is usually carried out at around 300°C but the high temperature lowered the surface reflectance of the catalyst during DRIFTS measurements; hence the signal-to-noise ratio was reduced in this temperature regime. In addition, due to the high reactivity of the nickel catalyst, active species on nickel are reacting very fast and cannot be captured at 300°C as a result of the limited time-resolution of the DRIFTS measurement. By lowering the temperature to 200°C, the coverage of adsorbed species was increased and more information on active species became accessible.

**Concluding remarks**

The results of this work exhibit practical relevance as the mechanistic investigations were focused on a commercial Ni/γ-Al₂O₃ catalyst that is used in industrial fluidized-bed methanation. Mechanistic DRIFTS studies of high Ni-loaded (> 50 wt.% Ni) methanation catalysts have not been reported in the literature. The modulation excitation technique was applied for the first time on CO methanation over a Ni catalyst. Based on controversial discussions [17, 20, 38, 42, 44, 45] about the mechanism of CO methanation, it was necessary to reconsider the fundamental steps of the CO methanation. In this thesis, it was found that the stepwise hydrogenation of surface carbon to methane is the most probable reaction pathway on Ni/γ-Al₂O₃. Sub-carbonyls and linear-CO species that are bonded to low coordination sites are very likely precursors in the formation of methane. Generally, the understanding of surface reactions on the catalyst is prerequisite for the improvement of catalysts.

The modulation of the C₂-hydrocarbons over the Ni catalyst under CO methanation conditions enabled to simulate the more complex composition of the biomass-derived producer gas. In this way, additional surface reactions that were not considered before can be implemented in a fluidized-bed methanation model that is developed at Paul Scherrer Institute [12]. So far, it was supposed that CO₂ is mainly produced via the water-gas-shift reaction at 300°C. The studies of this work showed
that CO\textsubscript{2} can also be formed by oxidation of carbon fragments that originate from decomposition of C\textsubscript{2}-hydrocarbons. It was also demonstrated that a lower temperature, such as 200°C, has an influence on the reaction pathway of C\textsubscript{2}-hydrocarbons. In particular, after decomposition of acetylene at 200°C, adsorbed methylene species remained on the catalyst and were most probably hydrogenated to methane. By now, it was assumed that adsorbed methylene species are converted to higher hydrocarbons [21]. On the contrary, carbon fragments (C- and/or CH-species) that arised from the decomposition of ethane, ethylene or acetylene at 300°C were the precursor in the formation of methane. Lower temperatures also favored the direct hydrogenation of unsaturated hydrocarbons. The interplay between hydrogenation and decomposition of C\textsubscript{2}-hydrocarbons proceeded in parallel to the CO methanation and the water-gas-shift reaction. In addition, adsorbed C-species that have its source from C\textsubscript{2}-hydrocarbon decomposition or CO dissociation can compete for adsorption sites or hydrogen on the catalytic surface. Competitive surface reactions also seemed to displace adsorbed carboxylate and carbonate species that may form as a consequence of the water-gas-shift reaction.

From the spectroscopic point of view, this work provides a comprehensive collection of vibrational modes of gas phase species and adsorbates that can be used as a reference data base for future DRIFTS measurements. This work contributes for better understanding of surface reactions on a commercial nickel catalyst and the results are valuable for interpreting kinetic data used to develop mathematical models that enable predictions for the performance of a methanation plant.
8 OUTLOOK AND RECOMMENDATIONS

In this chapter, opportunities and ideas for further investigation and improvement of methanation catalysts are presented. On one hand, the development of new catalysts can improve the overall methanation process and on the other hand, the understanding of catalytic surface reactions would result in improved mathematical models enabling to predict the performance of industrial fluidized-bed methanation.

In this work, the surface chemistry of high weight-loading Ni/γ-Al₂O₃ (50 wt.% Ni) was investigated during CO methanation. It was reported that low weight-loading Ni/γ-Al₂O₃ (Ni loading < 15 wt.%) shows two distinctive methanation sites [267, 268]. Consequently, a more detailed mechanistic study of Ni/γ-Al₂O₃ with lower Ni loading would be required as well, as CO methanation might proceed by another mechanism (e.g. via adsorbed methoxy) on that catalyst beside the surface carbide mechanism.

Biomass-derived producer gas contains a considerable amount of unsaturated hydrocarbons that can form carbon deposition on nickel during CO methanation and carbonaceous deposits, such as unreactive coke, can deactivate Ni catalysts. Effort should be put into the development of new methanation catalysts that are resistant to carbon deposition. For instance, structural promoters like boron would decrease the deactivation due to carbon deposition [275].

Another alternative to conventional supported metal methanation catalysts is the use of promising hydrogen storage alloys which should be further developed to create more efficient methanation catalysts. Improved or newly developed methanation
catalysts can be studied with the systematic methodology that was carried out in this work. As a consequence, methanation catalysts can be investigated with the same modulation technique considering C₂-hydrocarbons in the synthesis gas feed. In this way, the results of the mechanistic investigation of different catalysts can be well compared among each other. Additionally, a possible interaction of benzene with C₂-hydrocarbons over the methanation catalysts should be examined as well because benzene is also a component of biomass-derived producer gas. In combination with DFT calculations, structure-reactivity relationships between different catalysts could be clarified and reaction mechanisms can be elucidated.

In order to decrease the duration of the experiments, a DRIFTS reactor with lower dead volume needs to be used that enables to carry out shorter modulation periods. In addition, a FT-IR spectrometer with higher time resolution is required that is able to acquire interferograms as fast as possible. Adsorbates on surfaces are of particular relevance but in consequence of the DRIFTS technique, adsorbed species exhibit rather weak signals. Synchrotron IR-light features an enhanced brightness in comparison to common IR-light; thus the signal-to-noise ratio and the sensitivity are improved and measurements with enhanced spectral- and temporal resolution can be achieved. In combination with the modulation excitation technique, weak adsorbates could be identified that are not visible with ordinary methods.

Another issue that is of major interest is the aspect of sulfur poisoning of methanation catalysts through sulfur compounds (e.g. H₂S, C₄H₄S) in the biomass-derived producer gas. Modulation of sulfur species in the CO/H₂ feedstock combined with DRIFTS and phase sensitive detection allows elucidating deactivation and regeneration mechanisms on catalysts. In principle, the combination of DRIFTS and XAS (X-ray absorption spectroscopy) within concentration modulation spectroscopy would provide additional electronic/structural information about relevant adsorbates.

Recently, it was also shown that modulated excitation synchrotron-based high-energy X-ray diffraction (HXRD) enables observing very subtle structure-reactivity changes of catalysts [276]. This technique allows studying the influence of the support material, the promoter phase and the catalytically active metal phase at the same time. As far as CO methanation is concerned, the formation of surface carbides might be followed with a very high time-resolution.
The formation of different surface carbon species that arise during the synthesis of methane can also be analyzed by in situ RAMAN spectroscopy which is a complementary method of IR spectroscopy. RAMAN spectroscopy makes it possible to identify carbon phases that are not detectable by IR-methods. In this manner, the mechanism of hydrocarbon decomposition could be studied in more detail over different methanation catalysts and a more precise assignment of adsorbed carbon species can be carried out.

Further insights into the mechanisms of reactions that were observed in this work could be obtained by application of sum frequency generation (SFG) spectroscopy which is a reliable technique for identifying reaction intermediates on catalyst surfaces under methanation conditions [105]. This optical photon-in/out technique is very surface specific as all gas phase molecules are invisible, and enables to detect adsorbed species by means of vibrational frequencies with high time-resolution. SFG is usually applied on model catalyst systems and it provides information about the molecular conformation of adsorbed species.

Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) allows for studying the oxidation state and the chemical composition of the catalyst surface in situ at a pressure up to 13 mbar [105]. Surface modifications that are induced by the presence of CO and C₂-hydrocarbons during methanation can be investigated by means of this method. Thus, the formation of surface carbon species and mechanisms of catalyst deactivation can be examined.
9 **Supplement Information**

Time- and phase resolved DRIFTS spectra that are discussed but not shown in the chapters 6.2.3 and 6.2.6.1 are depicted here as supplement information.

Figure 9.1 describes $\text{C}_2\text{H}_4$ modulation under $^{13}\text{CO}/\text{H}_2$ methanation conditions at 300°C and refers to chapter 6.2.3.

Figure 9.2 shows $\text{C}_2\text{H}_2$ modulation under $^{13}\text{CO}/\text{D}_2$ methanation conditions at 200°C and refers to chapter 6.2.6.1.
Figure 9.1: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, C$_2$H$_4$ modulation (0.2 - 0 mol.%) over Ni/γ-Al$_2$O$_3$ under methanation conditions (10 mol.% H$_2$, 2 mol.% $^{13}$CO) at 300°C and 1.1 bar.
Figure 9.2: (a) Time-resolved and (b) phase-resolved DRIFTS spectra, C$_2$H$_2$ modulation (0.2 - 0 mol.%)
over Ni/γ-Al$_2$O$_3$ under methanation conditions (10 mol.% D$_2$, 2 mol.% $^{13}$CO) at 200°C and 1.1 bar.


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