Operando investigations of particle size and support effects during the Selective CO Methanation over oxide supported Ru nanoparticles in idealized and realistic H₂ feed gases

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I do not think there is any thrill that can go through the human heart like that felt by
the scientist as he sees some creation of the brain unfolding to success, such
emotions make a man forget food, sleep, friends, love, and everything

(Nicola Tesla 1856 - 1943)
To
The spirit of my father
and
My family
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1. Introduction
1. Introduction

1.1. H₂ for fuel cells: Possibilities for cleaning /ultra-purification

The increasing consumption of energy, mainly produced from the combustion of crude oil, natural gas and coal deposits, has resulted in negative ecological and climatic changes. This has stimulated an indispensable need for replacing combustion based technologies by more efficient and hence economically and environmentally friendly viable energy technologies. This transition requires, however, a clean and efficient energy carrier, which can be obtained from some sustainable sources at least on the long term. Therefore hydrogen emerged as a promising all-purpose fuel for transportation, heating, domestic uses, and for electricity generation. As a result, a new definition came about recently for describing all the economic activities related to the production and use of hydrogen which refers to “Hydrogen Economy”.

In principle, hydrogen can be produced by chemical processing of the solid or gaseous feedstock (e.g., crude oil, biomass or natural gas) by steam reforming, partial oxidation or autothermal reforming (oxidative steam reforming). The reaction pathways for producing syngas from different hydrocarbon starting molecules are represented by the following equations (1.a - f).

(Partial oxidation)

\[
\begin{align*}
\text{CH}_4 + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO} + 2 \text{H}_2 \quad (1.a) \\
\text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 + 2 \text{H}_2 \quad (1.b) \\
\text{C}_x\text{H}_y + \gamma/2 \text{O}_2 & \rightarrow x \text{CO} + (\gamma/2) \text{H}_2 \quad (1.c)
\end{align*}
\]

(Steam reforming)

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \quad (1.d) \\
\text{C}_x\text{H}_y + x \text{H}_2\text{O} & \rightarrow x \text{CO} + (x+y/2) \text{H}_2 \quad (1.e) \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 3 \text{H}_2 \quad (1.f)
\end{align*}
\]

Due to the harsh reaction conditions applied during these chemical processes, undesired reaction products are additionally formed during the reforming step including the deposition of coke (eq. 2.a – 2.c) and large amounts of CO₂ because of the thermally driven water gas shift (WGS) reaction, as indicated in eq. 2.d. Thus the final H₂ rich feed gas will basically consist of a mixture of CO, H₂O, CO₂, and H₂. This mixture contains roughly about 10%, 20%, 20% and 40% of the respective gases.
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\[
\begin{align*}
2 \text{CO} & \rightarrow \text{C} + \text{CO}_2 \quad (2.a) \\
\text{CO} + \text{H}_2 & \rightarrow \text{C} + \text{H}_2\text{O} \quad (2.b) \\
\text{C}_x\text{H}_y & \rightarrow z \text{C} + \text{C}_{x-z}\text{H}_{y-2z} + z \text{H}_2 \quad (2.c) \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (2.d)
\end{align*}
\]

The highest efficiency of converting H\textsubscript{2} into usable electric energy and the technically most viable method is the electrochemical conversion in Low Temperature Proton Exchange Membrane Fuel Cells (PEMFCs). The successful introduction of PEMFCs depends decisively on a cheap and reliable supply with contamination free hydrogen, where in particular CO concentrations have to be kept in the low ppm range to avoid poisoning of the platinum anode catalyst.\textsuperscript{3,7,10,11} Therefore, the purification of H\textsubscript{2} fuel is a must for these fuel cell applications to keep them economically efficient. Reducing the CO concentration down to the tolerable limits (≤ 10 ppm) is conventionally achieved in two stages. The first step involves the application of the catalyzed WGS reaction over two temperature ranges to achieve the desired enrichment of H\textsubscript{2}, and at the same time to decrease the CO concentration. In the high temperature shift (HTS) reaction the concentration of CO can be lowered from about 15% down to 2 – 3% by reaction over ferrochrome catalysts (Fe\textsubscript{2}O\textsubscript{3} / Cr\textsubscript{2}O\textsubscript{3}: 9 / 1) in a temperature range of 350 – 550 °C. This step is followed by a low temperature shift (LTS) reaction at temperatures ≤ 250°C on Cu/ZnO or CoMo catalysts, which further decreases the CO concentration down to an assumed about 1 - 0.5%.\textsuperscript{12-14} As the gas feed reaches lower CO concentrations the WGS reaction reaches the equilibrium point with the RWGS reaction (eq.2.d), which makes the process thermodynamically retarded. In other words the low concentration required for use in fuel cells can not be reached with a reasonable reaction rate via water gas shift reaction at these temperatures. Therefore it requires another step involving another catalytic reaction after reaching a CO concentration of ≤ 1.0 % for further cleaning and ultra-purification of H\textsubscript{2} fuel (≤ 10 ppm).

The preferential oxidation of CO (PROX) is frequently used to decrease the concentration of CO in H\textsubscript{2} fuels to the extremely low levels required for the operation of the low temperature proton exchange membrane fuel cells (PEMFC). However, this process is only profitable for large scale systems, where the costs of the additional O\textsubscript{2} dosing, monitoring units and their maintenance are low compared to the overall costs. Selective CO Methanation has emerged in recent years as a promising alternative for the PROX reaction
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especially in small scale (‘domestic’) applications. This depends basically on using the already existing infrastructure for transfer and distribution of natural gas. In this case H₂ can be produced locally from steam reforming of CH₄ (see eq.1d) followed by an intermediate step where WGS reaction is used to lower CO concentration to about 1.0 %. Afterwards selective CO methanation can be applied with the big advantage of using the H₂ present in feed gases to reduce the CO concentration to the tolerable limit required for use in fuel cells. Furthermore the additional CH₄ formed during the selective CO methanation reaction can be recycled and used for heating the small reformer unit which decreases the overall running costs.

1.2. Methanation and Fischer-Tropsch synthesis reactions

The hydrogenation of carbon monoxide in syngas (CO + H₂) had been a subject of numerous studies over a long time since the pioneering work of Paul Sabatier. The hydrogenation of CO can proceed in a single pathway producing methane or in Fischer Tropsch synthesis direction where syn gas can be polymerized to a wide range of hydrocarbons (CₓHᵧOz) ranging from light fuel gas (C₂-C₄) to the production of heavy organic compounds (e.g., wax, paraffin, distillates, etc).

1.2.1. Control of the reaction pathway between FT synthesis and methanation

The selectivity between methanation and FT synthesis can basically be controlled by the proper selection of the reaction conditions (T, p), the ratio of carbon source (CO + CO₂) to H₂ and the nature of the catalyst used. FT synthesis is favored at high temperature, and pressures (200 – 600°C & 5 – 100 bar) while the methanation reactions of CO and CO₂ are exothermic reactions (eq. 3.a & b), and therefore are favored at milder reaction conditions (150 - 200°C & 1 bar). The selectivity between FT synthesis and methanation is governed also by the C / H content in the reaction feed. Methanation (3.a and b) is largely favored at low ratios of CO : H₂ (<< 1:3) This is attributed to the strong interaction of CO with metal particles which retard the reaction at high concentration of CO by forming of strong adsorbed layer which limit the adsorption / desorption of reactants and products on / from active sites. This explanation is in agreement with the reported low activity for CO methanation at high CO and low H₂ concentrations. On the other hand FT synthesis require significantly higher ratios of CO : H₂ with an optimum value of 1:3 (syn gas composition). This drastic dependence of both reactions (FT synthesis and CO methanation) on the relative ratio of CO to H₂ presents an additional parameter to control the reaction pathway for different catalysts.
1. Introduction

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_R^0 = -206.2 \text{ KJ} / \text{mol} \quad (3.a) \\
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_R^0 = -164.9 \text{ KJ} / \text{mol} \quad (3.b)
\end{align*}
\]

1.2.2. Ruthenium as the best choice for CO / CO\textsubscript{2} hydrogenation

Ni was the first metal discovered to be active for the catalytic methanation of CO and CO\textsubscript{2}. A similar behavior was reported later also for Co\textsuperscript{19}, while other metals including Cu, Fe, Pt, and Pd were classified as poor methanation catalysts\textsuperscript{21,25}. Not surprisingly, the metals reported active for the production of higher hydrocarbons in Fischer Tropsch reactions showed varying tendencies for the methanation of CO with different selectivities\textsuperscript{21,25}. Fischer, Tropsch and Dilthey\textsuperscript{26} had discovered a descending tendency of the methanation for a group of metals (Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag), which already have a prominent activity in Fischer-Tropsch synthesis. The differences in methanation activity were basically related to the variation of the enthalpy of CO adsorption on different metals rather than H\textsubscript{2}, which showed largely similar chemisorptive characteristics over different metals\textsuperscript{27,22}. Thus the retardation of the reaction in the presence of high concentration of CO was attributed to the blocking of most of the active sites by the adsorbed CO, which empirically has ~ 2-fold higher adsorption enthalpies than H\textsubscript{2} on the surface of different metals\textsuperscript{21,22}.

Among all metals studied for CO hydrogenation related reactions (methanation / Fischer Tropsch), Ru showed the highest mass and turnover frequency based activities for CO methanation, and furthermore higher stability during reaction with time on stream\textsuperscript{28}. Furthermore, although the Ru catalyst itself shows limited activity for FT synthesis, however modification by other metal promoters produced significantly more active catalysts compared to the pure Ru catalysts. Nurunnabi et al. showed that Ru/Al\textsubscript{2}O\textsubscript{3} and Ru/SiO\textsubscript{2} catalysts exhibited low CO conversion and severe deactivation at 493 K, while addition of a small amount of Mn enhanced the activity and stability drastically\textsuperscript{29,30}. The addition of Mn improves the reducibility of Ru metal particles and prevents the oxidation during the reaction by water, which was claimed as the reason for deactivation.

Another feature recommending the use of Ru is the low affinity for carbide deposition during the reaction compared to other metal, e.g., Ni. For that reason Ru had been used also as a promoter for other metals. For example, it has been reported that a significant improvement in the stability and activity of supported Co catalysts for Fischer-Tropsch synthesis was observed upon doping it partly with Ru\textsuperscript{31-34}. 

One important parameter which decides the choice of a specific metal for a given reaction is the coadsorption of different reactants on the catalyst active sites, which increases the probability of reaction. For metals active in CO hydrogenation this feature was studied for the first time by McKee for Pt, Rh, Ir and Ru at 200°C. On the surface of Pt, CO was strongly adsorbed and the formed adlayer could not be removed by H₂ present in the feed gas. For Rh and Ir, however, coadsorption and subsequent reaction between CO_ad and H_ad species was proved by the formation of limited amount of CH₄. On the other hand Ru exhibited moderate chemisorption of CO with a simultaneously enhanced adsorption of H₂ in the presence of CO adlayer. In this case the supply of H_ad species is facilitated by the slightly less strongly chemisorbed CO on the surface of Ru and the tendency for coadsorption with H₂. These findings were even corroborated by the formation of methane at much lower temperatures and pressures (≤ 100°C & 100 Torr). Recent studies of the gas phase interaction of free Ruₙ⁺ clusters with CO and H₂ arrived at similar results. Lang et al. demonstrated that the coadsorption of CO with H₂ improves the dissociative adsorption of H₂ which explains the exceptional activity of Ru for CO methanation, while these small metal clusters were found to be inert for CO₂ methanation.

Earlier investigations of the methanation reaction over supported Ru catalysts mainly focused on the experiments for reactor layouts and catalyst comparison under realistic conditions, and on the other hand kinetic and adsorption experiments under idealized or semi realistic conditions. In spite of the importance of the previous studies the following points should be critically considered: i) In most of the cases the ratio of H₂/CO is much lower than those present in typical feed gases used in fuel cells, which is the main target of the emerging application of selective CO methanation, ii) the issue of CO selectivity in the presence of CO₂ was not critically discussed and measurements in the presence of either CO or CO₂ were the main source of information about their methanation activities and selectivities, and iii) in addition, the catalytic behavior, and the vibrational properties and composition of adlayer have been correlated only with structural information obtained using ex situ characterizations, which limits our understanding of the reactivity behavior and mechanistic interpretation.

1.3. Selective CO methanation: State of the art

Recent studies in different research groups can be categorized under i) the fundamental molecular scale studies of the methanation of CO and CO₂ over standard catalysts, which were previously established for CO / CO₂ hydrogenation reactions, and ii) the
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development and synthesis of more active catalysts or the improvement of the already present catalysts.\textsuperscript{78-92} The development of a highly active / selective catalyst depends on detailed understanding of the origin of its selectivity / activity. This requires an integrated assessment of the structural and electronic properties and changes therein during the reaction in addition to the simultaneous modification of the adsorbed adlayer. Afterwards, these parameters can be correlated with the changes in the catalytic performance to derive the reaction mechanism.

Focusing on the mechanistic understanding of selective CO methanation over supported Ru catalysts, several parameters affecting the performance of supported Ru catalysts should be discussed in the light of what had been published in recent years.

1.3.1. Composition of the reaction gas mixture

The sensitivity of the catalytic behavior to the composition of reaction gas mixture originates from its direct impact on the composition of the adlayer under reaction conditions, which can also modify the structure and chemical composition of the catalyst. Studies related to the application and mechanistic understanding of the Selective CO Methanation should take into consideration two important points. First of all, the selectivity should be tested for CO concentrations resulting in sub-monolayer coverages of CO\textsubscript{ad} species on the surface of metal particles (P\textsubscript{CO} \leq 0.01%), simultaneously in the presence of large amounts of CO\textsubscript{2} (up to 15%). The preferential adsorption of CO with Ru nanoparticles will prevent the adsorption and dissociation of CO\textsubscript{2} on the active sites, therefore the incomplete surface coverage is prerequisite for testing the inherent CO selectivity, whereas the dissociation (methanation) of CO\textsubscript{2} on the surface can occur on sites not blocked by CO.\textsuperscript{72,62} This is not possible at CO concentrations higher than 0.1%, whereas the selectivity (S = CO Conv. / CH\textsubscript{4} Form.) is always 100% regardless of the inherent selectivity of the catalyst for CO\textsubscript{2} dissociation (CH\textsubscript{4} formed only from CO). Testing the inherent selectivity of the catalyst is important to isolate the impact of the structural properties of the catalysts from the effects related to the change in adlayer. Second, the use of selective methanation in fuel cell applications comes after an initial cleaning of CO down to below 1 %, where the application of HT / LT-WGS reaction contributes to the enrichment of H\textsubscript{2} in the gas feed up to 60 – 70% beside additional amounts of CO\textsubscript{2} and H\textsubscript{2}O of about 15 – 20%. Therefore, very high ratios of H\textsubscript{2} / CO at least above 120 should be used if we consider the presence of about ca. 0.5% CO in the initial gas feed as the starting point for the ultra-purification of H\textsubscript{2}. Adjusting CO : H\textsubscript{2} ratios around this values is important to mimic the lower zone of reactor,
where the application of selective CO methanation becomes indispensable after the initial processing of the feed gas by water gas shift.

### 1.3.2. Partial pressure of CO and H₂

For the selective CO methanation the concentration of CO and H₂ in the reaction feed is decisive for the activity and the selectivity in the case CO₂ is included in the reaction feed.⁷¹ On one hand it was found that the selectivity for CO methanation in the presence of up to 15 % CO₂ in the reaction for Ru/Al₂O₃ (Ru particle size ≥ 2.0 nm) decreases drastically with the decrease of the concentration of CO reaching ≤ 40 % at a CO partial pressure ≤ 0.01 %.⁷² The drop of CO concentration in the gas mixture correlates to a decrease of the CO coverage on the surface, which increases the probability for CO₂, present in feed gas, for dissociative adsorption and thereby leads to a decreasing CO selectivity. The decreasing CO partial pressure in the reformate gas goes along with an increasing CO methanation activity. One possible explanation for that is the increasing supply of adsorbed Hₐd relative to COₐd on Ru particles which leads to higher reaction rates. The negative reaction orders for CO and the positive values for H₂ reported by Eckle et al.⁷¹ and by others ⁹³,⁹⁴ on different catalysts are in good agreement with the observed increasing activity with the increase of % H₂ in the reaction feed. Other components such as CO₂ which is technically already present in reformate gases or CH₄ either left after reforming of natural gas or resulting from the methanation process were found to have little effects on the methanation activity for CO, regardless of the nature of catalyst support used.⁷¹

### 1.3.3. Influence of water on catalytic performance

The most crucial issue in the discussion related to the impact of the gas composition on the reaction characteristics is the presence of water. This is true for the following reasons: i) although weakly adsorbing on metal particles compared to CO and H₂, water interacts strongly with the support and is able to modify it e.g., by the buildup of OH groups, ii) it may oxidize metal nanoparticles, and iii) induce undesired side reactions such as the water gas shift reaction.⁹⁵

Due to these points studying the effect of water is also challenging for the understanding reaction mechanism due to the difficulty to isolate the effects resulting from the adsorption of water on metal particles or on the metal oxide support from those related to the structural changes water may create in the catalyst surface. Earlier studies dealing with the effect of water on the hydrogenation of CO or CO₂ to
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methane, or the synthesis of higher hydrocarbons (Fischer-Tropsch reaction) under high pressure, pointed to a strong dependence of the reaction characteristics and mechanism on the presence of water. In the Fischer-Tropsch synthesis water was found to decrease the activity, mainly due to bulk oxidation of the metal particles. For bimetallic supported Ru-Co/γ-Al₂O₃ catalysts it was found that under Fischer-Tropsch synthesis conditions the activity decreases as the ratio of H₂O / (CO+H₂) in the reaction gas mixture was increased. This was explained by the oxidation of metallic Co nanoparticles. In these cases water induced changes in the activity/selectivity were attributed to an induced irreversible structuring of the catalyst, including the formation of a cobaltaluminate complex or oxidation of the metal nanoparticle (NP) surface upon the interaction with water.

For Fischer-Tropsch synthesis the nature of metal particles can also decide on the direction of the effect of water on activity. As an example, Claeys et al. reported an increase in Fischer-Tropsch activity over a silica gel supported Ru nanoparticles, which is opposite to the effect reported on Co based catalysts.

On other hand, for the selective methanation of CO / CO₂ mixtures, the effects resulting from the presence of water in the reaction feed were also recently outlined. In temperature screening measurements, Panagiotopoulou et al. found that the CO conversion remains practically unaffected in the presence of water, while the onset for CO₂ conversion is shifted to higher temperatures. Men et al. reported that the addition of water to the reaction gas mixture hinders the methane formation from a CO / CO₂ mixture on a Ni/CaO/Al₂O₃ catalyst, accompanied by a deterioration of CO₂ dissociation activity (i.e., lower CO₂ methanation) and thus an increase in CO selectivity. In contrast, Jimenez et al. reported that the CO conversion is 2-3 times faster in the presence of steam than in a dry reaction gas mixture for Ru/fishbone and Ru/platelet catalysts over a wide range of temperatures, while the CO₂ hydrogenation rate is unaffected. This increase of CO methanation activity is opposite to the behavior reported in the other studies discussed above. Once again similar to the results reported by Claeys et al. for Fischer-Tropsch synthesis the effect of water on the reaction behavior seems to depend also on the nature of the catalyst support.

So far the arguments related to the effect of water in the above studies of several groups focused on the general trend of the catalytic performance which were obtained basically from the kinetic data but did not yet differentiate between the changes of the adsorption
properties of CO and possible structural modification due to presence of water. Separation of the effects resulting from the changes in the adlayer due to the presence of water in the reaction feed from those related to permanent / reversible restructuring of the catalyst due to interaction with water are addressed in more detail in the present work in sections 3.2 and 3.4 (Results and Discussion).

1.3.4. Ru particle size effects on catalytic performance
Changes in the metal particle size result in drastic changes in the geometric, electronic as well as the adsorption characteristics of metals, which in turn impact the catalytic performance as reported for different reactions on various catalysts. Different studies have recently revealed a strong dependence of the CO$_2$ dissociation activity during selective CO methanation on the average particle size of metal nanoparticles. Panagiotopoulou et al., showed that the rate of CO$_2$ methanation strongly increases as the Ru loading for a Ru/TiO$_2$ catalysts increases, which goes along with an increase of the average Ru particle size. Using the same approach Eckle et al. showed a dominant dependence of the CO selectivity in the presence of 15.5 % CO$_2$ on the average Ru particle size for a Ru/zeolite catalyst. The decrease of Ru particle size from 1.9 to 0.9 nm resulting from decrease of Ru metal loading from 5.6 to 2.2 wt. %, resulted in an increase of the CO selectivity in semi-realistic reformate gas (0.01% CO, 3.0% N$_2$, 15.5% CO$_2$ and 80.9% H$_2$) from 80 to 100 %. Under similar reaction conditions, a 5.0 wt.% Ru/γ-Al$_2$O$_3$ catalyst with an average Ru particle size around 2.0 nm showed a selectivity of 42% only.

Full conversion of CO$_2$ was achieved over 2.2 wt.% Ru/zeolite at much higher temperature (410°C) than over a 5.0 wt.% Ru/γ-Al$_2$O$_3$ catalyst both in the absence and in the presence of 0.6 % CO in the reaction gas mixture. These observations referred to an intrinsic higher activity for the dissociation of CO$_2$ and subsequent methanation of the Ru/γ-Al$_2$O$_3$ (Ru particle size: 2-3 nm) catalyst compared to the Ru/zeolite catalyst (Ru particle size: 0.9 nm) depending on Ru particle size.

Although the decrease of Ru particle size limits the CO$_2$ dissociation activity and suppress the overall methanation, it results, however, in a prominent decrease of the activity of Ru nanoparticles (TOF rates) for the selective CO methanation as reported in several cases. The estimated turn over frequencies (TOF) were found to increase with increasing the Ru particle size upon increasing the Ru loading in the zeolite framework.

A similar behavior was also reported in earlier studies over differently loaded Ru/γ-Al$_2$O$_3$ catalyst under Fischer-Tropsch synthesis conditions, using relatively lower ratios of H$_2$ /
The reported findings were explained by assuming that the methanation of CO requires crystallite faces, which are more abundant on larger Ru nanoparticles than on smaller particles, as had been calculated by van Hardveld and Hartog. The increasing TOF values due to increase of the average diameter of Ru nanoparticles is, however, counterbalanced by the loss of activity due to the loss of active surface area of Ru with increasing Ru nanoparticles average diameter.

Careful scrutinizing the reported results showed contradictory trends in various cases, when comparing the Ru particle size with the Ru mass normalized activity, which is important for the price assessment of the price of the commercial use of a specific catalyst. The increase of the Ru particle size resulting from the increase of Ru loading was reported to go along with an increase of the Ru mass normalized activity. On the contrary, larger Ru particles obtained by reduction at high temperatures, or by the calcination of Ru/Al₂O₃ and Ru/TiO₂ catalysts at elevated temperatures (> 650°C) led to lower activities.

These opposing trends can be explained by the different approaches used in different studies for altering Ru particle size which makes the isolation of effects resulting from the Ru particle size hard to interpret in correlation with the CO methanation activity. These different approaches, especially the thermal activation in reactive gas mixtures (O₂, H₂ and CO), in addition to changing the Ru dispersion (average particle size) may also modify the metal oxide support material, which in turn affects the metal support interaction. As a direct result, the adsorption properties of metal nanoparticles will be modified and in turn the catalytic activity and selectivity. In this way we can not attribute changes in catalytic performance of the catalyst to changes in the metal particle size, since changes in the metal support interaction are also induced at the same time.

In total an open question referring to the impact of the method used in altering Ru particle size on the activity and selectivity will be addressed in more in sections 3.1 and 3.4 (Results and Discussion).

1.3.5. Nature of oxide support and metal support interactions

The proper selection of catalyst support and its characteristics is essential for controlling the structural and electronic properties of metal nanoparticles as well as their stability during reaction. One recent example reported by Eckle et al. is the substantially higher activity for Ru/zeolite catalysts compared to Ru/Al₂O₃. The higher reaction rate over a 5.6 wt.% Ru/zeolite catalyst compared to a 5.0 wt.% Ru/γ-Al₂O₃ catalysts, which have almost comparable Ru particle size, was attributed to the stronger metal-support interaction (MSI)
between Ru particles and zeolite matrix.\textsuperscript{71} Also findings of Panagiotopoulou et al. showed a strong dependence of the methanation activity on the nature of support material, with Ru/TiO\textsubscript{2} catalyst having a much higher catalytic methanation activity compared to non-reducible metal oxide supported Ru catalyst such as Ru/Al\textsubscript{2}O\textsubscript{3} and Ru/SiO\textsubscript{2} catalysts.\textsuperscript{68} Similar results were reported also by Tada et al.\textsuperscript{76,111} Solymosi et al. showed earlier that for supported Rhodium catalysts Rh/TiO\textsubscript{2} has about one order of magnitude higher CO methanation activity compared to other supported Rh catalysts such as Rh/Al\textsubscript{2}O\textsubscript{3}, Rh/SiO\textsubscript{2}, and Rh/MgO catalysts.\textsuperscript{112} Also, a significant increase of activity for CO\textsubscript{2} methanation was observed for Rh/TiO\textsubscript{2} catalyst, as reported by the same group.\textsuperscript{113} The authors attributed the high activity of supported TiO\textsubscript{2} catalysts to an enhanced electron charge transfer from TiO\textsubscript{2} to the Rh metal particles, which increases electron density into the antibonding 2π*orbital of CO. Thus, the metal-carbon bond becomes stronger, while at the same time the C-O bond is getting weaker. Accordingly this higher electron density on carbon atoms will be more attractive for the electrophilic H\textsubscript{ad} species in a subsequent hydrogenation step to form -CH-, -CH\textsubscript{2}, -CH\textsubscript{3} and finally CH\textsubscript{4}. Therefore, the overall hydrogenation rate of CO\textsubscript{ad} species is improved. These differences in adsorption properties of different catalyst and their impact on catalytic activity can only be understood in terms of the variation of the metal-support interaction.

Considering the metal-support interactions, two general aspects should be underlined. The first one is a structural change usually observed for reducible metal oxides, which have a tendency to overgrow the surface of metal nanoparticles especially under reductive reaction conditions (high temperature & H\textsubscript{2} atmosphere).\textsuperscript{114,115} The other effect is electronic in nature and is related to a modification of the electron density on the metal particles. Here, it should be emphasized that the electronic changes of the metal particles sometimes arise from the structural changes outlined in the previous point or due to the modification of the oxide support material (phase composition, doping, change of crystallite size, etc.).\textsuperscript{116} The exchange of electronic charge between the metal nanoparticles and the support depends on the difference between Fermi levels of both components of the catalyst (e.g., Ru and TiO\textsubscript{2}) in such a way which allows for a transfer of electrons from the metal oxide into the metal particles conduction band.\textsuperscript{117,118} Baddour et al. supplied evidence about the electron transfer from germanium supports into nickel metal particles, which was associated with an increase of catalytic activity, where a transfer of as little as one electron from the support to 10\textsuperscript{5} Ni atoms accounts for an
1. Introduction

increase the activity for formic acid decomposition by a factor of 1.33 to 3.0.\textsuperscript{119}

Such effects can obviously interfere with those resulting from the changes in metal particle size modifications. Therefore a straightforward strategy to disentangle these interfering contributions is mandatory for the correct understanding of the catalytic performance. The impact of metal-support interaction on the catalytic activity and selectivity are discussed in detail in section 3.5 (Results and Discussion).

1.4. Reaction mechanism and active intermediate

Two reaction mechanisms for the methanation of CO on supported metal catalyst had been discussed for a long time. One mechanism suggested disproportionation of the adsorbed CO as the first step for the methanation reaction followed by a stepwise hydrogenation of adsorbed CO species, resulting in the buildup of the adsorbed -CH, -CH\(_2\), -CH\(_3\) species.\textsuperscript{69,120,121} The other mechanism suggested that the hydrogenation of CO\(_{ad}\) species is the rate limiting step in the methanation of CO.\textsuperscript{94,122}

In earlier work by S. Eckle et al., the nature of reactive intermediate during CO / CO\(_2\) methanation was scrutinized by applying steady state isotope transient kinetic analysis (SSITKA) measurements, following the changes in the rate of exchange (decay / build-up) of different surface species (CO\(_{ad}\) and CH\(_x\)) upon switching from \(^{12}\)CO / H\(_2\) to \(^{13}\)CO / H\(_2\) gas mixtures. According to their reported findings the methanation reaction on Ru/γ-Al\(_2\)O\(_3\) catalyst proceeds through the formation of formyl surface species (HCO\(_{ad}\)). These authors calculated the rate of decay of the initial intensity related to the on top adsorbed CO\(_{ad}\) and HCO\(_{ad}\) species (off rate) after the exchange of the isotopes \(^{(12)}\)CO / \(^{13}\)CO and found that the off rate for the formyl (HCO\(_{ad}\)) species is largely similar to the reaction observed in the kinetic measurements, which means that this species is a preeminate reaction intermediate.\textsuperscript{72} Since the CO\(_2\) methanation reaction proceeds through the formation of CO\(_{ad}\) species resulting from the dissociation of CO\(_2\) in a preceding step, it could be also undoubtedly assumed that CO\(_2\) produce CH\(_4\) via the formation of formyl species (HCO\(_{ad}\)) as the reaction active intermediate. These results agree well with the findings reported by Inderwildi et al. who demonstrated by calculations that the hydrogenation of adsorbed CO\(_{ad}\) is the rate limiting step in the hydrogenation of CO over metal nanoparticles.\textsuperscript{123}

For the mechanistic interpretation of the relationship between Ru particle size and reaction behavior in the present work, we will focus on the comparison of the changes of the CO\(_{ad}\) and Ru-carbonyls adsorption related band intensities, which goes along with the changes in
the intensity of the reaction intermediate (HCO\textsubscript{ad}).\textsuperscript{72} In addition to the mechanistic information extracted from the changes of these species under reaction conditions, their sensitivity to structural changes of Ru nanoparticles (particle size and oxidation state) is used to supplement and support the information obtained from the structural characterization during reaction (\textit{operando} EXAFS / XANES) and after reaction by ex situ techniques (TEM, XPS and XRD), as discussed in section 3.4.

1.5. Overview and layout of the thesis

In addition to the increasing importance in technical applications of the selective CO methanation, it is also an ideal model reaction for testing the catalytic performance of supported Ru catalysts in hydrogenation reactions. The focus of the present work is the molecular scale understanding of the relationship between structure and catalytic performance of supported Ru catalysts, with emphasis on the disentanglement of metal particle size effects from the metal-support interaction for non-reducible (zeolite and Al\textsubscript{2}O\textsubscript{3}) and reducible (TiO\textsubscript{2}) oxide support materials.

The findings and mechanistic insights drawn from these studies were obtained using a multi-analytical approach, employing state of the art time on-stream reaction kinetic experiments, as well as time resolved \textit{operando} diffuse reflectance FTIR and X-ray absorption fine structure (XAFS) spectroscopy. These measurements were supplemented by a detailed elucidation of the composition and structural properties of the catalysts, studied by \textit{ex situ} characterization techniques, including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), high resolution transmission electron microscope (HR-TEM) imaging, and inductively coupled plasma optical emission spectroscopy (ICP-OES).

The experimental setups, synthesis recipes, work procedures, characterization techniques and data processing will be presented in the experimental part (section 2), with a concise but informative discussion of the scientific background of these techniques, which is necessary for understanding results and related discussion.

Results and discussion will be presented in five chapters in sections from 3.1 to 3.5. Each chapter starts with a graphical illustration to make it easier for the reader to gain an overview of the work, followed by an introduction of the specific topic of the chapter, and then presenting results and discussion.

Results presented are, either published (3.1, 3.2 and 3.4) or submitted / under revision (3.3-3.5). These results and the text therein are reproduced from the respective publications and will be presented in the following sequence:
1. Introduction

i) Section 3.1 focuses on the impact of Ru particle size, resulting from the variation of the calcination temperature of a Ru/zeolite catalyst, on the selectivity and activity of the CO methanation reaction. In principle, the pre-treatment of the Ru/zeolite catalyst for the selective CO methanation in CO$_2$-rich H$_2$ atmospheres involves a calcination step (catalyst activation) before the reaction. In this study, the correlation between changes in the catalytic performance (selectivity/activity) and Ru particle size will be a topic of discussion. These changes will be discussed in the light of the resulting changes in the relative coverages of CO on Ru nanoparticles during the reaction in different reaction atmospheres.

ii) Section 3.2 focuses on the influence of water on the average Ru particle size for Ru/Al$_2$O$_3$ and Ru/zeolite catalysts and the simultaneous changes of CO selectivity in a reformate gas containing very low concentration of CO (100 ppm) in the presence of large amount of CO$_2$. These changes will be concisely interpreted in the light of the mechanistic picture described in the previous section, based on the relationship between CO$_2$ dissociation activity (i.e., CO selectivity) and the average Ru particle size.

iii) Section 3.3 addresses the impact of increasing additions of water in reaction gas mixture on the activity of Ru/$\gamma$-Al$_2$O$_3$ and Ru/zeolite catalysts in medium CO concentration (6000 ppm) reformate gas and in more detail in the limited CO concentration (100 ppm). These results will focus on the effect of water on the catalytic activity and will extend the discussion about CO selectivity in the low CO concentration reformates (100 ppm), started in the previous section. These changes will be outlined and correlated to the changes in Ru particle size obtained from operando EXAFS measurements and ex situ TEM imaging. Results from time resolved EXAFS measurements will supply an insight into the changes of the oxidation state of Ru as well as the evolution of particle size during the initial activation phase up to the steady state. The discussion spans to the impact of water on the vibrational characteristics and changes in the CO adlayer in four different reformate gas mixtures for the medium (6000 ppm / SR-ref 6000) and low CO concentration (100 ppm) both in the presence (SR-ref 100) and in the absence of (ID-ref 100) CO$_2$. In addition, the impact of water was also studied in a CO-free CO$_2$ reformate gas.
Section 3.3 expands the insights presented in section 3.2 and 3.3 by following the structural and kinetic behavior changes of a Ru/γ-Al₂O₃ catalyst, which has originally poor selectivity for CO methanation, after temporary exposure to water containing reaction gas. In this approach the stability of the high CO selectivity obtained in the presence of water as well as the possible change in CO methanation activity, was tested after removing water from reaction gas mixture in a subsequent step (switching to dry gas mixture). *Operando* X-ray absorption spectroscopy during reaction in the presence of water and during a subsequent reaction in the absence of water extended the insights obtained from EXAFS results discussed in the previous two chapters. In these measurements we scrutinized the impact of the initial state of Ru species (reduced or oxidized) on the observed dispersion of larger Ru metal particles in the presence of water in the reaction gas mixture. Implications of these data and additional results from transmission electron microscopy and *in situ* IR spectroscopy on the role and influence of H₂O in/on the selective methanation reaction, also in technical applications, are discussed.

In section 3.5, the impact of the specific surface area of the oxide support on the activity and selectivity for CO methanation of Ru/TiO₂ catalyst is discussed in relation to the changes of the metal-support interaction resulting from the strong variation of support material surface area. The structure – reactivity dependence on the support surface area, and the resulting changes of Ru dispersion, were investigated using kinetic and *in situ* DRIFTS experiments, in addition to high resolution TEM. This study underlines the role and the importance of the metal support interaction for a specific catalyst and explains how it can be controlled by altering the oxide support surface area (crystallite size) which can critically modify the methanation activity.
2.1 Kinetic measurements

**Experimental**
2. Reaction gas reformates

2.1. Catalysts preparation and pre-treatments

Commercial Ru/zeolite and Ru/γ-Al₂O₃ catalysts were used as received without any pre-treatments, while the Ru/TiO₂ catalysts were synthesized (see Table 1). The Ru/TiO₂ catalysts were prepared by Sine E. Olesen in the group of Prof. Dr. Ib. Chorkendorff (Department of Physics - Technical University of Denmark). Different supports with increasing surface area, (TiO₂-1: Sigma Aldrich < TiO₂-2 (P25): Degussa < TiO₂-3(P90): Degussa < TiO₂-4: Schaeftlen) which are commercially available, were used to prepare Ru/TiO₂ catalysts using an incipient wetness impregnation method. Prior to synthesis, the pore volume of respective supports were measured, then RuCl₃ hydrate precursor (Sigma Aldrich) (typically 0.0635 g of Ru³⁺ salt per g of TiO₂ support) was dissolved in the appropriate amount of millipore water and was magnetically stirred for 30 min. The TiO₂ supports were dispersed into the Ru³⁺ millipore solution (depending on pore volume of TiO₂) at room temperature for 30 min, then dried at 25°C overnight.

Prior to all experiments, the catalysts were pre-treated in-situ by calcination, followed by reductive activation. Calcination involved either only heating in N₂ to 150°C and keeping it there for 30 min (Ru/zeolite and Ru/Al₂O₃ catalysts) or heating to 150°C in N₂, followed by exposure for 30 min to 10% O₂/N₂ at 150°C and finally flushing for 15 min with pure N₂ at the same temperature (Ru/TiO₂ catalysts). For the reductive activation, which is required to form metallic Ru nanoparticles, all catalysts were exposed to the respective reaction gas atmosphere during heating up from 150°C to the reaction temperature (190°C; heating plateau: 10 min), after that the reaction was run for 1000 min.

Table 1: Structural characteristic of supported catalysts used in different measurements.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>Ru loading / Wt. %</th>
<th>SA / m² g⁻¹</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/zeolite</td>
<td>Ion exchange</td>
<td>2.2</td>
<td>400</td>
<td>Clariant Produkte</td>
</tr>
<tr>
<td>Ru/γ-Al₂O₃</td>
<td>Incipient wetness impregnation</td>
<td>5.0</td>
<td>100</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Ru/TO₂-1</td>
<td>Incipient wetness impregnation</td>
<td>2.8</td>
<td>19.6</td>
<td>Synthesized</td>
</tr>
<tr>
<td>Ru/TO₂-2</td>
<td>Incipient wetness impregnation</td>
<td>2.2</td>
<td>63.5</td>
<td>Synthesized</td>
</tr>
<tr>
<td>Ru/TO₂-3</td>
<td>Incipient wetness impregnation</td>
<td>2.2</td>
<td>121.0</td>
<td>Synthesized</td>
</tr>
<tr>
<td>Ru/TO₂-4</td>
<td>Incipient wetness impregnation</td>
<td>2.1</td>
<td>235.4</td>
<td>Synthesized</td>
</tr>
</tbody>
</table>
2.2. Reaction gas reformates

Gas feeds ranged from idealized gas mixture (CO / CO₂ / H₂ / N₂) to realistic gas mixtures (CO + CO₂ + H₂O + H₂) as described in Table 2. Compositions were estimated by the balance of partial pressures of different gases against 1.0 atm, which correlate to the percentage in the gas mixture versus the total volumetric flow. The measured flow of gas mixture (ml min⁻¹) under ambient conditions (T, p) is normalized (Nml min⁻¹) to the standard conditions (0°C & 1.0 atm). In realistic reformate gases, a water is introduced by bubbling the dry gas mixture in water bath kept at fixed temperatures according to the Clausius - Clapeyron equation (eq.4g). As well known, the vapor pressure (p) above the condensed phase of matter under certain expands logarithmically on the temperature (T), whereas ΔH⁰_vap, R and C are the respectively vaporization enthalpy, universal gas constant, and the integration constant.

\[
\ln p = \frac{-\Delta H_vap}{RT} + C \quad \text{(4.g)}
\]

The flow of all water free gas reformates was adjusted at 41.6 Nml min⁻¹, while it was corrected (increased) in the presence of different amounts of water, to keep the amount of CO almost unchanged in all compositions (section 3.2 - 3.4). From GC measurements it was observed that the amount of CO after the addition of water decreases tangibly with increasing water in the feed. The controlled increase of gas flow decreases the loss of CO in the presence of water. This can be explained by the different mixing properties of different gases (i.e., solubility) with water in the gas phase after saturation.¹²⁴

<table>
<thead>
<tr>
<th>Reformate gas</th>
<th>CO / ppm</th>
<th>CO₂ / %</th>
<th>N₂ / %</th>
<th>H₂ / %</th>
<th>H₂ / CO Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-ref</td>
<td>0</td>
<td>15.5</td>
<td>0.0</td>
<td>84.5</td>
<td>--</td>
</tr>
<tr>
<td>ID-ref 100</td>
<td>100</td>
<td>0.0</td>
<td>0.0</td>
<td>99.99</td>
<td>9999</td>
</tr>
<tr>
<td>ID-ref 6000</td>
<td>6000</td>
<td>0.0</td>
<td>0.0</td>
<td>99.4</td>
<td>166</td>
</tr>
<tr>
<td>SR-ref 100</td>
<td>100</td>
<td>15.5</td>
<td>3.0</td>
<td>84.49</td>
<td>8449</td>
</tr>
<tr>
<td>SR-ref 6000</td>
<td>6000</td>
<td>15.5</td>
<td>3.0</td>
<td>80.9</td>
<td>135</td>
</tr>
</tbody>
</table>

Table 2: Composition of reaction gas mixtures used in the measurements.
2.3. Structural characterization of the catalysts

In this part different characterization techniques used in the elucidation of the structure of studied catalysts including the chemical composition, metal particle size, and support surface will be described.

2.3.1. Ru loading: ICP-OES method

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the loading (wt.%) of Ru in different catalysts, which is critical for the evaluation of the Ru mass based reaction rates. It is required for normalizing the activity of different catalysts with respect to the mass of Ru, and thus establishing an abstract comparison among them based on the mass of loaded Ru metal nanoparticles regardless of the method of preparation or the type of support.

The principle of work of emission spectro-analytical techniques depends basically on the measurement of ultraviolet or visible light emitted radiation after a thermal or electrical excitation of the sample. The emission thus requires a preceding atomization step, wherein the solid material of the catalyst is converted into free gaseous atoms. To do that, a hot and partially ionized gas (usually Ar plasma) is used for heating the sample, hence dissociating it into its atomic components. In the present case the sample is dissolved in aqua regia mixture, and then the resulting solution is sprayed into a plasma torch. The plasma is formed by exposing a flow of Ar to high frequency energy in the head of the atomization torch, resulting in a temperature above 5000°C, which is enough for the atomization of most of the powder catalyst. All measurements were done in the Institute of Analytical and Bioanalytical Chemistry (Ulm University) by Ms. Margit Lang. Only fresh samples were used for the analysis without any prior pre-treatments.

2.3.2 Catalyst surface area (SA) – BET method

The evaluation of the specific surface area of the catalyst (support) is important for accurate assessment of the catalytic performance and for the correct comparison of different catalysts. In spite of its oversimplified model, the BET theory is still widely accepted for the evaluation of surface area of catalysts / supports according to the model of Brunauer, Emmett and Teller. The BET theory is an extension of the Langmuir ideal monolayer adsorption model, where an infinite number of adsorbed layers can be formed, with each layer acting as an adsorption site for the following layer. On the basis that the multilayer has an infinite thickness at \( \frac{p}{p^0} = 1 \), the well-known BET equation could be formulated as shown in eq. 5a.
2.3. Characterization of the catalysts

The theory is based on physisorption of gases where \( p \) stands for the equilibrium pressure, \( p^\circ \) for the saturation pressure at a specific temperature, and \( n \) represents the quantity of adsorbed gas molecules at certain pressure (mole), while \( n_m \) (mol) is the monolayer capacity with an empirical constant \( C \). By plotting the left side of the equation versus \( p/p^\circ \), \( n_m \) (mol) can be obtained from the slope and intercept of the equation, which can be used to calculate the specific surface area \( SA \) (m\(^2\)g\(^{-1}\)) of catalyst from the knowledge of the absolute surface area of the adsorbate molecule used in the experiment (usually N\(_2\)), and the weight (wt.) of the investigated sample (eq. 5b). In that equation, \( N_A \) stands for the Avogadro’s number.

\[
\frac{1}{n} \left[ \frac{(p^\circ/p) - 1}{1} \right] = \frac{1}{n_m C} + \frac{(C - 1)}{n_m C} (p/p^\circ) \quad (5.a)
\]

\[
SA = \frac{(n_m \times N_A)}{wt} \quad (5.b)
\]

All measurements were done in the Institute of Inorganic Chemistry II (Ulm University) by Ms. Cornelia Egger. Only fresh samples were used for the analysis without any prior pre-treatments with N\(_2\) as adsorbate molecule.

2.3.3. Transmission Electron Microscopy (TEM)

Electron microscopy is a powerful technique for the determination of the size and shape of supported metal particles. In dealing with electron microscopes one should bear in mind the resolving power, which is defined as the minimum distance at which two points can be resolved as separate entities. The resolution of a light microscope is fundamentally limited by half the wavelength of the light hitting the sample, which is known as Abbe’s diffraction limit. Making use of the short wavelength associated with electrons (< 1Å), Ernst Ruska could develop electron microscopes and helped to resolve nanometer sized objects. In principle an electron beam of high energy / intensity passes through a condenser to illuminate the sample. As the electron beam passes through a thin layer of the specimen, a fraction of the electrons passes through the sample without suffering an energy loss. The transmitted electrons form a two-dimensional projection of the sample which is referred to as the bright field mode. Another mode defined as the dark field image is formed by the projection of the diffracted electrons.\(^{126}\)
2.3. Characterization of the catalysts

Although being able to resolve single atoms (1.0 Å) with the application of aberration corrected instruments, TEM still has some severe limitations which can be listed as follows:\textsuperscript{127} i) samples sensitive to electron beam damage such as zeolite and some MOFs, can not be imaged due to electron beam damage because of the interaction with the high energy electrons (100 - 200 keV),\textsuperscript{128} ii) it is hard to obtain \textit{operando} information, especially in studying real catalytic systems, due to the necessity for reduced pressure in the range of $10^{-6}$ mbar for normal TEM microscopes, which can increase up to 150 mbar in the best case when using the environmental TEM microscopes, iii) for supported metal particles over high surface area supports (> 200 m$^2$ g$^{-1}$) the low contrast due to the similar size of metal particles and support crystallites makes the differentiation between these particles quite hard.

Samples were prepared by dissolving very small amounts of the Ru powder catalyst (< 0.5 mg) in 2 ml of ethanol, which is sonicated for 10 min to make sure that the whole amount is completely dispersed in the liquid. Afterwards the dispersed catalyst was supported onto a holy carbon grid by drop coating of ethanol suspension. The grid was left a few minutes until ethanol evaporated, and then the drop coating step was repeated 2 more times to ensure appropriate coating and distribution of metal particles on the grid.

For the evaluation of the average particle size of Ru nanoparticles at least 500 particles were scanned per sample, and analyzed by iTEM processing software. From the knowledge of the Ru particle diameter one can eventually determine the surface dispersion according to the following set of equations, which are described in more detail in Ref.\textsuperscript{129}

By knowing the diameter ($d_i$ / m) for a number of Ru nanoparticles ($n_i$) measured by TEM, the volume-area mean diameter ($d_{VA}$) for all particles can be defined according to eq. 6.a.

In terms of metal atom volume ($V_m$ / m$^3$) and surface area ($a_m$ / m$^2$) the volume-area mean diameter can be defined also according to eq. 6.b, where D is the metal surface dispersion, which is defined by the ratio between the number of surface atoms ($N_S$) to the total number of atoms ($N_T$) in the surface and in the bulk.

\[
d_{VA} = \frac{\sum_{i} n_i d_i^3}{\sum_{i} n_i d_i^2} \quad (6.a)
\]

\[
d_{VA} = 6 \left( \frac{V_m N_T}{a_m N_S} \right) = 6 \left( \frac{V_m}{a_m D} \right) \quad (6.b)
\]

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2.3. Characterization of the catalysts

By rearranging the above two equations, the surface dispersion (D) can be calculated directly from the diameter of Ru nanoparticles (d_i) obtained from iTEM according to eq. 6c.

\[ D = 6 \left( \frac{V_m}{\sum_i n_i d_i^2} \right) / \left( \frac{a_m}{\sum_i n_i d_i^3} \right) \]  

All TEM measurements were carried out in the Electron Microscopy Group of Materials Science (Ulm University) by Dr. Johannes Biskupek.

2.3.4. X-ray Diffraction (XRD)

Since its discovery by Wilhelm Röntgen in 1895 X-ray diffraction found numerous applications which affected various branches of science. The first structural information from X-ray diffraction was obtained by Max von Laue who reported for the first time the diffraction pattern for CuSO_4 which won him the 1914 Nobel Prize in Physics. The precise determination of the crystal structure were determined by Bragg and his son, who got jointly the 1915 Nobel prize in physics for the analysis of a crystal structure using X-ray diffraction as well as for the formulation of the relationship between crystal spacing, X-ray wavelength, and the diffraction angle. X-ray diffraction is basically used for the evaluation of the metal particle size by the analysis of the line broadening using the Debye – Scherrer equation. It is also useful in the testing phase purity of materials, such as the identification of the ratio of anatase to rutile phases in titania.\(^{126}\) The evaluation of line broadening can be carried out either at an elementary level or at complete line profile analysis. The elementary evaluation of the line analysis produces an average over all crystallites therefore yielding an average particle size based on the use of Scherrer equation. The Fourier analysis of the whole line profile allows for the determination of the crystallite size distribution. The latter approach is known as Warren-Averbach method. In this work we have used the elementary line reflections. If we consider an X-ray beam possibly a number of lattice planes (N) with a specific lattice spacing (d_{hkl}), perpendicular to the diffracting plane (hkl), then the thickness of the whole crystallite \(L = N \cdot d_{hkl}\) can be calculated from peak width (\(\beta / \text{radians}\)) at the half of the peak maximum height via eq. 7.

\[ L_{hkl} = \frac{K \lambda}{\beta \cos \Theta} = \frac{0.9 \lambda}{\beta \cos \Theta} \]  

(7)
2.3. Characterization of the catalysts

In that equation \( \lambda \) refers to the X-ray wavelength, \( k \) (0.9) is an experimental constant, while \( \Theta \) stands for the angle between the beam and the normal on the reflecting lattice plane.

Like TEM techniques X-ray diffraction has also some drawbacks in the particle size determination, which limit its application in certain cases. First, for relatively low atomic number metals such as Fe, Co and Ni, there is a significant lack of contrast between the intensity of the reflection and overall scattering of X-ray. Second, single line analysis of XRD is confined by a lower (1.5 – 2.0 nm) and higher (> 100 nm) particle size cutoff limits. At the lower limit the broadening is too large, which makes it hard to distinguish diffraction peaks from the noise, while for the upper limit the broadening is too small to be evaluated.

Furthermore, XRD can not discriminate between single crystalline and polycrystalline particles, and only an average value for all crystallites can be obtained.

All XRD measurements for the Ru/TiO\(_2\) catalysts were performed after reaction for 1000 min in SR-ref 6000 reformate (see Table 2). Measurements were carried out in the Institute of Inorganic Chemistry II (Ulm University) by Mr. Samuel Blessing.

2.3.5. X-ray Photoelectron Spectroscopy (XPS)

The use of XP spectroscopy was developed by Kai Siegbahn in the mid-sixties and introduced in research laboratories in the early 1970s. The technique is basically useful in the analysis of the topmost layer of the surface (3 - 10 nm). The sample is irradiated by a monoenergetic X-ray beam (soft X-ray; \( E \leq 5 \) KeV) under vacuum, and the electrons emitted the surface are analyzed.

In principle, X-rays with frequency \( v \) (s\(^{-1}\)) can be absorbed by a specific element whenever the photon energy \( h_v \) matches, or is higher than the binding energy (\( E_b \)) of one of the inner core electrons, in such a way that the electron is emitted with a kinetic energy (\( E_{\text{kin}} \)) according to the photoelectric effect shown in eq. 8.

It should be noted that the work function of the spectrometer (\( \phi \)) should be considered when calculating the final binding energies of the emitted photoelectrons.\(^{130}\) By measuring the kinetic energy of emitted electrons and knowing the work function and the photon energy the binding energies of respective elements in the sample can be identified. Furthermore, changes in the oxidation state or the chemical environment surrounding a specific element can be also identified from the change in the standard value of the binding energy of that element.

\[
E_b = h_v - E_{\text{kin}} - \phi
\]
2.3. Characterization of the catalysts

In the present work XPS measurements were performed basically for the assessment of the changes in the atomic ratio of Ru to Ti in the topmost layer of Ru/TiO$_2$ catalysts as a function of the support surface area (see section 3.4). All spectra were recorded by Dr. Thomas Diemant using a PHI 5800 ESCA system (Physical Electronics) applying monochromatic Al-K$\alpha$ x-ray radiation (1486 eV) with a pass energy path of 29.35 eV for the detail spectra. All the spectra were recorded over a size of 1 mm at an emission angle of 45 $^\circ$ with an aperture size of 4 mm. An electron gun emitting a current of 20 $\mu$A was used for neutralizing the powder samples. Fitting of the spectra was carried out by the XPSpeak4.1 software, applying a Shirley background subtraction. Shifts resulting from the surface charging during the measurements were removed by normalization against the carbon standard 1s energy located at 284.4 eV.

The samples were scanned for Ru (3d) in the energy range from 274 to 294 eV in the 3d region. It should be noted that the major peak of C1s at ca. 284 eV interferes with the 3d$_{5/2}$ component of the Ru (3d) orbital at an average value of 284 eV. For the Ti (2p) region, we scanned in the energy range from 450 eV to 501 eV. In this range the Ru (3p$_{3/2}$) signal interferes with the Ti (2p$_{1/2}$) peak at an average energy around 465.5 eV.

The atomic surface ratio of Ru: Ti is determined by the ratio between the 3d$_{5/2}$ peak intensities of Ru and to the 2p$_{3/2}$ peak intensity of Ti using the tabulated atomic sensitivity factors for each peak. Spin orbital coupling energies of 5.71 and 4.2 eV were fixed for 2p$_{3/2}$ / 2p$_{1/2}$ and 3d$_{5/2}$ / 3d$_{3/2}$ components. Corresponding peak intensity ratios of 1:2 for the 2p$_{3/2}$ / 2p$_{1/2}$ and 2:3 for 3d$_{5/2}$ and 3d$_{3/2}$ signals, respectively, were used in the fitting process.
2.4 Kinetic measurements

2.4.1. Experimental set-up

The set-up used in kinetic experiments consists of 3 parts. The first is the gas mixing unit (see Fig. 1), wherein the reaction gases are regulated and mixed up together before entering the reactor. It consists of a combination of gas lines, control valves, and mass flow controllers for different gases (Bronkhorst F201C-FA-88V). The second part is the reaction chamber made of a quartz tube micro-reactor connected with a NiCr/Ni thermocouple in the middle for temperature monitoring and control during reaction. The reactor is housed inside an isolated oven chamber, where controlled heating during the post-treatments and the reaction can be achieved using a resistant wire (Horst HSQ 900). Third is the analysis unit used for separation and quantification of influent and effluent gases which uses on-line gas chromatography (GC; DANI 86.10). The GC is equipped with thermal conductivity detectors (TCD).

![Figure 1: Block diagram of the setup used in kinetic measurements.](image)

2.4.2. Plug flow reactor (Reaction rate / selectivity)

The working principle of a plug flow reactor, which was used for the determination of the absolute reaction rates is based on a mass balance between reaction gas mixtures flowing to the reactor and the effluent mass coming out on the other side after reaction, which contains
2.4 Kinetic measurements

reaction products in addition to the remaining reactants. This can be represented by eq. 9.a, considering the conversion of CO as dX_CO (see eq. 9b) taking place in a mass element of the catalyst bed (dm) packed in the reactor for an overall initial molar flow n_CO (mol min⁻¹) (see Fig. 2). In this case the reaction rate for CO methanation (conversion rate) per second can be represented by r_CO in (mol_CO s⁻¹ g_cat⁻¹) as indicated in eq. 9c.

The rate of CH₄ formation is given by the total out-coming molar flow of methane (CH₄) and the Ru mass according to eq. 9.d. This equation is valid for an initial (incoming) CH₄ concentration equal to zero. Finally, the CO₂ conversion rate is obtained from the difference between the rate of CH₄ formation and the rate of CO conversion.

The ratio of the catalyst to the inert material is adjusted depending on the catalytic activity of each catalyst such that the total conversion is kept to ≤ 20 % of the initial concentration of the limiting reactant (CO). The low conversion of CO is required to avoid i) heat transfer due to changes in temperature of the catalyst bed because of the exothermic reaction and ii) mass transfer due to a mass gradient inside the catalyst pore channels. These phenomena can lead to incorrect evaluation of the real reaction rate related to kinetic changes.

\[
\int_0^m \frac{dm}{n_{CO_{in}}} = \int_0^X_{CO} \frac{dX_{CO}}{r_{CO}} \quad (9.a)
\]

\[
X_{CO} = \frac{c_{in} \cdot c_{out}}{c_{in}} < 0.2 \quad (9.b)
\]

\[
r_{CO} = X_{CO} \frac{n_{CO_{in}}}{m_{Ru}} \quad (9.c)
\]

\[
r_{CH4} = \frac{n_{CH4_{out}}}{m_{Ru}} \quad (9.d)
\]
2.4 Kinetic measurements

The evaluation of the rate of \( \text{CH}_4 \) formation is similar to that of \( \text{CO} \) except that for \( \text{CH}_4 \) overall methane formation comes from \( \text{CO} \) and \( \text{CO}_2 \) conversions (i.e., methanation rate). Thus the selectivity (Sel. \%) can be defined as a ratio between conversion of \( \text{CO} \) and formation of \( \text{CH}_4 \) (conversion of \( \text{CO} + \text{CO}_2 \)) as indicated in eq. 9.e.

\[
\text{Sel.\%} \text{ CO} = \frac{\text{CO conv.}}{\text{CH}_4 \text{ Form.}} \times 100
\] (9.e)

The turnover frequency (TOF) based rate is important for the comparison of intrinsic activities of all Ru surface sites (including active sites). TOF (s\(^{-1}\)) values can be estimated by the knowledge of Ru mass normalized reaction rate (mol s\(^{-1}\) g\(_{\text{Ru}}\)), dispersion of Ru nanoparticles (D) and the atomic mass of Ru (At\(_{\text{Ru}}\); g mol\(^{-1}\)) as represented in eq. 9.f.

\[
\text{TOF} = \frac{r \times \text{At}_{\text{Ru}}}{D}
\] (9.f)

2.4.3. Gas chromatography (GC)

Chromatography encompasses a number of techniques which share the same general idea for the separation of mixtures of different chemical components based on the differential sorption between a mobile phase carrying the mixture and a stationary phase (gas/solid, liquid solid, Liquid/Liquid and gas/liquid). Chromatographic methods are classified in four basic categories according to the principle used in mixtures partition, including i) adsorption chromatography, ii) partition chromatography, iii) ion exchange
2.4 Kinetic measurements

chromatography and iv) size exclusion chromatography. Separation by gas chromatography depends on the differences in adsorption properties of the gaseous components on the stationary phases (first category). The separation of the components in a gas sample can be achieved by one of three approaches including frontal analysis, displacement development or elution development (for more information see Ref.\textsuperscript{132}).

DANI model (86.10 HT) gas chromatograph was used in all experiments presented in this thesis. This chromatograph use thermal conductivity detectors (TCD) having detection limit for different components (especially CO and CH\textsubscript{4}) down to \textasciitrans{5} ppm. The effluent gases were separated over two different sorption materials packed into stainless steel columns, which are housed inside an oven to adjust the required separation temperature (60 - 70°C). The heating is selected according to the amount of water present in the reaction gas feed. The first column, packed with a polymeric material (Hayesep Q) is used for separating polar components such as CO\textsubscript{2}, H\textsubscript{2}O and CH\textsubscript{3}OH, while a molecular sieve is used to separate the remaining non-polar components including O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4} and CO.

The process of gas separation starts by opening the separation loop in the way that 1.5 ml of the flowing gas mixture is injected into the first column to separate CO\textsubscript{2} and H\textsubscript{2}O from the gas mixture. Afterwards, the rest of the gas mixture is switched to the second column to separate O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4} and CO. A four ways value switches between the two columns, and the two TCDs which are thermostated at constant temperature (140°C). H\textsubscript{2} is used as a carrier gas for the components to be analyzed, whereas the difference in the thermal conductivity of the carrier gas caused by the presence of eluted components creates a difference in temperature, which can be measured using a wire with temperature dependent resistance. The chromatogram is obtained by plotting the electrical signal (mV) as a function of the elution time.\textsuperscript{133} Different components in the analyzed gas mixtures are standardized by reference gas mixture with exact composition prepared especially for this purpose. The peak areas of the reference test gas components are equivalent to a known composition (1% CO, 1% CO\textsubscript{2}, 1%O\textsubscript{2}, 0.5% CH\textsubscript{4}, 21.5% N\textsubscript{2} and balance H\textsubscript{2}), and can be used to calculate the absolute composition of reactant / product gases.
2.5. Diffuse reflectance infrared spectroscopy (DRIFTS)
Infrared spectroscopy is very crucial in studying solid catalysts due to the high sensitivity for changes in the nature and quantity of the adsorbed surface species (adlayer). In addition, it can be used to probe the structural changes and alteration of geometric and electronic properties. As an example the change of the oxidation state of metal particles affects the bond strength between the adsorbate and the catalyst surface site, which appears as a change in the position of absorption band characteristic for this adsorbate species. The reflectance modes have big advantage in studying real catalysts as it avoid the change of the physical state of the catalyst in the preparation of wafers (e.g., transmission modes).\textsuperscript{134,135}

2.5.1 Theoretical background of DRIFTS
The infrared reflectance methods include internal reflectance and external reflectance. Since in external reflectance the measured property is the reflected radiation from the surface, the material being used should be reflective or covered with a reflective thin layer. Hence, the sensitivity of the reflectance methods is affected by the refractive index and surface roughness, in addition to the infrared absorption properties of the active surface components. It should be noted that the surface reflected energy relative to the total incident energy is located in the range of 5 – 10 % for most of the materials and increases slightly on materials which are infrared active.\textsuperscript{136}

External reflectance includes specular and diffuse reflectance. In specular reflectance the reflection angle of radiation should equal the incidence angle of radiation on the surface, while in diffuse reflectance the energy that penetrate through surface particles is reflected back in all direction which can be collimated by spherical mirror (see Fig.3). The theoretical principle of DRIFT spectroscopy was firstly introduced by Kubelka and Munk.\textsuperscript{137}

\textbf{Figure 3:} The difference between specular (a) and diffuse reflectance (b).\textsuperscript{136}
2. 2. Diffuse Reflectance Infrared Spectroscopy (DRIFTS)

The intensity of reflected infrared due to the interaction with the surface is related to the surface coverage (concentration) of the interacting species, which is conventionally defined as Kubelka-Munk equation. The absolute reflectance \( R \) from infinitely thick layer is related to surface concentration \( c \) for certain species by eq. 10a, where \( S \) represents the scattering coefficient of the light, and \( k \) represents the absorption coefficient.

\[
F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S} \tag{10.a}
\]

For a weakly absorbing sample, which is a prerequisite for the appropriate application of Kubelka-Munk relationship, the absorption coefficient can be calculated using eq. 10b and \( c \), where \( \varepsilon \) is the molar absorptivity of the material, and \( c \) is the concentration of surface species.\textsuperscript{137} The data are evaluated according to a standard method described elsewhere.\textsuperscript{138} Absolute quantification of the adsorbed species is not possible with DRIFTS measurements due to the difficulty to determine the exact penetration depth and the broadening of the infrared beam on the surface. Nevertheless, DRIFT spectra can be employed in a semi-quantitative manner, since the evaluated intensities of absorption bands go along with the concentration of surface species.\textsuperscript{139}

\[
K = 2.303 \varepsilon c \tag{10.b}
\]

\[
F(R) = \frac{(1 - R)^2}{2R} = \frac{2.303\varepsilon c}{S} = \frac{c}{K'} \tag{10.c}
\]

\textbf{Figure 4:} Components of the in situ DRIFTS reaction cell.\textsuperscript{140}
2.2. Diffuse Reflectance Infrared Spectroscopy (DRIFTS)

2.5.2. Experimental set-up

The set-up for DRIFTS experiments includes a gas mixing unit similar to that one described in section 3.4.1 (Fig.1), a reaction cell, a spectrometer, and the control system with a software interface to run the whole assembly. The measurements were performed using a commercial in situ reaction cell (Harricks, HV-DR2), as illustrated in Fig. 4. The spectra were recorded using a Magna 6700 spectrometer (Thermo Fisher) equipped with an MCT narrow-band detector. The catalyst is normally filled inside the sample cup, which is located under a detachable cell dome.

The catalyst is heated during the reaction using a heating element and thermocouple built directly at the bottom of the sample cup. The set-up of the cell allows for the continuous flow of the pre-treatment / reaction gas mixtures through the catalyst bed, from the bottom to the surface, and then to the exhaust or to the gas chromatograph for further analysis and quantification of the gas composition coming out from the reaction cell.

The infrared laser beam is focused on the catalyst surface using an array of flat and elliptical mirrors. As illustrated in Fig. 5 the laser beam coming from the infrared source, located horizontally on the left hand side of the reaction cell, is directed using two mirrors (M1 and M2) to the elliptical mirror which collimate it on top of the catalyst surface. After that, the diffuse reflected infrared light on the opposite path of incident light is collimated back on the other part of the half spherical mirror, which directs it to the mirrors M3 and M4, and thereafter reflected to the detector. The spectrometer is controlled during the measurements by Omnic 7.3 software package.

**Figure 5:** Path of the incident and diffuse reflected infrared beam.
Gas mixtures were prepared exactly as described above for the kinetic measurements (section 2.4.2). The infrared spectra were collected during reaction by recording over a short time scale (20 scans per spectrum in 15 sec) during the initial reaction phase, where fast changes are expected to occur. Although the signal to noise ratio is relatively low for these spectra, however, they are mandatory to follow and resolve the fast changes in the adlayer during the initial activation phase of the reaction (e.g., see Fig. 24 in section 3.2.4). At extended reaction times, up to steady-state, the changes in the adlayer are slower or close to zero, therefore we can use a longer time scale (400 scans per spectrum in 4 min) to monitor the spectra.

The absorption band intensities for different surface species were evaluated in Kubelka-Munk units which are linearly related to the adsorbate coverage. Background removal of the spectra was done by dividing the measured absorption by the absorption obtained in spectra recorded in a flow of N$_2$ at 150°C, before heating up to 190 °C in reaction atmosphere.
2.6. X-ray Absorption Fine Structure Spectroscopy (XAFS)

Before the discussion of XAFS theory and related aspects (experimental set-up and data acquisition) the principle of production and use of synchrotron radiation as well as the physical properties of X-rays interaction with matter will be discussed.

2.4.1. Synchrotron radiation: Fundamentals

Synchrotron radiation emerged for the first time in 1947. It could feasibly be used as a research tool since around the mid-sixties.¹⁴¹ The development of X-ray absorption spectroscopy was one of the outcomes because of the high intensity and tunability of X-ray energies.¹⁴² In synchrotron rings, the electrons are produced and then injected inside evacuated pipelines, where they are accelerated close to the speed of light during the movement in a circular path using bending magnets. The moving electrons accelerate in the magnetic field as the magnets bends, and consequently emit electromagnetic radiation with wavelengths depending on their kinetic energy. According to the Lorenz equation, the force affecting a moving charge with velocity $v$, which is simultaneously exposed to an electric field $E$, under magnetic field with the flux $B$, can be described by eq. 11 (see chapter 2 of Ref.¹⁴¹). Accordingly, the radiant power of the orbiting electron packets depends largely on the applied magnetic fields.

$$F = e(E + vB)$$ (11)

In the classical synchrotron rings the radiation is usually produced due to the orbiting electrons in a simple dipole bent magnet as illustrated in Fig. 6a. On the other hand, the modern storage rings are based on “insertion devices”, which use multipole magnets including wigglers and undulators (Figs. 6b & c), in order to improve the characteristics of the radiant power and energy tunability. This is achieved by forcing the electron bunches to move in a sinusoidal path instead of the conventional elliptical path. Wigglers enhance the radiant power at high photon energies. Undulators are also indispensable as they make use of lower magnetic fields with a larger number of magnetic poles compared to wigglers (Fig. 6b), to keep the high intensity, but for much lower photon energies (Fig. 6c). By employing both devices together, the synchrotron radiation can be tuned over a wide range of photon energies and keeping, at the same time, the required high radiation intensity.
2.6. X-ray Absorption Fine Structure Spectroscopy (XAFS)

2.6.2. X-rays: Interaction with matter and Cross section

X-ray is an electromagnetic radiation consisting of two perpendicular wave components travel in vacuum at the speed of light \( c = 3.0 \times 10^8 \text{ m s}^{-1} \). Like all waves, X-rays are defined by a wavelength \( \lambda \) and frequency \( \nu \) whose product equals the speed of light (eq. 12.a). The energy of the electromagnetic wave is defined by eq.10b \( (h: \text{Planck’s constant}) \).

\[
c = \nu \lambda \quad \text{(12.a)}
\]

\[
E = h \nu = h c / \lambda \quad \text{(12.b)}
\]

X-rays occupy the upper part of the electromagnetic spectrum and cover the energy range from 100 eV to 100 keV. According to their energies, X-rays can be classified as hard X-rays with energies > 5 KeV, and soft X-ray with energies < 5 keV. The interaction of X-rays with matter induces different spectroscopic phenomena such as absorption, scattering (elastic and inelastic), diffraction, fluorescence, and photoemission.

X-ray absorption occurs when the photon gives up its complete energy to one of the core
2.6. X-ray Absorption Fine Structure Spectroscopy (XAFS)

Electrons, resulting in a transition to one of the uppermost empty energy levels, which creates an electron vacancy. The hole created can be filled by another electron from a higher energy level, either radiatively by a simultaneous emission of a photon (fluorescence) or non-radiatively by expelling of another electron (Auger process).

The extent of X-ray absorption at different atomic species is defined by the cross section of the photons with the respective matter (\(\sigma\)), which bears the unit area and depends critically on the incident photon energy. For comparison of different materials, the cross section is calculated as a mass normalized quantity, which represents an effective area per amount of element (see chapter 1 in Ref. 142). Another relevant parameter which is always defined with the cross section is the linear attenuation coefficient \(\mu\), which defines the loss of X-ray intensity as it penetrates into a specific material. The attenuation coefficient is related to the cross section via eq. 13.\(^{142}\) This equation also defines the probability of a particle interaction with X-ray in a thin layer having a thickness dx, with a volume density of the target particle \(\rho\). The inverse of the linear attenuation coefficient is equal to the absorption length. These parameters are crucial for the proper selection of the thickness and dilution of the sample under investigation.

\[
\rho \sigma \, dx = \mu \, dx
\]

2.6.3. Near / Extended X-ray Absorption Fine-Structure

The fine oscillations in the absorption coefficient near to the absorption edges of X-rays were first discovered by Hugo Fricke in 1920, who named this as X-ray absorption fine structure (XAFS). These features remained for 50 years vague and almost of no use until Stern, Sayers, and Lytle\(^{143,144}\) formulated the fundamentals of the XAFS theory in the early seventies of the last century.

Implicit in the XAFS spectra are three basic regions (e.g., Ru K-edge in Fig.7), shall be highlighted. The first region includes the pre-edge / edge jump for the absorbing metal, where the edge energy is element characteristic and can be used as fingerprint to identify the atomic composition. The second region extends for ca. 100 eV after the absorption edge and is abbreviated X-ray absorption near edge spectroscopy (XANES). The absorptivity oscillation as a function of energy over a few hundred electron volts after the XANES region is defined as Extended X-ray Absorption Fine Structure (EXAFS).

The basic difference between XANES and EXAFS is the type of information which can be extracted. On the one hand the shape and symmetry of the XANES spectra in addition to the
2.6. X-ray Absorption Fine Structure Spectroscopy (XAFS)

shifts of energy edge can supply qualitative information about the electronic structure (i.e., oxidation state) and changes of the adlayer for a specific element.\textsuperscript{145} This can be achieved by simple comparison of the normalized spectra with standard forms of the same element (metal foil or pure oxide powder), or by applying more sophisticated linear algebra techniques to obtain a detailed analysis of different components in the spectra.\textsuperscript{143} On the other hand, the analysis of EXAFS features provides valuable information both on the electronic properties as well as the structure (atomic structure, bond lengths and particle size) of the scattering and back-scattering atomic shells. This is, however, challenged by the extent of data reduction and analysis, which involves a more tedious procedure compared to the XANE spectra.

\textbf{Figure 7:} XAFS spectra at Ru K-edge over Ru/TiO$_2$ catalyst
(XAFS beamline; Elletra Synchrotron -Trieste-Italy, June 2014).

2.6.4. EXAFS theory

The use of EXAFS in studying non-crystalline structures was introduced first in 1971 by Sayers et al.\textsuperscript{143} Fourier analysis of EXAFS was used to invert the observed energy fluctuation into a radial structure function, wherefrom the geometrical information of the material (distances from the absorber, number of atoms surrounding, and widths of coordination shells) could be extracted. The example for the new emerging technique at that time compared the EXAFS spectra for amorphous and crystalline germanium (Ge) samples. Stern published later on a detailed description of EXAFS theory in 1974.\textsuperscript{144} As described in section 2.5, X-ray absorption follows the photoelectric effect (see eq.8), where an electron can be ejected with a kinetic energy ($E_{\text{km}}$) depending on the incident photon energy and the energy level of the bound electron. According to the assumption of De Broglie, the excited
2.6. X-ray Absorption Fine Structure Spectroscopy (XAFS)

electron can be considered as a wave with wavelength \( \lambda = 2\pi/k \), where \( k \) is defined as the photo-electron wave vector and can be related to the electron kinetic energy through eq.14.a.

\[
k = \sqrt{\left(\frac{8\pi^2 m}{\hbar^2}\right) \times E_{\text{kin}}} \quad (14.a)
\]

\( m \): electron mass ; \( \hbar \): Planck’s constant

In principle, the absorber atom is considered as the center of the outgoing electron wave which, however, can be scattered from the electron density of neighboring atoms leading to back scattered waves spreading in the opposite direction. The interference of the outgoing and the backscattered wave is destructive at some points in space around the absorber atom and instructive in other points (see Fig. 8), which creates the minima and maxima in the absorption coefficient as a function of the X-ray frequency / energy (see Fig. 7).

Different atoms around the absorber produce distinguishable features in the EXAFS spectra depending on the distance from absorber, the atomic mass and the former charger of the scatterer (i.e., elemental nature). The oscillating absorption coefficient (\( \mu \)) is directly proportional to the photoelectric excitation probability (\( p \)), which in turn depends on the density of allowed states at the final energy level (\( \rho (E_f) \)). This probability is described by the wave-functions of the ground and excited states (eq.14.b):

\[
p = \left(2 \pi^2 e^2 / \omega c^2 m^2\right) \left|<\psi_f| P \times E | \psi_i>\right|^2 \rho (E_f) \quad (14.b)
\]

\( e \): electron charge; \( \omega \): angular frequency; \( c \): speed of light; \( P \): momentum vector;
\( E \): electric field vector (X-ray); \( \psi_i / \psi_f \): ground / excited states wave-functions

**Figure 8:** Outgoing (solid) and backscattered electron wave (dashed circles).144
2.6. X-ray Absorption Fine Structure Spectroscopy (XAFS)

The basic EXAFS mathematical formula shown in eq. 14.c represents the oscillatory part of the absorption coefficient as a function of the photo-electron wave vector. Referring to the \( j \)th coordination shell, this equation relates the distance between the absorbing and the backscattering atoms (\( R_j \)) with the amplitude of backscattered wave (\( A_j \)); and the phase shift of the photo-electron wave (\( \varphi_j(k) \)).

\[
\chi(k) = \sum_{j=1}^{j} \{ A_j(k) \sin (2k R_j + \varphi_j(k)) \} \tag{14.c}
\]

The amplitude of the oscillating wave described according to eq.14.d includes important physical constants, which are very useful for understanding and interpretation of the EXAFS data. These parameters can be listed as: i) \( S_0^2 \) is called the electron reduction (damping) factor and represents the decay of intensity as a function of the photo-electron wave, ii) \( \lambda \) represents the mean free path of the photo-electron, iii) \( \sigma_j^2 \) is the Debye - Waller factor (DWF) which describes the disorder resulting from the displacement of atoms around their equilibrium positions in the lattice, basically due to thermal effects, iv) \( N_j \) represents number of the atoms around the absorber, and v) \( F_j(k) \) is a function of the wave vector and defines the scattering power of the neighbor atoms.

\[
A_j(k) = \frac{S_0^2 e^{-2R_j/\lambda}}{k R^2} \exp [-2\sigma_j^2 k^2] N_j F_j(k) \tag{14.d}
\]

2.6.5. Detection modes during XAFS measurements

X-ray absorption can be detected in transmission, fluorescence, or by measuring the electron yield. In transmission mode the absorption is measured directly by following the flux of the X-ray photons before (\( I_o \)) and after passing the sample (\( I \)). On the other hand, for the fluorescence and electron yield modes the absorption is followed indirectly, either by monitoring the intensity of the fluorescent X-ray photons (\( I_f \)) or by collecting the electron yield (\( I_{EY} \)) emitted from the surface, where both phenomena arise from the filling of the core-hole created during the absorption of the energetic X-ray photon. The positioning of the detector depends on the adopted mode of the measurement, as shown in Fig. 9.

In the transmission mode the sample is put in between two detectors (ionization chambers), while in the fluorescence mode one detector is put before the sample and the other one is put orthogonal to the beam (90° relative to X-ray path) at 45 ° relative to sample. A peculiar difference of the electron yield methods is the necessity to house and illuminate the sample.
inside the detector. Also the sample must be kept under vacuum in order to collect the ejected electrons. This feature in particular limits the use of this mode. In practice, transmission mode is straightforwardly used for diluted sample specimen, since the absorption is not very strong which allows for a measurable intensity. However, in some samples containing strongly absorbing elements, e.g., Au/CeO\(_2\) catalyst, the use of fluorescence is mandatory to have reasonable sensitivity.

![Detection modes: transmission (a); fluorescence (b); electron yield(c).](image)

2.6.6. XAS experiments / Work at the Synchrotron

The XAS experiments were performed at storage rings (Synchrotrons), which are in most cases non-university facilities. This requires easy transfer, and mounting of equipment to the beamline for a few days. Furthermore, the size and characteristics of the high intensity X-ray beam requires a special design of the reaction cell. In this section, the equipments and preparation of the measurements will be discussed briefly.

2.6.6.1. The reaction cell

The reaction cell used in this work consists of a stainless steel tube with a cylindrical channel (i.d. 4 mm) along the diameter, which contained the catalyst bed (length ca. 10 mm, around 25 mg catalyst) and allowed the gases to flow through (see Fig. 10). A second bore along the central axis of the ring and perpendicular to the catalyst bed allowed the X-ray
beam to pass through the catalyst bed. Under working conditions, the reaction cell is closed off by two kapton windows and sealed by two metallic O rings and screws from both sides (transmission mode). In some cases, when the fluorescence mode is used, one side of the cell is closed off with a stainless steel disk, where fluorescence photons are collected at 45° with respect to X-rays path. Heating the cell during the activation and reaction was achieved via thermoelectric coils passing along the reactor ring through 4 small holes evenly distributed around the reaction tube. The temperature was controlled and adjusted during reaction with a NiCr/Ni thermocouple temperature controller.

![Figure 10: In situ reaction cell for X-ray absorption measurements.](image)

2.6.6.2. Portable gas mixing unit:
The home built gas mixing unit illustrated in Fig. 11, which was used in all XAFS investigations, consists of 6 mass flow controllers (Bronkhorst F201C-FA-88V) controlled via a computer program (Flow View, Bronkhorst). This unit has the advantage of being easy to mount in the beamline and allows to use two XAS cells simultaneously, e.g., one for the catalyst pre-treatment and one for the basic experiment using a maximum of three MFC per cell (see also Ref. 23). The in situ XAS measurements were conducted with high purity gases (99.999%), which were passed through the reaction cell and the mixture flow was adjusted as described in section 2.2. Prior to the operando experiments, the catalyst was heated to 150°C, in situ, in a N₂ flow and kept for 30 min. Subsequently, the catalyst was heated up within 10 minutes to the reaction temperature (190°C) in the reaction gas mixture.

All EXAFS measurements were performed in idealized reformate at atmospheric pressure (ID-ref 6000; 0.6% CO, 3% N₂, balance H₂), in the absence (section 3.1) or in the presence of different amounts of water (sections 3.2 – 3.4).
2.6. X-ray Absorption Fine Structure Spectroscopy (XAFS)

Figure 11: Portable gas mixing unit for measurement at the synchrotron beamlines.

2.6.6.3. Recording XAS spectra at Ru K-edge

The spectra were collected in transmission mode at the Ru K-edge (22117 eV) using two ionization chambers filled with Ar/N₂ for X-ray detection. A ruthenium metal foil placed in between the second and an additional ionization chamber allowed for internal and simultaneous calibration during all measurements. The pre-edge region was measured in the range of 21867 - 22087 eV with a step size of 10 eV. For the XANES region (22087 - 22157 eV) and EXAFS region (22157 - 23317 eV), step widths of 0.5 and 0.98 eV were used, respectively.

2.6.6.4. EXAFS data evaluation:

To convert the fine oscillations of the absorption coefficient to the radial distribution function containing the structural information related to the absorber, a systematic procedure should be applied irrespective of the software used. In general, this involves the following steps as had been nicely described by van Bokhoven et al. This algorism include the following steps, i) isolation of the EXAFS function by data reduction (background subtraction, edge energy identification, atomic background determination and normalization and Fourier transformation), ii) calibration of reference spectra for potential components in the sample, and iii) fitting of the reduced EXAFS data with the calibrated references in a multi-shell analysis procedures. Several analysis codes have been developed since the eighties. We carried out the multiple shell analysis in the present work using the XDAP software with standard procedures described elsewhere. Theoretical references were calculated by the FEFF 8.0 code and calibrated by the standard spectra collected over a Ru foil and pure RuO₂ powder as experimental references, to determine the damping factor, the phase shifts and the mean free path of the electrons. For detailed description of the data reduction and fitting methodologies by XDAP software package see the PhD dissertation of S. Eckle.
3. Results and Discussion

The results and text in this part were reprinted (adapted) with permission from the *Journal of Catalysis* 298 (2013) 148 – 160: Ali M. Abdel-Mageed, S. Eckle, H. G. Anfang, and R. J. Behm, Selective CO methanation in CO$_2$-rich H$_2$ atmospheres over a Ru/zeolite catalyst: The influence of catalyst calcination, Copyright (2013) with the permission of Elsevier. S. Eckle has contributed to this work by discussions and further by revisions of the first draft of the published manuscript. H. G. Anfang supplied the Ru/zeolite catalysts and took part in the initial discussion.
3.1. Results and discussion

3.1.1 Introduction

The direct conversion of hydrogen into electric energy in fuel cells, in particular in proton exchange membrane fuel cells (PEMFC), is one of the most promising processes for energy conversion, with various applications, including transportation, stationary applications and mobile applications.\(^1\) The high sensitivity of low temperature fuel cells to carbon monoxide in the H\(_2\) feed, which acts as catalyst poison for the anode catalyst, requires that the CO concentration is kept at very low levels (≤ 10 ppm).\(^8\) Currently, H\(_2\)-rich feed gases are mainly produced by steam reforming of fossil fuels, which leaves substantial amounts of CO in the gas feed (reformate) and up to 20% CO\(_2\). The methanation of CO in reformate gases\(^9,6,15,16\) may be an attractive alternative to the commonly used preferential oxidation of CO (PROX) for CO removal.\(^7,149\) It is economically feasible, however, only if the reaction is highly selective for CO methanation, and reaction of the abundant CO\(_2\) with hydrogen is inhibited. In response to the increasing interest in using selective methanation (SelMeth) for complete removal of CO, the mechanistic understanding and the identification of the physical reasons underlying the high selectivity for CO methanation in CO\(_2\)-rich H\(_2\) streams, has been the subject of various studies.\(^76\)

Eckle et al. have recently studied the mechanism of the selective methanation reaction over highly active and selective Ru/zeolites catalysts, being particularly interested in the physical origin of the high selectivity.\(^62,71,72\) Main results of these studies were i) that these catalysts exhibit very small Ru particles (mean particle size 0.9 nm), ii) that the reaction proceeds via a formyl intermediate, and iii) that the high selectivity results from an inherently low activity of the very small Ru particles for CO\(_2\) dissociation and hence for CO\(_2\) methanation, in combination with a high activity of these nanoparticles (NPs) for CO methanation. For larger NPs, in contrast, the selectivity originates from CO\(_{\text{ad}}\) surface blocking of the active Ru surface. This effect decays at low CO partial pressures, leading to a decreasing selectivity at lower CO concentrations, as experienced, e.g., at the end of the reactor in practical applications. Further details as well as a comprehensive literature overview on the selective methanation reaction are given in previous papers.\(^71\)

The present study is aiming at a mechanistic understanding of the role of the calcination procedure which, is applied after catalyst synthesis, before activation of the pre-catalyst and its further use. It is known that this calcination step leads to a significant improvement of the activity and selectivity of the catalyst after subsequent reactive activation. The
mechanisms and physical origin for the observed increase in catalytic performance, however, are largely unknown. These are the topics of the present contribution. The structural changes of the catalyst imposed by the calcination procedure were determined by \textit{in situ} X-ray absorption spectroscopy (XAS) for different calcination temperatures. The resulting changes in catalytic reaction characteristics were evaluated by combined kinetic and \textit{in situ} IR spectroscopic measurements (diffuse reflection FTIR spectroscopy – DRIFTS). The reaction measurements were performed in different reaction mixtures including idealized (CO, H$_2$), and semi-realistic (CO, H$_2$, and CO$_2$) gas streams. Coupled with activity measurements, \textit{in situ} spectroscopic DRIFTS measurements were used to follow the evolution of different intermediates formed on the catalyst surface during the reaction, in particular the steady-state coverage of CO$_{\text{ad}}$, which acts as a precursor leading to the active intermediates involved in both CO and CO$_2$ methanation.

### 3.1.2 \textit{Operando} EXAFS measurements - Ru dispersion and particle size

The XAS measurements were performed in ID-ref 6000 gas reformate under steady-state conditions, where the Ru coordination number did not change any more during the measurement.\textsuperscript{62} Firstly, we present the XANES spectrum of Ru foil in comparison with spectra of differently calcined catalyst is introduced in Fig.12. In first glance, the spectra points to a completely metallic Ru species under the present reaction conditions.

![Figure 12: XANES spectra of a Ru foil and of differently calcined catalysts (A-D, with increasing calcination temperature).](image)
The $k^3$ weighted chi functions for the respective sets of catalysts are plotted in the $k$-range from 3.2 - 11.8 Å$^{-1}$ in the left panels in Fig. 13 (a-d), while the Fourier transforms in the $r$-space in the range of the first shell (Ru-Ru scattering, $r$-range: 1.0 - 6.0) are plotted in the right panels (e-h) for the four differently calcined catalysts. It should be noted a bi-shell fitting including Ru-Ru and Ru-O was tried and only Ru-Ru scattering shell could fit to the measured spectra. A characteristic signal in EXAFS measurements, appearing at 2.67 Å in r-space, reflects undoubtedly the metallic nature of Ru particles under reaction conditions for all four catalysts. Also, referring to previous XANES measurements carried out for differently loaded Ru/zeolite catalysts prior to the methanation reaction, the Ru nanoparticles embedded in the zeolite are completely oxidized before exposure to the reaction mixture. These RuO$_2$ nanoparticles are reduced within the first 2 minutes after exposure to the reaction atmosphere, which is too short to be resolved in these XAS measurements. The coordination numbers of the Ru-Ru shell in these catalysts were obtained by fitting the EXAFS data of the first shell of atoms at 2.67 Å to the Ru foil reference (see Fig. 13). Afterwards, the average particle size and the dispersion of the Ru nanoparticles (NPs) were calculated using the coordination number – particle size relationship determined by Karim et al., assuming hemispherically shaped Ru nanoparticles, reported to prevail under reduction conditions as reported by the author. The Ru coordination number was found to decrease with increasing calcination temperature, which is equivalent to a decrease in particle diameter. The structural parameters resulting from these fits as well as the calculated dispersions and particle sizes are summarized in Table 3. It should be noted that the goodness of the fit of data was always between 1 and 2. Moreover, the fitting parameters did not change significantly when applying different $k$ weightings ($k^3$ and $k^2$ weighting), which illustrates the quality of the fits of our data. Based on these data, the dispersion of the Ru NPs increases with increasing calcination temperature (particle size decreases), with the Ru/zeolite catalyst A calcined at the lowest temperature showing the lowest dispersion of 47.3% (particle size ~1.5 nm), while for the catalyst D calcined at the highest temperature this increased to 67.9% (particle size ~1 nm) (see Fig. 14). It should be noted that although the differences in particle sizes are small on an absolute scale, the relative differences are considerable. Especially for particles < 2 nm, such differences are expected to lead to considerable differences in the electronic and chemical surface properties.
3.1. Results and discussion

**Figure 13:** Left: $k^3$ weighted chi function, right: corresponding Fourier transforms (3.2 - 11.8 k-space) for the differently calcined catalysts under steady-state conditions in ID-ref 100 (190°C reaction temperature). Catalysts: a, e) catalyst D; b, f) catalyst C; c, g) catalyst B and d, h) catalyst A (EXAFS spectra: solid lines; fits: dotted lines).
3.1. Results and discussion

Figure 14: Average sizes of supported Ru nanoparticles as a function of calcination temperature, as calculated from the EXAFS data.

The assumed error in the coordination numbers results in considerable error ranges in the structural data (see table 3). Since, however, these errors mainly result from systematic errors which will equally affect all catalysts either upwards or downwards; we consider the trends and also the relative differences between the particle sizes to be significant. Hence, calcination in 10\% O\textsubscript{2} results in a reactive (re-)dispersion of the Ru oxide NPs to generate finely dispersed RuO\textsubscript{2} particles\textsuperscript{151,152} which we propose are located inside the zeolite pores. These nanoparticles are subsequently reduced to metallic particles, which are uniformly distributed in the zeolite matrix. In our picture, mobile RuO\textsubscript{2} species, which are formed during oxidation in 10\% O\textsubscript{2}/N\textsubscript{2} atmosphere, can penetrate better into the zeolite cages at higher calcination temperatures. This process can be driven by a better interaction of the oxide species with the zeolite pore surface (‘inner surface’), i.e., by the wetting properties of the support. Afterwards, during the initial stages of the reaction, these particles get mildly reduced, leading to small metal nanoparticles confined within the zeolite cages.\textsuperscript{151,153} This mechanism can very reasonably explain the unusual finding of an increasing Ru dispersion with increasing calcination temperature.

There are numerous reports in the literature dealing with the effect of the pre-treatment on the particle size of supported Ru catalysts for hydrogenation reactions etc., where this is controversially discussed.\textsuperscript{151-154} For example, there is disagreement on whether an oxidative treatment leads to pronounced particle sintering or just to moderate agglomeration. This may result, however, from the different support materials and pre-treatment conditions used in those studies.
### Table 3: Structural parameters derived from the EXAFS measurements in idealized reaction reformate (steady-state condition, 0.6 % CO, balance H₂, mass flow 40.6 Nml min⁻¹, reaction temperature 190°C) for the differently calcined Ru/zeolite catalysts (DW: Debye-Waller factor, r: Ru – Ru bond length, E₀: energy shift).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Coordination number</th>
<th>DW / 10⁻³ Å²</th>
<th>r / Å</th>
<th>E₀ / eV</th>
<th>Dispersion / %</th>
<th>Particle size /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>catalyst D</td>
<td>7.04</td>
<td>8.8</td>
<td>2.670</td>
<td>-2.13</td>
<td>0.68 ± 0.22</td>
<td>1.05 ± 0.36</td>
</tr>
<tr>
<td>catalyst C</td>
<td>7.23</td>
<td>7.2</td>
<td>2.670</td>
<td>0.80</td>
<td>0.63 ± 0.21</td>
<td>1.14 ± 0.38</td>
</tr>
<tr>
<td>catalyst B</td>
<td>7.89</td>
<td>8.0</td>
<td>2.668</td>
<td>-0.13</td>
<td>0.51 ± 0.17</td>
<td>1.41 ± 0.48</td>
</tr>
<tr>
<td>catalyst A</td>
<td>8.10</td>
<td>8.3</td>
<td>2.665</td>
<td>-0.60</td>
<td>0.47 ± 0.14</td>
<td>1.51 ± 0.51</td>
</tr>
</tbody>
</table>

Verdonck et al.,¹⁵⁵ who were one of the first to study the effect of different (reductive or oxidative) pre-treatment procedures on the Ru particle size in NaY zeolite catalysts, used catalysts which before oxidative treatment were always reduced in a flow of hydrogen at 400 – 600°C for 1 h. Calcination of the samples was carried out in a pure O₂ atmosphere at different temperatures (maximum 400°C), and before analysis of the Ru nanoparticle dispersion, the catalysts were reduced a second time in H₂. Those authors found that calcination leads to pronounced agglomeration of the formerly highly dispersed Ru nanoparticles, with Ru particle sizes around 100 nm, and results in a bimodal distribution, where small particles and very large particles coexist. The small particles were assumed to be located inside the zeolite and on the external surface, respectively. Analogously, we suggested previously on the basis of our own EXAFS results that on the activated catalyst only a small number of large particles is present on the external surface, while small particles inside the zeolite matrix dominate.⁶₂ A similar morphology is assumed also for the catalysts investigated in this study. On the other hand, McCarthy et al.¹⁵⁶ concluded that higher calcination temperatures lead to an increasing number of larger particles, which contrasts the present findings. The contradictory experimental results obtained by Verdonck et al.¹⁵⁵ and in this work can be rationalized by the rather different pre-treatment conditions used in both studies, and the use of a different zeolite support. In the present work, the catalyst is oxidized directly after synthesis in 10% O₂/N₂ and mildly reduced in situ under reaction conditions. Therefore, sintering of Ru nanoparticles due to high
temperature reduction is unlikely in the present case. This agrees with findings by Shoemaker and Apple, who confirmed by TEM imaging that different from high temperature reduction, high temperature oxidation of supported Ru/NaY catalysts does not lead to excessive particle sintering. Bond and coworkers also studied the pre-treatment effect on Ru catalysts supported on TiO$_2$, SiO$_2$ and Al$_2$O$_3$. For calcination temperatures very similar to ours (150°C, 350°C), they observed the formation of small Ru nanoparticles and explained this by a spreading of mobile RuO$_2$ over the surface. Mild reduction favored the formation of small Ru particles. Furthermore, Reyes et al. reported that the extent of particle agglomeration depends on the support acidity, which might provide an additional explanation for the particle agglomeration observed by Verdonck et al., since they used a rather basic zeolite support. In that picture, the acidic microporous zeolite support used in the present study is expected to limit the growth of metal particles. Wider support pores favor sintering of the Ru nanoparticles during high temperature treatment (reductive or oxidative), which consequently results in larger particles. For instance, it was reported by Tkachenko et al. that in the calcined state, ruthenium is present as highly dispersed, oxygen deficient RuO$_x$ nanoclusters. However, we cannot rule out in the present study that although the majority of Ru particles are encaged in the zeolite pores, a few larger NPs are present on the outer surface of the zeolite particles. This would also mean that the Ru NPs in the zeolite pores have slightly smaller sizes than the mean Ru particle size calculated from the EXAFS data. Overall, these results are compatible with our proposal that the number of larger Ru particles present on the outer surface of the zeolite particles is controlled by the calcination temperature, with higher calcination temperatures improving the Ru dispersion of these zeolite supported catalysts.

3.1.3 Reaction kinetics and selectivity for CO methanation

The kinetic measurements were carried out in two semi-realistic reaction reformates containing 6000 ppm CO (SR-ref 6000) and 100 ppm CO (SR-ref 100) on the 4 differently calcined catalysts. The activity is based on the reaction rate for CO methanation (CO consumption), while the selectivity for CO methanation is calculated from the ratio between CO consumption and CH$_4$ formation (CO plus CO$_2$ methanation) rates. Water was excluded from the reaction atmosphere in these measurements to make the reaction conditions as simple as possible; the effect of water vapor up to technically relevant contents (30%) is subject of ongoing studies and will be reported later.
3.1. Results and discussion

Figure 15 illustrates the temporal evolution of the Ru mass normalized reaction rate over 800 min for reaction in SR-ref 6000 at 190°C. While for all catalysts the changes in activity with time are rather small, a closer look reveals differences in the deactivation behavior. For the highest temperature calcined catalyst D, the rate increases slightly during the first 200 min, and then changes very little. Catalyst C remains at constant activity throughout the measurements, and the lower temperature calcined catalysts B and A deactivate steadily with time, by 18% for catalyst B and by 20% for sample A. These characteristics apply to both CO methanation and the total rate for methane formation. Under steady-state conditions in SR-6000, the differences in activity between the different catalysts are rather small, and the selectivity for CO methanation is at 100% for all catalysts (see table 4).

For comparing intrinsic activities, it is better to use turn-over frequencies (TOF). Due to the additional change in particle size and hence in Ru surface area, the differences in TOF between the differently calcined Ru/zeolite catalyst are rather small in SR-ref 6000 (factor ~1.1). Here it should be noted that the error ranges in the TOFs, which are caused by the errors in the particle size, are mainly associated with systematic errors that would affect all catalysts equally (see section 3.1.3). Therefore, differences between the different catalysts should be significant on a much smaller scale than indicated by the error range. Based on these data, the apparent increase in activity with increasing calcination temperature is solely due to the increase in Ru surface area. In fact, the increase in Ru surface area is slightly more pronounced than the increase in (Ru mass normalized) activity, resulting in a slight decrease of the TOF with increasing calcination temperature or decreasing particle size (see table 4). This will be discussed in more detail when discussing the reaction behavior and CO methanation behavior in SR-ref 100 later.

At the high CO concentrations in SR-ref 6000 (6000 ppm CO), the selectivity of the four catalysts for CO methanation is not affected by the change in Ru dispersion (see table 4) and remains at 100%. In accord with previous discussions, we assume that under these conditions the surface of the Ru NPs is completely covered by a strongly bound CO adlayer (see section 3.3.2), which inhibits the dissociation of CO$_2$ by blocking active surface sites, and this way prevents CO$_2$ methanation.

More information on the physical origin underlying the high selectivity of the Ru/zeolite catalyst and possible effects caused by the calcination procedure is gained from similar measurements using a reaction mixture with a much lower CO content (SR-ref 100), but
otherwise identical reaction conditions. In that case, the four catalysts showed a higher initial activity than in SR-ref 6000, at least for the catalysts A – C calcined at lower temperatures, and also the final activities are higher (Fig. 16 and Table 4). Furthermore, the evolution of the activity and selectivity with time shows more pronounced changes and differences between the four catalysts. For the catalyst D (highest calcination temperature), the reaction rate for CO consumption as well as that for CH₄ production increase during the first 200 min, followed by a subtle decrease.

**Table 4:** Ru mass normalized activities and turnover frequencies (TOFs) for CO and CO₂ methanation (Rₘₚ) and selectivities of differently calcined 2.2 wt.% Ru/zeolite catalysts in semi-realistic reformates with high (SR-ref 6000) and low (SR-ref 100) CO concentrations, as calculated from the CO consumption and CH₄ formation (reaction temperature 190°C, steady-state activities, error ranges in TOFs are derived from the errors in the calculated dispersion).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SR-ref 6000</th>
<th>SR-ref 100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rₘₚ / 10⁶ mol⁻¹ g₀₄⁻¹ s⁻¹</td>
<td>TOF / 10⁻³ s⁻¹</td>
</tr>
<tr>
<td>Catalyst D</td>
<td>39 / 39</td>
<td>5.8 ± 1.9 / 0.0</td>
</tr>
<tr>
<td>catalyst C</td>
<td>38 / 37</td>
<td>6.0 ± 2.0 / 0.0</td>
</tr>
<tr>
<td>catalyst B</td>
<td>34 / 34</td>
<td>6.8 ± 2.2 / 0.0</td>
</tr>
<tr>
<td>catalyst A</td>
<td>29 / 28</td>
<td>6.2 ± 1.8 / 0.0</td>
</tr>
</tbody>
</table>
3.1. Results and discussion

**Figure 15:** Reaction rates and selectivities for the selective methanation reaction over differently calcined, 2.2 wt.% Ru/zeolite catalysts under differential reaction conditions (catalyst diluted with SiO$_2$) in SR-ref 6000. Catalyst D (highest calcination temperature); catalyst C; catalyst B and catalyst A (lowest calcination temperature) (■: CH$_4$ formation rate, ◊: CO consumption rate, ▲: selectivity)
3.1. Results and discussion

During the entire time, CO consumption and CH₄ formation rates are identical, resulting in a constant selectivity of 100%. For the other three catalysts, the initial activation phase is missing, similar to observations in SR-ref 6000, and the deactivation more pronounced, with the activity decaying over the entire reaction time. After 800 min, where the activity has reached 75, 70 and 70% of the initial value for the catalysts C, B and A, respectively, further changes in the activity are small.

The selectivity behavior of the respective catalysts in SR-ref 100 reformate is quite different from that in SR-ref 6000. While for the Ru/zeolite catalyst D, the activity for the methanation of CO₂ is negligible and the selectivity is still at 100%, this changes when going to lower calcination temperatures. Here the selectivity (steady-state value) declined from 100% (catalyst D) via 84% (catalyst C) and 80% (catalyst B) to 70% (catalyst A) (see Table 4). During time-on-stream, the changes in selectivity are mostly small (catalysts A, B, C) or not existent (catalyst D), only for sample C there seems to be a decrease in selectivity with time. One should note, however, that at the very low CO concentrations in the reaction gas these measurements are at the limits of the resolution.

The TOFs increase by about a factor of 1.7 with particle size in SR-ref 100, while they were almost independent of Ru particle size for reaction in SR-ref 6000 (Table 4). The almost constant TOFs in SR-ref 6000 are explained by a surface blocking by CO_ads caused by the relatively high CO partial pressure, which is independent of particle size. The increasing TOFs in 100 ppm CO with increasing Ru particle size can be attributed to a particle size effect, which apparently has a stronger effect on the reactivity for CO methanation at these low concentrations of CO as compared to SR-ref 6000. The almost identical activities (TOFs) for catalyst D in the two reaction atmospheres are considered to be fortuitous, because of the very different reaction conditions, with a CO_ads limited reaction in the first case, due to the slow supply of CO from the gas phase and the inhibition of CO₂ dissociation, and a H_ads limited reaction (due to CO_ads surface blocking) in the second case. A more detailed discussion on these aspects is given in ref. 72.

We and others had reported earlier that the activity of supported ruthenium catalysts is significantly affected also by metal-support interactions, 72,48,85 and by the Ru loading, where the latter affects the particle size (increase in Ru loading results in increasing particle size). 62 In the present case, modifications in the metal-support interactions due to increasing calcination temperature appear at least feasible, e.g., due to differences in the zeolite surface composition.
More information on the possible role of metal-support interactions can be obtained by comparing the present results with those of a previous study, where we obtained increasing Ru particle sizes by increasing the Ru loading, while keeping the catalyst pre-treatment procedure. In that case, we obtained an increase of the TOF by a factor of about 2 when going from a catalyst with 0.9 nm particles to one with 1.6 nm sized Ru particles, both for reaction in SR-ref 6000 and in SR-ref 100, and especially a decrease in catalyst selectivity was observed with the increase in particle size for the highest loaded catalyst (5.6 wt%). Because of the identical activation treatment for all loadings, effects from changed metal-support interactions can be excluded in that case. Considering the similar trends in reaction behavior (activity, selectivity) in those and in the present experiments, we conclude that the change in activity in SR-ref 100 must be mainly due to the change in Ru particle size resulting from calcination at different temperatures, reflecting a dominant particle size effect. The different behavior of the activity in SR-ref 6000 with Ru particle size observed in the present study, however, indicates that in addition to particle size effects contributions from other effects are active as well. In that case, modifications in the metal-support interactions, caused by the different calcination temperatures, appear as most likely candidate. Also the more pronounced deactivation of the lower temperature calcined catalysts in SR-ref 100 can tentatively be explained by a particle size effect, by the higher activity of larger Ru particles for CO\textsubscript{ad} formation via CO\textsubscript{2} dissociation. Assuming that the formation of reaction inhibiting, carbon-containing species, which will block active Ru sites, is faster from CO\textsubscript{2} than from CO\textsubscript{ad}, the higher deactivation in SR-ref 100 is simply explained by the more facile interaction of CO\textsubscript{2} with the only partly CO\textsubscript{ad} blocked Ru particle surfaces. This interpretation is supported by the higher IR intensities of surface formates and carbonates (1590 and 1390 cm\textsuperscript{-1}) in CO free CO\textsubscript{2}-ref (15.5% CO\textsubscript{2}, 0% CO) as compared to that in CO\textsubscript{2} free ID-ref 100 (0% CO\textsubscript{2}, 0.01% CO).
3.1. Results and discussion

**Figure 16:** Reaction rates and selectivities for the selective methanation reaction over differently calcined 2.2 wt.% Ru/zeolite catalysts under differential reaction conditions (catalyst diluted with SiO$_2$) in SR-ref 100. Catalyst D (highest calcination temperature); catalyst C; catalyst B and catalyst A (lowest calcination temperature) (■: CH$_4$ formation rate, ◊: CO consumption rate, ▲: selectivity).
In addition to the increase in TOF for the CO methanation, also the TOF for CO$_2$ methanation in SR-ref 100 increased with increasing Ru particle size (decreasing calcination temperature), from about zero for catalyst D to 5.6 (see also Table 4). The extremely small particles dominant for the Ru/zeolite catalyst D showed very little activity for the methanation of CO$_2$. We had explained this earlier by a very low inherent activity of the very small Ru particles embedded in the zeolite matrix for the dissociation of CO$_2$. On the surface of larger Ru particles, the activity for CO$_2$ dissociation is higher than on the very small ones, which results in increasing methanation of CO$_2$, via formation and methanation of CO$_{ad}$. We had tentatively explained this by a stabilization of the final state for CO$_2$ dissociation, adsorbed CO, on the larger particles, which according to the Brønstedt-Evans-Polanyi (BEP) relation reduces the energy of the transition state for this reaction and this way also the barrier for CO$_2$ dissociation. This mechanism dominates in reaction gas mixtures with very low CO contents, while for higher contents the selectivity is determined by a site blocking mechanism, where active sites for CO$_2$ dissociation are blocked by a stable CO-adlayer.

3.1.4 In-situ spectroscopic measurements (DRIFTS)

In situ IR spectroscopic measurements (using DRIFTS) were performed to determine differences in the interaction of the reaction gas mixtures with the differently calcined Ru/zeolite catalysts, and thus unravel the reasons responsible for differences in the selectivity for CO methanation in CO$_2$-rich H$_2$ streams on these catalysts. The build-up of different intermediates and reaction spectators, besides the time dependent coverage of the CO$_{ad}$ adlayer, was followed with time in different reaction gas mixtures, including semi-realistic reformate containing both high and low concentrations of CO (SR-ref 6000 and SR-ref 100), idealized reformate (ID-ref 100) as well as CO-free CO$_2$ reformate (CO$_2$-ref) (compositions see Table 2, page 26).

3.1.3.1 Spectral regions and surface intermediates

The characteristic bands attributed to different functional groups of the adsorbed species present on the calcined Ru/zeolite catalysts under reaction conditions are illustrated in the series of spectra in Figures 17 - 20. The assignment of the different bands was discussed in detail previously, and we refer to this discussion for further details. The general characteristics of the spectra are similar in all reformates; only the respective intensities differ depending on the reaction gas atmosphere.
3.1. Results and discussion

Starting with the OH region, two characteristic bands appear at 3740 and 3640 cm\(^{-1}\), which are attributed to terminal silanol species and isolated OH\(_{ad}\) groups on the zeolite support\(^{48,71,163}\). The intensities of these two bands did not vary much during reaction for the four catalysts. In addition, overtones from gas phase CO\(_2\) are encountered in reformates containing CO\(_2\) (SR-ref 6000, SR-ref 100 and CO\(_2\)-ref), at 3700, 3600, 3540 and 3450 cm\(^{-1}\), which are superimposed on the OH signals.

In the CH\(_x\) band region, bands resulting from the (symmetric and asymmetric) vibrations of adsorbed CH\(_4\), CH\(_3\), and CH\(_2\) species are observed at 3016, 2928, and 2860 cm\(^{-1}\) over 1000 min on all four catalysts and in all reaction atmospheres, in agreement with earlier reports\(^{72,164}\). Finally, a shoulder present at 2906 cm\(^{-1}\) was assigned to C-H vibration of formates which according to the literature are mainly adsorbed on the surface of the zeolite support\(^{48}\), though adsorption of small amounts on the Ru nanoparticles or at the interface between Ru nanoparticles and support cannot be ruled out (for assignment and discussion see also ref.\(^{72}\)).

In the region of the CO vibrations, between 1850 and 2150 cm\(^{-1}\), a CO\(_{ad}\) band appears between ~2038 (SR-Ref 6000) and ~2026 cm\(^{-1}\) (low CO contents), depending on the gas mixture, which is related to linearly bound CO\(_{ad}\) on Ru\(^0\). This band is accompanied by a shoulder at 2075 cm\(^{-1}\) resulting from CO adsorbed on Ru\(^{6+}\) species or coadsorbed with O\(_{ad}\) on Ru\(^{72,165}\). The observed shift for linearly bound CO\(_{ad}\) depends on the CO\(_{ad}\) coverage and on the Ru dispersion in the different catalysts. A band at 1870 cm\(^{-1}\) is assigned to a bridge bonded CO\(_{ad}\) on two Ru atoms\(^{46}\). In the range of the OCO bending vibrations (1750 - 950 cm\(^{-1}\)), characteristic bands appeared at 1590 and 1390 cm\(^{-1}\) after around 100 min reaction time, which were attributed to surface formate species accumulating on the Ru/zeolite surface. A weak band at 1440 cm\(^{-1}\) (not marked)\(^{48}\) is attributed to surface carbonate species. Furthermore, a weak band at 1265 cm\(^{-1}\) may be related to C=O stretching vibration in a bridged surface carbonate\(^{166}\). We emphasize here that both the surface formate and the surface carbonate species building up on the catalyst surface could be ruled out as potential reaction intermediate in our earlier work, both for CO hydrogenation and for CO\(_2\) hydrogenation, in steady-state isotopic transient kinetic analysis (SSITKA) experiments\(^{72}\). Instead, they were considered as spectator species, which do not affect the rate of CO methanation.
Figure 17: DRIFT spectra recorded over 1000 min during reaction at 190°C in SR-ref 6000 reformate over 2.2 wt.% Ru/zeolite catalysts: catalyst D (highest calcination temperature), catalyst C; catalyst B and catalyst A (lowest calcination temperature) (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, 795, and 945 min).
Figure 18: DRIFT spectra recorded over 1000 min during reaction at 190°C in SR-ref 100 reformate over 2.2 wt.% Ru/zeolite catalysts: catalyst D (highest calcination temperature), catalyst C; catalyst B and catalyst A (lowest calcination temperature) (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, 795, and 945 min).
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**Figure 19:** DRIFT spectra recorded over 1000 min during reaction at 190°C in CO₂-ref reformate over 2.2 wt.% Ru/zeolite catalysts: catalyst D (highest calcination temperature), catalyst C; catalyst B and catalyst A (lowest calcination temperature) (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, 795, and 945 min).
3.1. Results and discussion

Figure 20: DRIFT spectra recorded over 1000 min during reaction at 190°C in ID-ref100 reformate over 2.2 wt.% Ru/zeolite catalysts: catalyst D (highest calcination temperature), catalyst C; catalyst B and catalyst A (lowest calcination temperature) (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, 795, and 945 min.)
3.1.3.2. CO\textsubscript{ad} steady state coverage and catalyst selectivity

Important mechanistic information on the selective CO methanation comes from the amount and nature of adsorbed CO during reaction, both in the absence and in the presence of CO\textsubscript{2}, which in a subsequent step can be hydrogenated to CH\textsubscript{4}.\textsuperscript{167,71} The selectivity for CO methanation of the zeolite supported Ru catalysts should be closely related to the relative contributions of CO and CO\textsubscript{2} to the total CO\textsubscript{ad} band intensity in the \textit{in situ} DRIFTS measurements. This will be discussed in the following, based on the intensities (peak heights) of the CO\textsubscript{ad} band for linearly adsorbed CO at 2042 cm\textsuperscript{-1}, which are plotted as a function of reaction time for the different catalysts and reaction gas atmospheres in Fig. 21.

**SR-ref 6000**: In this reaction atmosphere, both the CO\textsubscript{ad} intensity and its temporal evolution depend on the catalyst calcination temperature. For catalyst D (Fig. 21a), the intensity increases initially and reaches saturation after ~ 400 min. For the catalysts C and B calcined at lower temperatures (Figs. 21b and 21c), steady-state conditions with constant CO\textsubscript{ad} intensities are reached after 200 minutes, and for the catalyst A, the CO\textsubscript{ad} intensity hardly varies with time; if at all, it decreases slightly at the later stages. Furthermore, the steady-state CO\textsubscript{ad} intensity decreases with decreasing calcination temperature (Figs. 21a - d). This trend fits perfectly to the EXAFS results, since for constant catalyst loading one would expect more adsorbed CO with increasing Ru surface area. The intensities of the CO\textsubscript{ad} band under steady-state conditions in SR-ref 6000, where CO\textsubscript{ad} saturation is assumed, was set to 100% for each catalyst (see Table 5).

**ID-ref 100 and SR-ref 100**: Next we discuss the trends in CO\textsubscript{ad} formation in reformates with very low CO contents (100 ppm), both in the presence (SR-ref 100) or absence (ID-ref 100) of CO\textsubscript{2} (see Table 2, page 26). In these cases (Figs. 21a – d), the CO\textsubscript{ad} band intensities are significantly lower than in SR-ref 6000. The time dependent evolution of the intensities resembles that observed in SR-ref 6000, with an initial increase during the first 200 – 400 min, and constant intensities at later times. Interestingly, the ratio between the CO\textsubscript{ad} band intensities observed in the presence and absence of 15.5 % CO\textsubscript{2} differs significantly between the different catalysts. On the catalyst D, they are about identical, indicating that the additional presence of a large amount of CO\textsubscript{2} in the gas phase has no measurable influence on the amount of adsorbed CO\textsubscript{ad} formed under reaction conditions. With lower calcination temperatures (Figs. 21b - d), the CO\textsubscript{ad} intensities are higher in SR-ref 100 than in ID-ref 100, and this difference increases with decreasing calcination temperature. In a simple model, this can be explained by an increasing CO\textsubscript{ad} formation
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from CO₂, reflecting an increasing tendency for CO₂ dissociation. Since the COₐd coverages are in all cases far below COₐd saturation, with much lower COₐd band intensities than in SR-ref 6000, this must reflect an inherent property of the differently sized Ru nanoparticles rather than a COₐd induced inhibition of dissociative CO₂ adsorption.

The COₐd band intensities in both mixtures can be used to calculate the selectivity for CO methanation as the ratio of the COₐd intensity in ID-ref 100 (no CO₂) to that in SR-ref 100 (15.5 % CO₂). This assumes that i) COₐd formation from CO₂ is the rate limiting step for CO₂ methanation and that ii) the contribution from CO adsorption is identical in both gas mixtures. Considering that in both cases and for all catalysts the COₐd coverage is far from COₐd saturation, this latter assumption is plausible. The resulting ratios, which are listed in Table 5, can be compared with the selectivities determined from kinetic measurements in the previous section (see Table 5). Obviously, the CO selectivities obtained by comparison of the COₐd band intensities closely resemble the CO selectivities derived from the kinetic measurements. Furthermore, the relative COₐd signal intensities increase with decreasing dispersion of the catalysts.

Table 5: Relative COₐd band intensities (normalized to the intensity in SR-ref 6000) during CO methanation over differently calcined 2.2 wt.% Ru/zeolite catalysts. The selectivity is calculated as a ratio between COₐd intensity in ID-ref and SR-ref 100.

<table>
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<th>Catalyst</th>
<th>COₐd intensity SR-ref 6000 /%</th>
<th>COₐd intensity SR-ref 100 /%</th>
<th>COₐd intensity ID-ref 100 /%</th>
<th>COₐd intensity CO₂-ref /%</th>
<th>Selectivity /%</th>
</tr>
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<td>11</td>
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<td>18</td>
<td>83</td>
</tr>
<tr>
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<td>22</td>
<td>16</td>
<td>22</td>
<td>72</td>
</tr>
</tbody>
</table>
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**Figure 21**: Evolution of the CO$_{ad}$ band intensity (peak heights) during reaction at the differently calcined Ru/zeolite catalysts in different reaction atmospheres: catalyst D (highest calcination temperature), catalyst C; catalyst B and catalyst A (lowest calcination temperature) (■: SR-ref 6000, ●: SR-ref100, ▼: ID-ref 100, ▲: CO$_2$-ref).
3. Results and discussion

The above ideas are supported by the trends observed for CO\textsubscript{ad} formation in CO\textsubscript{2}-ref. In this gas mixture, which contains only CO\textsubscript{2} (15.5%) and H\textsubscript{2}, bands related to CO\textsubscript{ad} are observed as well, which must result from the dissociation of CO\textsubscript{2} (Note that a RWGS reaction via surface formate species for CO\textsubscript{2} conversions had been excluded in earlier work. The CO\textsubscript{ad} intensity also increases during the initial 200 – 400 min, similar to the behavior in the other gas mixtures, and then remains about constant.

The CO\textsubscript{ad} intensity varies significantly with the calcination temperature of the Ru/zeolite catalyst and thus with the particle size. In this case, we focus on the relative intensity with respect to that detected in the SR-ref 100 and ID-ref 100 gas mixtures.

For the catalyst D, where the CO\textsubscript{ad} signal is observed at 2026 cm\textsuperscript{-1}, the intensity is only half of that in the SR-ref 100 and ID-ref 100 gas mixtures. (It should be noted that for very low CO\textsubscript{ad} band intensities, these are hard to discriminate from small changes in the background signals, and that for the interpretation we always included a careful inspection of the raw data.) That points to a very low tendency for CO\textsubscript{2} dissociation to CO\textsubscript{ad} on this catalyst, in agreement with the identical intensity in the absence and presence of 15.5% CO\textsubscript{2} in ref 100 gas mixtures (SR-ref 100 and ID-ref 100). With decreasing calcination temperature, the CO\textsubscript{ad} band intensity increases and finally, for the catalyst A (lowest calcination temperature), it is about identical to that observed in SR-ref 100. Hence, the contribution from CO\textsubscript{2} dissociation to the CO\textsubscript{ad} band intensity rises with decreasing calcination temperature / increasing Ru particle size, and for catalyst A it represents the dominant contribution. This behavior agrees with the decreasing relative intensity of the CO\textsubscript{ad} band in ID-ref 100 compared to that in SR-ref 100. Overall, these results agrees very well with reaction model proposed before, according to which CO\textsubscript{2} methanation proceeds via CO\textsubscript{2} dissociation to CO\textsubscript{ad} and subsequent methanation of the CO\textsubscript{ad} and where the somewhat larger Ru nanoparticles formed at lower calcination temperatures have a higher inherent activity for the dissociation of CO\textsubscript{2} than the very small particles generated at higher temperatures (see section 3.2). It should be noted, however, that we assume these ‘larger’ particles (mean particle size 1.5 nm) to consist of coexisting small particles in the zeolite pores and a higher fraction of larger Ru particles (~10 nm size) on the outer surface of the zeolite particles, leading to a bimodal particle size distribution.
3.1.5 Conclusions

Applying a combination of kinetic measurements, *in situ* EXAFS and *in situ* DRIFTS measurements, we have investigated the influence of the initial calcination procedure on the structure and catalytic properties of Ru/zeolite catalysts in the selective methanation of CO in CO$_2$-rich reformates. The measurements and comparison with previous data lead to the following conclusions:

1. Calcination of the Ru/zeolite pre-catalyst increases the dispersion of the RuO$_2$ nanoparticles; according to our proposal this happens by driving Ru oxide from the outer surface of the zeolite particles, where much of it is initially located, into the zeolite matrix. Driving force for this process is the stabilization of the Ru oxide in the zeolite pores. After reactive pre-treatment in reaction gas, at the very beginning of the reaction, this results in very small Ru nanoparticles encaged in the zeolite pores. With increasing calcination temperature, the mean particle size decreases, from 1.5 nm (Ru dispersion ~47%) at the lowest calcination temperature (catalyst A) to 1.0 nm (Ru dispersion ~68%) upon calcination at the highest temperature (catalyst D). We tentatively propose that the decrease of the mean Ru particle size with increasing calcination temperature results from a temperature independent size of the Ru nanoparticles in the zeolite pores, which is largely determined by the size of these pores, and an increasing fraction of Ru oxide nanoparticles driven into the zeolite matrix with increasing calcination temperature. This way, the fraction of larger Ru nanoparticles remaining on the outer surface decreases with calcination temperature. This process is essentially completed at the highest calcination temperature (catalyst D).

2. The size of the Ru nanoparticles has pronounced effects on the activity and in particular on the selectivity of the Ru/zeolite catalyst in the selective methanation of CO in CO$_2$-rich reformates. In semi-realistic reformate with a relatively high CO concentration (SR-ref 6000), the variation in calcination temperature results does not change the inherent steady-state activity (TOF) with decreasing calcination temperature, when considering the statistical error. Because of the increasing Ru particle size, the Ru mass normalized CO methanation rate decreases slightly at the same time. This result, which agrees well with earlier reports of an increasing activity for larger Ru particle size, points to an electronic particle size effect, together with site blocking effects due to the high CO$_{ad}$ coverage.
3. At very low CO concentrations (100 ppm, SR-ref 100), the CO methanation rate also decreases with increasing calcination temperature, but now for both the Ru mass normalized rates and the TOF. Both are (slightly) higher than at higher CO concentration (SR-ref 6000), in good agreement with the negative reaction order for CO determined earlier. Because of the lower CO\textsubscript{ad} coverage, the activity variation reflects directly the electronic particle size effects, without additional site blocking effects. Except for the initial activation period observed for the catalyst D (highest calcination temperature), the activity decays with time, by in average ~25% over 800 min.

4. The selectivity of the Ru/zeolite catalyst depends sensitively on the composition of the reaction gas mixture and on the Ru particle size, where under present conditions the latter is determined by the calcination temperature. At higher CO concentrations in the reaction gas mixture, as present in SR-ref 6000 (6000 ppm CO), the selectivity is dominated by a site-blocking mechanism, where the active sites for dissociative CO\textsubscript{2} adsorption are blocked by strongly adsorbed CO\textsubscript{ad} species, which effectively inhibit this process, independent of the Ru particle size. This is underlined by the high CO\textsubscript{ad} band intensity in the DRIFTS measurements, which was shown earlier to be close to or identical to CO\textsubscript{ad} saturation. The relative CO\textsubscript{ad} band intensity in SR-ref 100 decreases progressively with decreasing calcination temperature, by up to 50% from catalyst D to A, reflecting the lower number of adsorbed CO\textsubscript{ad} molecules due to the lower Ru surface area.

5. At low CO concentration in the reformate, as present in SR-ref 100 and ID-ref 100, the CO\textsubscript{ad} coverage is much lower, which is also evidenced by the DRIFTS measurements. This leaves active sites for CO\textsubscript{2} dissociation accessible. Under these conditions, the selectivity is determined by the inherent activity of the Ru nanoparticles for dissociative CO\textsubscript{2} adsorption. The activity for CO\textsubscript{2} dissociation was found to increase with particle size. While for the smallest mean particle size (1.0 nm), obtained after calcination at the highest temperature (catalyst D) and subsequent reactive reduction, CO\textsubscript{2} dissociation is essentially inhibited and the selectivity is still at 100%, the tendency for CO\textsubscript{2} dissociation increases with increasing particle size, yielding a selectivity of 70% for the catalyst A calcined at the lowest temperature.

6. This interpretation is supported by the increasing relative steady-state CO\textsubscript{ad} band intensity in CO\textsubscript{2}-ref, which only consists of CO\textsubscript{2} and H\textsubscript{2} and where CO\textsubscript{ad} can result only
from CO$_2$ dissociation, with decreasing calcination temperature / increasing Ru particle size. While on the catalyst D (highest calcination temperature), this is much lower than the CO$_{ad}$ band intensity in reformate with a similar amount of CO$_2$, but 100 ppm CO in addition (SR-ref 100), the relative intensity of CO$_{ad}$ resulting from CO$_2$ dissociation increases with decreasing calcination temperature / increasing Ru particle size. For the catalyst A (lowest calcination temperature), it is identical to the CO$_{ad}$ band intensity in SR-ref 100. Hence, the contribution from CO$_2$ dissociation to CO$_{ad}$ formation, which is negligible for the catalyst D (highest calcination temperature), increases with decreasing calcination temperature / increasing Ru particle size. At the same time, the contribution from CO adsorption, which is indicated by the relative CO$_{ad}$ band intensity in ID-ref 100 compared to that in SR-ref 100, decreases.

7. The selectivities of the different catalysts calculated from kinetic measurements (ratio between CO conversions to CH$_4$ production rates) are comparable to those calculated from the CO$_{ad}$ band intensities in the DRIFTS measurements (ratio between the CO$_{ad}$ intensity in ID-ref 100 and SR-ref 100).

In total, these results yield a consistent picture of the role of catalyst calcination. They closely agree with our earlier findings for the effect of increasing Ru loading on these Ru/zeolite catalysts, where the reaction characteristics were also mainly affected by the increasing Ru particle size, leading to similar changes in the reaction behavior.
3.2. High selectivity of supported Ru catalysts in the Selective CO methanation - water makes the difference

The results and text content in this part were reprinted (adapted) with permission from *the Journal of the American Chemical Society* 137(2015) 8672-8675: Ali M. Abdel-Mageed, D. Eckle, and R. J. Behm, High selectivity of Supported Ru catalysts in the Selective CO Methantion – Water makes the difference. Copyright (2015) with permission from American Chemical Society.

S. Eckle has contributed to this work by critical discussions and further by revisions of the first draft of the published manuscript. H. G. Anfang supplied the Ru/zeolite catalysts and took part in the initial discussion (Clariant Produkte, Deutschland).
3.2. Results and discussion

3.2.1. Introduction

As described in the general introduction, the successful introduction of low-temperature polymer electrolyte membrane fuel cells (PEMFCs) relies decisively on an inexpensive and reliable supply with contamination free hydrogen, where in particular CO levels have to be in the low ppm range to avoid poisoning of the anode catalyst. For the removal of CO from H₂-rich feed gases to below these levels in small scale applications, e.g., in domestic operation, the selective methanation of CO is a highly attractive and promising alternative to the commonly used preferential oxidation of CO (PROX) because of its simpler operation. In the presence of high CO₂ concentrations in the feed gas, which are typical for H₂ generation by reforming processes, e.g., from natural gas, the methanation of CO must be highly selective to avoid intolerable losses of H₂ due to CO₂ methanation (see equations below). Therefore, a very high selectivity for CO methanation over the entire lifetime of the catalyst is an important if not the most important aspect for a successful catalyst.

It has been recently demonstrated that for supported Ru catalysts the selectivity for CO methanation, which is defined as the rate of CO conversion to the overall rate of CH₄ formation (conversion of CO + CO₂), depends sensitively on the Ru particle size. Ru/zeolite catalysts with Ru particle sizes of below 1 nm were found to exhibit CO₂ conversions just at the detection limit of the gas chromatograph (~5 ppm for CH₄) even at very low CO levels, where high selectivities are no more enforced by a surface blocking CO adlayer, as it is the case for higher CO contents. Ru/γ-Al₂O₃ catalysts with Ru particle sizes of 2 nm or more, in contrast, were found to be highly selective only at these higher CO concentrations, while at lower CO contents the CO₂ conversion increased significantly. The high selectivity of the Ru/zeolite catalysts was explained by an inherent inactivity of the very small Ru particles for CO₂ dissociation as a first step for CO₂ methanation, while for larger Ru particles this was found to be facile.

Our previous studies were performed in idealized reaction gas mixtures, with no or low water contents in the reaction gas mixture. Here we report on changes in the reaction gas mixtures with varying water contents.
behavior, in particular in the selectivity for CO methanation over supported Ru catalysts, which occur when changing from idealized to technically relevant reaction gas mixtures by stepwise increasing the amount of water in the reformate gas from 0 to 30% (see Table 2, page 26). To gain further insight into the physical origin of any changes in the reaction behavior, the catalytic performance was followed by combined kinetic and operando EXAFS measurements in the presence of increasing amounts of water in the reaction gas mixture. In addition, time resolved in situ IR spectroscopic (diffuse reflection FTIR spectroscopy – DRIFTS) measurements were employed to resolve changes in the CO\textsubscript{ad} vibrational characteristics correlated with the change of Ru particle size and in the selectivity.

3.2.2. Impact of water on CO selectivity

The changes in activity and selectivity over both catalysts were followed in a reformate gas mixture with a very low CO content (SR-ref 100 gas mixture: 0.01% CO + 3% N\textsubscript{2} + 15.5 CO\textsubscript{2} + balance H\textsubscript{2}), with different amounts of water (0 - 30%) added. The measurements were performed at fixed reaction temperature (190°C) and under differential reaction conditions. The low CO concentration results in a rather low CO\textsubscript{ad} coverage, far below saturation, which allows us to test the inherent selectivity of the catalyst in the presence of high CO\textsubscript{2} concentrations. At higher CO contents and hence high CO\textsubscript{ad} coverages, in contrast, blocking of active sites by adsorbed CO species hinders the dissociation of CO\textsubscript{2}, and leads to high selectivities, up to 100%, even for catalysts which at low CO\textsubscript{ad} coverages would be active for CO\textsubscript{2} dissociation or the Ru/γ-Al\textsubscript{2}O\textsubscript{3} catalyst, the addition of water to the reaction gas mixture caused only small changes in the activity for CO conversion, which decreased by up to 16% in the presence of 30% H\textsubscript{2}O (Fig. 22a). At the same time, however, it resulted in a tremendous decrease of the CO\textsubscript{2} conversion. The addition of 5, 15, or 30% water to the reaction gas mixture lowered the rate of CO\textsubscript{2} conversion to 22.0, 5.7 and ~ 0% of the value obtained in dry reformate, respectively (Fig. 22b). The decrease of the CO\textsubscript{2} methanation rate corresponds to an increase of the selectivity from 42% in dry atmosphere to 78, 92, and 100% in reaction atmospheres with 5, 15, and 30% H\textsubscript{2}O, respectively (Fig. 22c). Similar measurements performed with the Ru/zeolite catalyst revealed a decrease of the steady-state activity for CO conversion by ~41% (5% H\textsubscript{2}O) to ~75% (30% H\textsubscript{2}O), while the CO\textsubscript{2} conversion and the selectivity for CO methanation, which are below the detection limit of the GC (5 ppm) and at 100% already in dry reformate, were not measurably affected (Figs. 22b and 22c).
Figure 22: Steady-state Ru mass normalized reaction rates / selectivities for CO and CO$_2$ methanation obtained over a 5.0 wt.% Ru/Al$_2$O$_3$ catalyst (CO conversion: △; CO$_2$ conversion: □; selectivity: ○) and over a 2.2 wt Ru/zeolite catalyst (CO conversion: ▲; CO$_2$ conversion: ■; selectivity: ●) in a SR-ref 100 gas mixture (0.01% CO + 3% N$_2$ + 15.5 CO$_2$ + balance H$_2$) at 190°C after 1000 min on stream.

3.2.3. Impact of water on Ru particle size

To explore the physical origin of the enhanced selectivity upon increasing the amount of water in the reaction gas mixture on the Ru/Al$_2$O$_3$ catalyst, we performed in operando EXAFS measurements under similar reaction conditions in the presence of 0, 5 and 15% water in the reaction gas mixture (higher water contents were not possible from technical reasons). Data evaluation and EXAFS parameters are given in the supporting information. EXAFS spectra of the Ru K-edge, which were recorded on the Ru/Al$_2$O$_3$ catalyst under steady-state reaction conditions, are presented in Figure 23. They include the $k^3$-weighed chi functions in the k-range of the first Ru-Ru shell (Figs. 23a, b) as well as the corresponding Fourier transforms (Figs. 23c, d). The data indicate a distinct decrease of the Ru-Ru coordination number (CN) upon reaction in the presence of 15% water compared to reaction under dry conditions, from 8.93 (dry reformate) to 7.45 (15% water containing reformate) (structural parameters resulting from the data evaluation are discussed in more detail in section 3.3.2, Table8). Applying the commonly used relationship between coordination number and particle size, which is based on the assumption of a hemispherical particle shape,$^{150}$ the decrease of the CN values corresponds to a decrease of the Ru particle size from 2 nm in dry reformate to 1.2 nm in 15% H$_2$O containing reformate gas under steady-state conditions (Fig. 24a).
3.2. Results and discussion

Figure 23: $k^2$-weighted chi function (a, b) and corresponding Fourier transforms (3.2 – 13.0 Å) (c, d) obtained on a 5.0 wt% Ru/Al$_2$O$_3$ catalyst during reaction in idealized reformate gas mixture (0.6% CO, balance H$_2$) containing 0% water (upper panels) or 15% water (lower panels), as well as typical TEM images / particle size distributions of the catalysts after 1000 min reaction in the same atmosphere (e, f) (solid lines: EXAFS data; dashed lines: fits; scale bars in the TEM images indicate 10 nm).
Transmission electron microscopy (TEM) measurements of the Ru particle size distribution on the Ru/\(\gamma\)-Al\(_2\)O\(_3\) catalyst, performed once after reaction in dry reformate and once after reaction in 15% H\(_2\)O containing reformate, support the above findings. Typical TEM images and particle size distributions are presented in Figs. 23e and 23f. After reaction in dry reformate we obtained a mean particle size of 2.2 nm, while after reaction in 15% H\(_2\)O containing reformate the particle size distribution was shifted to lower values, yielding a mean particle size of 1.68 nm. Hence, the ex situ TEM measurements reveal a similar trend as the in operando EXAFS measurements, and even the absolute values are rather similar, considering that in these TEM images very small Ru nanoparticles, in the sub-nanometer range, are not detected, while they contribute fully to the coordination number and hence to the mean particle size derived from the EXAFS measurements.

Similar EXAFS measurements performed with the 2.2 wt.% Ru/zeolite catalyst showed a decrease of Ru particle size from 1.05 (Table 3; sample D / page 57) to 0.86 nm upon addition of 5% H\(_2\)O to the reaction gas mixture (see Appx., Fig. S1), equivalent to an increase of the dispersion of the Ru NPs from 68% (dry reformate) to 82.5% (5% H\(_2\)O containing reformate). Using differently loaded and differently calcined Ru/zeolite catalysts we had shown earlier that the mean Ru particle size and the selectivity for CO methanation in dry, CO\(_2\)-rich reformate gas (SR-ref 100), but under otherwise similar reaction conditions, are strictly correlated with each other. The selectivity was found to increase with a decreasing mean particle size of the Ru nanoparticles, and similar trends were reported also by other groups. Considering also the observed lower stability of adsorbed CO on very small Ru nanoparticles, the enhanced selectivity for CO methanation was interpreted by a decrease of the inherent activity for CO\(_2\) dissociation on very small Ru NPs. According to the Brønsted-Evans-Polanyi (BEP) relation, the activation barrier for this step increases with decreasing stabilization of the final product CO\(_{ad}\).

We propose that the decrease in Ru particle size during reaction in wet reaction gas mixtures is caused by a water assisted rupture of Ru-Ru bonds, which eventually leads to smaller Ru NP sizes and thus a higher dispersion of the catalyst. Solymosi et al. had shown already earlier that the adsorption of CO on Ru catalysts results in the formation of Ru-dicarbonyl species, which goes along with the disruption of Ru-Ru bonds, and that this process is accelerated by the presence of water. Ru-dicarbonyl related bands were observed also in the present work, but their intensity is very low due to the presence of H\(_2\), consistent with the earlier observations of Solymosi.
Similar observations were reported by Mitsushima et al.\textsuperscript{17,18} By following the changes at the Ru K-edge spectra these authors found that CO adsorption results in a decrease of the coordination number and the disappearance of the extended oscillations characteristic for Ru back scatterers, together with the appearance of Ru-O and Ru-C peaks in the FT transform. They concluded that small Ru nanoparticles are formed and that these are stabilized by adsorbed OH species.

\textbf{Figure 24}: a) Ru particle size in a Ru/Al\textsubscript{2}O\textsubscript{3} catalyst as a function of the amount of water in the SR-ref 6000 reaction gas mixture. b) Intensity evolution of the band related to on top adsorbed CO in CO\textsubscript{2}-ref gas mixture containing different amounts of water: dry CO\textsubscript{2}-ref (▲), 5\% H\textsubscript{2}O containing CO\textsubscript{2}-ref (▼), and 30\% H\textsubscript{2}O containing CO\textsubscript{2}-ref (■). c) Reaction rates for CO methanation (▲) and CO\textsubscript{2} methanation (■) and selectivities for CO methanation (●) during reaction first in dry SR-ref 100 reformate (D) at 190°C, followed by switching to wet SR-ref 100 reformate (W) (15\% H\textsubscript{2}O in the feed gas) and back again to dry (D) SR-ref 100 reformate (open red symbols: dry; filled blue symbols: wet).
3.2. Results and discussion

3.2.4. CO\textsubscript{2} dissociation activity and stability of CO selectivity

Our proposal is strongly supported by the results of a series of DRIFTS measurements, where we monitored changes in the adlayer, in particular the evolution of the CO\textsubscript{ad} coverage, with time on stream on the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst during exposure to CO-free reformate gas containing 15.5% CO\textsubscript{2} (no CO) and different contents of water vapor (CO\textsubscript{2}-ref, balance H\textsubscript{2}). As shown in Fig. 24b, the intensity of the bands related to linearly adsorbed CO\textsubscript{ad}, which is thought to be an intermediate in the CO\textsubscript{2} methanation reaction,\textsuperscript{10} initially increased with time on stream and then saturated for the dry CO\textsubscript{2}-ref (see inset in Fig. 24b). For 5% water containing CO\textsubscript{2}-ref, it initially increased and then decreased with longer time on stream.

Finally, for the 30% water containing CO\textsubscript{2}-ref mixture the general behavior of the CO\textsubscript{ad} related intensity is rather similar, but the decay at longer times is more pronounced. The CO\textsubscript{ad} related intensity reached after 1000 min on stream in 5% and 30% water containing CO\textsubscript{2}-ref was only $\frac{1}{4}$ and $\frac{1}{12}$, respectively, of that observed in dry CO\textsubscript{2}-ref reformate. The latter amount of CO\textsubscript{ad} is comparable to findings for Ru/zeolite in dry CO\textsubscript{2}-ref reformate, which are known to be 100% selective even at very low CO contents (SR-ref 100) under those conditions.\textsuperscript{23}

This observation directly indicates that the presence of water reduces the formation of CO\textsubscript{ad} from CO\textsubscript{2}, in perfect agreement with the mechanistic explanation presented above, where we had proposed that the water assisted dispersion of the Ru nanoparticles leads to a decreasing probability for CO\textsubscript{2} dissociation, and hence an inherently lower activity for CO\textsubscript{2} methanation with increasing H\textsubscript{2}O content / decreasing Ru particle size. The different trends observed for increasing time on stream in Fig. 24b can be explained on the same basis. In the absence of water, it takes some time before the steady-state CO\textsubscript{ad} coverage is reached. In that case, the CO\textsubscript{ad} intensity increases steadily with time and then saturates. We assume that this induction period is needed for the formation of the appropriate Ru particles ($\approx$ 2.0 nm) supporting the observed CO\textsubscript{ad} coverage. With increasing water content, the water assisted dispersion of the Ru nanoparticles becomes more effective. This leads to a counteracting decrease of the Ru nanoparticles due to the increasing water assisted dispersion and a decreasing CO\textsubscript{ad} formation on the smaller Ru NPs than in dry reaction gas mixture. As a result, the maximum CO\textsubscript{ad} band intensity is lower and followed by a steady decline of the CO\textsubscript{ad} band intensity. For 30% water content, these effects are more
pronounced than for 5% water content. These results fully support the mechanistic proposal described above.

Finally, in order to test for a direct influence of adsorbed water on the reaction characteristics by site blocking effects, which was proposed by Panagiotopoulou et al. as origin for the improved selectivity for CO methanation in the presence of water,\textsuperscript{13,19} we performed transient experiments, starting with reaction in dry SR-ref 100, then switching to 15% water containing SR-ref 100 reaction gas and finally back again to dry SR-ref 100 reformate (Fig. 3c), where the latter was demonstrated before to have a rather high activity for CO\textsubscript{2} conversion, equivalent to a low selectivity for CO methanation (see Fig. 22). Interestingly, after changing back to the dry reaction gas mixture the catalyst maintains the high selectivity observed in the presence of water, with a very low rate for CO\textsubscript{2} methanation, and does not return to the relatively high CO\textsubscript{2} methanation rate and low selectivity for CO methanation typical for reaction in dry SR-ref 100 reformate. Apparently, the changes induced by the reaction in water containing reformate gas are irreversible on the time scale of these experiments (1000 min). This result also points to a structural change as origin of the increased selectivity, fully supporting the previous conclusions, rather than to water induced modifications in the adlayer. The latter should quickly approach a new steady-state composition at present reaction conditions (190°C), in particular for weakly adsorbed species such as H\textsubscript{2}O.

These findings of a distinct and stable improvement of the selectivity for CO methanation are highly relevant for technical applications of these catalysts for the Selective Methanation of CO in CO\textsubscript{2}-rich reformate gases, e.g., for the removal of CO trace impurities from H\textsubscript{2}-rich feed gases for PEMFCs. First, the contents of H\textsubscript{2}O in technical reformates tend to drive the Ru catalysts to smaller particle sizes and hence to higher selectivities. Second, the high stability of the small Ru NPs generated upon temporary addition of H\textsubscript{2}O to the feed gas allows for a simple procedure for the regeneration of the catalyst, which means mainly to re-disperse the Ru particle, and then operate again with the technical reaction gas mixture (without addition of water) over an extended time. This would be particularly important for applications of PEMFCs for house heating (domestic applications’), where the catalyst system should survive 50,000 h of operation.
3.2.5. Conclusions

In summary, we have shown for Ru/Al₂O₃ that a Ru catalyst which is poorly selective for the methanation of CO in CO₂-rich reformate gases at low CO contents, becomes highly selective, up to 100% selectivity, in the presence of higher amounts of H₂O in the gas feed, as typical for technical applications. This behavior is explained by a combination of two effects, i) a pronounced, H₂O induced decrease of the mean Ru particle size, and ii) a pronounced decrease in the activity for CO₂ dissociation with decreasing Ru particle size, which we had explained earlier by a decreasing stabilization of CO₂ad and hence, according to the BEP principle, an increasing barrier for CO₂,ad dissociation with decreasing Ru particle size. We consider the dispersive effect of water to be a general effect for supported Ru catalysts, which would allow to simply reactivate these catalysts in technical applications of the Selective CO Methanation, e.g., in fuel gas processing for PEMFCs, by occasional addition of water.
3.3 Water assisted dispersion of Ru nanoparticles: Impact on the activity / selectivity of supported Ru catalysts during selective methanation of CO in CO\textsubscript{2}-rich H\textsubscript{2} feeds

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S. Eckle and D. Widmann contributed to this work by discussions about the results, and revisions of the first draft of the published manuscript. H. G. Anfang supplied the Ru/zeolite catalysts and took part in the initial discussion (Clariant Produkte, Deutschland).
3.3. Results and discussion

3.3.1 Introduction

Focusing on supported Ru catalysts as the main interest of the present work, specifically a commercial Ru/Al₂O₃ catalyst and a Ru/zeolite catalyst, we had investigated the calcination temperature on the activity and in particular on the selectivity in different reaction atmospheres (section 3.1), in addition to the effect of water on the selectivity for CO methanation in low concentration CO reformate (section 3.2). Together with earlier results discussed in the previous sections we could demonstrate that there are two mechanisms leading to a high selectivity for CO methanation, either a blocking of the active sites for CO₂ methanation / dissociation by adsorbed CO, which is dominant at higher CO partial pressures, or an inherently low activity for CO₂ dissociation, which was observed for very small Ru nanoparticles in the 1 nm range and below.⁶²,¹⁶⁸ So far, however, these studies were limited to idealized or semi-realistic reaction conditions, where water either was excluded or limited to 5% at most.

For technical applications, however, water concentrations may reach up to 30%. The effect of high water contents on the reaction behavior and on the reaction mechanism has been discussed controversially. This is topic of the present work; where we report results of a combined kinetic and in situ spectroscopy study on the selective methanation of CO in CO₂-rich reformate gases on supported Ru catalysts. We are particularly interested in structural and chemical changes of the Ru nanoparticles with increasing water content and their correlation with changes in the reaction behavior in medium (6000 ppm) and low (100 ppm) CO concentrations.

Previous studies on the effect of water in related reactions, e.g., the hydrogenation of CO or CO₂ to methane,⁶⁷,⁶⁸,⁸⁰,⁸² or the synthesis of higher hydrocarbons (Fischer-Tropsch reaction) under high pressure³¹,⁹⁷,⁹⁸,¹⁰⁰,¹⁰²,¹⁶⁹,¹⁷⁰ indicated that the presence of water causes a decrease in the activity, which was often attributed to bulk oxidation of the metal particles. Only Claeys et al. reported an increase in Fischer-Tropsch activity over a supported Ru catalyst.¹⁰³ Tavasoli et al. found an increased deactivation of Ru-Co/γ-Al₂O₃ catalysts under Fischer-Tropsch synthesis conditions as the ratio of H₂O / (CO+H₂) in the reaction gas mixture was increased, which they attributed to the oxidation of metallic Co nanoparticles.¹⁰³ Water induced changes in the activity/selectivity were attributed to an induced irreversible reconstruction of the catalyst, including the formation of a cobaltaluminate complex or oxidation of the metal nanoparticle (NP) surface upon the interaction with water.¹⁶⁹,¹⁰²
Water induced effects were observed also for the selective methanation of CO/CO₂ mixtures. Panagiotopoulou et al. found that in temperature screening measurements the CO conversion remains practically unaffected in the presence of water, while the onset for CO₂ conversion is shifted to higher temperatures. These authors suggested that water mainly affects the CO₂ methanation by irreversibly blocking the active sites for the reverse water gas shift (RWGS) reaction. Men et al. observed that the addition of water to the reaction gas mixture hinders the methane formation from a CO/CO₂ mixture on a Ni/CaO/Al₂O₃ catalyst, accompanied by an increase in CO selectivity. The effect of water on the reaction behavior seems to depend also on the nature of the catalyst support. Jimenez et al. reported that the CO conversion is 2-3 times faster in the presence of steam than in a dry reaction gas mixture for Ru/fishbone and Ru/platelet catalysts over a wide range of temperature, while the CO₂ hydrogenation rate is unaffected. This is opposite to the behavior reported in the other studies discussed above.

In the following we will first present and discuss the effect of increasing water contents on the reaction kinetics as determined in kinetic measurements, which were performed in different reaction gas mixtures, including idealized (CO, H₂), and semi-realistic (CO, H₂, and CO₂) reformates, with high (6000 ppm) and low (100 ppm) CO contents and with different amounts of water added (0 – 30% H₂O). Then we focus on the results of in situ extended X-ray absorption fine structure (EXAFS) measurements, where we are particularly interested in water induced structural changes, i.e., in the size and composition of the Ru nanoparticles. The EXAFS data are complemented by transmission electron microscopy (TEM) results acquired ex situ, after the reaction. This is followed by in situ IR spectroscopic measurements (diffuse reflection FTIR spectroscopy – DRIFTS), which focus on water induced changes in the composition of the adlayer under reaction conditions, in particular of linearly bound COₐd species, and their correlation to changes in the activity and selectivity of the reaction and structural changes. Finally, the results will be discussed in terms of a mechanistic picture derived earlier, which correlates the selectivity for CO methanation to the Ru particle size, with small Ru nanoparticles exhibiting a low activity for CO₂ dissociation.

### 3.3.2 Kinetic measurements

The activity and selectivity of the Ru/Al₂O₃ and Ru/zeolite catalysts at high (6000 ppm) and low (100 ppm) CO concentrations and changes therein with time-on-stream and with increasing water content were followed by kinetic measurements in different reformate gas mixtures (see Table 2; page 26). The activity is calculated from the CO consumption rate,
while the selectivity for CO with respect to CO\(_2\) conversion is determined from the ratio of CO conversion to CH\(_4\) formation. We will first characterize the reaction behavior in SR-ref 6000 (0.6% CO, 3% N\(_2\), rest H\(_2\)), which is characteristic for realistic gas mixtures, and then for gas mixtures with a very low CO content (SR-ref 100 - 100 ppm CO, 3% N\(_2\), rest H\(_2\)), which corresponds to gas mixtures close to the end of a methanation stage.

### 3.3.2.1 Reaction in SR-ref 6000 (Effect of water on activity)

Both for the Ru/Al\(_2\)O\(_3\) and Ru/zeolite catalysts the activity for CO methanation decreases with increasing amount of water in the reaction feed (see Fig. 25) by factors of 1.4 and 1.9 respectively; from 4.67×10\(^{-6}\) mol g\(_{Ru}\)^{-1} s to 3.3×10\(^{-6}\) mol g\(_{Ru}\)^{-1} s for the Ru/Al\(_2\)O\(_3\) catalyst and from 53.7×10\(^{-6}\) mol g\(_{Ru}\)^{-1} s to 29.0×10\(^{-6}\) mol g\(_{Ru}\)^{-1} s for the Ru/zeolite catalyst when going from 5% to 30% water content (see Table 6). The lower activity, especially for the Ru/zeolite catalyst, is clearly related to the presence of water in the reformate gases and not caused by changes in the space velocity upon addition of water to the dry gas. This was confirmed by measurements at higher flow rates (46.6 and 51.5 Nml min\(^{-1}\)), where the water in the reaction gas mixture was replaced by N\(_2\) (Appx. Fig. S2). The resulting decrease of the reaction rate is relatively low. For an increase in the gas flow to 51.5 Nml min\(^{-1}\), the activity decreased by a factor of 1.3, while in the presence of 30% H\(_2\)O in the SR-ref 6000 gas mixture with the same total flow (51.5 Nml min\(^{-1}\)) it decayed by a factor of 1.9.

A similar reaction behavior, with an increasing selectivity for CO methanation in the selective methanation reaction, was reported by Panagiotopoulou et al. for different supported Ru as well as Rh catalysts in water concentrations up to er30%.\(^{67,68}\) They found that the presence of water shifted the CO conversion curve to higher temperature, but that at the same time the temperature window between the maximum CO conversion and the onset of CO\(_2\) conversion became wider. These authors assumed that CO\(_2\) methanation proceeds via the reverse water gas shift (RWGS) reaction, where water is a reaction product, and explained the decreasing CO\(_2\) methanation activity by decaying contributions from the RWGS reaction with increasing water content in the feed.

In principle, there are two possibilities to explain the water induced loss of activity for CO methanation and Fischer-Tropsch like reaction.\(^{31,96,97,98,100,170}\) On the one hand, this was attributed to surface oxidation caused by the presence of water. In this case, oxidation of the active metallic sites is held responsible for the loss of catalyst activity. Surface oxidation by water was proposed as one of the reasons for deactivation in a number of studies on the Fischer-Tropsch synthesis, e.g., for supported cobalt catalysts.\(^{96,31,102}\) Tavasoli et al.
suggested for a Ru promoted Co/γ-Al₂O₃ catalyst that the deactivation mechanism depends on the water content in the reaction. At a relatively high water content with p_H₂O / p_H₂ + p_CO ratios > 0.75, they detected oxide formation by X-ray diffraction and temperature programmed reduction, and related the deactivation to surface oxidation of the metal particles. For lower water contents, they attributed the water induced loss of activity to sintering of the Co particles. Also, Jacobs et al. reported that the observed loss of activity in the Fischer-Tropsch synthesis reaction over Co/Al₂O₃ catalysts for high H₂O/CO ratios was accompanied by surface oxidation. At lower H₂O/CO ratios, reversible kinetic effects, such as surface blocking by adsorbed species were held responsible for deactivation.

### Table 6: Ru mass normalized activities for CO conversion / CH₄ formation (RST), and selectivities of the 5.0 wt.% Ru/Al₂O₃ and the 2.2 wt.% Ru/zeolite catalysts, respectively, in semi-realistic reformates with high (SR-ref 6000) in the presence of varying amounts of water (reaction temperature 190° C).

<table>
<thead>
<tr>
<th>% water in</th>
<th>Corrected</th>
<th>RST *10⁻⁶ / mol gₐₘ⁻¹ s⁻¹</th>
<th>RST *10⁻⁶ / mol gₐₘ⁻¹ s⁻¹</th>
<th>Selectivity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>41.6</td>
<td>4.67 / 4.64</td>
<td>53.7 / 52.0</td>
<td>100 / 100</td>
</tr>
<tr>
<td>5</td>
<td>42.9</td>
<td>4.46 / 4.57</td>
<td>48.0 / 49.0</td>
<td>100 / 100</td>
</tr>
<tr>
<td>10</td>
<td>44.1</td>
<td>4.46 / 4.40</td>
<td>41.0 / 42.0</td>
<td>100 / 100</td>
</tr>
<tr>
<td>15</td>
<td>46.6</td>
<td>4.30 / 4.14</td>
<td>37.0 / 38.0</td>
<td>100 / 100</td>
</tr>
<tr>
<td>30</td>
<td>51.5</td>
<td>3.3 / 3.40</td>
<td>29.0 / 29.0</td>
<td>100 / 100</td>
</tr>
</tbody>
</table>

In the other reaction model the loss of CO hydrogenation activity in the presence water is attributed to the competitive adsorption of H₂O and CO, which decreases the number of active sites available for CO and H₂ adsorption, and consequently leads to a lower activity for CO methanation. For the Ru/zeolite catalyst we found a significantly higher activity for CO conversion than for the Ru/Al₂O₃ catalyst, both under dry conditions, with 53.7×10⁻⁶ mol/gₐₘ s compared to 4.67×10⁻⁶ mol/gₐₘ s for the Ru/Al₂O₃ catalyst, and also for increasing amounts of water (see Table 6). The higher activity under dry conditions was suggested to be due to a significantly higher dispersion of the Ru/zeolite catalyst compared to the Ru/Al₂O₃ catalyst. The CO conversion was found to be stable with time on-stream, with very small changes only in the first 100 min, and this was independent of the water content. Similar to the CO methanation activity, also the water induced loss of activity is significantly higher for the Ru/zeolite than for the Ru/Al₂O₃ catalyst (see Table 2). Most likely, this is also related to the
much higher dispersion of the Ru/zeolite catalyst (Ru dispersion: 68.0%, Ru particle size: 1.0 nm) compared to that of the RuAl₂O₃ catalyst (Ru dispersion: 35.6%, Ru particle size: 2.0 nm). This will be discussed in more detail after the presentation of the spectroscopic data. As an alternative explanation, Wang et al. suggested that dealumination of the zeolite, accompanied by a partial collapse of the zeolite network, may be responsible for the high loss of activity upon adding water.¹⁷¹ The selectivity for CO methanation was found to be 100 for both catalysts (Fig. 25). Most simply, this is explained by site blocking effects, where a complete monolayer of adsorbed CO inhibits adsorption and subsequent dissociation of CO₂ on the surface, which keeps the selectivity for CO methanation at 100%.⁶²

3.3.2.2 Reaction in SR-ref 100 (Effect of water on selectivity)

The effect of water on the activity and selectivity was investigated also at a much lower concentration of CO (100 ppm – SR-ref 100), using the same approach as described above for SR-ref 6000. Both the Ru/Al₂O₃ (Fig. 26) and the Ru/zeolite (Fig. 27) catalyst showed higher activities than obtained in the corresponding measurements at 6000 ppm of CO, regardless of the water content (5, 15, and 30% water in the reaction gas mixture). This result agrees well with the negative reaction order for CO determined for CO methanation on these catalysts under dry conditions earlier.⁷¹ Steady-state is reached for both catalysts after around 400 min. Interestingly, and different from the findings for reaction in SR-ref 6000, the response to the addition of water in SR-ref 100 reformates differs significantly for the two catalysts. For the Ru/Al₂O₃ catalyst, the addition of water to the reaction gas had little effect on the activity for CO conversion, it merely decreased by a factor of 1.17 for 30% H₂O content. For the Ru/zeolite catalyst, in contrast, addition of water resulted in a decrease of the activity for CO conversion by factors of 1.8, 2.2, and 3.9, respectively, from 55.9 x10⁻⁶ mol/g₉Ru s in the absence of water to 32.2 x10⁻⁶ mol/g₉Ru s for 5% water, 25.3 x10⁻⁶ mol/g₉Ru s for 15%, and to 14.8 x10⁻⁶ mol/g₉Ru s for 30% H₂O (see Table 7). In this case the limited coverage of CO on Ru NPs exacerbates the effect of water on activity, since a higher number of active sites can be blocked by adsorption of H₂O molecules.
3.3. Results and discussion

Figure 25: Ru mass normalized reaction rates determined on the Ru/Al$_2$O$_3$ catalyst (CO conversion: □; CH$_4$ formation: ●) and on the Ru/zeolite catalyst (CO conversion: ◊; CH$_4$ formation: ■) in SR-ref 6000 reformate containing different amounts of water (a-e) (reaction temperature 190°C, differential reaction conditions).
Table 7: Ru mass normalized activities for CO conversion / CH₄ formation (Rₜₛₜ), and selectivities of the 5.0 wt. % Ru/Al₂O₃ and the 2.2 wt.% Ru/zeolite catalysts, respectively, in semi-realistic reformates with 100 ppm CO concentration (SR-ref 100) in the presence of varying amounts of water (reaction temperature 190°C).

<table>
<thead>
<tr>
<th>% water in gas reformate</th>
<th>Rₜₛₜ *10⁻⁶ / mol g⁻¹ s⁻¹ (Ru/Al₂O₃)</th>
<th>Rₜₛₜ *10⁻⁶ / mol g⁻¹ s⁻¹ (Ru/zeolite)</th>
<th>Selectivity / % Ru/zeolite / Ru/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.4 / 24.5</td>
<td>55.9 / 53.5</td>
<td>100 / 42.4</td>
</tr>
<tr>
<td>5</td>
<td>10.9 / 14.0</td>
<td>32.2 / 32.0</td>
<td>100 / 78.0</td>
</tr>
<tr>
<td>15</td>
<td>9.99 / 10.8</td>
<td>25.3 / 24.0</td>
<td>100 / 92.5</td>
</tr>
<tr>
<td>30</td>
<td>8.83 / 8.90</td>
<td>14.8 / 14.3</td>
<td>100 / 100</td>
</tr>
</tbody>
</table>

Pronounced differences in the water induced effects are observed also for the selectivity for CO conversion. For the Ru/Al₂O₃ catalyst, where under dry conditions the selectivity is much lower than that of the Ru/zeolite catalyst, the CO₂ conversion decreased by factors of 1.8, 2.3 and 2.8, respectively, in the 5%, 15%, and 30% water containing reaction gas mixtures. This results in an increase of the selectivity from 42% (dry gas) via 78% (5% H₂O) and 92% (15% H₂O) to finally 100% for the 30% H₂O containing reaction gas mixture, respectively (see Table 7). For the Ru/zeolite catalyst, in contrast, it reached 100% during all measurements, both in dry and wet (5%, 15% and 30% H₂O content) reaction atmospheres.
3.3. Results and discussion

**Figure 26:** Ru mass normalized reaction rates (CO conversion: □; CH₄ formation: ●) and selectivities (▲) for the selective methanation of CO on the Ru/Al₂O₃ catalyst in SR-ref 100 reformate containing different amounts of water (a-d) (reaction temperature 190°C, differential reaction conditions).
3.3. Results and discussion

Figure 27: Ru mass normalized reaction rates (CO conversion: ◊; CH₄ formation: ■) and selectivities (▲) for the selective methanation of CO on the Ru/zeolite catalyst in SR-ref 100 reformate containing different amounts of water (a-d) (reaction temperature 190°C, differential reaction conditions).
3.3. Results and discussion

3.3.3. Particle size / structural changes and nature of Ru species during reaction

Possible changes in the size and chemical composition of the Ru nanoparticles during the reaction were monitored by operando EXAFS measurements. Fig. 28 shows the steady-state EXAFS spectra of the Ru k-edge including k^3-weighted chi functions in the k-range 3.2 - 13.2 Å⁻¹ in the left panels (Figs. 28a - d). These spectra were recorded in idealized reformate (ID-ref 6000, 0.6% CO, rest H₂, see Table 2 / page 26) with different water contents (0%, 5%, 10%, and 15%) under similar reaction conditions as used in the kinetic measurements after about 200 min on stream, when steady-state conditions were reached. The corresponding Fourier transforms in r-space, in the range of the first shell (Ru-Ru scattering), are shown in the right panel (Figs. 28e - h). A long sequence of oscillations toward high k-values, which is observed in all spectra, is characteristic of backscattering at heavy metals such as Ru (Figs. 28a - d). In the Fourier transform a characteristic peak at 2.67 Å, fits well to the Ru-Ru distance.

The data could be fitted well with backscattering at a single Ru shell, while attempts to fit the spectra with multiple shell structures including both Ru-Ru and Ru-O were unsuccessful. This indicates that under steady-state conditions the Ru NPs are in a metallic state, despite the presence of water. A completely metallic state of the Ru NPs is supported also by the absence of a CO_ad band at 2075 cm⁻¹ and higher, which would be characteristic of CO adsorbed on oxidic Ru^{δ+} species (see Fig. 31 in section 3.3.4.1).

These findings agree well with previous results obtained in our group for Ru/zeolite catalysts during reaction in dry reformate gases of similar composition.¹⁶²,¹⁶⁸ Those measurements showed that the oxidic Ru^{δ+} species disappear shortly after the start of the reaction.

The coordination number (CN) of the Ru-Ru shell was obtained by fitting the EXAFS data of the first Ru-Ru shell at 2.67 Å to the calibrated Ru foil reference (see Fig. 28). Using the coordination numbers obtained upon reaction in gas mixtures with different water contents, at steady-state conditions, the average particle sizes and the dispersion of the Ru nanoparticles (NPs) were calculated. Here we used the coordination number – particle size relation determined by Karim et al.,¹⁷² which assumes hemispherical Ru NPs. The data indicate a decrease in CN of the Ru NPs in the presence of water (see Table 8), which points to an increasing dispersion of the Ru NPs with increasing water content in the reaction gas. Eckle et al reported a Ru particle size in the range of ~2 - 3 nm for a similar Ru/Al₂O₃ catalyst after methanation reaction in SR-ref 6000.⁷¹,⁷²
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Figure 28: Left: $k^3$ weighted chi function, right: corresponding Fourier transforms (3.2 – 13.0 k-space) obtained for the Ru/Al$_2$O$_3$ catalyst during reaction in idealized reformate gas (0.6% CO, balance H$_2$) with 0% water (a, e); 5% water (b, f); 10% water (c, g) and 15% water (d, h) 200 min after the reaction start (reaction temperature 190°C, solid line: EXAFS data; dashed line: fits)
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Table 8: Structural parameters of the Ru/Al$_2$O$_3$ catalyst obtained from fitting the EXAFS spectra (reaction conditions: idealized reformate gas (0.6% CO, balance H$_2$) containing different amounts of water, steady-state conditions, reaction temperature 190°C).

<table>
<thead>
<tr>
<th>% Water</th>
<th>CN</th>
<th>DW /10$^3$Å$^2$</th>
<th>$r$ / Å</th>
<th>E$_0$/ev</th>
<th>Dispersion /%</th>
<th>Particle size /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.93 ± 0.89</td>
<td>3.23</td>
<td>2.665</td>
<td>7.8</td>
<td>35.6 ± 3.1</td>
<td>2.00 ± 0.61</td>
</tr>
<tr>
<td>5</td>
<td>7.96 ± 0.80</td>
<td>3.23</td>
<td>2.675</td>
<td>8.67</td>
<td>49.6 ± 11.8</td>
<td>1.48 ± 0.39</td>
</tr>
<tr>
<td>10</td>
<td>7.57 ± 0.75</td>
<td>4.53</td>
<td>2.676</td>
<td>6.7</td>
<td>57.5 ± 14.7</td>
<td>1.26 ± 0.32</td>
</tr>
<tr>
<td>15</td>
<td>7.45 ± 0.76</td>
<td>3.76</td>
<td>2.672</td>
<td>8.65</td>
<td>59.1 ± 15.3</td>
<td>1.21 ± 0.31</td>
</tr>
</tbody>
</table>

With increasing amount of water in the reaction gas mixture, the mean particle size decreased from 2.0 nm (0% H$_2$O) to 1.2 nm (15% H$_2$O) (see Table 8). Assuming an error in the CN of 10% results in an uncertainty range for the particle size of 1.4 – 2.6 nm for reaction in dry gas mixture,$^{145}$ while for reaction in a gas mixture with 15% water this range is 0.9 – 1.5 nm. Nevertheless, considering that the uncertainty is largely due to systematic errors, the trend to larger Ru particle sizes with increasing water contents derived from these data is assumed to be highly reliable, despite the rather large error range.

Exploiting the time resolution of the in situ EXAFS measurements, we investigated the initial phase of the reaction on the Ru/Al$_2$O$_3$ catalyst in more detail. The fresh catalyst, which was exposed to air for a long time, exhibits mainly oxidic Ru species. These oxidic Ru species exist before and also after heating in N$_2$. However, as has been observed in the EXAFS spectra (see Appx. Fig. S3), they might get partially reduced by reaction with carbonaceous species which are possibly adsorbed on them.$^{173}$ After switching to the reaction gas mixture, the oxidic Ru species are quickly reduced. EXAFS spectra recorded 2 min after the onset of reaction in dry, 5% and 10% H$_2$O containing gas mixtures (0.6% CO, rest H$_2$) showed mainly metallic Ru NPs with characteristic peaks at 2.67 Å. Obviously, at these water concentrations the equilibrium concentration of RuO$_2$ or other oxidic Ru species is too low to be detected. This is different for reaction in a gas mixture with 15% water, where a shoulder at 2.012 Å, indicative of the presence of oxidic Ru species, can be observed until 28 minutes after the start of the reaction. Hence, in the presence of higher water contents in the reaction gas
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mixture Ru reduction is slowed down, and a mixture of oxidic and metallic species coexists during the initial formation range, for the first 28 min (see Fig. 29).

Table 9: Structural parameters of the Ru/Al₂O₃ catalyst obtained from the EXAFS spectra after increasing times on stream (idealized reformate gas (0.6% CO, balance H₂) containing 15 % H₂O, reaction temperature 190°C).

<table>
<thead>
<tr>
<th>Time / min</th>
<th>Scatterer</th>
<th>CN</th>
<th>DW/10⁻³Å²</th>
<th>r / Å</th>
<th>E₀ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Ru-Ru / Ru-O</td>
<td>4.38 / 1.24</td>
<td>1.46 / 3.14</td>
<td>2.677 / 2.012</td>
<td>6.29 / -2.90</td>
</tr>
<tr>
<td>28</td>
<td>Ru-Ru / Ru-O</td>
<td>6.01 / 0.65</td>
<td>2.54 / -3.10</td>
<td>2.673 / 2.018</td>
<td>9.25 / 0.00</td>
</tr>
<tr>
<td>55</td>
<td>Ru-Ru</td>
<td>6.58</td>
<td>3.11</td>
<td>2.668</td>
<td>8.41</td>
</tr>
</tbody>
</table>

Table 10: Structural parameters of the Ru/zeolite catalyst determined from EXAFS spectra measured in idealized reformate gas (0.6% CO, balance H₂) containing 5% H₂O after different reaction times. The data were fitted by Ru-Ru backscattering.

<table>
<thead>
<tr>
<th>Time / min</th>
<th>CN</th>
<th>DW/10⁻³ Å²</th>
<th>r / Å</th>
<th>E₀ / eV</th>
<th>Particle size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>6.07</td>
<td>0.00774</td>
<td>2.663</td>
<td>0.05</td>
<td>0.83</td>
</tr>
<tr>
<td>97</td>
<td>6.53</td>
<td>0.00854</td>
<td>2.670</td>
<td>-0.24</td>
<td>0.87</td>
</tr>
<tr>
<td>144</td>
<td>6.56</td>
<td>0.00805</td>
<td>2.668</td>
<td>0.07</td>
<td>0.865</td>
</tr>
<tr>
<td>178</td>
<td>6.49</td>
<td>0.00772</td>
<td>2.665</td>
<td>-0.037</td>
<td>0.863</td>
</tr>
</tbody>
</table>

The CNs of the metallic Ru species obtained after 2 min and after 28 min on stream with 15% water in the feed gas (see Table 9) indicate a higher dispersion than obtained in the later stage of the reaction, under steady-state conditions (after 200 min). After 55 min the catalyst was found to be completely metallic, with only one characteristic peak at 2.672 Å (see Figs. 29c, f). Overall, the data demonstrate that the reduction of the initially oxidic Ru species is slowed down with increasing amount of water (15%) in the reaction gas mixture. Under steady-state conditions, however, the Ru is completely reduced to metallic Ru, independent of the water content, at least up to 15%. Similar measurements performed on the 2.2 wt.% Ru/zeolite
3.3. Results and discussion

catalyst revealed identical trends, although the Ru particles are generally much smaller. For reaction in dry reaction atmosphere we obtained a mean Ru particle size of 1.0 nm, which perfectly agrees with our earlier findings.\textsuperscript{62,168}

For reaction in 5\% H\textsubscript{2}O containing reaction gas, the steady-state particle size is even smaller, at about 0.8 nm (see Table 10). Looking at the time dependence of the Ru NP size in the presence of 5 \% H\textsubscript{2}O in the reaction gas, this increased during the initial 70 min and leveled off at a constant value of 0.86 nm at 180 min. The fit of the EXAFS data showed exclusively Ru in the metallic state, even in the presence of 5\% H\textsubscript{2}O in the gas feed (see Appx., Fig. S1). A similar trend was also observed over Ru/Al\textsubscript{2}O\textsubscript{3} catalysts (see Appx., Table S2).

The results obtained by the \textit{in situ} EXAFS experiments were cross-checked by (\textit{ex situ}) high-resolution TEM measurements, evaluating the Ru particle size of three Ru/Al\textsubscript{2}O\textsubscript{3} catalyst samples after reaction in ID-ref 6000 reaction gas mixtures containing 0\%, 5\% or 15\% water, respectively. Representative TEM images of the three catalyst samples and the resulting particle size distributions are shown in Fig. 30. The particle size distributions reveal a downshift of the Ru NP size distribution after reaction in H\textsubscript{2}O containing reaction gas mixtures compared to the samples exposed to H\textsubscript{2}O containing reaction gas mixtures. This is reflected by mean particle sizes of 2.2 nm (reaction in dry atmosphere), 1.78 nm (reaction in 5\% H\textsubscript{2}O containing reformate) and 1.68 nm (reaction in 15\% H\textsubscript{2}O containing reformate) (see Fig. 30). These values are slightly larger than those obtained by the \textit{operando} EXAFS measurements (2.0 nm, 1.48 nm, and 1.21 nm for the same samples, see Table 8), but they exhibit the same trend, namely a decreasing mean particle size with increasing H\textsubscript{2}O content in the reaction gas mixture. The difference in absolute numbers can be understood by the differences in the cut-off limit of both techniques. In the EXAFS measurements the average CN is integrated over all Ru particles, while TEM imaging does not detect the very small Ru clusters (< 1.0 nm). This results in a slightly higher apparent mean particle size, in agreement with our observations.

A dispersion of Ru nanoparticles upon interaction of oxidizing agents such as O\textsubscript{2} or H\textsubscript{2}O with either the Ru nanoparticles or with their or their oxidic precursors had been reported already before and explained in different ways.
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Figure 29: Left: $k^3$ weighted chi function, right: corresponding Fourier transforms ($3.2 - 11.5$ k-space) obtained for the Ru/Al$_2$O$_3$ catalyst during reaction in idealized gas mixture (0.6% CO, balance H$_2$) containing 15% water 2 min (a, d); 28 min (b, e); and 55 min (c, f) after the onset of the reaction (reaction temperature 190°C, solid line: EXAFS data; dashed line: fits).

Ran et al.$^{174}$ reported that the reduction of Ru nanoparticles supported on carbon nanotubes (CNTs) in a 1:1 CH$_4$/H$_2$ mixture yields much smaller Ru nanoparticles if 0.6% water is added to the reducing atmosphere than in the absence of water. The authors ascribed the high dispersion of the Ru NPs to the presence of oxygen-containing groups formed during the water pretreatment of the support, and to uniform defects on the tube-walls. In this case, the carbon nanotubes provide anchoring and nucleation sites for Ru nanoparticles during reduction, a situation very different from the present case.
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Figure 30: TEM images and particle size distribution of the Ru/Al$\text{}_2$O$_3$ catalyst after 1000 min exposure to idealized reformate gas (ID-ref 6000) in the absence of water (a), in the presence of 5% H$_2$O (b) and in the presence of 15% H$_2$O (c) in the reaction gas (reaction temperature 190°C, scale bar indicates 10 nm).

We had recently demonstrated that calcination of a Ru/zeolite catalyst in air at temperatures up to 500°C before the actual activation procedure (same procedure as applied in the present paper, i.e., drying in N$_2$ at 150°C and subsequent heating to the reaction temperature of 190°C in the reaction gas mixture) results in increasingly smaller Ru nanoparticles than obtained
without calcination, with mean particle sizes decreasing from 1.5 nm to 1.0 nm. This was explained by a thermally induced transfer of mobile Ru oxide species from the outer surface of the zeolite into the pores of the zeolite matrix during calcination and subsequent reduction of the resulting Ru oxide nanoparticles during activation and reaction. A stabilization of the Ru oxide in the pores was suggested as driving force for this process.

Considering that in the present case both the experimental conditions are considerably milder, using much lower temperatures and H$_2$O instead of O$_2$ as oxidation agent, and that in the non-porous Al$_2$O$_3$ support stabilization in pores is not possible, we have little evidence for a purely oxidative dispersion of the Ru nanoparticles by interaction with H$_2$O.

A second mechanism suggested for the explanation of the observed size decrease of the Ru nanoparticles is based on the oxidative disruption of the metallic Ru-Ru nanoparticles due to a synergetic effect resulting from the simultaneous interaction of CO and H$_2$O with Ru$_x$ nanoparticles. Such type of oxidative Ru-Ru bond breaking was reported earlier by a number of groups. Solymosi et al. reported that the adsorption of CO on Ru/Al$_2$O$_3$ at 170 - 350 K leads to the disruption of Ru NP, which is accompanied by a shift of the CO$_{ad}$ band from 2020 - 2040 cm$^{-1}$ to 2140 cm$^{-1}$, and similar results were obtained also before for supported Rh catalysts. These authors reported that disruption in the presence of water is considerably faster than under dry conditions, especially in the presence of hydrogen (oxidative disruption). According to them, the driving force behind the disruption of Ru-Ru bonds is the high bond energy of the Ru-CO bond. In the presence of H$_2$, the Ru carbonyl species formed during oxidative disruption process are reduced by H$_{ad}$, which results in tiny Ru clusters that subsequently may agglomerate to small Ru nanoparticles. Mizushima et al. arrived at similar conclusions for Ru catalysts using different support materials (γ-Al$_2$O$_3$, MgO, SiO$_2$ and TiO$_2$). In their picture, Ru clusters can be recovered by desorption of CO, These earlier results were later supported by similar findings in infrared spectroscopy measurements on Ru/SiO$_2$ catalysts, where they equally observed Ru$^0$-CO carbonyl species. They concluded that the adsorption of CO on Ru/SiO$_2$ catalysts results in a disruption of Ru-Ru bonds in the metal nanoparticles, liberating free Ru$^0$-CO species, and that part of these species interact with silanol groups on the support surface, replacing the protons from the hydroxyl groups.
Overall, this process increases the mean dispersion of the Ru NPs. Likewise, Chin et al. concluded on the formation of Ru$^{5+}$ monocarbonyl and multicarbonyl species during adsorption of CO (1% CO/He), indicated by strong bands at 2075 - 2139 cm$^{-1}$.\textsuperscript{57,181} This happened, however, only in the presence of oxygen. Similarly, Robbins et al. reported that the bands at 2084 and 2140 cm$^{-1}$ can be assigned to (TiO$_2$)Ru-(CO)$_3$ surface species formed during the adsorption of CO on a Ru/TiO$_2$ catalyst at 310 K.\textsuperscript{60} 

The present EXAFS results are fully compatible with the mechanistic picture described in the previous paragraphs. From our data, we cannot distinguish whether larger Ru NPs are dispersed by direct oxidation upon reaction with water and subsequent reduction, or whether the oxidative disruption step itself is due to coadsorption of CO and H$_2$O on the Ru NPs. In any case, it was not observed to be active in the absence of water, with only CO and H$_2$ in the feed. It should be noted that the reduction process of the oxidic species resulting from oxidative disruption must be sufficiently fast to be outside the time resolution of both EXAFS and DRIFTS measurements.

Consequences of the H$_2$O induced dispersion of the Ru nanoparticles on the reaction behavior will be discussed later in section 3.4, after the presentation and discussion of the DRIFTS measurements.

### 3.3.4 In situ DRIFTS measurements

The interaction of the different reaction atmospheres with both catalysts in the presence of varying amounts of water (5-30%) was characterized by sequences of \textit{in situ} DRIFTS measurements. We were particularly interested in the adsorbed CO-adlayer intensities, to identify H$_2$O induced modifications in the adlayer, which in turn may provide more insight into the origin of the H$_2$O induced modifications of the activity and selectivity. In the following we will only briefly introduce the observed surface species, for a more detailed discussion we refer the reader to previous reports.\textsuperscript{71,72}

#### 3.3.4.1 SR-ref 6000 (Effect of water on activity):

Spectra recorded during reaction in realistic reformate (SR-ref 6000) on the Ru/Al$_2$O$_3$ and Ru/zeolite catalysts, with different amounts of water in the reaction gas mixture, are presented in Figures 31 (Ru/Al$_2$O$_3$ catalyst) and 32 (Ru/zeolite catalyst), respectively. In the left panel we show detail spectra of the OH region (3450 – 3800 cm$^{-1}$). Due to large changes in the background in this region they are presented as raw spectra. The right panel shows detail spectra from the CO region (2150 - 1780 cm$^{-1}$) and the OCO bending (1750 - 1200 cm$^{-1}$) regions (absorption in Kubelka Munk units). Because of the extremely low intensities of the
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CH-, CH₂- and CH₃- species in the presence of water, which are at or below the detection limit, the detail spectra of the CHₓ region are not shown (2700-3200 cm⁻¹).

In the OH region, two characteristic bands at 3733 and 3623 cm⁻¹ (left panels) are assigned to terminal and isolated OH_ad groups adsorbed on the catalyst support. On the Ru/Al₂O₃ catalyst (Fig. 31; left panels) the OH band interferes with the OH band of molecularly adsorbed water, therefore it was not possible to quantitatively evaluate them. On the Ru/zeolite catalyst (Fig. 32; left panels), these two peaks appear at 3736 and 3630 cm⁻¹. The peak at 3736 cm⁻¹ is also characteristic of the silanol group of zeolite support.¹⁸²,⁴⁸

In the CO region, a peak around 2040 cm⁻¹ is assigned to linearly (‘on top’) adsorbed CO_ad species. Its position varies with the water concentration (Ru/Al₂O₃: 2034 - 2024 cm⁻¹; Ru/zeolite: 2045 - 2038 cm⁻¹). The other band (1928 - 1905 cm⁻¹) is attributed to bridge bonded CO_ad species. The ratio of linearly adsorbed to bridge bonded CO_ad on Ru/Al₂O₃ increases with increasing water content in the reaction gas mixture. For the Ru/zeolite catalyst the intensity of the bridge bonded CO_ad species is extremely low compared to Ru/Al₂O₃ catalysts, resulting in a ratio of 6.5. This decreases even more with increasing amount of water, and at a water content >10% it has vanished completely (see Fig. 32; right panels). The increasing fraction of linearly adsorbed CO on both catalysts is likely to be related to the water induced decrease in Ru particle size (see Appx., Fig. S4).

The intensities of the CO_ad related bands were found to decrease with increasing water content in the reaction gas mixture. This decrease in CO_ad coverage goes along with a decrease of the activity, as discussed above. Although H₂O is expected to mainly adsorb on the support, part of it may be adsorbed also on the Ru particles, resulting in a competition between H₂O and CO molecules for adsorption sites. A band observed at higher wavenumbers (2075 – 2086 cm⁻¹) at the Ru/zeolite catalyst had been interpreted as due to adsorption of CO on partially oxidized Ru atoms (Ru⁰⁺).⁷¹,⁵⁶ The intensity of this band is very low and it deteriorates further in the presence of water, similar to the behavior of linearly adsorbed and bridge bonded CO_ad species.

In the present work, CO_ad related bands at around 2140 cm⁻¹, which had been reported earlier and attributed to the formation of Ru⁰⁺ monocarbonyl and multicarbonyl species,¹⁸³,⁵⁷,⁵⁹ were extremely weak and just above the noise level, both in CO/N₂ atmosphere nor in CO/H₂ atmosphere.
Figure 31: DRIFT spectra recorded over 800 min during reaction on the Ru/Al₂O₃ catalyst in SR-ref 6000 gas reformate containing different amounts of water (a-e) (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, and 795 min, reaction temperature 190°C).
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Figure 32: DRIFT spectra recorded over 800 min during reaction on the Ru/zeolite catalyst in SR-ref 6000 gas reformate containing different amounts of water (a-e) (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, and 795 min, reaction temperature 190°C).
In the spectral region of OCO bending vibrations two characteristic peaks appeared at 1594 and 1390 cm\(^{-1}\) on the Ru/Al\(_2\)O\(_3\) catalyst and at 1586 and 1385 cm\(^{-1}\) on the Ru/zeolite catalyst, respectively. Bands in this range had been assigned earlier to bidentate surface formate species, which act as spectator in the reaction.\(^{71}\) The intensities of these bands decrease with increasing water content in the feed gas. Apparently, the reaction with adsorbed water molecules accelerates the decomposition rate of these species (for more information see Appx, Fig. S5). A weak band at 1460 cm\(^{-1}\), which was related to surface carbonates,\(^{48}\) is more prominent on the Ru/zeolite catalyst than on the Ru/Al\(_2\)O\(_3\) catalyst.

The time evolution of the linearly adsorbed CO\(_{ad}\) band intensity during time on stream is plotted for different water concentration in Fig. 33 (Fig. 33a: Ru/Al\(_2\)O\(_3\); Fig. 33b: Ru/zeolite catalyst).

For the Ru/Al\(_2\)O\(_3\) catalyst, low and medium water concentrations (0% - 15%) result in approximately constant CO\(_{ad}\) band intensities, only for 30% it decays with time, mainly after 600 min on stream. For the Ru/zeolite catalyst, the intensities are generally lower. At low water concentrations (0%, 5%) the intensity initially increases during the first 300 min and then decreases continuously, with the decay in intensity being much more pronounced for 0% water than for 5% water content. For 10% water content the CO\(_{ad}\) intensity increases first and then saturates, and for the higher water concentrations (15%, 30%) it is about constant.

To compare the effect of water on a more quantitative scale, we plotted the CO\(_{ad}\) intensities obtained after 300 min (filled symbols) and at the end of the measurements (~ 300 min, open symbols), where in most cases steady-state was reached, for different water concentrations (Fig 33c: Ru/Al\(_2\)O\(_3\) catalyst, Fig. 33d: Ru/zeolite catalyst). Both catalysts show a more or less steady decline of the linearly adsorbed CO\(_{ad}\) band intensity as the amount of water in the gas mixture is increased. The relative CO\(_{ad}\) band intensity (relative to the maximum CO\(_{ad}\) band intensities observed in dry SR-ref 6000 gas mixture) decreased from 91.1 (5% H\(_2\)O) to 40.1% (30% H\(_2\)O) for the Ru/zeolite catalyst, while for the Ru/Al\(_2\)O\(_3\) catalyst the respective values are 89.9 and 6.3% (see also Table 11). The decline of the CO\(_{ad}\) band intensity correlates, at least in trends, with the decrease of the Ru mass normalized activity (see Table 6 and Fig. 25), which is compatible with a competition of CO and H\(_2\)O for similar adsorption sites. Although water adsorption on most metal surfaces is weaker than CO adsorption,\(^{184,185,95}\) a measurable H\(_2\)O coverage can build up on the surface due to its much higher partial pressure as compared to the CO partial pressure. This fits well to the observed decrease of the CO\(_{ad}\) band intensity.
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with increasing water content in the gas mixture, (Fig. 33c, d), which is accompanied by a decrease of the reactivity.

The steady-state intensity of the CO\textsubscript{ad} band on the Ru/Al\textsubscript{2}O\textsubscript{3}, catalyst in dry gas mixture is 2.6 times higher than in the mixture containing 30% water. In the case of the Ru/zeolite catalyst, this difference is even a factor of 16.0. The decrease is more pronounced in the DRIFTS results than in the kinetics, where the reaction rates decreased only by 29% for the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst and by 48% for the Ru/zeolite catalyst, when going from a dry reaction gas mixtures to one containing 30% water. Obviously, water also has an impact on the coverage of other adsorbed reaction intermediates (CH\textsubscript{x} etc.), which fits well and may be responsible for the lower activity. For water contents \(> 5\%\) in the respective gas mixtures, the broad peak of the OH stretch vibration in water in the range from 3150 to 3450 cm\(^{-1}\) makes an evaluation of the CH\textsubscript{x} intensities impossible. However, for 5% H\textsubscript{2}O containing gas mixtures this is possible and indicates a sizable decrease of the CH\textsubscript{x} related band intensities as compared to dry reformate.

**Table 11:** Relative band intensities of linearly adsorbed CO on the Ru/Al\textsubscript{2}O\textsubscript{3} and Ru/zeolite catalysts, respectively, at different water concentrations in the SR-ref 6000 reaction gas mixture.

<table>
<thead>
<tr>
<th>Water Content / %</th>
<th>Relative intensity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru/Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>91.1</td>
</tr>
<tr>
<td>10</td>
<td>71.9</td>
</tr>
<tr>
<td>15</td>
<td>58.5</td>
</tr>
<tr>
<td>30</td>
<td>40.1</td>
</tr>
</tbody>
</table>
3.3. Results and discussion

Figure 33: Left panel: Time evolution of the band intensity of linearly adsorbed $\text{CO}_{\text{ad}}$ (a) Ru/Al$_2$O$_3$, (b) Ru/zeolite catalyst in a SR-ref 6000 gas mixture containing different amounts of water (0: ■; 5: ▲; 10: ●; 15: ♦; 30▼), right panel steady-state intensity (●) and the corresponding reaction rates (○) as a function of water content for Ru/Al$_2$O$_3$ (c) and Ru/zeolite (d) catalysts.

3.3.4.2 ID-ref 100 and SR-ref 100 (selectivity correlation)

Changing to reaction gas mixtures with very low CO contents (ID-ref 100 and SR-ref 100), the build-up of different surface species is rather similar to that observed in SR-ref 6000, but the intensities are generally lower (Figs. 34a, b and Figs. 35a,b). Because of the low CO concentration (100 ppm) in the reaction gas mixture, which results also in low absorption intensities, and the water induced decrease in the $\text{CO}_{\text{ad}}$ band intensity we could not extend the measurements to water contents above 5%. The evolution of the $\text{CO}_{\text{ad}}$ band intensities in the 2 different reaction gas reformates (see Table 1), in the absence and in the presence of 5% water, is shown in Fig. 36 (Fig. 36a, b: Ru/Al$_2$O$_3$:catalyst, Fig. 36c, d: Ru/zeolite catalyst).

For the Ru/Al$_2$O$_3$ catalyst, the $\text{CO}_{\text{ad}}$ band intensities obtained in the two low-CO reformates in H$_2$O free gas mixtures differ significantly. While in SR-ref 100 it is close to the saturation value in SR-ref 6000 (94.0%), it is reduced to almost half in the ID-ref 100 gas mixture. (51.0%, see Table 12)
3.3. Results and discussion

Hence, on this catalyst and under these reaction conditions, CO\textsubscript{ad} formation via CO\textsubscript{2} dissociation/conversion contributes significantly to the CO\textsubscript{ad} band intensity, but the efficiency for CO\textsubscript{2} dissociation decreases with increasing H\textsubscript{2}O content. This increase in relative band intensity fits well to the increase in selectivity from 42% (0% H\textsubscript{2}O) to 78.0% (5% H\textsubscript{2}O) determined in the kinetic measurements. Comparing with the EXAFS / TEM results described before, we attribute the increase of the catalyst selectivity to the decrease of the mean Ru particle size. The significantly lower CO\textsubscript{ad} band intensity and hence also CO\textsubscript{ad} coverage on the smaller Ru nanoparticles formed in the presence of H\textsubscript{2}O in the reaction gas implies that adsorbed CO is less stable on the smaller Ru NPs, which according to the above discussion would result in a higher dissociation barrier for adsorbed CO\textsubscript{2}. Since CO\textsubscript{ad} formation from CO\textsubscript{2} is an intermediate step for CO\textsubscript{2} methanation on these catalysts,\textsuperscript{72} this fits perfectly to the higher selectivity in the presence of water in the feed.

The situation is distinctly different for the Ru/zeolite catalyst. In this case the relative CO\textsubscript{ad} intensity in the low-CO reformates (ID-ref 100 and SR-ref 100) is much lower, only 6.5% of that in SR-ref 6000 (CO\textsubscript{ad} saturation coverage) under dry conditions. It is also much lower than that obtained for Ru/Al\textsubscript{2}O\textsubscript{3}. The latter finding has been explained by a lower adsorption energy of CO on the very small Ru nanoparticles of the Ru/zeolite catalyst, together with a very low activity (= high barrier) for CO\textsubscript{2} dissociation.\textsuperscript{62} Therefore, the CO\textsubscript{ad} coverage in SR-ref 100 is about the same as that in ID-ref 100. In the presence of 5% water, the relative intensity decreases to 82.0% of the saturation intensity in SR-ref 6000 and to 2.1 and 2.6%, respectively, for the ID-ref 100 and SR-ref 100 reformates (see Table 12). The low CO\textsubscript{ad} coverage goes along with a decrease in the CO methanation activity in SR-ref 100 by almost 40% compared to SR-ref 6000. The time dependent evolution of the intensities resembles the behavior observed in SR-ref 6000, with an initial increase during the first 200 – 400 min (see Fig. 36), and constant intensities with proceeding reaction time. Furthermore, almost identical CO\textsubscript{ad} band intensities are found for the two low-CO reformates, SR-ref 100 and ID-ref 100, for dry and 5% wet water containing gas mixtures, indicating that the additional 15.5% CO\textsubscript{2} present in SR-ref 100 do hardly contribute to the CO\textsubscript{ad} intensity. Hence, CO\textsubscript{ad} formation via CO\textsubscript{2} dissociation/conversion is negligible under these conditions. This agrees well with the observation of 100% selectivity for CO methanation for this catalyst, both in absence and in the presence of water.\textsuperscript{62, 168} The presence of water did not cause any marked changes in the reaction behavior of this catalyst, except for the somewhat lower CO\textsubscript{ad} band intensities and reaction rate.
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Table 12: Relative intensities of linearly adsorbed CO on the Ru/Al$_2$O$_3$ (left) and Ru/zeolite (right) catalysts in different reformate gases under dry conditions and with 5% water.

<table>
<thead>
<tr>
<th>Water %</th>
<th>Relative CO$_{ad}$ intensity / % (Ru/Al$_2$O$_3$ / Ru/zeolite)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SR-ref 6000</td>
</tr>
<tr>
<td>0</td>
<td>100 / 100</td>
</tr>
<tr>
<td>5.0</td>
<td>91.5 / 82.0</td>
</tr>
</tbody>
</table>

Figure 34: DRIFT spectra recorded over 800 min during reaction on the Ru/Al$_2$O$_3$ catalyst in a) SR-ref 100; b) ID-ref 100 and c) CO$_2$-ref reformate gas containing 5% water (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, and 795 min, reaction temperature 190°C).
3.3. Results and discussion

**Figure 35**: DRIFT spectra recorded over 800 min during reaction on Ru/zeolite catalyst in a) SR-ref 100, b) ID-ref 100 and c) CO\textsubscript{2}-ref reformate gas containing 5% water (from bottom to top: 0, 1, 2, 3, 5, 7, 15, 35, 105, 195, 345, 495, 645, and 795 min, reaction temperature 190°C).

### 3.3.4.3 CO\textsubscript{2}-ref (CO\textsubscript{2} dissociation activity)

In addition to comparing the selectivity / CO\textsubscript{ad} formation in low-CO reformates with and without CO\textsubscript{2} present in the reaction gas (ID-ref 100 and SR-ref 100) and the effect of water hereon, we also investigated the effect of water on the CO\textsubscript{2} dissociation activity on the two catalysts in a CO free gas mixture containing 15.5% CO\textsubscript{2} (CO\textsubscript{2}-ref). Again we compared the reaction in dry gas and in reformate containing 5% water. In this case, the band related to CO\textsubscript{ad} solely results from CO\textsubscript{2} dissociation / conversion on the Ru NPs. Sequences of spectra
3.3. Results and discussion

recorded during exposure to CO$_2$-ref are presented in Fig. 34 for the Ru/Al$_2$O$_3$ catalyst and in Fig. 35 for the Ru/zeolite catalyst (bottom panel). The time evolution of the band intensities related to linearly adsorbed CO is illustrated again in Fig. 36 (left panels: Ru/Al$_2$O$_3$, right panels: Ru/zeolite, upper panels: dry reformate, lower panels: 5% water).

Figure 36: Time evolution of the band intensity of linearly adsorbed CO on the Ru/Al$_2$O$_3$ catalyst (left panel), and on the Ru/zeolite catalyst (right panel) during reaction in dry (a, c) and 5% water containing (b, d) reformate gas mixtures (■: SR-ref 6000, ●: SR-ref100, ▼: ID-ref 100, △: CO$_2$-ref, reaction temperature 190°C).

Both in the absence and presence of H$_2$O, the CO$_{ad}$ intensity reaches steady-state after 200 – 400 min on stream, similar to the behavior in the other gas mixtures in Fig. 36. In both cases the CO$_{ad}$ intensity, which results from the dissociation of CO$_2$, is lower than the CO$_{ad}$ intensity in SR-ref 100 and ID-ref 100 (see Table 12).

For the Ru/Al$_2$O$_3$ catalyst, the intensity of the CO$_{ad}$ species in dry CO$_2$-ref reaction gas is almost equal to that in SR-ref 100 and SR-ref 6000 reformates, and higher than the CO$_{ad}$ band intensity in ID-ref 100. Apparently, despite the absence of high CO concentrations, CO$_{ad}$ forms a monolayer which can block active sites and thus inhibit the methanation reaction.
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This observation is in good agreement with earlier reports, where the high CO\textsubscript{ad} coverage was explained by a high activity of larger Ru NPs for the dissociation of CO\textsubscript{2} to CO\textsubscript{ad} and O\textsubscript{ad} species\textsuperscript{72}. In the presence of 5% water, the CO\textsubscript{ad} intensity in CO\textsubscript{2}-ref decreased to a similar intensity as that of SR-ref 100. This observation fits to the kinetic results, where an increasing water concentration led to a higher CO selectivity on the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst, which is essentially unselective under dry reaction conditions\textsuperscript{67,68}.

In recent steady-state isotope transient kinetic analysis (SSITKA) experiments we could show, however, that the CO\textsubscript{2} methanation reaction on the Ru/zeolite and the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst does not proceed via a formate based mechanism, but presumably via dissociative adsorption of CO\textsubscript{2}\textsuperscript{72}. In separate kinetic experiments it could also be excluded that the reverse water gas shift (RWGS) reaction contributes significantly to the CO\textsubscript{2} methanation reaction. Following our previous mechanistic proposal for the selectivity of Ru/zeolite catalyst\textsuperscript{71,72,62,168} the extremely low CO\textsubscript{ad} intensity in CO\textsubscript{2}-ref on that catalyst is explained by an inherently low activity of the highly dispersed Ru NPs (mean diameter 0.9 -1.0 nm) for the dissociation of CO\textsubscript{2}\textsuperscript{62,168}.

The lower activity of very small Ru NPs can be understood in terms of the Brønstedt–Evans–Polanyi (BEP) concept\textsuperscript{162}. On larger Ru NPs the dissociation products of CO\textsubscript{2} (CO\textsubscript{ad} + O\textsubscript{ad}) are better stabilized compared to very small NPs, which is supported also by the very low CO\textsubscript{ad} band intensity on the Ru/zeolite catalyst in ID-ref 100 and SR-ref 100, which is much lower than what was observed on the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst.

This stabilization of the final state should lower also the energy of the transition state, and consequently the barrier for CO\textsubscript{2} dissociation. For the Ru/zeolite catalyst with its very small Ru NPs, additional effects of H\textsubscript{2}O on the CO\textsubscript{ad} intensity resulting from CO\textsubscript{2} dissociation are small. For the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst, which exhibits a considerable activity for CO\textsubscript{2} dissociation under dry conditions, the addition of water resulted in a significant decrease in the activity for CO\textsubscript{2} dissociation. This agrees perfectly with the H\textsubscript{2}O induced decrease of the Ru NPs derived from TEM imaging and in particular from the in situ EXAFS measurements.

Following this argumentation, the presence of water lowers the reaction rate for CO\textsubscript{2} conversion in SR-ref 100 reformate via a H\textsubscript{2}O induced Ru-Ru bond breaking (see section 3.3.3) and a resulting decrease of the Ru NP size. This way, the selectivity for CO methanation increases with increasing H\textsubscript{2}O content. This behavior can also be observed here.
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3.3.5 Mechanistic consequences of the addition of H₂O

The data presented in the preceding sections clearly demonstrate that the presence of water vapour in the reaction gas mixture, which is characteristic also for technical applications of the SelMeth reaction, results in a more or less pronounced decay in activity, depending on the CO content and on the catalyst, and in a significant improvement of the selectivity for CO methanation of the Ru/Al₂O₃ catalysts at low CO partial pressures. Under these latter conditions, which are typical for the catalyst at the end of a methanation stage, the selectivity is rather poor in dry reformate, e.g., at around 40% at 100 ppm CO and 15.5% CO₂, but increases to 100% at 30% water content. On the Ru/zeolite catalyst, where the selectivity is already 100% in dry reformate under these conditions, the addition of water vapour does not affect the selectivity.

As mentioned in the introduction, a water induced modification of the methanation of CO/CO₂ containing reformates had been observed already earlier on Ru and also on Rh catalysts by Panagiotopoulou and his coworkers.⁶⁷–⁶⁸ They observed decay in the activity for the conversion of CO/CO₂ mixtures with increasing water content in the reaction gas mixture, which was mainly caused by a decrease in CO₂ conversion with increasing water content, while the CO conversion remained stable. They explained this by a competition of H₂O and CO, which is produced as reaction intermediate, and also CO₂ for the same adsorption sites. Furthermore, they assumed that the methanation of CO₂ molecules proceeds via the reverse water gas shift reaction, where water is a reaction product, and explained the low CO methanation activity by a decreasing RWGS activity with increasing water content in the feed.

The latter assumption is in contradiction with previous reports which stated that on Ru catalysts the RWGS is active only at temperatures above 300°C,⁷¹,⁸⁰ and with own measurements of the WGS activity of the Ru/Al₂O₃ and the Ru/zeolite catalyst in 30% H₂O and 0.6% CO, balance H₂. At 190°C reaction temperature both catalysts were inactive for the WGS reaction. Since the WGS reaction is known to start at much lower temperatures than the RWGS reaction,¹⁸⁶ it is highly unlikely that CO₂ methanation proceeds via the RWGS reaction at present reaction temperatures.

Blocking of active sites for CO methanation by adsorption of H₂O seems to be unlikely in view of the considerably stronger adsorption of CO and hydrogen than H₂O on Ru. Considering, however, that the H₂O partial pressure is much higher than that of CO in these
measurements, site blocking by adsorbed H₂O molecules may play a role in the methanation reaction.

Nakamura et al. reported that the co-adsorption of water with CO at 20 K results in an abnormally red shifted CO band from 2145 to 1356 cm⁻¹ on a Ru(0001) surface for individual COₐd (‘singleton COₐd’) species surrounded by a H₂O bilayer.¹⁸⁷,¹⁸⁸ In our measurements we did not observe such a shift in the COₐd related band (see section 3.3.1), only a decrease of the COₐd band intensity with increasing water content. Nevertheless, the rather small decrease of the CO methanation activity with increasing water content in the more CO-rich SR-ref 6000 may at least partly be related to a competitive adsorption of CO and H₂O, and the related site blocking by adsorbed H₂O molecules.

The situation is different for CO₂ methanation. Although blocking of Ru active sites by adsorbed water molecules can hinder also the dissociation of CO₂, e.g., by reducing the number of sites available for CO₂ adsorption or for accommodating the dissociation products of CO₂ (COₐd + Oₐd), such site blocking effects should equally reduce the COₐd coverage and the CO₂ coverage, as long as there are no other effects which would be selectively reduce the CO₂ₐd coverage. Therefore it appears unlikely that the drastic increase in selectivity in the low-CO reformate SR-ref 100 can mainly be rationalized by such kind of site blocking effects as described above.

We therefore favor a different mechanistic explanation, which is closely related to the mechanistic model proposed recently to explain the complete selectivity of the Ru/zeolite catalyst even in reformate gas mixtures with a very low CO content (SR-ref 100).⁷² According to that model the high selectivity of the Ru/zeolite catalyst for CO methanation, in the presence of substantial amounts of CO₂ in the reaction gas mixture, is due to an intrinsically low activity of very small Ru nanoparticles for CO₂ dissociation as a first step for CO₂ methanation.⁷² In contrast, for the Ru/Al₂O₃ catalyst, where larger Ru nanoparticles prevail, the selectivity was attributed to a site blocking effect, where adsorbed CO molecules block active sites for the adsorption and dissociation of CO₂. In the latter case, the selectivity depends sensitively on the CO content in the reaction gas, which agrees fully with the decreasing selectivity for CO methanation with decreasing CO content in the gas mixture, down to 42% in SR-ref 100 observed for the Ru/Al₂O₃ catalyst. The gain in selectivity with decreasing Ru particle size was explained by a decreasing inherent activity for CO₂ dissociation for these particles, due to an increasing energy barrier for CO₂ dissociation.
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Following the Brønstedt-Evans-Polanyi (BEP) relation, the latter is supported by the decreasing stabilization of the reaction product CO$_{ad}$ on smaller Ru NPs (see section 3.3.3). A similar particle effect is proposed also as physical origin for the increasing selectivity for CO methanation (= decreasing activity for CO$_2$ methanation) of the Ru/Al$_2$O$_3$ catalyst with increasing water content in the reaction gas mixture. In this case, it is induced by the additional interaction with water during the reaction, rather than by stabilization by the zeolite pores. The observed water induced decrease of the mean Ru particle size, from 2.0 in dry ID-ref 6000 reformate to 1.48 nm / 1.2 nm for Ru/Al$_2$O$_3$ in the presence of 5% / 15% water vapor, fits even quantitatively to the improved selectivity. Assuming that at 30% water content the Ru particle size on the Ru/Al$_2$O$_3$ catalyst during reaction is even below 1.2 nm, the Ru particle size required for 100% selectivity for CO methanation in SR-ref 100 mixture is very similar to that of the Ru/zeolite catalyst in dry SR-ref 100 reformate (Ru particle size 1.0 nm), where also 100% selectivity are reached. Similar to the present findings for the Ru/Al$_2$O$_3$ catalyst in H$_2$O containing reaction gas, the selectivity of the Ru/zeolite catalyst (in dry, low-CO SR-ref 100 reaction gas mixture) was found to decrease with increasing particle size.

In combination these findings strongly support a particle size effect as physical origin for the improved selectivity for CO methanation of the Ru/Al$_2$O$_3$ catalyst with increasing water content in the reformate gas mixture. For the Ru/zeolite catalyst, in contrast, the selectivity in low-CO reformate gas mixture is not affected by the addition of water vapour to the reaction gas, since already in dry reaction gas the Ru particle size is small enough (ca. 1 nm) to reach 100% selectivity under these conditions (100 ppm CO).

3.3.6 Conclusions

Employing a combination of kinetic measurements, in situ EXAFS and in situ DRIFTS measurements, we have investigated the impact of water on the activity and selectivity for CO methanation in the selective methanation of CO in CO$_2$-rich reformate gases on Ru/Al$_2$O$_3$ and Ru/zeolite catalysts. The results of these measurements and comparison with findings in previous studies led us to the following main findings and conclusions:

1. At higher CO concentrations (6000 ppm), the addition of up to 30% water to the reformate gas (15.5% CO$_2$) leads to a decrease in activity for both catalysts, but does not affect the selectivity. The latter stays at 100%, independent of the water content. This is attributed to a blocking of sites for the dissociative adsorption of CO$_2$ on the Ru nanoparticles, which is considered as intermediate step for CO$_2$ methanation, by CO$_{ad}$.
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2- At low CO concentrations (100 ppm), the addition of up to 30% water to the reformate gas also causes a decrease in activity for both catalysts, but in this case the decay is much more pronounced for the Ru/zeolite catalyst. Furthermore, it results in a distinct modification of the selectivity for CO methanation on the Ru/Al₂O₃ catalyst, where it increases from 42% (dry reformate gas) to 100% in the presence of 30% water in the reformate gas mixture. On the Ru/zeolite catalyst, where the selectivity is already at 100% in dry reformate gas, addition of water does not cause any changes therein.

3- The increased selectivity in the presence of water in the reformate gas, in particular at low CO contents, goes along and is attributed to a water induced decay in the mean Ru particle size, which is very pronounced for the Ru/Al₂O₃ catalyst (from 2.0 nm in dry reformate to 1.48 / 1.2 nm in the presence of 5 / 15% H₂O in the reaction gas), while for the Ru/zeolite, where the Ru particles are very small already in dry reaction gas, this effect is less pronounced (1.0 nm in dry reformate to 0.86 nm in the presence of 5% H₂O in the reaction gas).

4- The higher selectivity for CO methanation with decreasing Ru particle size agrees fully with our earlier mechanistic interpretation that the high selectivity of Ru/zeolite catalysts (in dry reaction gas) is largely due to the much smaller size of the Ru nanoparticles on this catalyst compared to those on a Ru/Al₂O₃ catalyst, which essentially inhibits the conversion of CO₂ to CO even in the absence of a site blocking CO adlayer. In the present case

5- We suggest that the decay in Ru particle size is caused by an oxidative disruption process, which may be assisted by the presence of CO, and the subsequent reduction of very small oxidized Ru nanoparticles / clusters by reaction with hydrogen present in the reaction gas atmosphere.

6- For both Ru catalysts the relative CO₆d band intensity was found to decrease with increasing amount of water in the reaction gas mixture (SR-ref 6000). This is tentatively attributed to a competitive adsorption of water molecules on CO adsorption sites, which explains also the observed decrease in the Ru mass normalized reaction rate with increasing water content.

7- The higher magnitude of the relative decrease in activity observed for the Ru/zeolite catalyst compared to the Ru/Al₂O₃ catalyst is tentatively explained by a dominant site blocking effect due to H₂O adsorption for the former catalyst, while for the Ru/Al₂O₃ catalyst this is counteracted and largely compensated by the decrease in Ru particle size.
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The latter results in a higher Ru surface area and also in electronic modifications, as evidenced by the decreasing tendency for CO₂ dissociation and the decreasing COₐd adsorption energy.

Overall this work has demonstrated that increasingly realistic reaction conditions, in this case the presence of significant amounts of water vapor in the reformate gas, result in a considerable improvement of the selectivity of the Ru/Al₂O₃ catalyst, which is little selective in dry reformate at very low CO contents, while the Ru/zeolite catalyst maintains its 100% selectivity also under these conditions.
3.4 Improved performance of Ru/γ-Al₂O₃ catalysts in the selective methanation of CO in CO₂-rich reformate gases upon transient exposure to water containing reaction gas

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D. Widmann and S. Eckle have contributed to this work by discussions and helped in the revision and improvement of the first draft of the manuscript.
3.4. Results and discussion

3.4.1 Introduction

Several groups have recently investigated the impact of technically relevant amounts of water in the reaction gas mixture (up to 30%) on the catalytic activity and selectivity of supported Ru catalysts for the selective CO methanation in the presence of significantly large amounts of 15.5% CO₂ in the reaction feed gases. 67,68,71,80,82,189

For a Ru/γ-Al₂O₃ catalyst it could be demonstrated in section 3.3 that the presence of 5% to 30% H₂O in the reaction atmosphere (CO / CO₂ / H₂) results in i) significantly smaller Ru nanoparticles and ii) much higher selectivities for the CO methanation compared to activation and reaction under strictly dry conditions (0% H₂O). Furthermore, we found a direct correlation between the water content in the reaction atmosphere, the Ru particle size, and the selectivity towards CO methanation. With increasing water content in the reaction feed the Ru particle size decreased and simultaneously also the rate for CO₂ dissociation decayed, leading to a lower CO₂ methanation rate. The CO methanation rate also decreased with increasing water content, but at a much lower extent. Therefore, this results in an overall higher CO selectivity.

This is in accordance with a mechanistic picture which we derived earlier for reaction under dry conditions over Ru/zeolite catalysts, 62,168,168 where we explained the higher selectivity for CO methanation of small Ru nanoparticles by their lower activity for CO₂ dissociation and, hence, CO₂ methanation. The activity for CO methanation on Ru/Al₂O₃, in contrast, was slightly lower under wet reaction conditions than under dry conditions, most probably due to the competitive adsorption of CO and H₂O during reaction and, hence, lower COₐd coverages in wet reaction conditions than under dry conditions. 189

In the present study we expanded on the investigations presented in section 3.2 and are mainly interested in further clarifying the origin of the increased selectivity in the presence of water, which may not be exclusively attributed to the decrease of the Ru particle size. For instance, water may also lower the CO₂ methanation activity by blocking active sites for (dissociative) CO₂ adsorption and reaction. Second, we are interested in the stability of the small Ru particles created in the presence of water after changing to a water free-gas mixture. This may be crucial from a technical point of view, if one wants to use a transient water treatment for catalyst reactivation. Finally, changing the Ru nanoparticles dispersion in the presence of water vapor may result also in changes in the adlayer when going from wet to dry reaction gas mixtures. This may, however, also change the CO / CO₂
methanation activities (under dry reaction conditions) and, hence, lead to changes in the selectivity.

In order to disentangle the effects caused by the activation of the catalyst (under dry and wet conditions) and those occurring during subsequent reaction in different, wet and dry reaction atmospheres, we performed transient measurements, following changes in the catalytic performance of a Ru/γ-Al₂O₃ catalyst due to changes in the reaction atmosphere, upon switching between wet and dry reaction conditions and vice versa, together with changes in the catalyst structure and chemical state.

Following this approach, the catalysts were always first dried in N₂ at 150 °C, similar to the procedure in our previous studies, and afterwards activated by heating to 190 °C in either dry reaction feeds or reaction feeds containing different amounts of water (up to 15%). In the latter case, water was subsequently bypassed and a dry reaction gas mixture was admitted to the catalysts in order to identify changes in activity and selectivity resulting from the activation under wet conditions. The reaction behavior was characterized by combined kinetic and in situ IR spectroscopic measurements (diffuse reflection FTIR spectroscopy – DRIFTS). Furthermore, the evolution of the Ru particle size and oxidation state was determined using in operando EXAFS and ex situ TEM measurements at different stages of the reaction.

In the following, we will first evaluate the influence of activation and temporary reaction in wet reaction gas mixture on the reaction characteristics and the structure (Ru particle size) of the catalyst in subsequent reaction in dry atmosphere. Here exposure to wet reaction gas takes place during Ru nanoparticle formation. Second, we performed similar sequences of measurements on a catalyst which was first activated in dry reaction atmosphere to form reduced metallic Ru nanoparticles before addition of water vapor, followed by subsequent change back to dry reaction gas. In the third section we finally present and discuss changes in the adlayer as detected by in situ Infrared spectroscopy during similar reaction sequences, and during exposure to a CO₂/H₂ mixture to evaluate the activity of the catalyst for CO₂ dissociation under these reaction conditions.

### 3.4.2 Activation of Ru/Al₂O₃ under wet conditions

We will start by measuring and comparing the activity and selectivity for CO methanation over the Ru/Al₂O₃ catalyst in dry reformate gases containing medium or low CO concentrations together with large amounts of CO₂ (SR-ref 6000: 0.6% CO, SR-ref 100:
Results and discussion

3.4.2.1 Activity / selectivity of Ru/Al₂O₃ in medium CO reformate (SR-ref 6000)

Fig. 37a shows the result of the reference measurement, illustrating the activity in SR-ref 6000 during 1000 min time-on-stream under dry reaction conditions, after drying the catalyst in N₂ at 150°C for 30 min and subsequent activation of the catalyst in a dry reaction atmosphere during the temperature increase to 190°C. This resulted in a Ru mass normalized activity of $4.4 \times 10^{-6}$ mol g$_{Ru}$⁻¹ s⁻¹ and no deactivation during 1000 min reaction (Table 13), which agrees closely with results of measurements on an identical Ru/Al₂O₃ catalyst under comparable activation / reaction conditions.² In the presence of 6000 ppm CO in the reaction feed the selectivity is always 100% (CO conversion ~ CH₄ formation), since under those conditions the selectivity is governed by site blocking of the active sites for CO₂ adsorption and dissociation by adsorbed CO species, which completely cover the surface.

To determine the effect of activating the catalyst under wet reaction conditions, we next measured the activity of the same catalyst after drying in N₂ for 30 min at 150°C (as usual) followed by activation of the catalyst in SR-ref 6000 reformate gas containing 5 and 15% water, respectively, while the temperature was increased to 190°C within 10 min (activation), and finally followed by 750 min reaction under similar conditions (see Figs. 37b and 1c; left panels). In the presence of water in SR-ref 6000 reformate the catalyst showed CH₄ formation rates of 4.1 and $4.2 \times 10^{-6}$ mol g$_{Ru}$⁻¹ s⁻¹ for 5% (W1) and 15% H₂O (W2), respectively (Table 13). These values are only slightly lower than the rate measured under dry conditions. Hence, differences in the activity between operation under dry or wet conditions, after preceding activation in the same reaction mixture, are rather small. This trend and also the absolute rates are consistent with our earlier results on the effect of increasing water concentrations on the CO activity in SR-ref 6000 on an identical catalyst used in the previous chapter ($4.5$ and $4.3 \times 10^{-6}$ mol g$_{Ru}$⁻¹ s⁻¹).

After 750 min reaction in a wet atmosphere containing 5% and 15% water, respectively, we changed to dry reaction gas mixture by switching off the wet reaction gas mixture from the micro-reactor, by bypassing the reactor. After 30 min waiting time (constant for all
3.4. Results and discussion

similar switching experiments), where the catalyst was left standing in the initial wet reaction gas, the catalyst was exposed to a dry reaction gas mixture (SR-ref 6000, D1 and D2 after preceding reaction with 5% or 15% H₂O, respectively). We tested in a separate experiment the effect of purging the reactor by dry N₂ for the same period of time (30 min) instead of keeping it in reaction gas mixture, and found only a slightly lower (17%) steady state activity in that case (for more information see Appx, Fig. S6).

**Figure 37**: Ru mass normalized CO methanation rates at 190°C in SR-ref 6000 reformate during 1000 min on stream a) in the absence of water (D, ○), b) in the presence of 5% H₂O (W1, ●), and c) in the presence of 15% H₂O (W2, ●), as well as during subsequent reaction in dry SR-ref 6000 (D1, D2, ○).
Table 13: Steady-state CH₄ formation rate (~CO conversion) on a Ru/γ-Al₂O₃ catalyst in SR-ref 6000 reformate before (W) and after (D) the switch from wet to dry reaction conditions.

<table>
<thead>
<tr>
<th>H₂O/ %</th>
<th>Flow / Nml min⁻¹</th>
<th>W – Rate / 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹</th>
<th>D - Rate / 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹</th>
<th>TOF / 10⁻³ s⁻¹ (W / D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>41.6</td>
<td>---</td>
<td>4.4</td>
<td>--- / 1.33</td>
</tr>
<tr>
<td>5</td>
<td>42.9</td>
<td>4.1</td>
<td>7.6</td>
<td>0.83 / 1.67</td>
</tr>
<tr>
<td>15</td>
<td>46.6</td>
<td>4.2</td>
<td>7.5</td>
<td>0.71 / 1.39</td>
</tr>
</tbody>
</table>

* TOF values are based on dispersion of Ru measured by EXAFS during wet measurements (Table8)

After having changed again to dry SR-ref 6000 feed, the catalyst activity for CO methanation is significantly higher than before under wet reaction conditions (Figs. 37b and 1c). Moreover, it is also significantly higher compared to the rate for reaction under dry conditions after activation of the catalyst under dry reaction conditions (Fig. 37a). Compared to activation in dry conditions, a ~ 3-fold higher initial activity was observed (Figs. 37b and c; right panels). This activity decayed with time on stream until it levelled off about 200 min after the switch from wet to dry conditions to reach a steady-state activity which is still by a factor of ~ 1.8 higher (D1: 7.6 x 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹; D2: 7.5 x 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹) than the corresponding steady-state rate after activation and operation under dry reaction conditions (D: 4.4 x 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹). These results indicate already that a significantly different catalyst state is reached after activation under dry and wet reaction conditions. A likely explanation for the physical origin of these differences is that the different activation procedures result in different particle sizes, with smaller Ru nanoparticles after activation under wet reaction conditions.

3.4.2.2 Activity / selectivity of Ru/Al₂O₃ in low-CO reformate (SR-ref 100)

In the light of our previous findings smaller Ru particles should result also in significantly enhanced selectivities in SR-ref 100 after activation under wet reaction conditions, given the lower activity for CO₂ methanation of smaller Ru particles. For testing this we performed similar measurements as described above in SR-ref 100 gas mixture. In this case the low CO concentration in the reaction atmosphere results in a rather low CO ad coverage, far below the surface saturation coverage,⁷² which allows for testing the intrinsic selectivity of the Ru nanoparticle catalyst in the presence of high CO₂ concentrations.
3.4. Results and discussion

Also in this case we first performed a reference measurement in dry SR-ref 100, following the activation of the catalyst by heating over 10 min from 150°C (after drying) to 190°C in the dry reaction feed. The catalyst behavior is drastically different compared to reaction in SR-ref 6000, showing only a poor selectivity for CO conversion (Fig. 38a). The observed CO\textsubscript{2} methanation activity under-steady state conditions is $14.0 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1} (Table 14) compared to $9.9 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1} for the methanation of CO, resulting in an overall CO selectivity of only 41%. Previous measurements on an identical catalyst showed about similar reaction rates and selectivities (see results in 3.3.1). The significantly higher CO reaction rates in SR-ref 100 compared to that observed in SR-ref 6000 reflects the negative reaction order of CO in the CO methanation over supported Ru catalysts under these reaction conditions reported earlier.\textsuperscript{71}

The impact of activating the catalyst in wet reformate was tested in a similar way as described above, by first exposing the catalyst to SR-ref 100 containing different amounts of water (activation and reaction until reaching steady-state conditions), and afterwards switching to dry SR-ref 100. In the presence of 5 and 15% water the rate of CO\textsubscript{2} methanation quickly assumed values of 2.7 and $0.9 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1} and, hence, much lower compared to dry SR-ref 100. The CO reaction rate, in contrast, was slightly higher in the presence of water ($11.4$ and $12.3 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1}), with changes with time being negligible. This results in much higher selectivities of 81 and 93% respectively (Figs. 38b and 2c, right panels) compared to 41% upon reaction in dry SR-ref 100 (Fig. 38a). These changes of the selectivity in the presence of water are consistent with earlier results over Ru/Al\textsubscript{2}O\textsubscript{3} where the reaction occurred continuously in the presence of similar amounts of water (see results in 3.2.1).

The poor selectivity of the catalyst after drying only, in dry SR-ref 100 reformate, results from the rather high rate of CO\textsubscript{2} methanation, which is significantly higher than that for CO methanation (see above). After changing back again from the water containing reaction gas mixture (SR-ref 100 + 5% H\textsubscript{2}O) to water free SR-ref 100, the rate of CO methanation as well as the rate of CO\textsubscript{2} methanation increased slightly, from $11.4 \times 10^{-6}$ to $11.9 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1} and from $2.7 \times 10^{-6}$ to $2.9 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1}, respectively (Figs. 38b and 8c, left panels; Table 14). For switching from SR-ref 100 + 15% H\textsubscript{2}O to the dry SR-ref 100 gas mixture, these changes were somewhat more pronounced than for the change from SR-ref 100 + 5% H\textsubscript{2}O, with the rate of CO methanation increasing from $12.3$ to $13.3 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1} and that of CO\textsubscript{2} methanation increasing from $0.9 \times 10^{-6}$ to $1.9 \times 10^{-6}$ mol g\textsubscript{Ru}\textsuperscript{-1}s\textsuperscript{-1}. 

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Figure 38: Ru mass normalized reaction rates (left panels, CO methanation: ■, □, CO\(_2\) methanation: ▼, ▼) and selectivities (right panels, ▲, ▲) at 190°C a) in dry SR-ref 100 (□, ▼, ▲), b) in the presence of 5% (■, ▼, ▲) and c) in the presence of 15% H\(_2\)O (■, ▼, ▲), as well as during subsequent reaction in dry SR-ref 100 (b, c): □, ▼, ▲).
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Hence, it is mostly the increase in the rate of CO\textsubscript{2} methanation which is responsible for the decrease of selectivity from 93 to 88 upon going to water free reformate. In both cases, however, the selectivity for CO methanation in dry reaction gas is still rather high (80\% and 88\%) for the catalysts activated and operated in the presence of 5 and 15\% water, respectively. In fact, the selectivity is similar to that observed during reaction in the presence of 5 and 15\% water, and much higher than observed for reaction in dry SR-ref 100 after only drying in N\textsubscript{2} (Fig. 38).

It is tempting to explain the lower rate for CO\textsubscript{2} conversion as well as the increase of CO conversion, which are characteristic for small Ru nanoparticles, by an increase of the Ru dispersion during reaction in wet reformate, which persisted after changing back to dry reformate. In order to test this idea, we examined the Ru particle size by TEM measurements once after activation and reaction in dry reaction feed and once after activation and subsequent reaction (750 min) in wet reformate (15\% H\textsubscript{2}O), followed by reaction in dry reaction feed. The particle size distributions presented in Fig. 39 clearly show that the mean Ru particle size of a catalyst activated and operated in dry reaction gases (ID-ref 6000) is about 2.2 nm, in agreement with findings in previous studies on the same catalyst, while it is only 1.6 nm for a catalyst which was first exposed to ID-ref 6000 containing 15\% H\textsubscript{2}O during activation and during reaction for 750 min, followed by reaction in dry ID-ref 6000 reformate for 1000 min. Obviously, activation of the catalyst and subsequent reaction in wet reformate results in a much smaller Ru particle size which is maintained also during the subsequent reaction under dry conditions. These structural results provide a simple and straightforward explanation for the findings of a higher Ru mass normalized activity and selectivity for CO methanation under dry reaction conditions after activation in wet reformate than after activation in dry reformate.

These above observations in combination agree fully with a mechanistic model that we have proposed in a number of previous studies, where we had observed an increase in CO selectivity / decrease in CO\textsubscript{2} methanation rate with a decreasing Ru particle size (increasing dispersion).\textsuperscript{168} According to that model the decrease of Ru particle size results in an increase of the energy barrier for the dissociation of CO\textsubscript{2}, which originates from a decreasing stabilization of the dissociation products, in particular CO\textsubscript{ad} on the smaller metal particles, as explained by the Evans-Brønstedt-Polanyi (BEP) relationship.\textsuperscript{162} This results in a decrease of the CO\textsubscript{2} dissociation rate and subsequently of the CO\textsubscript{2} methanation rate.
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Table 14: Steady-state activity and selectivity over a Ru/γ-Al₂O₃ catalyst in SR-ref 100 reformate upon changing between wet (W) and dry (D) conditions and vice versa.

<table>
<thead>
<tr>
<th>H₂O / %</th>
<th>Dry (D1)</th>
<th>Wet (W)</th>
<th>Dry (D2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rate (CO / CO₂) / 10⁻⁶ mol g⁻¹ Ru s⁻¹</td>
<td>Sel. / %</td>
<td>Rate (CO / CO₂) / 10⁻⁶ mol g⁻¹ Ru s⁻¹</td>
</tr>
<tr>
<td>0</td>
<td>9.0 / 14.0</td>
<td>41</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>---</td>
<td>---</td>
<td>11.4 / 2.7</td>
</tr>
<tr>
<td>15</td>
<td>---</td>
<td>---</td>
<td>12.3 / 0.9</td>
</tr>
<tr>
<td>15</td>
<td>11.6 / 12.2</td>
<td>46</td>
<td>11.8 / 2.1</td>
</tr>
</tbody>
</table>

Figure 39: TEM images and Ru particle size distributions on the Ru/Al₂O₃ catalyst a) after activation and reaction (1000 min) at 190°C in dry SR-ref 6000, and (b) after activation and reaction (700 min) in SR-ref 6000 in the presence of 15% water followed by 800 min reaction in dry reaction feed at 190°C.
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To further test the stability of the small Ru particles formed in the presence of water under subsequent dry reaction conditions, we performed an additional long-term kinetic experiment, during which the catalyst was first activated and operated (170 min) in the presence of water (SR-ref 6000 + 15% H₂O), before the reaction was run for 80 hours in dry SR-ref 6000 (see Appx, Fig. S7). Again, the catalyst activity was much higher compared to that of a catalyst activated under dry reaction conditions, and there was almost no deactivation with time-on-stream after the initial 200 min after the switch from wet to dry conditions. Even after 80 hours reaction in dry SR-ref 6000 the activity was still higher by a factor of ~1.8 compared to that of a catalyst activated and operated under dry conditions only, providing clear evidence for the high stability of the small Ru particles formed upon interaction with the wet reaction gases during subsequent operation in dry reformate. Hence, the increase of Ru dispersion in the presence of water during the methanation reaction is largely irreversible under present reaction conditions.

Although the dispersion of Ru in case of reaction in the presence of 15% H₂O is higher (59%) than the dispersion resulting from reaction in the presence of 5% H₂O (48%) in the reaction gas mixture, the activity increase compared to a catalyst activated in dry reaction conditions in both cases is about the same both during the initial reaction phase and at steady state. This can be explained by the lower turnover frequency (TOF) in case of the higher dispersion, resulting from running the catalyst in the presence of 15% H₂O, whereas higher TOF values are observed over larger Ru particles formed in the presence of 5% H₂O. Thus the gain in reactivity due to a higher dispersion is counterbalanced by the lower intrinsic activity (TOF) which decreases with decreasing Ru particle size / increasing dispersion. Similar effects were reported in refs. 64,66,68,71,107,108,168

In total, activating the dried catalyst (after drying in N₂ at 150°C) first in wet reaction gas (5% and 15% H₂O at 190°C) and subsequent reaction in dry reformate results in a significantly higher activity and selectivity for CO methanation than obtained for the same reaction after activation and reaction in dry reformate directly. TEM images revealed that the smaller Ru particles obtained by activation and reaction under wet reaction conditions (particle size 1.6 nm) as compared to activation plus reaction under dry conditions (particle size 2.2 nm) are maintained also during the subsequent reaction in dry reformate, at least for up to 80 hours reaction. The ‘irreversible’ change of the Ru particle size is held responsible for the higher activity and selectivity of a catalyst activated in wet reformate as compared to a catalyst activated in dry reformate.
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3.4.3. Wet activation of pre-reduced Ru/Al₂O₃

In the previous section we had tested the influence of wet activation on the activity / selectivity of the Ru/Al₂O₃ catalyst in the subsequent methanation of CO in dry reformate. In that case, the wet activation includes and may dominate the process of Ru nanoparticle formation. In this section we will, in contrast, investigate the effect of exposing a completely reduced catalyst, which has previously been activated by exposure to dry reaction gas, to wet reformate. As described above, activation under dry conditions results in rather large Ru nanoparticles with an average diameter of 2.2 nm and a selectivity of only 41% in SR-ref 100 reformate. The experiments are performed in the same way as described above, operating the catalyst in SR-ref 6000 to follow changes in the activity and in SR-ref 100 to test the CO selectivity.

3.4.3.1 Activity / selectivity of Ru/Al₂O₃ in medium CO reformate (SR-ref 6000)

The catalyst was first activated and operated in dry SR-ref 6000 reformate (D1) for 180 min, then it was exposed to wet reformate gas by introducing water directly to the gas mixture (W; SR-ref 6000 + 15% H₂O). After 550 min reaction water was removed from the reaction atmosphere and the reaction was performed once again in dry SR-ref 6000 (D2), using the same procedure for gas exchange as described above (see chapter 3.4.2.1).

The activity measured in the initial dry run (D1) is similar to that in Fig. 37a (4.2 x 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹) and remained almost unchanged when adding 15% of water to the reaction atmosphere (W1, 4.5 x 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹) (Fig. 40). Upon changing back to dry reaction conditions (D2), however, the CO methanation activity first increased to 15.1 x 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹ and then reached a steady-state activity of 7.7 x 10⁻⁶ mol g⁻¹ Ru⁻¹ s⁻¹ after ~200 min.

As described above, the selectivity in SR-ref 6000 is always 100%, independent of the presence or absence of water. Obviously, the activity of the Ru/Al₂O₃ catalyst in dry SR-ref 6000 reformates depends fully on whether the catalyst was exposed for a longer time to wet reformate or not. In the end it does not matter whether the exposure to wet reformate occurred in the initial activation phase, during Ru nanoparticle formation, or whether this happened in a later stage, after activation and Ru nanoparticle formation had been finished already. Keeping in mind that activation under dry conditions results in rather large Ru nanoparticles (D1, mean Ru particle size of 2.2 nm), the comparably higher reaction rates under dry conditions after exposure to water containing reformate, under otherwise identical reaction conditions (D2), clearly indicate that there was a re-dispersion of Ru nanoparticles during reaction in the presence of water. In that case, regardless of the initial
state of the catalyst, the addition of water to the reaction atmosphere always results in the formation of smaller Ru nanoparticles as compared to activation / reaction under dry reaction conditions.

3.4.3.2 Activity / selectivity of Ru/Al₂O₃ in low CO reformate (SR-ref 100)

Following the same approach as described above, the selectivity was tested in the same sequence in SR-ref 100 by subsequently exposing the Ru/Al₂O₃ catalyst to i) dry, ii) wet, and again iii) dry reaction gas, where the first exposure to dry gas included the initial activation. The corresponding rates and selectivities are shown in Fig. 41 and listed in Table 14. After activation in the absence of water, the selectivity in dry SR-ref 100 (D1) is 46 % and thus close to the value reported previously for the same catalyst.\(^7\) Two The addition of 15% H₂O to the reaction atmosphere resulted in an overall CO selectivity of 85 % (W; after 150 min). This increase in selectivity originates mainly from a significant decrease in the activity for CO₂ methanation, from 12.2 x 10⁻⁶ under dry conditions to 2.1 x10⁻⁶ mol g\(_{Ru}^{-1}\) s⁻¹ in the presence of 15% water. The rate for CO methanation, in contrast, remained almost unchanged. Upon changing back again to the dry SR-ref 100 gas mixture (D2), the rate for CO methanation increases from 11.8 x 10⁻⁶ to 15.6 x 10⁻⁶ mol g\(_{Ru}^{-1}\) s⁻¹. In parallel, the rate of CO₂ methanation and, hence, CO₂ dissociation decreased to an even lower value of 1.6 x 10⁻⁶ mol g\(_{Ru}^{-1}\) s⁻¹ (Table 14). In total, this results in a further increase in CO selectivity from 85% (W) to 90% (D2).

**Figure 40:** Time on stream Ru mass normalized CO methanation rate at 190°C in dry SR-ref 6000 reformate (D1: ○), during subsequent reaction in the presence of water (W, 15% H₂O; ●), and after switching back to dry SR-ref 6000 reformate (D2: ○).
Hence, also these findings indicate that the increase of activity and selectivity for CO methanation under dry reaction conditions induced by the preceding activation / reaction in wet reaction gas is independent of whether the exposure to wet reformate occurred during Ru particle formation from oxidic Ru species, in the activation stage (Figs. 37-39) or subsequently for a catalyst with metallic Ru nanoparticles, which were formed during activation in dry gas feed (SR-ref 6000 or SR-ref 100).

**Figure 41:** Ru mass normalized reaction rates in steady-state (upper panel) (CO methanation: ■, □, CO₂ methanation: ▽, △) and selectivities (lower panel) (▲, △) at 190°C in dry SR-ref 100 (D1; □, ▽, △), during subsequent reaction in the presence of water (W, 15 % H₂O; ■, ▽, △), and after switching back to dry SR-ref 100 (D2, □, ▽, △) at 190°C.
3.4.4 Structural modifications of the Ru/Al₂O₃ catalyst

To support the conclusions on the Ru particle size derived in the previous two sections from kinetic data we performed time resolved \textit{in operando} EXAFS measurements during the reaction in dry ID-ref 6000, followed by a change to wet ID-ref 6000 (+ 5% H₂O) reformate gas over the Ru/γ-Al₂O₃ catalyst after heating and drying in N₂ at 150 °C for 30 min. First the measurement in dry reformate was run until reaching steady-state, where no more changes in activity and selectivity are observed (200 min). Afterwards the gas mixture was bypassed and saturated with 5% H₂O and changed back again into the reaction cell where EXAFS spectra were also recorded with time on stream up to 150 min.

Fig. 42 shows the EXAFS spectra for the Ru k-edge including \( k^3 \)-weighted chi functions in the \( k \)-range 3.2 - 13.3 Å\(^{-1} \) in the left panels (Figs. 42a - d) and the corresponding Fourier transforms in the \( r \)-space shown in the right panels (Figs. 42e - h). After introducing the wet gas mixture into the reaction cell, the amplitude of the chi-function decreased progressively with time-on-stream (Figs. 42b - d) compared to the amplitude observed in the absence of water (Fig. 42a). A characteristic peak at 2.672 - 2.665 Å in the Fourier transforms fits well to the distance of a Ru-Ru shell. Its amplitude was damped with time-on-stream after switching from dry to wet conditions.

\textbf{Table 15:} EXAFS fit procedure and structural parameters of Ru in dry ID-ref 6000 gas mixture (D) and at different time intervals after switching to ID-ref 6000 + 5 % H₂O feed (W1: 60 min; W2: 90 min; W3: 140 min).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>CN</th>
<th>( r / \text{Å} )</th>
<th>( DW / \text{Å}^2 )</th>
<th>( E_0 / \text{eV} )</th>
<th>Dispersion / %</th>
<th>( d_{\text{Ru}} / \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>8.91</td>
<td>2.665</td>
<td>7.27</td>
<td>3.23</td>
<td>35.6</td>
<td>2.01</td>
</tr>
<tr>
<td>W1</td>
<td>8.60</td>
<td>2.667</td>
<td>6.29</td>
<td>2.37</td>
<td>39.9</td>
<td>1.80</td>
</tr>
<tr>
<td>W2</td>
<td>7.94</td>
<td>2.675</td>
<td>6.42</td>
<td>3.76</td>
<td>47.3</td>
<td>1.44</td>
</tr>
<tr>
<td>W3</td>
<td>8.10</td>
<td>2.672</td>
<td>6.59</td>
<td>4.03</td>
<td>49.9</td>
<td>1.53</td>
</tr>
</tbody>
</table>
The structural parameters of Ru were extracted by evaluating the EXAFS data using standard procedures described elsewhere. The coordination number (CN) and other related structural parameters were obtained by fitting the EXAFS data of the first Ru-Ru shell with the calibrated Ru foil reference (see Table 15). In dry ID-ref 6000 reformate the Ru particles showed a CN of 8.9, which decreased upon the addition of water (i.e., upon switching from dry ID-ref 6000 to ID-ref 6000 + 5 % H₂O) gradually with time-on-stream to 8.1 after 150 min after the switch. The CN number reached after 150 min is very similar to the value obtained for a Ru/Al₂O₃ catalyst operated under identical conditions without any prior exposure to reaction in dry ID-ref 6000. The observed decrease of CN reflects a significant decrease in the Ru particle size / increase of the Ru dispersion upon adding water to the reaction gas, decreasing the size of the larger Ru nanoparticles formed during initial activation / reaction in dry reformate (see section 3.3.3).

The average particle diameter and the dispersion of the Ru NPs were calculated using a commonly employed relationship between CN and particle size defined elsewhere. This is based on the assumption of hemispherical Ru particles on the surface. In that case the mean Ru particle diameter decreased after changing to wet reformate with time-on-stream. Starting with 2.0 nm in dry ID-ref 6000 before the change, it reached a steady-state value of 1.53 nm about 140 min after switching from dry to wet ID-ref 6000 gas mixture (see Fig. 43).
3.4. Results and discussion

**Figure 42:** k3 weighted chi functions & Fourier Transforms (FT) recorded on the Ru/\(\square\)-Al\(_2\)O\(_3\) catalyst during reaction in ID-ref 6000 (a, e) and at various times after addition of 5% H\(_2\)O to the reaction gas mixture (b, f: 60 min; e, g : 90 min; d, h : 140 min) - solid line: EXAFS data; dashed line: fits.
3.4. Results and discussion

**Figure 43:** Ru particle sizes obtained from *in operando* EXAFS measurements during the CO methanation at 190 °C in dry ID-ref 6000 (D) and at various times after the switch from dry to wet reaction conditions (W1: 60 min; W2: 90 min; W3: 140 min).

The resulting Ru particle size is essentially identical to that obtained after drying in N\textsubscript{2} and subsequent activation and reaction in wet reformate containing 5%, 10% and 15% H\textsubscript{2}O previously (see section 3.2.2). In that study we determined Ru particle sizes of 1.48 nm (5\% H\textsubscript{2}O), 1.26 nm (10\% H\textsubscript{2}O), and 1.21 nm (15\% H\textsubscript{2}O) under steady-state conditions. This increase in the Ru dispersion in the presence of water was explained by a water assisted oxidative disruption of Ru-Ru bond, which was discussed in more detail in earlier reports.\textsuperscript{53,56,178,179,180,57}

The similar Ru particle size obtained for activation and reaction in the presence of 5\% H\textsubscript{2}O and for initial activation and reaction in dry reformate, followed by reaction in wet reformate with the same amount of H\textsubscript{2}O fully supports our above tentative conclusion that the interaction with wet reformate leads to a lower or decrease of the Ru particle size, independently of whether this occurred during the initial activation stage, during Ru nanoparticle formation from the oxidic precursor, or whether it happened only after the activation procedure, when the reduced Ru nanoparticles are already formed.

Obviously, the initial state of the catalyst, oxidic RuO\textsubscript{x} after drying in N\textsubscript{2} only or metallic Ru nanoparticles reached after drying and reaction in dry reformate, has essentially no influence on the catalyst state during subsequent operation under wet reaction conditions.
3.4.5 Time evolution of the adlayer

The time evolution of surface species formed during the reaction, in particular changes in the coverage of on top adsorbed and bridged CO\textsubscript{ad} species, was followed using \textit{in situ} DRIFT spectroscopy. As for the kinetic measurements, also here the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst was either activated and operated in dry conditions (SR-ref 6000) or first activated and operated under wet reaction conditions, and subsequently exposed to the dry reformate. In the discussion we will focus on the spectral region between 1100 and 2200 cm\textsuperscript{-1}, since this contains the vibrational bands being most important for the understanding of the observed changes in catalyst structure and adlayer structure. For more information about the adlayer and its reaction related changes we refer to previous studies\textsuperscript{72} and discussion in section 3.2.3.

3.4.5.1 On top adsorbed / bridged CO\textsubscript{ad}

Following the sequence described in the kinetic measurements, the fresh catalyst was either exposed to dry reformate only (activation and reaction in dry reformate) or it was first activated and operated in SR-ref 6000 containing 5 or 15\% H\textsubscript{2}O, respectively, prior to the reaction in dry SR-ref 6000 reformate. Spectra recorded at different reaction times during reaction in dry reformate, after activation in dry or wet reformate, are presented in Fig. 44. Most prominent in all spectra (Fig. 44a-c) are the absorption bands at around 2030 cm\textsuperscript{-1} and 1920 cm\textsuperscript{-1}, which are assigned to linearly, on top adsorbed and bridge bonded CO\textsubscript{ad} species.\textsuperscript{56,164,165,167} Moreover, there is also a weak absorption band at 1756 cm\textsuperscript{-1} in all spectra, which is related to hydroformyl species (HCO\textsubscript{ad}) resulting from hydrogenation of CO\textsubscript{ad}.\textsuperscript{72} This species was previously identified as dominant reaction intermediate during the methanation of CO and CO\textsubscript{2} over a Ru/Al\textsubscript{2}O\textsubscript{3} catalyst. For the catalyst activated under dry reaction conditions, there is also a significant absorption band at around 1662 - 1652 cm\textsuperscript{-1}, which is attributed to the bending vibration of H\textsubscript{2}O adsorbed on the support.\textsuperscript{190} Interestingly, this band is larger upon dry activation than after activation and initial reaction in wet reaction gas mixture. Reasons for that are not yet resolved. The two bands appearing at 1590 and 1390 cm\textsuperscript{-1} are characteristic for antisymmetric and symmetric bending of surface formate species,\textsuperscript{71} and the band at 1190 cm\textsuperscript{-1} was attributed to metal-O-C stretch vibrations in adsorbed methoxy or ethoxy groups, which accumulated on the catalyst support surface during the reaction.\textsuperscript{191} Also these bands are much more pronounced for the catalyst operated under dry conditions only than for those pretreated in wet reformate first.
The temporal evolution of the bands related to the CO\textsubscript{ad} species during reaction in wet and dry SR-ref 6000 reformate are shown in Fig. 45. After an initial increase in the CO\textsubscript{ad} coverage for about 100 min, steady-state is reached for all three samples, and the CO\textsubscript{ad} intensities (on top and bridge bonded) do not change any more. Similar to the behavior of Ru/zeolite and Ru/Al\textsubscript{2}O\textsubscript{3} catalysts during the CO methanation in the presence of water reported earlier (see section 3.3.3), the addition of water to the reaction gas mixture results in a decrease of the total CO\textsubscript{ad} coverage compared to that in dry gas mixture. This was explained by a mutual site blocking by CO\textsubscript{ad} and H\textsubscript{2}O\textsubscript{ad}.

Upon changing from water containing to water free SR-ref 6000 feed gas (see Fig. 45) the coverage of on top adsorbed CO\textsubscript{ad} increased by about 15\% and 35\% compared to the reaction in 5\% and 15\% water containing reformate, while the coverage of bridge bonded CO\textsubscript{ad} decreased slightly, by about 3\%. The overall band intensity, however, is still below that obtained for continuous reaction under dry conditions only (Fig. 45a and Table 16). Given the higher total exposed Ru surface area for catalysts with smaller Ru particle size as obtained after activation under wet reaction conditions, one would expect a higher CO\textsubscript{ad} coverage on these samples. On the other hand it is well known that CO adsorption is less strong on smaller Ru particles than on larger ones.\textsuperscript{62} In total, this results in a lower CO\textsubscript{ad} coverage for Ru/Al\textsubscript{2}O\textsubscript{3} with smaller Ru particles under otherwise identical, dry reaction conditions. In addition to the total CO\textsubscript{ad} coverage, there are also significant differences in the relative coverages of on top and bridge bonded CO\textsubscript{ad} between the spectra obtained in dry SR-ref 6000 after activation and operation under dry or wet reaction conditions, respectively. After activation and reaction in reformate with 0\%, 5\%, and 15\% water, respectively, we determined intensity ratios for on top / bridge bonded CO\textsubscript{ad} of 0.8, 1.3 and 1.4 for reaction in dry reformate. Hence, this clearly increases with increasing water content during the preceding activation of the catalyst and hence with decreasing Ru particle size (2.0 nm, 1.5 nm, and 1.2 nm, see above).

The same behavior was also observed if the experiment was started with dry SR-ref 6000 before introducing water into the reaction gas mixture consistent with the results of the kinetic and EXAFS measurements discussed in section 2.2 (see Appx; Fig. S8). Thus, also these \textit{in situ} DRIFTS results fully agree with and support our previous conclusion that the state of the catalyst after operation in wet reformate is independent of the preceding activation procedure. Comparable correlations between Ru particle size and the relative population of on top and bridge bonded adsorbed CO were reported also in a number of previous studies.\textsuperscript{47,192} This was explained by formation of linearly bound CO\textsubscript{ad} species for
adsorption on low coordination edge and corner atoms, whose relative contribution increases with decreasing particle size.\textsuperscript{193,194}

Table 16: Relative intensity of surface species during transient measurement in SR-ref 6000 gas mixture (W1, W2 / D1, D2) with respect to standard dry (D) measurement, and the corresponding ratio on top / bridge CO\textsubscript{ad} surface species.

<table>
<thead>
<tr>
<th>Surface species</th>
<th>SR-ref 6000</th>
<th>SR-ref 6000 (+) 5% H\textsubscript{2}O</th>
<th>SR-ref 6000 (+) 15% H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D</td>
<td>W1</td>
<td>D1</td>
</tr>
<tr>
<td>CO\textsubscript{ad} (terminal)</td>
<td>100</td>
<td>80</td>
<td>95</td>
</tr>
<tr>
<td>CO\textsubscript{ad} (bridge)</td>
<td>100</td>
<td>85</td>
<td>65</td>
</tr>
<tr>
<td>Bidentate formate</td>
<td>100</td>
<td>12</td>
<td>45</td>
</tr>
<tr>
<td>CO\textsubscript{ad} (terminal / bridge)</td>
<td>0.81</td>
<td>0.95</td>
<td>1.31</td>
</tr>
</tbody>
</table>
Figure 44: Series of DRIFT spectra recorded during the CO methanation on the Ru/γ-Al₂O₃ catalyst in dry SR-ref 6000 at 190°C after a) drying in N₂ at 150°C, and b, c) after activation in wet SR-ref 6000 gas mixture(b): 5% H₂O (c): 15% H₂O). Spectra were recorded after 15, 75, 135, 195, 255, 315, 375, 435, 495, 555, 615, and 675 min reaction (from bottom to top).
Figure 45: Temporal evolution of the intensity of absorption bands related to different species adsorbed on the Ru/γ-Al₂O₃ catalyst (■, □: on top adsorbed COₐd; ●, ○: bridge bonded COₐd; ▲, △: bidentate formate) during CO methanation at 190°C; a) in dry SR-ref 6000 (D; □, ○, △); b), c), during reaction in the presence of 5% (b, W1) and 15% (c, W2) H₂O, respectively (■, ●, ▲), and during subsequent reaction in dry SR-ref 6000 (D1; D2, □, ○, △).
Another notable consequence of the activation in wet reformate is the lower coverage of surface formates compared to that obtained after activation in dry SR-ref 6000. These species were identified as spectator species during CO/CO2 methanation using SSITKA measurements. In the presence of 5 and 15% water in the reaction gas, their band intensity is only 12 and 6%, respectively, of that obtained in the dry measurements (Table 16). Furthermore, the intensities obtained after changing from wet to dry gas mixture (D1 and D2) are only 45 and 29% of that measured on the catalyst after dry operation only. Hence, the formate coverage decreases with increasing Ru dispersion. This goes along with a decrease of the bridge bonded COad band intensity and an increase of activity.

In total the decrease in Ru particle size induced by the presence of water in the reaction gas goes along with a significant increase of the ratio between on top adsorbed COad and bridge bonded COad species during subsequent reaction in dry reformate, which stays constant during time-on-stream. This result further underlines the permanent decrease of the Ru particle size induced during subsequent CO/CO2 methanation in dry reformate by the temporary presence of water as compared to the Ru particle size in dry conditions only.

3.4.5.2 CO2 dissociation

In a number of previous studies we had found that the activity of supported Ru/Al2O3 and Ru/zeolite catalysts for CO2 dissociation to COad is closely related to their selectivity for CO methanation in CO containing reformate, with increasing CO2 dissociation activity and decreasing CO methanation selectivity for increasing Ru particle size. The correlation between Ru particle size and activity for CO2 dissociation can thus be used as further evidence for our proposal of a water induced increase in Ru particle dispersion as origin for the observed increase of selectivity / decrease of particle size upon treatment in wet reformate.

The activity for CO2 dissociation during the reaction in dry CO-free CO2-ref reformate was tested after drying in N2 at 150°C and after subsequent activation and reaction for 750 min in wet SR-ref 6000 gas mixture containing 5% and 15% H2O, following the changes in the intensity of the band at 2022 cm⁻¹ related to on top COad and the mode at 1889 - 1893 cm⁻¹ related to bridge bonded COad (Fig. 46).

After activation and reaction (550 min) in SR-ref 6000 containing 5% and 15% H2O, the COad intensity resulting from dissociation of CO2 in dry CO2-ref decreased significantly when going from dry to wet pre-treatment, resulting in COad intensities (steady-state) of only 48% and 44% (Figs. 47b and c, Table 17) compared to the intensity obtained over the only dried catalyst in N2 after heating up to 190°C in CO2-ref (Fig. 47a).
3.4. Results and discussion

Figure 46: Series of DRIFT spectra recorded during 750 min reaction on the Ru/γ-Al₂O₃ catalyst at 190°C in dry CO₂-ref after a) drying in N₂ at 150 °C followed by heat-up to 190°C in CO₂-ref (10 min) and b), c) after activation in wet SR-ref 6000 gas mixture (b) 5% H₂O, c) 15% H₂O). Spectra were recorded after 15, 75, 135, 195, 255, 315, 375, 435, 495, 555, 615, and 675 min reaction in CO₂-ref (from bottom to top).
Figure 47: Temporal evolution of the intensity of absorption bands related to different species adsorbed on the Ru//γ-Al₂O₃ catalyst (□: On top adsorbed CO\\textsubscript{ad}; ○: bridge bonded CO\\textsubscript{ad}; Δ: bidentate formate) in CO₂-ref at 190°C, a) after drying in N₂ at 150°C and heating up to 190°C in CO₂-ref (10 min), and b), c) after activation and reaction (550 min) in wet SR-ref 6000 gas mixture (b) 5% H₂O, c) 15% H₂O).
3.4. Results and discussion

Hence, after activation and reaction in wet reformate (5% and 15% H$_2$O, respectively) the Ru/Al$_2$O$_3$ catalyst is much less active for CO$_2$ dissociation in dry reformate compared to a catalyst activated in dry reformate. This fully agrees with our previous mechanistic proposal that the higher inherent selectivity for CO methanation of smaller Ru particles (at low CO concentrations) originates from their lower activity for CO$_2$ dissociation. Furthermore, the observed decrease of the CO$_{ad}$ coverage in CO rich reformate gases after identical pre-treatment, activation and temporary operation in wet reformate, also fully agrees with our interpretation that the lower activity for CO$_2$ dissociation is correlated with and due to a lower stability of adsorbed CO on smaller Ru particles, in accordance with the BEP principle.$^{162}$ Finally, the stability of the low CO$_{ad}$ band intensity with time on stream is further evidence for the stability of the small Ru particles formed by activation and reaction in wet reformate also under subsequent dry reaction conditions.

**Table 17**: Relative intensity of surface species in CO$_2$-ref reformate at 190 °C after activation and reaction in SR-ref 6000 containing different amounts of water compared to standard dry CO$_2$-ref, and ratio between terminal and bridge bonded CO$_{ad}$ surface species in the respective gas mixtures.

<table>
<thead>
<tr>
<th>Surface species</th>
<th>Intensity in dry CO$_2$-ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After drying in N$_2$ at 150 °C</td>
</tr>
<tr>
<td>CO$_{ad}$ (terminal)</td>
<td>100</td>
</tr>
<tr>
<td>CO$_{ad}$ (bridge)</td>
<td>100</td>
</tr>
<tr>
<td>Bidentate formate</td>
<td>100</td>
</tr>
<tr>
<td>Ratio (terminal / bridge)</td>
<td>1.4</td>
</tr>
</tbody>
</table>
3.4. Results and discussion

3.4.6: Conclusions

Extending our efforts to better understand the role of water in the selective CO methanation in CO$_2$-rich reformates, we have investigated changes in the catalyst structure, in the adlayer composition and in the catalytic performance of a Ru/Al$_2$O$_3$ catalyst and their correlation upon transient changes in the reaction atmosphere, from wet to dry reaction atmosphere and vice versa, by combined kinetic measurements, in operando EXAFS and DRIFTS measurements, and ex-situ catalyst characterization. From these measurements, which in particular aimed at disentangling effects caused by Ru particle formation during the activation of the catalyst (under dry and wet conditions) and those occurring during reaction in different, wet and dry, reaction atmospheres, we arrived at the following conclusions:

1. Activating the dried catalyst (drying in N$_2$ at 150°C) first in wet reaction gas (5, 15% H$_2$O, > 180 min at 190°C), followed by reaction in dry reformate results in a significantly enhanced activity and selectivity in dry reformate (0% H$_2$O) as compared to activation and reaction in dry reformate directly. TEM imaging revealed that the smaller Ru particles obtained upon activation and reaction in wet reaction atmosphere (TEM based particle size 1.6 nm) as compared to activation and reaction under dry conditions (TEM based particle size 2.2 nm) are maintained also during the subsequent reaction in dry reformate. Based on long-term kinetic measurements, these smaller Ru particles are stable under reaction in dry conditions, at least for the time range of our experiments (80 hours). The ‘irreversible’ change of the Ru particle size is held responsible for the higher activity and selectivity of a catalyst activated in wet reformate as compared to a catalyst activated in dry reformate.

2. The opposite procedure, activating the dried Ru/Al$_2$O$_3$ catalyst in dry reformate (metallic Ru only, particle size 2.0 (EXAFS) – 2.2 (TEM) nm) and then changing to wet reaction conditions (5% H$_2$O) results in a decrease of the Ru nanoparticle size under reaction conditions compared to the state reached upon activation and reaction in dry reformate. After 150 min reaction in wet reformate, in operando EXAFS measurements indicated a particle size of 1.5 nm. This points to a water assisted dispersion of the pre-existing metallic Ru nanoparticles under wet reaction conditions. In parallel, the selectivity for CO methanation increased, as expected for smaller Ru particles.
3.4. Results and discussion

3. After about 150 min reaction in wet reformate, following the activation in dry reformate, both the Ru particle size as well as the catalytic performance of the Ru/Al₂O₃ catalyst (activity and selectivity) are almost identical to those of a catalyst activated in wet reformate directly. Obviously, the initial state of the catalyst, oxidic RuOₓ after drying only or metallic Ru nanoparticles after activation and reaction in dry reformate, has essentially no influence on the catalyst state during subsequent operation under wet reaction conditions. Hence, for reaction in wet reformates both the Ru particle size and the reaction behavior under steady-state conditions are solely determined by the reaction atmosphere, with significantly smaller Ru nanoparticles as compared to dry reaction conditions, and not by the preceding activation procedure. This is in contrast to the findings for the opposite sequence (activation + initial reaction in wet atmosphere, followed by reaction in dry reformate), where the small Ru nanoparticles formed during activation are maintained during reaction.

4. The decrease in Ru particle size induced by the presence of water in the reaction gas goes along with a significant increase of the ratio between on top adsorbed CO_{ad} and bridge bonded CO_{ad} species during subsequent reaction in dry reformate, which remains constant during time-on-stream. This finding further underlines the permanent change of the Ru particle size induced by the temporary presence of water.

5. The comparison of the CO_{ad} coverages obtained from CO₂ dissociation in an idealized, CO-free reformate shows that after activation and reaction in wet reformate (5% and 15% H₂O, respectively) the Ru/Al₂O₃ catalyst is much less active for CO₂ dissociation in dry reformate compared to a catalyst activated in dry reformate directly. This fully agrees with our previous proposal that the higher selectivity for CO methanation of smaller Ru particles at low CO concentrations originates from their lower intrinsic activity for CO₂ dissociation.

Overall, these results fully support our previous proposal that the selectivity of supported Ru catalysts for CO methanation is largely determined by the Ru particle size. Furthermore they indicate that even for reaction in dry reformate, where at low CO concentrations the Ru/Al₂O₃ catalyst normally suffers from a rather poor selectivity for CO methanation, the selectivity of the Ru/Al₂O₃ catalyst may be enhanced to up to 100% selectivity down to lowest CO concentrations by a preceding activation phase in wet reformate, e.g., by artificially adding water vapor to the feed.
3.5. Selective CO methanation on Ru/TiO$_2$ Catalysts: Influence of metal-support interactions

Results and text content in this part were reprinted (adapted) with permission from *ACS Catalysis* 5 (2015) 6753–6763: Ali M. Abdel-Mageed, Widmann, S. E. Olesen, I. Chorkendorff, and R. J. Behm, Improved performance of Ru/Al$_2$O$_3$ catalysts in the selective methanation of CO in CO$_2$-rich reformate gases upon transient exposure to water containing reaction gas. Copyright (2015) with permission from American Chemical Society.

D. Widmann has contributed to this work by discussions and helped in the revisions and improvement of the first draft of the manuscript. The set of catalysts used in this work were synthesized by Sine E. Olesen who is working in the research group of Prof. I. Chorkendorff.
3.5. Results and discussion

3.5.1. Introduction

In the previous chapters we demonstrated that both activity and in particular the selectivity of Ru nanoparticle catalysts can be varied in a wide range by varying the Ru particle size, allowing to reach 100% selectivity in CO₂-rich reformate gases down to very low CO concentrations. In the present study we report results of a different approach, where we tried to modify the metal-support interaction (MSI) in a very controlled way, namely by systematically increasing the surface area of the support, while essentially maintaining other important properties such as Ru loading or Ru particle size. Because of their well-known tendency of exhibiting pronounced MSIs, we used a set of 4 Ru/TiO₂ supported catalysts with widely varying TiO₂ surface areas, while keeping the Ru loading and particle size as well as the phase composition of the support largely unchanged. In this work we focus on the state and performance of the catalysts under steady-state reaction conditions.

Before moving to the results we will briefly summarize the main results of previous studies pertinent for this work. There seems to be general agreement in the meantime that under conditions of low CO contents in the reaction gas, where the selectivity is not determined by site blocking effects, due to blocking of sites for CO₂ dissociation by adsorbed CO, the Ru particle size is the decisive parameter for the selectivity of these catalysts. Lower CO₂ methanation activities with decreasing Ru particle size originate from a decreasing CO₂ dissociation activity with decreasing Ru particle size, which in turn results in an increase of the selectivity for CO methanation. This behavior was explained by a lower stability of the CO₂ dissociation product CO_ad with decreasing particle size, which according to the Brønsted–Evans–Polanyi (BEP) principle results in a higher activation barrier for CO₂ dissociation. The intrinsic activity, in terms of turnover frequencies (TOFs), of Ru catalysts for CO methanation, in contrast, decreases with decreasing Ru particle size. This was explained by a structural effect, assuming a higher CO methanation activity on the crystallite facets, whose relative abundance decreases with decreasing Ru particle size. For the Ru mass normalized activity, however, this may be different, since a decreasing Ru particle size always goes along with an increase in dispersion. Hence, there is a counterbalance between activity gain (due to higher Ru surface area) and activity loss (due to lower TOFs) with decreasing particle size, which can result in either a decrease or an increase in Ru mass normalized. Both situations have been observed, depending on the exact nature of the catalyst and the conditions during catalyst activation as well as during reaction. 

It was, for
example, reported that the increase of Ru particle size resulting from the increase of Ru loading on a Ru/TiO$_2$ and Ru/zeolite catalysts results in an increased Ru mass normalized activity.$^{62,68}$ On the other hand, formation of larger Ru particles by reduction$^{110,111}$, or calcination$^7$ at elevated temperatures resulted in lower Ru mass normalized activities. Wherever TOFs were reported, however, these increased with increasing particle size.

It is well known that also the nature of the support material has a pronounced influence on the catalytic performance of supported Ru catalysts in the selective CO methanation. Comparison of differently supported Ru catalysts revealed that Ru catalysts supported on TiO$_2$ are among the most active and selective catalysts for this reaction.$^{68,76,111}$ Similar findings were reported for other metals (Rh and Pd), where TiO$_2$ supported catalysts also showed significantly higher CO methanation / hydrogenation activities compared to catalysts based on other support materials, e.g., Al$_2$O$_3$, MgO, or SiO$_2$.$^{112,113,116,198,199}$

Already in the late 70s of the last century, Tauster et al. demonstrated that for group VIII small metal particles supported on reducible metal oxides, in particular on TiO$_2$, that the oxide not only acts as an otherwise inert stabilizer for small metal nanoparticles but that interactions between metal und support (strong metal-support interactions (SMSI)), may alter the (electronic and / or structural) properties of the metal nanoparticles upon reduction at elevated temperatures.$^{114,117,200}$ This may result in drastic changes of their chemisorption properties and catalytic performance.$^{112,117}$ Therefore, a mechanistic understanding of Ru/TiO$_2$ catalysts and of the ongoing surface processes requires the separation and disentangling of Ru particle size effects and possible metal-support interactions.$^{201}$

In the following we will first present results of kinetic measurements, comparing the activity and selectivity of the different Ru/TiO$_2$ catalysts for selective CO methanation in CO$_2$-rich reformates containing medium (6000 ppm) and low (100 ppm) CO concentrations (section 3.2). Next we present results of in situ IR spectroscopy measurements (Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)), where we determined the (relative) amounts and types of adsorbed surface species formed during the reaction, focusing on the evolution of adsorbed CO species (section 3.3). Finally we evaluated the tendency for CO formation via CO$_2$ dissociation in CO-free CO$_2$-rich reformate gas. Based on these data we will try to disentangle in a systematic way the contributions arising from different effects, including Ru particle size effects, metal-support interactions and possible other effects on the reaction characteristics.
3.4.1. Ru/TiO₂ catalyst characterization

The Ru loadings of the various Ru/TiO₂ catalysts used in this study, as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), are 2.8, 2.2, 2.2, and 2.1 wt.% for Ru/TiO₂-1, Ru/TiO₂-2 and Ru/TiO₂-3, and Ru/TiO₂-4, respectively (see Table 18) and hence rather similar to each other. The surface areas of the Ru catalysts, in contrast, differ significantly, ranging from 20 m² g⁻¹ to 235 m² g⁻¹ for Ru/TiO₂-1 and Ru/TiO₂-4, respectively. Accordingly, also the TiO₂ crystallite sizes of the samples differ significantly from each other. Based on XRD measurements the crystallite size of the TiO₂ particles decreases from 52 nm for Ru/TiO₂-1 to about 9 nm for Ru/TiO₂-4, respectively. This trend fits quite well, at least qualitatively, to the observed increase in surface area.

Table 18: Physical properties, catalytic activities for the selective CO methanation at 190 °C (in SR-ref 6000) and selectivities for CO methanation (in SR-ref 100) of various Ru/TiO₂ catalysts with different specific surface areas.

<table>
<thead>
<tr>
<th>Structural parameter</th>
<th>Ru/TiO₂-1</th>
<th>Ru/TiO₂-2</th>
<th>Ru/TiO₂-3</th>
<th>Ru/TiO₂-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru loading / wt. %</td>
<td>2.8</td>
<td>2.2</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Surface area / m² g⁻¹</td>
<td>20</td>
<td>64</td>
<td>121</td>
<td>235</td>
</tr>
<tr>
<td>Pore diameter / nm</td>
<td>3.45</td>
<td>3.08</td>
<td>3.05</td>
<td>2.27</td>
</tr>
<tr>
<td>Ru / Ti (atomic ratio / XPS)</td>
<td>0.076</td>
<td>0.043</td>
<td>0.016</td>
<td>0.012</td>
</tr>
<tr>
<td>TiO₂ crystallite size / nm</td>
<td>52.4</td>
<td>19.3</td>
<td>14.0</td>
<td>8.8</td>
</tr>
<tr>
<td>Ratio anatase / %</td>
<td>92</td>
<td>83</td>
<td>89</td>
<td>97</td>
</tr>
<tr>
<td>Ru particle size / nm</td>
<td>2.3</td>
<td>1.8</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Ru dispersion / %</td>
<td>43</td>
<td>55</td>
<td>68</td>
<td>71</td>
</tr>
<tr>
<td>Reaction rate / 10⁻⁶ mol g⁻¹ s⁻¹</td>
<td>2.7</td>
<td>20</td>
<td>30.0</td>
<td>11.1</td>
</tr>
<tr>
<td>TOF / 10⁻³ s⁻¹</td>
<td>0.65</td>
<td>3.7</td>
<td>4.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Selectivity / %</td>
<td>58</td>
<td>76</td>
<td>90</td>
<td>95</td>
</tr>
</tbody>
</table>
3.5. Results and discussion

The XRD measurements provide additional information on the phase composition of the support material. For all support materials the most prominent diffraction peaks were detected at 25.3° and 48.1°, which are related to the (101) and (200) planes of anatase.\(^{202,203}\) Hence, in all samples TiO\(_2\) is predominantly present as anatase. In addition, there are also weaker reflections at 27.4°, 36° and 55°, which are assigned to the (110), (101) and (211) planes of rutile.

The diffractograms indicate that in all catalysts TiO\(_2\) is present as a mixture of anatase and rutile, as it is well known for TiO\(_2\)-2 (P25). Taking the intensity ratio of the (101) reflection of anatase and of the (110) reflection of rutile as a measure, there are no significant differences in the phase composition of the four Ru/TiO\(_2\) catalysts (see Table 18 and Fig. 48).

The chemical composition of the catalyst surfaces was characterized by XPS measurements, evaluating the Ru(3d) and Ti(2p) signals of the four samples after calcination and reaction for 1000 min in SR-ref 6000 reformate gas at 190 °C. The spectra presented in Fig. 49 show that the binding energy (BE) for the 3d\(_{5/2}\) state of Ru is between 279.5 and 280.0 eV, which refers to a largely reduced catalyst.\(^{204}\) The BEs of the Ti (2p\(_{3/2}\)) signals are between 458.1 eV and 458.8 eV, which is typical for Ti\(^{4+}\).\(^{205,206}\) The relative ratio of oxidic to reduced Ru could not be determined by XPS because of instantaneous surface oxidation upon exposure to air, during catalyst transport to the spectrometer. \textit{In-situ} XANES spectra on Ru/TiO\(_2\)-3, which were recorded under reaction conditions, however, revealed almost completely metallic Ru species during CO methanation. Based on these results we consider Ru to be present as metallic species under reaction conditions, as it was previously reported also for Ru/Al\(_2\)O\(_3\) and Ru/zeolite catalysts using XANES / EXAFS experiments.\(^{71,168}\)

Highly important is also the atomic ratio of Ru : Ti atoms in the topmost layers of the Ru/TiO\(_2\) catalysts, which was calculated from the intensity ratio of the Ru (3d\(_{5/2}\)) and Ti (2p\(_{3/2}\)) peaks, taking into account the tabulated sensitivity factors for the respective signals. The Ru : Ti ratio is found to decrease continuously with increasing surface area, by a factor of about 3 when going from Ru/TiO\(_2\)-1 to Ru/TiO\(_2\)-4 (see Table 18). This significant decrease of the Ru : Ti ratio at (almost) constant Ru loading and Ru dispersion is clearly correlated with the increase of support surface area.
3.5. Results and discussion

Figure 48: X-ray diffraction patterns of Ru/TiO$_2$ catalysts with different TiO$_2$ surface areas: a) Ru/TiO$_2$-1; b) Ru/TiO$_2$-2; and c) Ru/TiO$_2$-3 and d) Ru/TiO$_2$-4.
3.5. Results and discussion

**Figure 49:** XP spectra of the Ti(2p) and Ru(3d) peaks of Ru/TiO$_2$ catalysts with different TiO$_2$ surface areas: a) Ru/TiO$_2$-1, b) Ru/TiO$_2$-2, c) Ru/TiO$_2$-3, d) Ru/TiO$_2$-4. Thin lines indicate contributions from the Ti(2p) (Ti(2p$_{3/2}$): ca. 458.8 eV, Ti(2p$_{1/2}$): ca. 464.5 eV) and the Ru(3p) states (Ru(3p$_{3/2}$): ca. 462.7 eV, Ru(3p$_{1/2}$): 484.9 eV) in the Ti(2p) region (left panels) and of the Ru(3d) peaks (Ru(3d$_{5/2}$): ca. 280.0 eV, Ru(3d$_{3/2}$): ca. 284.2 eV) and the C(1s) peak (284.4 eV) in the Ru(3d)/C(1s) peak region (right panels).

TEM images taken of all samples after reaction in SR-ref 6000 for 1000 min at 190°C are shown in Fig. 50, together with the corresponding particle size distributions. These images clearly illustrate that the TiO$_2$ nanoparticles decrease in size with increasing surface area, in agreement with the XRD results, and that the Ru nanoparticles are well separated and highly dispersed on the TiO$_2$ surface. The Ru size distributions reveal that the mean Ru particle size decreases slightly with increasing surface area, from 2.3 nm (Ru/TiO$_2$-1) to 1.5 nm (Ru/TiO$_2$-4). While the differences in Ru particle size are rather small for Ru/TiO$_2$-2, Ru/TiO$_2$-3 and Ru/TiO$_2$-4 (1.8, 1.6, and 1.5 nm, respectively), the mean Ru particle size for Ru/TiO$_2$-1 catalyst (2.3 nm) differs significantly (see Table 18). Based on the particle size distributions we also calculated the dispersions, assuming hemispherical Ru particles.
and $1.5 \times 10^{15}$ Ru atoms cm$^{-2}$. The resulting Ru dispersions are 43, 55, 68, and 71% for the Ru/TiO$_2$-1, Ru/TiO$_2$-2, Ru/TiO$_2$-3 and Ru/TiO$_2$-4 catalysts, respectively. Overall, the differences in Ru loading, Ru particle size (or Ru dispersion) and TiO$_2$ phase composition of the four Ru/TiO$_2$ catalysts are rather small compared to the differences in catalyst surface area, which grows by more than one order of magnitude from Ru/TiO$_2$-1 to Ru/TiO$_2$-4, from 20 to 235 m$^2$ g$_{cat}^{-1}$. The influence of the different structural properties on the reaction characteristics will be discussed in more detail below, after presenting the results of the kinetic and in situ IR spectroscopic studies.

**Figure 50:** TEM images and particle size distributions of Ru NPs supported on TiO$_2$ with different surface areas: a) Ru/TiO$_2$-1 b) Ru/TiO$_2$-2; c) Ru/TiO$_2$-3, and d) Ru/TiO$_2$-4. Measurements were performed ex-situ, after reaction in SR-ref 6000 gas reformate at 190°C for 1000 min (Ru/TiO$_2$-1: black; Ru/TiO$_2$-2: red; Ru/TiO$_2$-3: green; Ru/TiO$_2$-4: blue).
3.5.3 Activity and selectivity for CO methanation

The performance of the Ru/TiO$_2$ catalysts in the selective methanation reaction was determined in kinetic measurements at atmospheric pressure and at 190°C in two different reaction atmospheres. First the catalytic activity for CO methanation was determined in SR-ref 6000 (6000 ppm, 3.0% N$_2$, 15.5% CO$_2$, balance H$_2$). In this reformate, high selectivities of essentially 100% are known to result from surface blocking by adsorbed CO, which blocks the active sites for CO$_2$ adsorption and dissociation, as had been demonstrated in previous measurements on Ru/Al$_2$O$_3$ and Ru/zeolite catalysts.$^{72,72}$ Similar results were obtained for the Ru/TiO$_2$ catalysts investigated in the present study in SR-ref 6000, and they are similarly attributed to site blocking by CO$_{ad}$. Therefore, the inherent selectivity of the catalyst for CO methanation in the presence of large amounts of CO$_2$ (15.5%) has to be determined in a reformate containing much lower CO contents (SR-ref 100: 100 ppm CO, 3.0% N$_2$, 15.5% CO$_2$, balance H$_2$).

This low CO partial pressure results in a much lower CO$_{ad}$ coverage on the Ru surface. Accordingly, there are active sites available for CO$_2$ dissociation and CO$_2$ methanation, and the selectivity is no longer governed by adlayer site blocking. Technically, such low CO concentrations are met at the end of methanation reactor, and also under these condition a high selectivity is mandatory to avoid intolerable losses of H$_2$ due to methanation of CO$_2$. $^{72}$

First the activity of the different Ru/TiO$_2$ catalysts was evaluated during 1000 min time on stream in SR-ref 6000, until almost no changes in activity were detected anymore and steady-state conditions were reached. The temporal evolution of the Ru mass normalized activities of the different catalysts is illustrated in Fig. 51. The data show for all catalysts an initial activation period, ranging over the first 50 - 300 min of the reaction, where the activity increases with time on stream. This is followed by a continuous decrease in reaction rate (deactivation). This temporal evolution (activation / deactivation) and its origin are topic of ongoing work in our laboratory, whose results will be reported later. In the present work, we focus on the catalytic activities of the different supported Ru catalysts under steady-state conditions, after 1000 min reaction at 190 °C (see Fig. 52b). The Ru mass normalized activity increases almost linearly with increasing support surface area, from $2.7 \times 10^{-6}$ mol g$_{Ru}$-1 s$^{-1}$ for the 20 m$^2$ g$^{-1}$ (Ru/TiO$_2$-1) catalyst to $30.0 \times 10^{-6}$ mol g$_{Ru}$-1 s$^{-1}$ for the 121 m$^2$ g$^{-1}$ (Ru/TiO$_2$-3), catalyst (see Table 18).
Figure 51: Temporal evolution of the Ru mass normalized CH₄ formation rates during the selective CO methanation in SR-ref 6000 gas mixture at 190°C on Ru/TiO₂ catalysts with different surface areas: a) Ru/TiO₂-1, b) Ru/TiO₂-2, c) Ru/TiO₂-3, and d) Ru/TiO₂-4.
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Figure 52: a) Average Ru particle diameter (▼) and Ru dispersion (○) after reaction for 1000 min in SR-ref 6000 at 190°C, b) steady state Ru mass normalized CH₄ formation rates (●) in SR-ref 6000 gas mixture at 190°C and corresponding turn over frequencies (♦), c) Ru mass normalized activity (CO conversion: ■; CH₄ formation: ●) and corresponding CO selectivity (▲) in SR-ref 100 reformate at 190°C, all as a function of TiO₂ surface area (SA).

A further increase of the catalyst surface area to 235 m² g⁻¹, however, results in an unexpected loss of activity to only 1.1 × 10⁻⁶ mol g⁻¹ s⁻¹ (Ru/TiO₂-4). Overall this results in a volcano type dependence of the CO methanation activity on the catalyst surface area, with the highest reaction rate observed on the Ru/TiO₂-3 catalyst with a surface area of 121 m² g⁻¹. Note that for the latter catalyst the Ru mass normalized activity is comparable to
that reported for a commercial, highly active and selective Ru/zeolite catalyst (Clariant Produkte).  

We also calculated the TOFs of the various catalysts, using the Ru dispersion as calculated from the Ru particle size distribution (see section 3.5.2) in order to determine the intrinsic catalytic activities of the Ru nanoparticles. As shown in Fig. 52, these exhibit the same volcano like dependence on the catalyst surface area as the Ru mass normalized activities (see Table 1). While the TOF increases by a factor of about 7, from \(0.65 \times 10^{-3} \text{ s}^{-1}\) to \(4.4 \times 10^{-3} \text{ s}^{-1}\), when going from the Ru/TiO\(_2\)-1 to the Ru/TiO\(_2\)-3 catalyst, it is again much lower, by a factor of about 2.5, for Ru/TiO\(_2\)-4 \((1.8 \times 10^{-3} \text{ s}^{-1})\). Considering the distinct increase in activity (mass normalized activity as well as TOF) with increasing surface area and decreasing particle size (Ru/TiO\(_2\)-1, Ru/TiO\(_2\)-2, and Ru/TiO\(_2\)-3), this contradicts previous findings of an increasing TOF based activity with increasing Ru particle size (see above). This discrepancy with previous results indicates already that the differences in the catalytic activity between these three catalysts does not originate from particle size effects alone. The same is true also for the significant decrease in activity for the catalyst with the highest surface area (Ru/TiO\(_2\)-4) as compared to Ru/TiO\(_2\)-3, in spite of the almost identical Ru loading and Ru particle size (2.2 wt.% and 1.6 nm vs. 2.2 wt.% and 1.5 nm). Here it has to be noted that differences in the TiO\(_2\) phase composition can also be excluded as reason for the observed differences in the catalytic performance, since this is rather similar for all catalysts, and does not follow at all the trend connected in the catalytic activity. Possible reasons for the discrepancy will be discussed in more detail below, after evaluation of the adsorption properties of the different catalysts.

In the above measurements, all catalysts were 100% selective for CO methanation due to CO\(_{\text{ad}}\) site blocking (see above in this section).

To gain further information on temperature effects, we performed another set of experiments, where the reaction temperature was increased from 190 to 270°C during the CO methanation in SR-ref 6000, after having reached a steady-state situation at 190°C (temperature programmed reaction, heating ramp 5°C min\(^{-1}\)). While for the first three catalysts the CO conversion increased continuously with temperature over the whole temperature range, until reaching full conversion, the Ru/TiO\(_2\)-4 with the highest surface area \((235 \text{ m}^2 \text{ g}^{-1})\) catalyst showed a moderate increase in CO conversion only from 190°C to 220°C, followed by a decrease in activity for even higher temperatures (see Fig. 53). At that temperature, the catalyst becomes increasingly active for the reverse water gas shift.
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reaction, producing mainly CO and H₂O and no longer CH₄. The other three catalysts, in contrast, were only active for the methanation reaction (CO and CO₂ methanation) in the entire temperature range investigated. Up to at least 220°C, all catalysts are 100% selective for CO methanation. For higher temperatures, CO₂ methanation sets in, most likely due to a decreasing COₐd coverage, with different relative contributions for the different catalysts.

Figure 53: Relative CO conversion during a temperature programmed reaction (190 °C – 270 °C) in SR-ref 6000 reformate gas of Ru/TiO₂-1 (●), Ru/TiO₂-2 (▲), Ru/TiO₂-3 (◊), and Ru/TiO₂-4 (♦) after reaching a steady state situation at 190 °C.

The activities of the four Ru/TiO₂ catalysts for CO methanation as well as for total methane formation, from CO and CO₂, in SR-ref 100 at 190°C are shown in Fig.52, together with the corresponding selectivities. The trend in the total methane formation activity is similar to that described above for reaction in SR-ref 6000. The activity first increases from Ru/TiO₂-1 to Ru/TiO₂-3, reaching a maximum activity for the latter catalyst, and then decreases again for the Ru/TiO₂-4 catalyst. This decrease in activity, however, is much less pronounced compared to reaction in SR-ref 6000. Another remarkable difference is the activity for methane formation from CO₂, which is given by the difference between CO conversion and methane formation. This difference is most prominent for the Ru/TiO₂-1 and Ru/TiO₂-2 catalysts (see Fig. 53c), and hardly present any longer for Ru/TiO₂-4. Calculations of the respective selectivities for CO methanation show that these are 58, 76, 90, and 95% on Ru/TiO₂-1, Ru/TiO₂-2, Ru/TiO₂-3, and Ru/TiO₂-4, respectively. Hence, in contrast to the catalyst activity, there is no maximum
for Ru/TiO₂-3, but a steady increase with increasing surface area of the catalysts. Taking into account previous findings on the origin of the selectivity, as described in the introduction, this increase in selectivity is proposed to originate at least partly from the decreasing Ru particle size, which decreases in the same order, from 2.3 nm (Ru/TiO₂-1) to 1.5 nm (Ru/TiO₂-4). Although these changes in Ru particle size are rather small, it is well known from previous studies on other Ru catalysts that such changes may be sufficient to induce significant changes in selectivity. Similar results of an increasing selectivity for CO methanation with decreasing Ru particle size have been reported in various previous studies, where variation of the Ru particle size was realized by i) a decreasing Ru loading on Ru/zeolite, ii) an increasing calcination temperature on Ru/zeolite, iii) a decreasing reduction temperature on Ru/Al₂O₃ and Ru/TiO₂, or iv) a pre-treatment in the presence of water in the reaction feed on Ru/Al₂O₃ (see section 3.4). Hence, the present observations are in good agreement with previous findings and clearly demonstrate a general dependence of the CO selectivity on the Ru particle size, independent of the nature of the metal oxide support (reducible or non-reducible) or exact procedures for catalyst preparation and pre-treatment. This behavior was previously explained by a lower activity of small Ru nanoparticles for the dissociation of CO₂, which was attributed to a lower stability of the dissociation products of CO₂ (COₐd + Oₐd) on these very small particles. According to the Brønstedt-Evans-Polanyi(BEP) relation the activation barrier for the CO₂ dissociation increases with decreasing stabilization of the final product COₐd + Oₐd.
3.5.4 Adlayer formation

In order to gain additional information on the chemical properties of the Ru nanoparticles and possible changes therein with increasing surface area of the catalysts, we followed the build-up of adsorbed species during the reaction by in-situ IR spectroscopy. In situ DRIFT spectra were recorded upon interaction of the different Ru/TiO₂ catalyst samples with the SR-ref 6000 reformate at 190°C until reaching steady-state conditions (after 800 min), applying identical pre-treatment and reaction conditions as described above for the kinetic measurements (see section 3.5.3). Since we were particularly interested in the nature and the amount of adsorbed CO, formyl and formate species formed on the catalyst surface during reaction, we focus here on the spectral region between 1200 cm⁻¹ and 2200 cm⁻¹. The evolution of these species, which are known to act as reaction intermediate (COₐd, formyl species) and spectator species (formate), respectively,¹⁷¹,¹⁷² can provide valuable information on the differences in the catalytic performance. Sets of spectra showing these regions, which were recorded during the CO methanation at different reaction times (from 0 to 735 min) on the different catalysts, are presented in Fig. 54. Sets of spectra covering the OH-region (around 3700 cm⁻¹) and the CHₓ-region (around 3000 cm⁻¹) are presented in the Supporting Information (Fig. S9).

From the spectra presented in Fig. 54 it is obvious that both the type as well as the amount of surface species formed on the catalyst surface during reaction differ significantly for the different catalysts. A weak band appearing in the range 2135 -2145 cm⁻¹, together with another band at around 2078 cm⁻¹, is considered to be characteristic for the CO vibration in Ru-multicarbonyl surface species.⁵⁷,²⁰⁷
Figure 54: DRIFT spectra recorded during the selective CO methanation (SR-ref 6000 gas mixture, 190°C) on the different Ru/TiO$_2$ catalysts after different reaction times (from bottom to top after 0, 1, 5, 9, 15, 75, 135, 255, 495, 615, and 735 min, respectively. a) Ru/TiO$_2$-1, b) Ru/TiO$_2$-2, c) Ru/TiO$_2$-3, and d) Ru/TiO$_2$-4.

For all samples, the intensity of these two bands was found to reach a maximum within the first minutes of reaction, followed by a continuous decrease with time on stream afterwards. Moreover, this band is much more intense on the catalysts with higher surface areas (Ru/TiO$_2$-3 and Ru/TiO$_2$-4) than on the samples with lower surface areas. When reaching steady-state conditions, this band has completely vanished for the Ru/TiO$_2$-1 catalyst. In the range from 2060 to 1980 cm$^{-1}$ there are various other surface species which are attributed to CO adsorbed in an on-top configuration on Ru particles. While the band at around 2058 cm$^{-1}$ was assigned to on-top adsorbed CO on small Ru clusters.$^{56,69,167}$
band in the range of 2009 - 2019 cm\(^{-1}\) was proposed to be characteristic for a CO\(_{\text{ad}}\) species adsorbed on slightly larger Ru particles.\(^{50,69}\) The respective intensities of these bands (multicarbonyl and CO\(_{\text{ad}}\)), as indicated by the corresponding peak heights (KM units) for all four catalysts, are illustrated in Fig. 55.

![Figure 55: Intensity of adsorbed CO surface species (peak heights) during reaction in SR-ref 6000 after 1000 min (steady state) as a function of the support surface area: a) Ru-carbonyl associated bands (2078 cm\(^{-1}\)) and b) on top adsorbed CO\(_{\text{ad}}\) (2060 - 2052 cm\(^{-1}\) and 2009 - 2025 cm\(^{-1}\); empty and filled columns, respectively).](image)

Finally, a band related to surface formates was observed at 1554 cm\(^{-1}\).\(^{40,55}\) The band intensity related to this species increases with increasing surface area (Fig. 55), from being absent on the lowest surface area catalyst (Ru/TiO\(_2\)-1) to low intensities on the Ru/TiO\(_2\)-2 and Ru/TiO\(_2\)-3 catalysts to a very pronounced band for the Ru/TiO\(_2\)-4 catalyst with the highest surface area. For the latter catalyst it is by factors of 15 and 13 higher compared to the Ru/TiO\(_2\)-2 and Ru/TiO\(_2\)-3 catalysts, respectively. The much higher steady-state
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coverage of surface formates on the Ru/TiO$_2$-4 catalyst is suspected as a potential reason for the much lower activity of the Ru/TiO$_2$-4 catalyst.

Despite the similar Ru loadings and Ru dispersion a quantitative comparison of the absolute amount of adsorbed surface species between different catalysts is hardly possible from these spectra. On a qualitative scale, all bands for CO$_{ad}$ are most prominent on the Ru/TiO$_2$-3 catalyst, which shows also the highest activity for CO methanation. On the less active Ru/TiO$_2$-2 and Ru/TiO$_2$-4 catalysts, in contrast, the band intensities are much lower. For the sample with the lowest surface area and lowest activity (Ru/TiO$_2$-1) they are hardly visible under steady-state conditions. Moreover, for the Ru/TiO$_2$-3 catalyst, and to a lesser extent also for Ru/TiO$_2$-4, there is also a characteristic peak at 1982 cm$^{-1}$, which was previously attributed to a CO$_{ad}$ species adsorbed on-top of highly dispersed, low coordinated Ru clusters isolated from other metal particles.$^{60, 69, 208}$ A band characteristic for bridge bonded CO$_{ad}$ species, located at 1932 cm$^{-1}$, was only observed on Ru/TiO$_2$-1. This latter finding agrees well with results from a number of previous studies where the relative population of on top and bridge bonded adsorbed CO was reported to depend sensitively on the Ru particle size, with a higher fraction of bridge bonded CO$_{ad}$ for larger particles.$^{47, 192, 204}$ Hence, the presence of larger Ru particles increases the possibility of adsorption in a bridge bonded configuration.$^{55, 180}$

A band appearing at 1765 cm$^{-1}$ had been assigned to adsorbed formyl surface species (HCO$_{ad}$) which are formed upon reaction between adsorbed CO$_{ad}$ and H$_{ad}$.$^{123, 72, 209}$ This species had been identified as an active reaction intermediate, since the rate of its off-reaction, as identified in an isotope exchange experiment switching from $^{12}$CO/H$_2$ to $^{13}$CO/H$_2$, was rather similar to the CO methanation rate.$^{72}$ This species appears for all catalysts, but with different intensities depending on the catalyst, as shown in Fig.54. Its coverage first increases gradually with increasing support surface area, from Ru/TiO$_2$-1 to Ru/TiO$_2$-3, but decreases again for even higher surface area (Ru/TiO$_2$-4, see Fig. 56a). Hence, also the intensity of this species is correlated in the same way with the activity for CO methanation (see Fig. 52b) as described above for the CO$_{ad}$ species.
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Finally, a band related to surface formates was observed at 1554 cm\(^{-1}\). The band intensity related to this species increases with increasing surface area (Fig.56b), from being absent on the lowest surface area catalyst (Ru/TiO\(_2\)-1) to low intensities on the Ru/TiO\(_2\)-2 and Ru/TiO\(_2\)-3 catalysts to a very pronounced band for the Ru/TiO\(_2\)-4 catalyst with the highest surface area. For the latter catalyst it is by factors of 15 and 13 higher compared to the Ru/TiO\(_2\)-2 and Ru/TiO\(_2\)-3 catalysts, respectively. The much higher steady-state coverage of surface formates on the Ru/TiO\(_2\)-4 catalyst is suspected as a potential reason for the much lower activity of the Ru/TiO\(_2\)-4 catalyst.

In a simple picture the largely different CO\(_{ad}\) band intensities on the different catalysts may be expected to result from significant differences in the CO\(_{ad}\) coverages due to a modification of the CO adsorption properties of the Ru nanoparticles. Considering, however, that for all catalysts CO\(_2\) methanation is completely suppressed in SR-ref 6000 due to surface blocking by a dense CO adlayer, resulting in 100% selectivity, the actual

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**Figure 56:** a) Intensity of adsorbed formyl surface species (HCO\(_{ad}\) – 1760 cm\(^{-1}\)), and b) of the surface formate species related band (HCOO\(_{ad}\) – 1554 cm\(^{-1}\)) for Ru/TiO\(_2\) catalysts with different support surface areas (SA).

![Graph showing intensity of adsorbed formyl and formate species](image-url)
CO$_{ad}$ coverages on the different samples cannot differ to an extent as indicated by the very different IR intensities in Figs. 54 and 55. Most simply, the rather low CO$_{ad}$ band intensities in particular of the highest surface area (Ru/TiO$_2$-4) catalyst may be due to a significantly lower number of accessible adsorption sites than expected from the dispersion of the Ru particles. This may be caused by a partial overgrowth of the Ru nanoparticles by TiO$_x$ species. Such behavior is a characteristic feature of strong metal-support interactions (SMSI), and had been reported earlier, e.g., for oxide supported Pt or Ru catalysts.$^{114,200}$

**Figure 57**: High resolution TEM images of Ru nanoparticles particles on different titania supports (a: Ru/TiO$_2$-1; b: Ru/TiO$_2$-2; c: Ru/TiO$_2$-3; d: Ru/TiO$_2$-4).

Experimental evidence for such SMSI effects in the present case is provided by high resolution TEM images, which are shown in Fig. 57. For Ru/TiO$_2$-4, the image resolves lattice fringes of TiO$_2$ crystallites through Ru nanoparticles as also indicated by the low contrast between Ru and TiO$_2$ particles in the TEM micrographs, which is indicative of a partial overgrowth of Ru by small reduced TiO$_X$ (x < 4)islands. Similar features are
detected also for the Ru/TiO$_2$-3 catalyst, but to a much lower extent, while for the other catalysts with even lower surface area (Ru/TiO$_2$-1 and Ru/TiO$_2$-2) they could not be observed. Hence, both the low CO$_{ad}$ absorption intensity and the TEM images point to a partial overgrowth of the Ru nanoparticles on the Ru/TiO$_2$-4 catalyst, which can explain also the low activity of this catalyst.

Further information on the adsorption properties of the various Ru catalysts can be obtained by determining the stability of the CO adlayer under reaction conditions.

**Figure 58:** Series of DRIFT spectra recorded during 750 min desorption in N$_2$ at 190°C (0, 1, 3, 5, 7, 9, 15, 75, 105, 195, 255, 435, 495, 675, and 795 min) after surface saturation in SR-ref 6000 at 190°C for 300 min on Ru/TiO$_2$-1, Ru/TiO$_2$-2, Ru/TiO$_2$-3, and Ru/TiO$_2$-4).

For this purpose, we performed another experiment where we switched from reaction atmosphere to inert atmosphere (N$_2$ only) at 190 °C. The catalyst surface was first saturated with CO$_{ad}$ / carbonyl species during reaction for 250 min, before their
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decomposition / desorption with time was followed for 800 min under isothermal conditions. The spectra recorded during desorption in N₂, and after saturation of the catalyst surface in SR-ref 6000, are presented in Fig. 58. The temporal evolution of the CO\textsubscript{ad} bands (see Fig. 8) reveals an increasing stability of the CO\textsubscript{ad} species adsorbed on the Ru nanoparticles with increasing surface area of the respective catalyst. The time required for complete desorption of the CO\textsubscript{ad} species clearly increases with increasing support surface area. While they were almost completely desorbed in less than 10 min for the lowest surface area catalyst (Ru/TiO\textsubscript{2}-1), it took about 250 and 450 min to reach a CO\textsubscript{ad} / Ru-carbonyl free surface for the Ru/TiO\textsubscript{2}-2 and Ru/TiO\textsubscript{2}-3 catalysts, respectively. On the Ru/TiO\textsubscript{2}-4 catalyst, even after 800 min flushing in N₂ there were still about 50\% of the adsorbed CO / Ru-carbonyl species present (see Figs. 58 and 59).

This increasing stability of CO\textsubscript{ad} on Ru nanoparticles with increasing surface area of the catalysts (Ru/TiO\textsubscript{2}-1 < Ru/TiO\textsubscript{2}-2 < Ru/TiO\textsubscript{2}-3 < Ru/TiO\textsubscript{2}-4) cannot be explained by a geometric reduction of the number of accessible surface sites, but points to electronic effects, e.g., by an increasing electron donation to CO\textsubscript{ad} species, which will affect both the Ru-CO and the C-O bond. Such a transfer of electronic charge from the support into metal nanoparticles was demonstrated for the first time by Raymond et al. for nickel metal particles supported on germanium. In that case a transfer of only one electron from the support to about 10,000 Ni atoms was proposed to result in an increase of the activity for formic acid decomposition by a factor of 1.3 to 3.0\textsuperscript{119} The increase in CO adsorption strength demonstrated above points to such kind of metal-support interactions, which increase with increasing catalyst surface area. Since in the present work the increase in surface area of the catalysts goes along with a slight decrease in Ru particle size, we obtain an increase of the CO adsorption strength with decreasing Ru particle size, which is opposite to the trend derived previously on other metal oxide supported Ru catalysts (Ru/zeolite,\textsuperscript{62} Ru/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{72}) Furthermore, the change in electronic and chemical properties due to metal-support interactions may also be responsible for the increasing activity for CO methanation with increasing surface area, at least for surface areas up to 121 m\textsuperscript{2} g\textsubscript{cat}\textsuperscript{-1} (Ru/TiO\textsubscript{2}-1 to Ru/TiO\textsubscript{2}-3). For the Ru/TiO\textsubscript{2}-4 catalyst with the highest surface area, however, the measured activity becomes significantly lower because of the partial overgrowth of Ru nanoparticles by TiO\textsubscript{x} species, as described above.
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Overall, these results indicate increasing metal-support interactions with increasing TiO$_2$ support surface area / decreasing TiO$_2$ crystallite size, which result in a stabilization of adsorbed CO and which are presumably also responsible for the observed increase in TOF based CO methanation activity. In addition to these electronic modifications, strong-metal support interactions (SMSI) lead to a partial overgrowth of Ru by TiO$_2$, which significantly reduces the number of accessible Ru surface sites and hence the number of adsorbed CO and formyl species as well as the CO methanation activity.
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3.5.5. Interaction of Ru/TiO₂ with CO₂ and origin of selectivity

So far we have not addressed the increasing selectivity with increasing surface area of the various Ru/TiO₂ catalysts observed for reaction in SR-ref 100, i.e., under reaction conditions where the inherent activity / selectivity of the catalyst is dominant rather than COₐd site blocking. According to the Brønstedt-Evans-Polanyi (BEP) principle, a higher stability of the dissociation product (COₐd) should result in a lower activation barrier for CO₂ dissociation and, hence, in a lower selectivity of the catalyst for CO methanation under these conditions. This, however, is in contrast to the finding in the kinetic measurements described above, where the selectivity was found to increase in the order Ru/TiO₂-1 < Ru/TiO₂-2 < Ru/TiO₂-3 < Ru/TiO₂-4 with decreasing Ru particle size, while the CO adsorption strength increased. On the other hand, in previous studies on closely related Ru/zeolite and Ru/Al₂O₃ catalysts, the selectivity was also observed to increase significantly with decreasing Ru particle size, up to 100% for 1 nm Ru particle size, but in that case the CO adsorption strength decreased with decreasing particle size. Hence, in that case expectations based on the BEP principle agreed with the experimental finding. To better understand this apparent discrepancy, we directly tested and compared the CO₂ dissociation activity of all Ru/TiO₂ catalysts by in-situ IR spectroscopic measurements in CO free CO₂-ref (15.5% CO₂, balance H₂).

The sets of spectra presented in Fig. 60, which were recorded during 1000 min exposure to CO₂-ref reaction gas at 190 °C, show for all catalysts except Ru/TiO₂-1 two dominant peaks in the CO region, one at around 2075 cm⁻¹ and one at around 2010 cm⁻¹, where the former one essentially disappears during time on stream. The band related to the Ru-multicarbonyl species (~2075 cm⁻¹) exhibits a small red shift, down to 2072 cm⁻¹, compared to the SR-ref 6000 gas mixture. This shift can be explained by the rather low coverage of COₐd resulting from the CO₂ dissociation. The band at 2018 – 2009 cm⁻¹ associated with on top adsorbed COₐd species shows a similar red shift compared to the SR-ref 6000 gas mixture, it appeared in the range 2005-1992 cm⁻¹. Bands at 2009, 2058 and 1982 cm⁻¹, which had been detected in the presence of CO in the reaction gas mixture, did not appear in CO-free reformate gas.

Also in these measurements we will focus on the situation reached under steady-state conditions. We will estimate the tendency for CO₂ dissociation, which is directly correlated with the selectivity for CO methanation, from the amount of COₐd present under steady-state conditions during exposure to CO₂-ref. This is determined from the intensity of the
CO\textsubscript{ad} related band under steady-state conditions, after normalization to the intensity obtained under saturation conditions, during exposure to SR-ref 6000.

**Figure 60:** DRIFT spectra over different surface area Ru catalysts at different reaction times (from bottom to top: 0, 1, 5, 9, 15, 75, 135, 195, 255, 495, 615, and 735 min) in CO\textsubscript{2}-ref gas mixture at 190°C. a) Ru/TiO\textsubscript{2}-1, b) Ru/TiO\textsubscript{2}-2, c) Ru/TiO\textsubscript{2}-3, and d) Ru/TiO\textsubscript{2}-4 (OCO stretch vibration region).

The normalized intensities, which are presented in Fig.61, clearly show that the formation of CO\textsubscript{ad} and Ru-carbonyl species from the dissociation of CO\textsubscript{2} decreases with increasing support surface area and, hence, decreasing Ru particle size. The relative intensities of the carbonyl related band decrease from 17% over Ru/TiO\textsubscript{2}-2 catalyst to 0.4 % over Ru/TiO\textsubscript{2}-4. (Note that the normalization results in measurable contributions from the Ru-
multicarbonyl species, although on an absolute scale the band intensities are very low.)
Interestingly, the lowest surface area catalyst (Ru/TiO$_2$-1) did not show any formation of Ru-carbonyl species, which resembles the behavior in SR-ref 6000 (see section 3.3), where they were also absent. For the on-top adsorbed CO$_{ad}$ species, the relative band intensity is about 125% for the Ru/TiO$_2$-1 catalyst, and it decreased with increasing support surface area, reaching 41% for the Ru/TiO$_2$-4 catalyst (see Fig.61). Note that the relative intensity $>100\%$ for CO$_{ad}$ observed on the Ru/TiO$_2$-1 catalyst is possible due to the much lower intensity for the bridge bonded CO.

These trends in the coverages of CO$_{ad}$ and multicarbonyl species from CO$_2$-ref agree well with the observed increase of the selectivity with increasing surface area in SR-ref 100, which goes along with a decreasing Ru particle size. Hence, also for the Ru/TiO$_2$ catalysts the selectivity for CO methanation is correlated with their CO$_2$ dissociation activity. Moreover, also in the present case the activity for CO$_2$ dissociation decreases with decreasing of Ru particle diameter, as observed earlier for Ru/zeolite and Ru/Al$_2$O$_3$.$^{62}$ Different from the latter cases, however, this is not correlated with a stabilization of the dissociation product CO$_{ad}$, as expected in a simple picture based on the BEP principle. Hence, for catalysts with significant metal-support interactions the physical origin for the increasing selectivity with decreasing Ru particle size below ca. 2 nm may be different than in the previous cases. This is topic of ongoing studies in our laboratory.

**Figure 61:** Normalized intensity of adsorbed surface species (empty columns: 2071 cm$^{-1}$; filled columns: 2009-1999 cm$^{-1}$) resulting from dissociation of CO$_2$ in CO$_2$-ref on a) Ru/TiO$_2$-1, b) Ru/TiO$_2$-2, c) Ru/TiO$_2$-3, and d) Ru/TiO$_2$-4.
3.5.6 Conclusions

Employing a combination of kinetic and *in situ* spectroscopic measurements as well as detailed *ex situ* catalyst characterization, we could show for the selective CO methanation reaction on a set of Ru/TiO$_2$ catalysts with rather similar Ru loading, Ru particle size, and TiO$_2$ phase composition that both the activity (Ru mass based activity and TOFs) and the selectivity of these catalysts in two reaction mixtures with medium (0.6%) and very low (0.01 %) CO contents depend sensitively on the BET surface area of the catalysts. The activity increases first up to a maximum surface area of 121 m$^2$ g and then decreases again for the catalyst with the highest surface. The selectivity for CO methanation is 100% for reaction in reformate gases with medium CO content, due to site blocking for CO$_2$ dissociation by CO$_{ad}$, it increases steadily for reaction in reformate with very low CO content, where site blocking effects are little relevant, reaching close to 100% for the catalyst with the highest surface area. The variation in reaction behavior with increasing catalyst surface area goes along with and is affected by the following effects:

i) An increasing dispersion / decreasing Ru particle size (with increasing surface area), which similar to previous findings for other supported Ru catalysts (Ru/zeolite, Ru/Al$_2$O$_3$) dominates the CO$_2$ dissociation activity, results in an increasing selectivity for CO methanation under conditions of low CO contents, where CO$_{ad}$ site blocking effects are negligible (particle size effect).

ii) The increasing Ru dispersion activity also causes the CO methanation activity to increase, up to the Ru/TiO$_2$-3 catalyst with a surface area of about 121 m$^2$ g$^{-1}$. With further increasing surface area, counteracting strong metal-support interaction (SMSI) effects overcompensate this by reducing the surface area available for reaction, as evident from the CO$_{ad}$ uptake at saturation (steady-state in SR-ref 6000). Accordingly, the activity drops sharply for the latter catalyst due to an SMSI effect.

iii) Metal-support interactions are evidenced also by an increasingly stronger CO adsorption on the Ru particles with increasing BET surface area. Considering that with increasing surface area also the Ru particle size decreases, this variation of the CO adsorption strength is in contrast to previous observations on other oxide supported Ru catalysts (Ru/zeolite, Ru/Al$_2$O$_3$), where the CO adsorption energy was found to decrease with increasing Ru dispersion / decreasing Ru particle size. This observation points to an MSI effect for the CO
3.5. Results and discussion

adsorption energy which overcompensates the particle size effects dominant in the latter catalysts.

iv) Metal-support interactions must be responsible also for the disparate trends for CO adsorption strength and for the selectivity for CO methanation / activity for CO\textsubscript{2} dissociation, with an increasing selectivity for CO methanation / decreasing activity for CO\textsubscript{2} dissociation together with an increasing CO adsorption strength with increasing surface area / increasing Ru dispersion, where the latter is opposite to the trend for the CO adsorption energy observed in previous studies on Ru/zeolite and Ru/Al\textsubscript{2}O\textsubscript{3} catalysts and opposite to the trend expected from simple arguments based on the BEP principle.

Overall, the data clearly demonstrate the role of metal-support interactions in the selective CO methanation on Ru/TiO\textsubscript{2}, which affect the reaction behavior in addition to the Ru particle size effects well known for other supported Ru catalysts. Metal-support interactions also provide an additional parameter to modify and steer the catalytic behavior of the Ru catalyst, which is highly relevant also for further catalyst optimization for technical applications.
4. Thesis Summary
4. Thesis Summary

4.1. English Summary

In this thesis work the impact of the Ru particle size and of metal-support interactions on the catalytic performance of supported Ru catalysts for the Selective CO Methanation in CO₂ rich H₂ feed gases was investigated. These results were obtained by using a multi-analytical approach, employing state of the art time on stream reaction kinetic experiments, as well as time resolved *operando* FTIRS and X-ray absorption fine structure (XAFS) spectroscopy, in addition to a complete catalyst characterization with *ex situ* analysis techniques. The most important results and general conclusions from these studies in combination will be summarized in the following two sections. Afterwards, the final message from this work will be presented at the end of the summary as a general conclusion.

4.1.1. Ru particle size effects on activity and selectivity

i) An increasing calcination temperature of the Ru/zeolite catalyst, up to 500 °C in 10% O₂ / N₂, results in a decrease of the Ru particle size from 1.5 to 1.0 nm. This goes along with a gradual increase of the selectivity for CO methanation in CO₂ rich gas mixture, from ca. 70 to 100%. In CO free reformate gas, the increasing selectivity is reflected by a decreasing coverage of COₐd surface species resulting from the dissociation of CO₂. At the same time, the Ru mass normalized activity over this Ru/zeolite catalyst decreases by 18 and 30% upon increasing Ru particle size, from 1.0 nm to 1.5 nm for the reformate gases containing 100 and 6000 ppm CO, respectively. TOF values, in contrast, increased by about 10 and 40% with increasing Ru particle size. Hence, calcination at higher temperatures has a positive effect on the Ru mass normalized activity, due to a higher (accessible) Ru surface area with increasing Ru dispersion. In this case the decrease of TOF based activity due to the decrease of Ru particle size is overcome by the higher dispersion, resulting in higher mass normalized activity for Ru/zeolite catalysts with smaller Ru particles.

ii) The addition of water to the reaction gas mixture led to a distinct increase of the selectivity of the Ru/γ-Al₂O₃ catalyst from ca. 42 to 100%, as the amount of water in the reaction atmosphere was increased from 0 to 30%. *Operando* EXAFS and *ex situ* TEM measurements indicated a significant decrease of the Ru particle size with increasing the amount of water in the reaction gas mixture. As for the Ru/zeolite catalyst, this decrease in Ru particle size goes along with an increase of the selectivity for CO methanation also for Ru/Al₂O₃. The presence of water and the resulting decrease of the Ru particle size did not result in significant changes of the activity of
The Ru/Al₂O₃ catalyst. For the Ru/zeolite catalyst, in contrast, there is a pronounced decrease of the activity in the presence of water, which is most probably caused by a water induced dealumination of the zeolite framework.

iii) The occasional addition of water to the reaction gas mixture during the CO methanation reaction on a poorly selective catalyst (Ru/Al₂O₃) induces an increase in CO selectivity, which does not decrease again after removal of water from the reaction gas mixture. Furthermore, an increase of the CO methanation activity in subsequent reaction in dry reformate as compared to activation and reaction in dry reformate directly was observed. These changes in activity and selectivity were demonstrated to go along with an increase of the Ru dispersion on this catalyst upon its exposure to water containing reaction gas mixtures. Moreover, these structural changes in the presence of water persist after switching again to a dry reaction gas feed. From these findings it can be concluded that the drastic increase of the selectivity of Ru/Al₂O₃ originates from an irreversible structural change, i.e., a decrease of the Ru particle size, rather than from blocking of active sites due to adsorption of H₂O on the Ru NPs. The higher Ru mass normalized activity of Ru/Al₂O₃ after removal of water from the feed is again attributed to the increased surface area of Ru. This is similar to the already described findings for the Ru/zeolite catalyst; this effect also overcompensates the lower turnover frequency (TOF) in case of higher dispersion.

iv) The increase of the specific surface area (from 20 to 235 m²g⁻¹) of the TiO₂ catalyst support resulted in a decrease of the average Ru particle size (increase of Ru dispersion) from 2.3 nm down to 1.48 nm for Ru/TiO₂ catalysts having similar Ru loading. Additionally, this resulted in an increase of the selectivity for CO methanation from 58 to 95%. Considering the increasing stability of CO_ad with increasing support surface area / decreasing Ru particle size, this increase cannot originate from Ru particle size effects only, as it was reported for (non-reducible) Ru/Al₂O₃ and Ru/zeolite catalysts. Hence, it is proposed that for Ru/TiO₂, in addition, metal support interactions are responsible for the increasing selectivity for CO methanation / decreasing activity for CO₂ dissociation with increasing surface area. Moreover, there is also a strong contribution of metal-support interactions on the catalytic activity for CO methanation on Ru/TiO₂ catalysts. While for non-reducible Ru catalysts (Ru/Al₂O₃, Ru/zeolite), the activity in terms of TOFs is always increasing with increasing Ru particle size, a completely different trend is observed for Ru/TiO₂ catalysts with different surface areas. Here, the TOF first increases and afterwards
4. Thesis Summary

decreases with increasing Ru particle size / decreasing surface area. This clearly demonstrates that, in addition to Ru particle size effects, the activity of Ru/TiO₂ is determined also by metal-support interactions, whose extent sensitively depends on the catalyst surface area / TiO₂ crystallite size. This point will be discussed in more detail in the following section.

4.1.2. Metal-support interaction effects on activity and selectivity

The impact of metal-support interactions, and changes therein on the catalytic activity and selectivity for CO methanation is summarized in the following:

i) The mass normalized activity of the most active Ru/TiO₂ catalyst is significantly higher than that of a Ru/γ-Al₂O₃ catalyst with similar surface area and similar Ru particle size. Fundamental differences in the catalytic properties of both catalysts could be demonstrated by their significantly different adsorption properties under reaction conditions. The Ru/TiO₂ catalyst showed a high abundance of both on top adsorbed COₐd species as well as surface stabilized Ru-multicarbonyl species. On the Ru/γ-Al₂O₃ catalyst, in contrast, a significantly higher fraction of bridge bonded COₐd species compared to on top adsorbed COₐd is observed, and there are almost no Ru-carbonyl species present. These observations clearly demonstrate that the adsorption properties of Ru nanoparticles with similar size can be strongly modified by the nature of the catalyst support. These differences are most likely related to an electronic modification of the Ru metal particles due to (strong) metal-support interactions.

ii) For Ru/TiO₂ catalyst, the increasing TiO₂ support surface area resulted in an increase of the metal-support interaction. This conclusion is based on the strong modification of the adsorption properties of the Ru nanoparticles on different Ru/TiO₂ catalysts with similar Ru loading and Ru particle diameter, but different TiO₂ surface areas. With increasing surface area also the stability of COₐd and Ru-carbonyl species increased, reaching the highest COₐd stability on the Ru/TiO₂ catalyst with highest surface area (235 m²g⁻¹). Here the stronger adsorption with increasing catalyst surface area / decreasing TiO₂ particle size is explained by and increasing strong metal-support interactions, which result in a higher electron donation from TiO₂ crystallites to Ru nanoparticles as well as in an increased probability for the electron back donation. This finally leads to a strong carbon-metal bond in the COₐd species.

In summary, it could be clearly demonstrated in this work that the Ru particle size as well as the nature of the metal oxide support have an immense impact on the activity of supported Ru catalysts for the CO methantion as well as for the CO₂ methanation. Due to
its influence on the latter reaction, this results also in significant changes of the selectivity for CO methanation, which is highly relevant for technical applications, e.g. the removal of CO from H₂-rich reformates in the presence of much higher amounts of CO₂ (6000 ppm CO, 15.5% CO₂). For catalysts based on non-reducible oxides with weak or moderate metal-support interactions only (Ru/zeolite and Ru/Al₂O₃) the selectivity for CO methanation is determined almost exclusively by the Ru particle size. With increasing Ru dispersion and, hence, decreasing mean diameter of the Ru nanoparticles, the selectivity continuously increases. From the results of the in situ IR measurements during the CO/CO₂ methanation on these catalysts with various Ru particle sizes it was demonstrated that this behaviour is a result of decreasing stability of the dissociation products of adsorbed CO₂ (COₐd) with decreasing size of the Ru nanoparticles. Here different Ru particle sizes were realized by calcination at different temperatures or the addition of water to the reaction atmosphere for Ru/zeolite or Ru/Al₂O₃, respectively. According to the Brønsted–Evans–Polanyi (BEP) principle the destabilization of the dissociation products results in an increasing energy barrier for CO₂ dissociation and, hence, an increasing selectivity for CO methanation with decreasing Ru particle size. For catalysts supported on reducible oxides (e.g., Ru/TiO₂), on the other hand, (strong) metal-support interaction have to be considered in addition to Ru particle size effects. Although the selectivity for CO methanation, still increases with decreasing Ru particle size (decreasing activity for CO₂ dissociation and methanation), an increasing stability of the CO adlayer during reaction was observed. This behavior contradicts the above described BEP principle, which accordingly is proposed to be valid for non-reducible catalyst supports only. Therefore, for Ru/TiO₂ catalysts metal-support interactions and changes therein are assumed to strongly affect also the CO selectivity.

Similar conclusions can be drawn with respect to the intrinsic activity for CO methanation (TOFs), which were found to continuously increase with increasing Ru particle size for catalysts based on non-reducible support materials (Ru/zeolite or Ru/Al₂O₃), but not for Ru/TiO₂. Hence, also in the evaluation of the CO methanation activity and any conclusions based on these results, e.g. on the reaction mechanism, one has to distinguish between catalysts based on reducible and non-reducible support materials.
4.2 German Summary (Zusammenfassung)


4.2.1 Einfluss der Ru Partikelgröße auf die Selektivität und Aktivität

i) Die Kalzinierung eines Ru/Zeolith Katalysators bei zunehmend höheren Temperaturen, bis 500 °C, in 10% O₂/N₂ führt zu einer Abnahme der Ru Partikelgröße von 1.5 bis 1.0 nm und zugleich zu einer Erhöhung der Selektivität für die CO-Methanisierung in CO₂ reichen Gasgemischen von ca. 70 auf 100%. Diese zunehmende Selektivität spiegelt sich auch in einer abnehmenden Bedeckung von adsorbiertem CO (COₐd) wieder, das aus der Dissoziation CO₂ in CO freiem Gasgemisch gebildet wird. Gleichzeitig nimmt die auf die Ru Masse normalisierte Aktivität des Ru/Zeolith Katalysators in Brenngasen mit 100 bzw. 6000 ppm CO bei Erhöhung der Ru Partikelgröße von 1.0 nm auf 1.5 nm um 18 bzw. 30% ab. Die TOF-Werte hingegen nehmen mit zunehmender Partikelgröße um etwa 10 bzw. 40% zu. Eine Kalzinierung des Katalysators bei hohen Temperaturen hat somit aufgrund der zunehmenden Ru Oberfläche mit abnehmender Ru Partikelgröße einen positiven Einfluss auf die Ru-Masse normalisierte Aktivität. In diesem Fall überwiegt die Zunahme der Aktivität aufgrund der zunehmenden Dispersion die Abnahme der TOF-basierten Aktivität mit abnehmender Ru Partikelgröße.

ii) Die Zugabe von Wasserdampf zur Reaktionsgasmischung führt zu einem deutlichen Anstieg der Selektivität des Ru/γ-Al₂O₃ Katalysator von ca. 42 auf 100% für Reaktionsgasmischung mit 0 bzw. 30% Wasser. Hier konnte durch operando EXAFS und ex situ TEM Messungen nachgewiesen werden, dass die Zugabe von Wasser zu einer signifikanten Abnahme der Ru Partikelgröße führt, die mit dem Wassergehalt im

iii) Die kurzzeitige Zugabe von Wasser zum Reaktionsgasgemisch während der CO Methanisierung über einem wenig selektiven Katalysator (Ru/Al\textsubscript{2}O\textsubscript{3}) führt zu einer drastischen Erhöhung der Selektivität, die auch nach der Entfernung von Wasser aus dem Reaktionsgasgemisch bestehen bleibt. Zudem wurde in anschließenden Messungen unter trockenen Bedingungen eine deutlich höhere Aktivität für die CO Methanisierung beobachtet als direkt unter trockenen Bedingungen, ohne die Zugabe von Wasser. Es konnte gezeigt werden, dass diese Änderungen in der Aktivität und Selektivität des Ru/Al\textsubscript{2}O\textsubscript{3} Katalysators mit einer Erhöhung der Ru Dispersion einhergehen, die durch die (temporäre) Anwesenheit von Wasser im Reaktionsgasgemisch verursacht wird. Diese strukturellen Änderungen in der Anwesenheit von Wassers bleiben auch nach einem Übergang zu trockenen Reaktionsbedingungen bestehen. Aus diesen Ergebnissen kann es geschlossen werden, dass die drastische Erhöhung der Selektivität eine Folge von irreversiblen strukturellen Änderungen ist (Abnahme der Ru Partikelgröße), und nicht durch eine Blockierung aktiver Stellen durch die Adsorption von Wasser auf der Ru Oberfläche verursacht wird. Zudem kann die höhere massenormalisierte Aktivität des Ru/Al\textsubscript{2}O\textsubscript{3} Katalysators unter trockenen Bedingungen wieder der höheren Ru Oberfläche zugeschrieben werden. Wie bereits für den Ru/Zeolith Katalysator beschrieben überwiegt dies die geringere TOF der Katalysatoren mit höherer Dispersion.

iv) Die Erhöhung der spezifischen Oberfläche (von 20 auf 235 m\textsuperscript{2} g\textsuperscript{-1}) des TiO\textsubscript{2}-Trägermaterials führte zu einer Abnahme der mittleren Ru Partikelgröße von 2.3 nm auf 1.48 nm auf Ru/TiO\textsubscript{2} Katalysatoren mit ähnlicher Ru Beladung. Gleichzeitig hat auch die Selektivität für die CO Methanisierung von 58 auf 95% zugenommen. Angesichts der zunehmenden Stabilität von auf Ru adsorbiertem CO (CO\textsubscript{ad}) mit zunehmender Katalysatoroberfläche kann die zunehmende Selektivität allerdings nicht
alleine auf Ru Partikelgrößeneffekte zurückgeführt werden, wie es für nicht reduzierbare Ru/Al₂O₃ und Ru/Zeolith Katalysatoren der Fall ist. Es wird davon ausgegangen, dass für Ru/TiO₂ zusätzlich Metall-Träger-Wechselwirkungen für die Zunahme der Selektivität bzw. die Abnahme der Aktivität für die CO₂ Methanisierung mit zunehmender Katalysatoroberfläche verantwortlich sind.


4.3.2. Metall – Trägerwechselwirkung

Die Auswirkungen der Metall-Träger-Wechselwirkungen und Veränderungen darin auf die katalytische Aktivität und Selektivität für CO-Methanisierung wird im Folgenden zusammengefasst:


Zusammenfassend konnte in dieser Arbeit deutlich gezeigt werden, dass sowohl die Ru Partikelgröße als auch die Natur des Trägermaterials einen entscheidenden Einfluss auf die Aktivität geträgerten Ru Katalysatoren haben, für die CO Methanisierung ebenso wie für die CO$_2$ Methanisierung. Aus den Einflüssen auf die CO$_2$ Methanisierung ergeben sich dabei gleichzeitig auch Änderungen in der Selektivität zugunsten der CO Methanisierung, die in technischen Anwendungen von großer Bedeutung ist, z.B. in der Entfernung von CO aus wasserstoffreichen Brenngasen in der Anwesenheit von sehr viel höheren CO$_2$ Konzentrationen (15.5% CO$_2$).


Zu ähnlichen Schlussfolgerungen kommt man, wenn man die intrinsische Aktivität der Ru Katalysatoren (TOFs) vergleicht. Für Katalysatoren mit schwachen Metall-Träger Wechselwirkungen nimmt diese mit zunehmender Ru Partikelgröße kontinuierlich zu, aber nicht für Ru/TiO$_2$. Folglich muss auch bei der Bewertung der Aktivität für die CO Methanisierung und bei daraus gezogenen Schlussfolgerungen, z.B. bezüglich des Mechanismus der Reaktion, zwischen Katalysatoren mit reduzierbaren und nicht-reduzierbaren Trägermaterialien unterschieden werden.
5. References
5. References


5. References


References


5. References


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5. References


5. References


5. References


5. References


5. References


5. References


5. References


6. Appendix
6.1 Supplementary Tables:

**Table S1:** The dilution ratios of the catalysts used in the kinetic measurements

<table>
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<tr>
<th>Catalyst</th>
<th>Gas Reformate</th>
<th>Dilution</th>
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<td>2.2 wt.% Ru/zeolite</td>
<td>SR-ref 100</td>
<td>1: 400</td>
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<td>SR-ref 100 + (H₂O : 5 – 30%)</td>
<td>1: 250</td>
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<tr>
<td></td>
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<td></td>
<td>SR-ref 6000 + (H₂O : 5 – 30%)</td>
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Table S2: EXAFS measurements fit data and structural parameters of Ru/Al₂O₃ catalyst with time on stream during the reaction in ID-ref 600 reaction gas mixture containing 5% H₂O reaction temperature 190°C.

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<th>Time</th>
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<th>DW/10⁻³Å²</th>
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6.2 Supplementary Figures:

**Figure S1**: Left: $k^3$ weighted chi function, right: corresponding Fourier transforms (3.2 – 11.6 k-space) for fresh Ru/zeolite catalyst measured in ID-ref 6000 saturated with 5% H$_2$O after different reaction times (4 min: a, b; 72 min: c, d; 144 min: e, f).
Figure S2: Kinetic measurement over 2.2 Ru/zeolite catalyst under dry reaction conditions at normal flow (41.6 Nml min$^{-1}$: ■) and at higher flow rates (46.6:Δ & 51.5: ● Nml min$^{-1}$) but by replacing the water in the reaction gas mixture by N$_2$ for comparison with measurements in the presence of 15 (▲) and 30% H$_2$O (▼).

Figure S3: Left: $k^3$ weighted chi function, right: corresponding Fourier transforms (3.2 – 11.6 k-space) for the fresh Ru/$\gamma$-Al$_2$O$_3$ catalyst measured in air (a, c) and after being heated to 150°C in N$_2$ (b, d).
Figure S4: Ratio between on top adsorbed and bridge bonded adsorbed CO\textsubscript{ad} as a function of water content in the SR-ref 6000 gas mixture at steady state reaction conditions.

Figure S5: Left panel: Evolution of the intensity of adsorbed bidentate formate with time on stream (Ru/Al\textsubscript{2}O\textsubscript{3}: a; Ru/zeolite: b) in SR-ref 6000 gas mixture containing different amounts of water (0 %: ■; 5 %: ▲; 10 %: ●; 15 %: ○; 30 %: ▼). Right panel: (c, d) steady-state intensity of adsorbed bidentate formate as a function of the water content (Ru/Al\textsubscript{2}O\textsubscript{3}: ▶; Ru/zeolite: ▶).
Figure S6: Ru mass normalized CO methanation rates at 190°C on changing from wet SR-ref 6000 reformate (W; 15% H₂O; block blue symbols) to dry SR-ref 6000 gas reformate (D; open red symbols) in cases the catalyst is purged for 30 min between the wet and dry experiments (♦, ◊ or left standing in wet SR-ref 6000: ●, ○).

Figure S7: Ru mass normalized CO methanation rates at 190°C during repeated switching from wet (SR-ref 6000 + 15 % H₂O) to dry reaction atmosphere (SR-ref 6000) and back, and finally reaction in dry SR-ref 6000 for in total 80 hours on stream (filled blue circles: wet; empty red circles: dry)
Figure S8: Temporal evolution of the intensity of absorption bands related to different species adsorbed on the Ru/γ-Al₂O₃ catalyst (■, □: on top adsorbed COₐd; ●, ○: bridge bonded COₐd; ▲, △: bidentate formate) during CO methanation at 190°C; in dry SR-ref 6000 (D1; □, ○, △) then reaction in the presence of 5% (W; ■, ●, ▲), and back again to dry SR-ref 6000 (D2; □, ○, △).

Figure S9: DRIFT spectra recorded at different reaction times during the CO methanation in SR-ref 6000 gas mixture at 190°C on RuTiO₂ catalysts with different surface areas, from bottom to top, after 0, 1, 5, 9, 15, 75, 135,195, 255, 495, 615, and 735 min. a) Ru/TiO₂-1, b) Ru/TiO₂-2, c) Ru/TiO₂-3, and d) Ru/TiO₂-4. OH stretch vibration region: 3900 – 3400 cm⁻¹ (raw data), CHₓ region: 3100 – 2750 cm⁻¹.
6.5. List of Publications:


6.5. Conference participation


Selective methanation of CO in CO$_2$-rich H$_2$ feeds: Effect of calcination temperature on the catalyst selectivity.


2. Selected as a young researcher to participate in the 59$^{th}$ meeting of Nobel Laureates in Lindau-Germany, dedicated for chemistry, Jun.27 to Jul.3. 2009.

1. Participated in the synchrotron light application meetings, organized by the ministry of Higher education and scientific research and SESAME program (Synchrotron-light for Experimental Science and Applications in the Mid-East), Cairo-Egypt, Nov, 17- 22, 2008.
6.6. Curriculum Vitae:
The curriculum vitae was removed from the electronic version of this work for the purpose of personal data protection.
6.7. Acknowledgement

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6.7. Declaration

I hereby certify that this dissertation has been composed by me and is based on my own work. Results presented in this thesis work had been published in the journals listed below. The published content was used for this thesis based on a license agreement permitted by respective journal publishers.


Ulm, 16. 02. 2016

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Ali Mohamed Abdel-Mageed Namies

(Born in Baltim, Egypt)