Structure–function relationship for CO2 methanation over ceria supported Rh and Ni catalysts under atmospheric pressure conditions

Natalia M. Martin, Felix Hemmingsson, Andreas Schaefer, Martin Ek, Lindsay R. Merte, Uta Hejral, Johan Gustafson, Magnus Skoglundh, Ann-Christin Dippel, Olof Gutowski, Matthias Bauer and Per-Anders Carlsson

In situ structural and chemical state characterization of Rh/CeO2 and Ni/CeO2 catalysts during atmospheric pressure CO2 methanation has been performed by a combined array of time-resolved analytical techniques including ambient-pressure X-ray photoelectron spectroscopy, high-energy X-ray diffraction and diffuse reflectance infrared Fourier transform spectroscopy. The ceria phase is partially reduced during the CO2 methanation and in particular Ce3+ species seem to facilitate activation of CO2 molecules. The activated CO2 molecules then react with atomic hydrogen provided from H2 dissociation on Rh and Ni sites to form formate species. For the most active catalyst (Rh/CeO2), transmission electron microscopy measurements show that the Rh nanoparticles are small (average 4 nm, but with a long tail towards smaller particles) due to a strong interaction between Rh particles and the ceria phase. In contrast, larger nanoparticles were observed for the Ni/CeO2 catalyst (average 6 nm, with no crystallites below 5 nm found), suggesting a weaker interaction with the ceria phase. The higher selectivity towards methane of Rh/CeO2 is proposed to be due to the stronger metal–support interaction.

1 Introduction

The conversion of CO2 to methane (methanation) has received wide interest during the last decade because of societal challenges related to climate change and finiteness of fossil fuels, which drive the change of the energy economy towards a system with a higher share of renewables.1-4 The methanation reaction from CO2 and H2 has the potential to (re-)use CO2 not only as an environmentally friendly carbon source but also as an alternative to H2 storage provided that the process can be made sufficiently efficient. In this context, CO2 conversion promoted by heterogeneous catalysis arouses interest.

Methanation of CO2 has previously been investigated for a number of catalytic systems based on transition metals supported on various oxides.5-10 Nickel is one of the most studied metal catalysts for the methanation reaction, but some previous results have shown deactivation of Ni catalysts even at low temperatures due to formation of mobile Ni carboxyls or carbon deposition.11,12 Ruthenium and rhodium supported on various metal oxides have been shown to be highly active for the hydrogenation of CO2 and also the most selective catalysts towards formation of methane.10,13,14 Among the support materials, alumina, ceria and titania have shown superior catalytic activity. CeO2 is one of the most interesting support materials in catalysis, mainly because of its high reducibility and high oxygen storage capacity, which are key to the functionality of ceria in many applications.15-17 Although many ceria supported metal catalysts, with high stability and activity, have been reported,18 the origin of their good performance is not unambiguously understood but attributed to various factors, which need to be clarified by confirming the active sites and the corresponding mechanism for the reaction. Operando characterization techniques are superior tools to obtain detailed structural information so as to understand the structure of active sites and reaction mechanisms under practical conditions. All these factors are necessary for a knowledge-based development of high-performance catalysts.

We have recently shown that supported Rh and Ni catalysts are active for methane production from CO2 hydrogenation under atmospheric pressure conditions and at relatively low temperatures (≤625 K).19 The selectivity towards...
methane formation was found to be higher for Rh as compared to Ni when supported on ceria. Thus a detailed comparison of these two systems during CO₂ methanation can reveal information about the active sites and reaction intermediates responsible for the enhanced activity towards methane production over Rh/CeO₂. Several other studies, including our previous work, have shown a support-dependent reaction mechanism toward CO₂ methanation via either a CO route (for catalysts supported on non-reducible oxides) or a formate route (for catalysts supported on reducible oxides). In related work we have shown that, for Rh catalysts supported on non-reducible oxides, the linearly adsorbed CO species is a more active precursor during the hydrogenation of CO₂ as compared to the bridge-bonded CO species, which is attributed to the smaller particle sizes of the Rh-based catalysts. Even though the previous work suggested a different reaction path for the catalysts supported on reducible oxides, the correlation between activity/selectivity and structural properties for ceria-based catalysts was still not fully understood and the oxygen vacancies on the surface of CeO₂ have been shown to play an important role in a number of catalytic reactions. In this work we investigate how the choice of the active metal may influence the catalytic activity and selectivity for ceria supported catalysts. For this, Ni and Rh supported on CeO₂ have been chosen and compared and the results show that the metal particle sizes are different for the two catalysts. It is suggested that for the highly dispersed catalyst (Rh/CeO₂), the stronger interaction of Rh with the ceria support leads to its enhanced activity during the methanation of CO₂. Special attention is paid to the identification of surface species and the influence of the ceria support during the CO₂ methanation reaction. The scope of this work is to relate catalytic activity with observed chemical or structural changes of the active metal (Rh or Ni) and the support phase. To this end, we have employed a combined array of high-energy X-ray diffraction (HE-XRD), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) under time-resolved, in situ conditions. This unique combination of methods allows for addressing both the chemical and structural dynamics important for the CO₂ conversion specifically targeting the site requirement. The results provide evidence that an active state of the ceria-based catalysts is rich in Ce⁴⁺ sites which can be associated with oxygen vacancies on reduced ceria activating CO₂ molecules forming formate, an important species for the reaction mechanism. Further, the results show the reversible oxidation of Ni during the transient CO₂ hydrogenation and the lack of adsorbed CO species for the Ni/CeO₂ sample. This may be related to the increased particle sizes, as determined from transmission electron microscopy (TEM) measurements on the as-prepared catalyst, indicating that Ni interacts more weakly with the ceria support. It is suggested that the linearly adsorbed CO species can be later hydrogenated to methane over the Rh/CeO₂ catalyst, while the weaker interaction between the CO and the Ni/CeO₂ catalyst leads to its fast desorption and thus lower methane selectivity.

2 Experimental section

2.1 Catalyst preparation and ex situ characterization

The catalysts were prepared by incipient wetness impregnation using ceria powder samples (99.5 H.S.A. 514, Rhone-Poulenc). The ceria samples were calcined in air at 875 K for 2 h starting from room temperature with a heating rate of 5 K min⁻¹ to remove carbonaceous impurities and stabilise the structure of the support materials. Precursor solutions of nickel and rhodium were prepared by dissolving Ni(NO₃)₂·6H₂O (Alfa Aesar) and Rh(NO₃)₃·6H₂O (Alfa Aesar) salts in Milli-Q water (18 MΩ cm). To increase the solubility of the rhodium salt, 25 droplets of 70% HNO₃ were added. The specific amount of precursor solution to obtain 3 wt.% of the metal was added to 3 g of each support. The theoretical metal loading is expected to be close to the actual loading as previously reported for incipient wetness impregnation.²¹ The impregnated ceria samples were instantly frozen with liquid nitrogen, freeze-dried for 24 h and finally calcined in air at 825 K for 1 h. The specific surface area of the catalysts was determined by nitrogen sorption at 77 K (Micromeritics Tristar 3000) using the Brunauer–Emmett–Teller (BET) method.²² The samples were dried in a N₂ flow at 500 K for 3 h prior to the measurements.

Structural characterization by transmission electron microscopy (TEM) imaging was performed using a JEOL 3000F microscope (300 kV, Cs = 0.6 mm). The catalysts were ground and dry dispersed onto plasma cleaned (10 s) lacy carbon copper grids. Rh and Ni/NiO nanoparticles were identified through their (111) plane spacings (ca. 2.1 Å for metallic Rh and 2.0/2.4 Å for Ni/NiO, respectively) which fall between the (200) and (220) plane spacings of the CeO₂ support (2.7 and 1.9 Å, respectively).

2.2 In situ characterization

2.2.1 High-energy X-ray diffraction. The structure of the samples during the CO₂ methanation reaction was studied by high-energy X-ray diffraction, in time-resolved in situ mode, in the second experimental hutch (EH2) of the P07 beamline at PETRA III at Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany.²¹ A photon energy of 85 keV was employed in all measurements and a large 2D 400 × 400 mm² Perkin Elmer XRD1621 detector with a pixel size of 200 × 200 µm² adapted for high-energy X-ray radiation was used for the recording of diffraction patterns. The methanation reaction was performed under transient operation conditions and atmospheric pressure by introducing H₂ pulses (2 vol% in Ar) into an otherwise constant CO₂ flow (0.5 vol% in Ar) at 623, 573 and 523 K, respectively. The pulses were 10 min long and were repeated 4 times to give a total duration of the experiment of 80 min.

2.2.2 Ambient-pressure X-ray photoelectron spectroscopy. The chemical surface composition of the samples during the CO₂ methanation reaction was studied by ambient-pressure
X-ray photoelectron spectroscopy at the soft X-ray beamline 9.3.2 at the Advance Light Source (ALS) in Berkeley, USA equipped with a Scienta R4000 HiPP system allowing for operando studies up to several hPa. All spectra were recorded in normal emission with photon energies of 435 eV for Rh 3d and C 1s, and 450 eV for Ce 4d. Measurements of Ce 3d levels were not possible at this beamline due to the limited range of photon energy (200–900 eV) and therefore we only measured the Ce 4d levels in this work. Prior to the measurements, the samples were prepared by drop-coating a silicon wafer with a layer of the powder sample, mounted on a specially designed sample holder with a BN-heater and were held by tantalum clips. Binding energies are referenced to either the X\textsuperscript{−} peak in the Ce 4d spectra at 122.8 eV (ref. 25) (for the 450 eV photon energy) or the C 1s peak at 284.8 eV (for the 435 eV photon energy). For the analysis of the recorded XPS spectra, a deconvolution procedure with a Doniach–Sunjić\textsuperscript{26} line shape convoluted with a Gaussian was used. The spectra were normalized to the background at the low binding energy side and a Shirley-type background was subtracted from all the spectra.\textsuperscript{27} Prior to the measurements the samples were exposed to 1.33 × 10\textsuperscript{−}5 hPa O\textsubscript{2} and the temperature was increased from room temperature to about 600 K to remove any C impurities. The recorded Ce 4d spectrum was considered to correspond to CeO\textsubscript{2} and was later used to determine the stoichiometry of the ceria. Oxidation and reduction measurements were performed in situ at 595 K by exposing the catalyst to either O\textsubscript{2} or H\textsubscript{2}. The C 1s level was measured continuously during the exposure and core-level spectra were recorded after a stable signal was observed. The methanation reaction was performed under a gas mixture of CO\textsubscript{2} and H\textsubscript{2}, with a total pressure of 0.2 hPa and a partial pressure ratio of 1:14 (CO\textsubscript{2}:H\textsubscript{2}) at temperatures from 515 to 625 K.

2.2.3 Infrared spectroscopy. Infrared spectroscopy was carried out in diffuse reflectance mode using a BRUKER Vertex 70 spectrometer equipped with a nitrogen-cooled MCT detector and a high-temperature stainless steel reaction cell (Harrick Praying Mantis\textsuperscript{TM} high temperature reaction chamber) with KB windows. The temperature of the sample holder was measured using a thermocouple (type K) and controlled with a PID regulator (Eurotherm). Individual mass flow controllers were used to introduce feed gases into the reaction cell, with a total flow of 100 ml min\textsuperscript{−}1. The samples were pre-treated at 625 K with 2 vol% O\textsubscript{2} in Ar for 10 min and 0.8 vol% H\textsubscript{2} in Ar for 10 min and a background spectrum was collected. The experiment was performed by introducing a flow of 0.2 vol% CO\textsubscript{2} and 0.8 vol% H\textsubscript{2} into the reaction cell and a spectrum was measured after 20 min in the reaction mixture at 625 K when a steady state signal was observed. The region between 790–3800 cm\textsuperscript{−}1 was investigated with a spectral resolution of 4 cm\textsuperscript{−}1.

3 Results and discussion

3.1 Ex situ characterization of the as-prepared catalysts

The surface area and microstructure of the calcined catalysts were characterized prior to the in situ investigations. A summary of the specific surface area measurements is provided in Table 1. The high resolution TEM micrographs of the two catalysts are shown in Fig. 1. The diameter of the CeO\textsubscript{2} nanoparticles of around 7 nm found by TEM is consistent with the specific surface area found by the BET method for both catalysts. The Rh crystallites are on average smaller than the Ni crystallites (average diameters of 4 and 6 nm for N = 11 and 10, respectively) as illustrated in Fig. 1. Particles 2–3 nm in diameter constitute nearly half of the found Rh crystallites, while no Ni crystallites smaller than 5 nm in diameter are found. The identified metallic crystallites however cannot account for the full loading of the catalysts, particularly in the case of Rh, indicating that there is an additional material that does not produce fringes in the electron micrographs with the characteristic spacings of the respective metals. Such a material could be present as a highly dispersed, possibly non-crystalline phase. For Ni, the presence of an oxidised material, formed during the calcination and maintained during storage, is indicated by the presence of d = 2.4 Å lattice planes.

3.2 In situ characterization of the redox behavior

Similar to our recent publication,\textsuperscript{20} an oxidation/reduction experiment was performed over the Rh/CeO\textsubscript{2} catalyst to obtain information on the characteristics of the catalyst under oxidation or reduction conditions. Fig. 2 shows the XPS spectra of the Rh 3d and Ce 4d levels upon exposure of the Rh/CeO\textsubscript{2} catalyst to 1.33 × 10\textsuperscript{−}5 hPa O\textsubscript{2} or 1.33 × 10\textsuperscript{−}6 hPa H\textsubscript{2} at 595 K. The exposure to either O\textsubscript{2} or H\textsubscript{2} has been monitored by recording the C 1s or Rh 3d levels continuously. When constant signals were obtained, the relevant core levels were still recorded during the gas treatment. Due to the superposition of several components in the O 1s core level arising not only from the sample but also from the silicon wafer used as the substrate, we will exclude the O 1s core level in the XPS analysis.

For the reduced sample, the Rh 3d\textsubscript{5/2} XPS data in Fig. 2(a) show the presence of a main peak at 307.3 eV typical for bulk metal Rh (Rh\textsuperscript{0}) and a minor peak at 308.2 eV, associated with oxidised rhodium,\textsuperscript{28} suggesting partial oxidation of Rh. The sustained oxidation state of Rh suggests the existence of a strong metal–support interaction between Rh and ceria, thus rhodium oxide is not easily reduced by H\textsubscript{2} exposure. For the oxidised sample, the bulk Rh component decreases in intensity and the Rh oxide peak increases. In addition, a new weak component at 309.1 eV forms, which has previously been assigned to Rh species (Rh\textsuperscript{3+}) located on the ceria lattice.\textsuperscript{29} However, the metallic Rh component is still present after the sample has been exposed to 1.33 × 10\textsuperscript{−}5 hPa O\textsubscript{2} at 595 K for a long time period (∼1 h). Thus, the Rh 3d XPS results suggest that Rh is not fully oxidised or reduced during the oxidation/reduction treatment, which is likely due to small Rh nanoparticles interacting strongly with the ceria support as previously reported for reducible oxides\textsuperscript{30–32} and also supported by the high degree of dispersion observed by TEM for the as-prepared catalysts and the AP-XPS measurements during CO\textsubscript{2}}
methanation at higher pressures (see section 3.3.2 below). The strong metal–support interaction between Rh and the ceria support facilitates good anchoring of the Rh particles and favors the catalytic activity for CO₂ methanation as will be discussed in more detail below.

In addition, XPS was used to determine the oxidation state of ceria during the oxidation/reduction treatment. The synthesized Rh/CeO₂ was reduced to Rh/CeOₓ when exposed to 1.33 × 10⁻⁶ hPa H₂ at 595 K. The Ce 4d spectra exhibit an intrinsically broad spectral shape with several contributions due to different electron coupling mechanisms. The curve fitting of these spectra is difficult. However, the spectra allow for differentiation between Ce⁴⁺ and Ce³⁺ and changes in the oxide’s oxidation state can be monitored. Particularly useful to this end are the signals designated as W” and X” in Fig. 2(b). These signals are interpreted to originate from the spin orbit split 4d⁹O₂p⁶4f⁰ final state configuration. Thus their intensity should be proportional to the Ce⁴⁺ concentration in the sampling volume of the XPS measurement. We used the W” and X” signals, located at binding energies of 126.1 and 122.8 eV, respectively, to estimate the stoichiometry (x in CeOₓ) of the oxide. The “degree of oxidation” refers to the amount of Ce⁴⁺ and Ce³⁺ in the oxide: “100% oxidised” refers to all Ce present as Ce⁴⁺ (CeO₂) and “0% oxidised” refers to all Ce present as Ce³⁺ (CeO₁.₅), i.e., reduced ceria. The presence of Ce³⁺ is usually associated with the formation of oxygen vacancies on the ceria surface. Comparison with the sample exposed to O₂ during a heating ramp to 600 K, for which we assumed a CeO₂ stoichiometry, indicates that the reduced sample contains about 23% (±5%) Ce³⁺, designated as Rh/CeO₂ₓ=0.89±0.03. The redox behaviour of the Rh/CeO₂ catalyst has been found to be reversible when switching between reduction/oxidation periods as previously reported. Thus, the results indicate that the Ce³⁺ species formed by the reduction in H₂ can be regenerated to Ce⁴⁺ by oxygen.

3.3 In situ studies of the CO₂ methanation reaction

3.3.1 HE-XRD measurements under atmospheric pressure conditions. To obtain insight into the crystalline structure of Rh and Ni and into any changes the ceria support may undergo during the methanation reaction, transient hydrogenation of CO₂ was investigated under in situ conditions by HE-XRD. The results of time-resolved measurements during periodic variation of the feed gas composition between 2 vol% H₂ + 0.5 vol% CO₂ and 0.5 vol% CO₂ at 625, 575 and 525 K for 10 min over the Rh/CeO₂ and Ni/CeO₂ samples are shown in Fig. 3 and 4, respectively. The cycles of CO₂ + H₂/CO₂ were repeated 4 times leading to a total duration of the experiment of 80 min. The data are presented as difference diffractograms to facilitate the observation of the major changes occurring during the pulsed experiments. Transient operating conditions were used to facilitate the observation of active vs. spectator species during the CO₂ methanation reaction.

Some clear changes could be observed in the XRD patterns between the CO₂ and CO₂ + H₂ pulses during the time-resolved measurements. Selected XRD patterns are shown at the bottom of Fig. 3 and 4 together with the pattern recorded from the ceria reference sample (green). For simplicity, the ceria reference pattern is only included in the panel presenting the measurements conducted at 625 K. The main reflections are due to scattering from the ceria lattice except the highlighted reflections around 3 Å⁻¹ which will be discussed more below. For both samples the ceria phase undergoes changes during the pulsed CO₂ hydrogenation experiment. During the CO₂ pulse, Ce seems to be in an oxidised state similar to the ceria reference, while the shift toward lower q (i.e., larger d spacing) during the CO₂ hydrogenation suggests a reduction of the ceria support due to formation of more Ce³⁺ species which have a larger ionic radius than Ce⁴⁺.

In addition, there are some differences observed between the ceria supported Rh and Ni catalysts. For the Rh/CeO₂ catalyst, a weak broad reflection is observed at q = 2.85 Å⁻¹ during the CO₂ methanation (see the inset), similar to the observations in our recent work of CO₂ hydrogenation over Rh/Al₂O₃. As already mentioned in our previous work, this corresponds to a d spacing of the reflecting planes of 2.2 Å.

### Table 1 Metal loading, calcination temperature and specific surface area of the catalyst samples used in this study. The catalytic performance at 625 K as reported in ref. 19 is also included for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal loading (wt%)</th>
<th>Calc. temperature (K)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>CO₂ conversion</th>
<th>CH₄ production</th>
<th>CO production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/CeO₂</td>
<td>3.0</td>
<td>825</td>
<td>125</td>
<td>~46%</td>
<td>~41%</td>
<td>~0.05%</td>
</tr>
<tr>
<td>Ni/CeO₂</td>
<td>3.0</td>
<td>825</td>
<td>128</td>
<td>~44%</td>
<td>~30%</td>
<td>~0.14%</td>
</tr>
</tbody>
</table>

Fig. 1 High-resolution TEM micrographs of the (a) Rh/CeO₂ and (b) Ni/CeO₂ catalysts. The inset in (a) shows a 2 nm Rh crystallite with a plane spacing of 2.2 Å. For Ni/CeO₂ in (b), spacing consistent with both metallic and oxidised Ni was found as indicated by the outlined areas. The inset diffractogram shows the corresponding crystalline reflections used for identifying the two phases. The white dashed lines indicate the (111), (200) and (220) reflections from the CeO₂ support.
which is close to the \(d\) spacing of metallic Rh (\(\sim 2.1\ \text{Å}\)) \(^{37}\) (ref no. #171677). The small difference in the cell parameter from metallic bulk Rh here is attributed to the strong interaction between the small Rh nanoparticles and oxygen.
in the ceria support. We therefore denote the reflection at \( q = 2.85 \, \text{Å}^{-1} \) as \( R_{\text{h, sup}} \). When in the presence of \( \text{CO}_2 \) only, the ceria is fully oxidised and the formation of (amorphous) Rh oxides cannot be excluded (cf. XPS results in Fig. 2), which may explain the lower intensity of \( R_{\text{h, sup}} \). During \( \text{CO}_2 \) methanation, however, the presence of Rh oxides is unlikely and the ceria is somewhat reduced, which results in an increased intensity of the \( R_{\text{h, sup}} \). For the \( \text{Ni/CeO}_2 \) catalyst, a new peak appears at \( q = 3.1 \, \text{Å}^{-1} \) as the intensity of the peak at \( q = 3.0 \, \text{Å}^{-1} \) decreases during the \( \text{CO}_2 + \text{H}_2 \) pulse. The corresponding \( d \) spacing of the peak at \( q = 3.1 \, \text{Å}^{-1} \) is \( d = 2.02 \, \text{Å} \), which is similar to the tabulated values for Ni available in the ICSD data collection\(^37\) (ref no. #260172). Thus, the results obtained for the Ni supported catalyst suggest that Ni is reduced to a metallic state during the \( \text{CO}_2 \) methanation reaction.

Based on the XRD results it can be concluded that under \( \text{CO}_2 \) methanation conditions the ceria is slightly reduced for both samples; crystalline Rh is influenced by the ceria support and does not resemble the bulk Rh structure, whereas the Ni phase exists as metallic Ni with a structure close to that of bulk Ni.

### 3.3.2 AP-XPS measurements under near-ambient pressure conditions.

To understand better the chemistry of methane formation over \( \text{Rh/CeO}_2 \), AP-XPS was used to study the interaction between \( \text{CO}_2 \) and \( \text{H}_2 \) and the catalyst. The result of a time-resolved measurement of the C 1s level during heating in a gas mixture of \( \text{CO}_2 \) (0.0133 hPa) and \( \text{H}_2 \) (0.1867 hPa) from 515 to 625 K is shown in Fig. 5(a). Already at 515 K, the mass spectra reveal the formation of methane with no indication of the rWGS reaction (i.e., no CO formation). Several components are observed in the spectra of the C 1s level, which will be discussed in more detail below. Increasing the temperature of the reaction mixture does not result in any significant changes of the C 1s spectra. The mass spectrometry data show a slight increase of the methane production up to 615 K and above this temperature the methane production starts to decrease and CO can be observed (i.e., the selectivity increases for the rWGS reaction). The mass spectrometry data are not presented in the present work since a detailed kinetics study for these samples has already been reported in our recent publication\(^19\) and a summary is given in Table 1.

Fig. 5(b–d) show a series of XPS spectra collected for the \( \text{Rh/CeO}_2 \) catalyst under \( \text{CO}_2 \) (0.0133 hPa) and \( \text{H}_2 \) (0.1867 hPa) at 515 K. In the C 1s region, there are several contributions observed in addition to the weak component at about 293.5 eV from gaseous \( \text{CO}_2 \). The strong peak at 285 eV with a shoulder at higher binding energy can be attributed to C\(_x\)/CO species on Rh. The component at about 285 eV with a slightly lower intensity can be observed before the catalyst is exposed to the \( \text{CO}_2 + \text{H}_2 \) mixture (not shown) and therefore it is suggested that some C is already present on the catalyst prior to \( \text{CO}_2 \) hydrogenation. However, we cannot exclude that some \( \text{CO}_2 \) is fully dissociated on the \( \text{Rh/CeO}_2 \) catalyst during the methanation reaction since previous studies have reported facile decomposition of CO over Rh deposited on reduced ceria.\(^35\) Thus, reduced ceria facilitates the (complete) decomposition of \( \text{CO}_2 \) or CO when \( \text{CO}_2 \) or \( \text{CO}_2 + \text{H}_2 \) interact with the \( \text{Rh/CeO}_2 \) catalyst. Further, another strong component is observed at around 290 eV with a shoulder on the low binding energy side (289.5 eV) which resembles the formate/carboxylate peaks on \( \text{CeO}_x/\text{Cu}(111) \) previously observed by Graciani et al.\(^38\) This component appears to be slightly
shifted to a higher binding energy as compared to the study by Graciani et al., and therefore, it is suggested that the carboxylate species are likely formed at the interface between ceria and Rh. It is interesting to note that no signals could be detected for CH$_x$ species at around 285–286 eV, which implies that any other surface intermediates produced by the hydrogenation of CO$_2$ or CO are short-lived.

In the corresponding spectra for the Rh 3d and Ce 4d regions shown in Fig. 5(c and d), a clear change is seen in the line shape of the Ce 4d spectrum indicating the reduction of ceria, with the formation of Ce$^{3+}$ (i.e., oxygen vacancies), and a change in the Rh 3d spectrum is observed indicating the reduction of RhO$_x$, similar to the results of the reduction treatment discussed above. The Rh 3d spectrum shows a similar behavior to when the catalyst was exposed to H$_2$ indicating still the presence of small amounts of Rh–O species during the methanation reaction. In the corresponding Ce 4d spectrum some signs of a change in the oxidation state to reduced ceria during CO$_2$ methanation are evident. Similar to the H$_2$ exposure, the synthesized Rh/CeO$_2$ is rapidly reduced to Rh/CeO$_x$ when exposed to the CO$_2$ + H$_2$ reactant mixture. The recorded spectrum after the H$_2$ exposure is included for comparison (dotted red). Further reduction of the ceria is observed during the methanation reaction as compared to the H$_2$ exposure, which is likely due to the higher H$_2$ pressure used during the methanation reaction (0.1867 hPa) as compared to the H$_2$ treatment (1.33 × 10$^{-6}$ hPa). The net amount of Ce$^{3+}$ formed during exposure to the CO$_2$ + H$_2$ mixture is found to be about 40% (±5%) (Rh/CeO$_{1.80±0.03}$).

3.3.3 DRIFTS measurements under atmospheric pressure conditions. In situ DRIFT spectroscopy was employed to study the interaction of CO$_2$ and H$_2$ with the ceria supported Rh and Ni catalysts in order to identify the adsorbed species present during methanation. A detailed DRIFTS study of CO$_2$ hydrogenation over the studied catalysts under transient operation conditions has been presented in our previous publication, and therefore, here we focus our attention on the different surface species formed during the reaction and how these differ depending on the choice of the active metal.

The DRIFTS results from a steady-state measurement obtained after the Rh/CeO$_2$ and Ni/CeO$_2$ catalysts have been exposed to a flow of 0.2 vol% CO$_2$ and 0.8 vol% H$_2$ at 625 K for 20 min are presented in Fig. 6. The interaction between the Rh- and Ni-based catalysts with 0.2 vol% CO$_2$ and 0.8 vol% H$_2$ at 625 K results in the development of intense absorption bands between 1200–1600 cm$^{-1}$, indicating the formation of formate and carbonate species. Although it is difficult to assign these peaks to specific structures on the surface, it is clear that formate and carbonate species are present on the surface of both catalysts. Some differences are observed between the investigated catalysts. The intensity of the IR bands is much higher for the Ni/CeO$_2$ sample indicating that some higher amounts of formates and carbonates are present on this sample during the CO$_2$ methanation reaction. Also the Ni/CeO$_2$ sample shows a sharp peak around 1000 cm$^{-1}$ typical for C–O symmetric stretching expected when formates/carbonates/carbonyls are present. However, its origin is not fully understood at this moment and the formation of some other species over the Ni/CeO$_2$ catalyst during CO$_2$ hydrogenation reaction is not excluded.

For the Rh/CeO$_2$ sample, some additional peaks at 2020 and 1740 cm$^{-1}$ appear. These peaks can be attributed to CO species linearly bound on reduced Rh sites (Rh–CO, 2020 cm$^{-1}$) and bridge-bonded CO at the Rh/ceria interface (1740 cm$^{-1}$) (see Table 2 for reference). This indicates that the Rh/ceria interface plays a role in the CO$_2$ hydrogenation reaction over Rh/CeO$_2$. The broad peak at 1800 cm$^{-1}$ may indicate the presence of some bridge-bonded CO species on Rh. No vibrations from CO species adsorbed on Rh$^+$ sites (2800–3000 cm$^{-1}$) could be seen for the Rh/CeO$_2$ sample indicating that the formed CO during the methanation reaction adsorbs only on metallic Rh. The adsorbed CO species may arise from either the direct dissociation of CO$_2$ over metallic Rh or from

![Fig. 6](image-url)
cles are present on the surface of the Rh/CeO$_2$ catalyst during the reaction. Since with IR spectroscopy we are not able to observe C species on the surface, the results suggest that the C species observed by AP-XPS during the methanation reaction are formed as a consequence of the complete decomposition of CO$_2$. Regarding the chemical state of the catalyst during the CO$_2$ methanation reaction, the results provide evidence of small Rh particles (partially oxidised even under reducing conditions due to the strong interaction with the ceria support) on partially reduced ceria denoted as Ce$^{3+}$. The results strongly indicate that the presence of Ce$^{3+}$ formed during the reduction of ceria is highly connected to the high activity of the Rh/CeO$_2$ catalyst. For the comparative study on Ni/CeO$_2$, the results show a similar behaviour to Rh/CeO$_2$ with reduction of ceria during the methanation of CO$_2$. Thus, Ce$^{3+}$ is linked to the increased activity for CO$_2$ hydrogenation over ceria-based catalysts while the metal surface is likely to act as the supplier of hydrogen for the subsequent hydrogenation of activated CO$_2$. The main differences between the two catalysts are the reversible oxidation of Ni under the transient operation conditions and the lack of adsorbed CO species for the Ni/CeO$_2$ sample, which may be related to the increased particle sizes. It is suggested that the linearly adsorbed CO species can be hydrogenated to methane subsequently over the Rh/CeO$_2$ catalyst, while the weaker interaction between CO and the Ni/CeO$_2$ surface leads to fast desorption of CO. Rh seems to be more active and selective towards CH$_4$ than Ni likely due to its stronger interaction with the ceria support which can facilitate further steps during CO/C$_2$ hydrogenation to methane.

The promoting effect of ceria is mainly related to its ability to undergo changes in its oxidation state (Ce$^{3+}$–Ce$^{4+}$ redox couple) with the consequent formation/annihilation of surface defects (O vacancies). Some previous reports have suggested Ce$^{3+}$ as the active site for CO$_2$ adsorption and conversion along with a valence change from Ce$^{3+}$ to Ce$^{4+}$. A recent study by Wang et al. on Ru supported on ceria showed also that the surface oxygen vacancies on ceria rather than on Ru are more likely to be the active sites in CO$_2$ methanation. This supports our interpretation that the Ce$^{3+}$ species, associated with oxygen vacancies, are the active sites for CO$_2$ hydrogenation.

Although CO$_2$ methanation is a comparatively simple reaction, its mechanism appears to be difficult to establish. Still, there are discussions on the nature of the intermediate compounds involved in the reaction process and on the methane formation scheme. Traditionally, transient studies are used to distinguish between intermediate or spectator species, but our recent transient DRIFTS measurements where the catalysts are subjected to alternating pulses of CO$_2$ and CO$_2$ + H$_2$ indicate that both formates/carbonates and some CO species form under transient operation conditions. It is difficult to study the stability of such species from a temperature ramped AP-XPS study as the selectivity of the catalyst changes at higher temperatures. Further, from the DRIFTS measurements we are not able to separate the different formate/carbonte/carboxylate species and thus we cannot confirm or deny that any of these species is the reaction intermediate. In related work, Graciani et al. suggested the less stable carbonate species to be the reaction intermediate for CO$_2$ hydrogenation to methanol over CeO$_2$/Cu(111), ruling out the formate reaction pathway due to the high stability of these species. Even though we see that the formate species are efficient as transient species, further measurements are
needed to confirm if formates are indeed a reaction intermediate in the CO₂ methanation over Rh/CeO₂. Still, from the results we have achieved so far, we consider the most likely reaction pathway to involve the formation of formates and propose that the hydrogen molecules can dissociate on the metallic sites and react with the activated CO₂ to form formates (HCOO) at the metal-support interface (see eqn (1) below). The formates can then dissociate into CO + OH and this step needs available metallic sites from where CO can be later hydrogenated to methane.

\[
\text{CO}_2 + H \rightarrow \text{COOH} \rightarrow \text{CO} + \text{OH}
\]

From the transient experiments where the catalysts are subjected to alternating pulses of CO₂ and CO₂ + H₂, we can conclude that the Ce³⁺ species needed to activate the CO₂ molecules are re-generated during the methanation reaction since we observe a reversible change in the oxidation state of ceria under these conditions. Since hydrogen is the only reactant introduced into the feed during the reaction, we think that hydrogen, after being dissociated on Rh, may spill over to the ceria leading to the reduction of the ceria support.

By comparison with our recent study of CO₂ methanation over Rh/Al₂O₃, which also showed a comparable activity to Rh/CeO₂, we cannot exclude that formates are also important in the reaction mechanism for CO₂ methanation over Rh/Al₂O₃ even though a smaller amount of formates is formed when alumina is used as the support. The results of our studies do not provide a conclusive assignment of a reaction path for the CO₂ to CH₄ conversion over the highly active Rh/CeO₂ catalyst. However, the results reveal some of the important initial steps in the CO₂ methanation reaction over Rh/CeO₂, which may be used as a starting point for further investigations. In order to reach a final conclusion concerning the reaction mechanism, it will be helpful to investigate the H₂ + CO reaction, the CO dissociation and the reactivity of surface C formed on the Rh catalyst.

4 Conclusions

Ceria supported Rh and Ni catalysts were structurally characterized during CO₂ hydrogenation to methane. In situ measurements employing AP-XPS, HE-XRD and DRIFT spectroscopy revealed that the Ce³⁺ species are likely the active sites in CO₂ methanation for ceria-based catalysts. The mechanism of the methanation reaction is complex and even though we are not able to reach a final conclusion, our results suggest that the formates created from the activated CO₂ molecules by Ce³⁺ play an important part in the reaction mechanism and are dissociated to CO and OH species. A stronger interaction between the metal and the support for the Rh/CeO₂ catalyst, as evident from its high degree of dispersion and as supported by the TEM measurements, leads to more strongly bound CO from formate dissociation, and thus a higher methane selectivity.

Conflicts of interest

There are no conflicts to declare.

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