Cobalt@Silica Core-Shell Catalysts for Hydrogenation of CO/CO\(_2\) Mixtures to Methane

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CO\(_2\), hydrogenation reactions for hydrocarbon synthesis, such as methane, are becoming more and more important in terms of the energy transition. The formation of the byproduct water leads to a hydrothermal environment, which necessitates stable catalyst materials under harsh reaction conditions. Therefore, novel nanostructured core-shell catalysts are part of scientific discussion, since these materials offer an exceptional resistance against thermal sintering. Here we report on a core-shell catalyst - Co@mSiO\(_2\) - for the hydrogenation of CO/CO\(_2\) mixtures towards methane. CO methanation experiments reveal a rapid temperature-depended deactivation for temperatures above 350 °C caused by coking and possible blocking of the pores. In comparison to a Co/mSiO\(_2\) reference catalyst with the same Co particle size a significantly higher methane selectivity was found for CO\(_2\) hydrogenation, which we attribute to the confinement effect of the core-shell structure and therefore a higher probability of CO readsoption. Finally, the simultaneous CO/CO\(_2\) co-methanation experiments show a high flexibility of the catalyst materials on different gas feed compositions.

Introduction

In the wake of a restructuring energy sector, the power-to-gas technology is often discussed to be an important tool to buffer the fluctuating nature of renewable energies.\(^{[1,2]}\) Here, either CO or CO\(_2\) react with hydrogen to form methane, according to Equations (1) and (2). As unwanted side reactions the (reverse) water-gas shift [Equation (3)], as well as the Boudouard reaction [Equation (4)] can occur.\(^{[3]}\)

\[
\begin{align*}
\text{CO} + 3\text{H}_2 &\rightarrow \text{CH}_4 + \text{H}_2\text{O}; \Delta H_{f}^{298}K = -206 \text{ kJ mol}^{-1} \quad (1) \\
\text{CO}_2 + 4\text{H}_2 &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O}; \Delta H_{f}^{298}K = -165 \text{ kJ mol}^{-1} \quad (2) \\
\text{CO} + \text{H}_2\text{O} &\rightarrow \text{CO}_2 + \text{H}_2; \Delta H_{f}^{298}K = -41 \text{ kJ mol}^{-1} \quad (3) \\
2\text{CO} &\rightarrow \text{C} + 2\text{CO}_2; \Delta H_{f}^{298}K = -172 \text{ kJ mol}^{-1} \quad (4)
\end{align*}
\]

Both CO and CO\(_2\) methanation reactions are usually catalyzed by supported transition metals. Ni is the most common methanation catalyst, due to its high activity and methane selectivity.\(^{[4,5]}\) Co performs very similar, whereas Fe has a high activity but suffers from a poorer methane selectivity.\(^{[6]}\) As supports, conventional systems mostly rely on porous Al\(_2\)O\(_3\), SiO\(_2\) or TiO\(_2\) due to their high surface area to accommodate the metal nanoparticles.\(^{[7]}\) The active metal is immobilized onto the pore surface by the formation of nanoparticles from a precursor solution via various methods, being incipient wetness impregnation one of the most important procedures.\(^{[8]}\)

Catalyst preparation by impregnation methods leads to a rather stochastic distribution of the size and the spatial location of the active nanoparticles within the catalyst volume. The control of the distribution is possible within certain limits by adjusting the synthesis parameters empirically. Consequently, the loss in active surface area by migration and subsequent coalescence of single atoms or aggregates as well as Ostwald ripening is hardly avoidable, leading to deactivation under reactions conditions.\(^{[9]}\) A rather novel concept to overcome these limitations are the so-called core-shell catalysts, where an active metal core is encapsulated by a supporting porous shell. These systems offer an improved sinter resistance and allow to tailor the combination of physical and chemical functionalities on the nanoscale, as well as to generate a confinement effect.\(^{[10-14]}\) Wang et al.\(^{[15]}\) prepared various Ni@SiO\(_2\) catalysts by a modified Stöber process and investigated their catalytic performance for the CO methanation in a slurry reactor. While they found that an increase in the core size leads to a declining activity, they also encountered a rapid deactivation which they ascribe to a changing shell structure, i.e. a loss of mesopores and pore volume. Han et al.\(^{[14]}\) developed a Ni@SiO\(_2\) catalyst by a modified Stöber process and compared the core-shell catalyst with an impregnated catalyst for the methanation of CO exhibiting a superior activity. Unfortunately, the authors do not...
account for the significantly different particle size, due to the
different synthesis method, which greatly affects structure-
sensitive reactions. Pang et al.\textsuperscript{[19]} examined Co@SiO\textsubscript{2} catalysts in
the dry reforming of methane and found that the core size as
well as shell thickness need to be carefully balanced in order
to ensure a high activity as well as to avoid coking and oxidation
of Co cores.

The reaction mechanisms of CO and CO\textsubscript{2} hydrogenation are
still under debate in literature.\textsuperscript{[17,18]} Miao et al.\textsuperscript{[19]} reviewed
possible mechanisms during CO and CO\textsubscript{2} methanation focusing
mainly on Ni and Ru catalysts. In general, two different routes are
claimed: On the one hand the associative mechanism meaning H atoms assisted C–O bond breaking and on the other
hand the dissociative mechanism, where the C–O bond breaking
takes place before the hydrogenation. Furthermore, they suggest that CO is more active in methanation than CO\textsubscript{2}. A
detailed study on the mechanism of CO hydrogenation to CH\textsubscript{4}
at 260°C is given by Chen et al.\textsuperscript{[18]} They investigated a Pt-
promoted Co/SiO\textsubscript{2} catalyst with particle size of 15 nm at
different H\textsubscript{2}/CO ratios using steady-state isotopic and transient
kinetic analysis (SSITKA) as well as back and forward chemical
transient analysis. From the gained results they postulate that
the CH\textsubscript{4} formation rate is mainly controlled by CH\textsubscript{2} hydro-
genation rather than CO dissociation. According to literature a
lot of parameters influence the CH\textsubscript{4} formation, such as the
active metal, the support material, as well as temperature,
pressure and H\textsubscript{2}/CO ratio. In addition, carbon formation plays
an important role. Chen et al.\textsuperscript{[20]} reported that amorphous
carbon formed on the cobalt surface during methanation can
easily be removed under reaction conditions, whereas graphitic
carbon is deposited irreversibly. This inactive carbon is mainly
located on the terrace sites of the cobalt and decreases the CH\textsubscript{4}
selectivity because of blocking the favored sites for CH\textsubscript{4}
hydrogenation.

Methane is claimed to play a crucial role in the energy
infrastructure in the next decades, as it can be generated from
electrical energy via water electrolysis as hydrogen source and
any carbon source.\textsuperscript{[22–25]} The latter is still a matter of debate, but
will include point sources, e.g. from the steel industry, which raises questions about the composition of the feed gas in terms of
H\textsubscript{2}, CO and CO\textsubscript{2} content as well as impurities. Particularly, the
methanation of process gases, such as blast furnace or
converter gas, requires the methanation reactor to operate over
a wide range of CO/CO\textsubscript{2} feed ratios. However, studies focusing
on this topic are scarce. Schöß et al.\textsuperscript{[22]} conducted a process-
based analysis and concluded that process gases, indeed, are a
viable carbon oxide source for methanation. Similar processual
studies have been published by Man et al.\textsuperscript{[23]} and Yi et al.\textsuperscript{[24]} In
turn, there are only a few studies, which focus on the
simultaneous CO/CO\textsubscript{2} methanation from a catalyst point of
view, although an influence is to be expected as evidenced
during the simultaneous Fischer-Tropsch synthesis (FTS) and
the selective methanation of CO.\textsuperscript{[25–28]} Riedel et al.\textsuperscript{[28]} observed a
significantly shifted product distribution to methane upon an
increasing CO\textsubscript{2} content in the syngas during FTS, which they
explained with a different kinetic regime induced by the co-
presence of CO and CO\textsubscript{2}. In contrast, Visconti et al.\textsuperscript{[29]} found that
CO\textsubscript{2} acts as an inert species as long as CO is present under FTS
conditions over a Co-Al\textsubscript{2}O\textsubscript{3} catalyst, due to the stronger
adsorption of CO over CO\textsubscript{2} on the metallic active sites. This is in
line with what most studies on the selective methanation of CO
conclude. Here, CO\textsubscript{2} is only hydrogenated once CO has been
fully removed from the feed.\textsuperscript{[31–33]} Razzaq et al.\textsuperscript{[34]} investigated the methanation of coke oven gas over various supported
Ni–Co catalysts and determined ZrO\textsubscript{2}–CeO\textsubscript{2} to be the optimal
support.

In this paper, we investigate the applicability of cobalt-
based core-shell catalysts in the CO\textsubscript{2} methanation. The novel
material consists of a cobalt nanoparticle as core, which is
encapsulated in an amorphous, mesoporous silica shell. Furthermore, Co@silicalite-1 materials with cores embedded in a
crystalline, microporous matrix are reported. Full character-
ization of the materials is provided, e.g. by atomic absorption
spectroscopy (AAS), N\textsubscript{2} physisorption, powder X-ray diffraction
(PXRD), H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}–TPR) as well as
electron microscopy, to relate the morphological and structural
properties to the catalytic performance. The novel
catalyst materials are studied for the methanation of CO/CO\textsubscript{2}
mixtures and the results are compared to those obtained with a
reference catalyst, which possesses the same surface properties
and Co particle size distribution. The findings are discussed
with respect to the unique features of the core-shell structure,

as well as in terms of flexibility towards the feed gas mixture.

Experimental Section

Catalyst Synthesis

The material synthesis follows a bottom-up synthesis route
previously established by Kruse et al.\textsuperscript{[35]} (Figure 1), in which colloidal cobalt oxide nanoparticles are prepared first (CoO\textsubscript{x} material A) and
subsequently encapsulated with mesoporous, amorphous silica to
yield a core-shell catalyst (CoO\textsubscript{x}@silicalite-1, material B). The silica can
subsequently be converted into a crystalline, microporous zeolite
matrix in which the cobalt oxide particles are embedded
(CoO\textsubscript{x}@silicalite-1, material C).

Material A was prepared via a solvothermal treatment of a mixture of 3.32 g cobalt nitrate (Cobalt(II) nitrate hexahydrate; 97.7 %,
Alfa Aesar) and 6.64 g polyvinylpyrrolidone (PVP, MW 1.300,000, high
purity grade, Amresco) dissolved in 375 mL ethanol (96 vol%, VWR
Chemicals) at 180°C in a PTFE-lined autoclave for 3 h. Subse-
quently, 50.0 g of the resulting cobalt oxide suspension were
directly used in a Stöber process via dissolving it together with
1.95 g cetyltrimethylammoniumbromide (CTAB, high purity grade,
AMRESCO) as porogen in an ethanol/water mixture and adjusting the pH to a value of 9 by the addition of 12.4 mL aqueous ammonia solution (NH₄OH, 30%, p.a. CARL Roth). After the dropwise addition of 6.40 mL tetraethylorthosilicate (TEOS, for synthesis, MERCK) as silicon source the reaction mixture was stirred for 2 h at room temperature to achieve material B after collecting the solids via centrifugation and calcination at 500 °C for 6 h. This material was used as catalyst and as precursor for the subsequent zeolite synthesis. Therefore, the solid was dissolved in an aqueous mixture of sodium hydroxide (25 wt% solution, ≥ 99% p.a., CARL Roth) as well as tetrapropylammoniumhydroxide (TPAOH, 40% w/w aq., ALFA Aesar) as structure directing agent and sulfuric acid (0.1 M, for analysis, MERCK) for adjusting the pH. The reaction mixture with a molar ratio of 1.0000 SiO₂:0.0148 Na₂O:0.0428 TPAOH:0.0204 H₂SO₄:0.426240 H₂O:0.014711 OH⁻ was treated at 175 °C for 30 h in a PTFE-lined autoclave. Afterwards the product was collected by centrifugation and calcined at 500 °C for 6 h leading to material C. As a reference material supported Co₃O₄/mSiO₂ (material D) was prepared with a cobalt loading of 1 wt%. Therefore, Co₃O₄ nanoparticles (material A) and mesoporous silica particles were synthesized separately according to the procedure described above. Afterwards, the Co₃O₄ particles are deposited on the silica particles by rotary evaporation. Due to their size, the Co₃O₄ particles could not enter the pores of the support and are, therefore, deposited solely on the external surface of the silica particles. In order to avoid the agglomeration of multiple Co₃O₄ cores, the loading was reduced to 1 wt% Co. After deposition, PVP was removed by calcination at 500 °C for 3 h. Thermo gravimetric analysis (TGA) before and after calcination confirmed the successful removal of PVP (see Figure S1 in SI).

Characterization

Transmission electron microscopy (TEM) was performed on a Jeol 1400 microscope operating at 120 kV. The TEM samples were prepared by suspending a small amount of the catalyst material in ethanol under ultrasonication. One droplet of the resulting suspension was applied on a graphitized copper grid (200 mesh). Typically, around 200 particles were considered for the statistic evaluation of the cobalt oxide particle size distribution using the software image J for image processing. For scanning electron microscopy (SEM) a Hitachi S-5200 electron microscope was used. The samples were prepared by dropping 20 μL of the catalyst suspension on a silicon wafer glued to a SEM sample holder. The contact between sample holder and wafer was achieved by using conductive silver. To minimize charge effects, the samples were sputtered with platinum before measuring. X-ray powder diffraction patterns were recorded on a STOE STADI-p diffractometer using Cu–Kα radiation (1.54184 Å) equipped with a DECTRIS MYTHEN 1 K strip detector. The measurement was performed in the 20 interval 0–70° in steps of 0.015°.

Nitrogen adsorption and desorption measurements were executed at 77 K using a high resolution Micromeritics 3Flex instrument with a special microport pie having a 0.1 Torr pressure transducer. Prior to the measurement the samples were degassed under vacuum at 300 °C for 4 h. For the mesoporous material B, the surface area was calculated via the Brunauer-Emmett-Teller (BET) model in the p/p⁰-region between 0.05 and 0.25 and the pore size distribution was determined by analyzing the desorption branch using the Barrett-Joyner-Halenda (BJH) method. For the microporous material C, the micropore volume, the micropore surface area as well as the external surface area were calculated via the t-plot method using the Rouquerol plot for the total surface area. For determining the micropore size distribution the Horwath-Kawazoe model was applied. H₂-TPR was measured on the Micromeritics 3Flex instrument, as well. Before the measurements, the samples were dried at 120 °C for 30 min in an Argon flow. Afterwards, the samples were cooled down to 50 °C and gas was switched to 10% H₂ in Ar. After baseline stabilization the temperature was ramped up to 650 °C with a linear heating rate of 10 K/min.

The quantitative characterization of the catalyst materials was done at Mikroanalytisches Labor Kolbe (Oberhausen, Germany). After drying and acidification of the samples the Co content was determined by atomic absorption spectroscopy (AAS) with an AAS Model Analyst 200 from PerkinElmer. For the analysis of the Si content the samples were treated with a so-called Wurzschmitt acidulation and measured with a photometric method at a UV/VIS Model Spectro 50 Plus from Analytikjena.

For ex-situ RAMAN spectroscopy of the catalyst powder an inVia confocal Raman microscope from Renishaw was used. The excitation source was a diode-pumped solid state (DPSS) laser with a wave length of 532 nm, while the laser power was adjusted to 5 mW. The spectra were recorded between 3200 cm⁻¹ and 150 cm⁻¹ as well as between 2100 cm⁻¹ and 1000 cm⁻¹ for survey and detail spectra, respectively. The acquisition time for each spectrum was 30 s and two spectra were accumulated each time.

Experimental Setup and Catalytic Measurements

All measurements were conducted in a fixed-bed reactor operated at atmospheric pressure. A self-designed metal block oven was used for reactor heating, which was controlled by a thermostate, placed at the external reactor wall. All tubing was heated at ca. 120 °C as well, in order to prevent water from condensing inside the set-up and to preheat the reactant flow. The gas flow rates were controlled by mass flow controllers (Bronkhorst Mättig).

A tubular quartz-glass reactor with an inner diameter of 6 mm was filled with the corresponding amount of the catalyst powders (75–200 μm) to achieve 1.92 mg cobalt inside the reactor for the methanation experiments of CO or CO₂. For co-methanation of CO/CO₂ mixtures a catalyst amount containing 2.88 mg cobalt is diluted with 300 mg Al₂O₃ in the same size fraction leading to a catalyst bed length of ca. 10 mm. Quartz wool was used to hold the powder in place inside the reactor. Prior to the reaction the catalyst is reduced in-situ in flowing H₂ at 430 °C for 10 h (heating ramp 1 K/min⁻¹). After reduction, the reactor was cooled down in inert gas atmosphere. The performance of the catalysts was determined in the temperature range from 200 to 400 °C. For this purpose, the formation and consumption rate of the involved carbonaceous compounds are calculated based on the inlet and outlet molar flow rates and the cobalt mass according to Equation (5).

\[ \frac{n_{\text{in}} - n_{\text{out}}}{m_{\text{Co}}} \]

For the methanation of CO or CO₂ each temperature was kept constant for 42 min. The conversion and selectivity are averaged over the last 24 min and the standard deviation is calculated from the respective data. The total flow rate was set to 50 mL_{STP} min⁻¹, corresponding to a weight hourly space velocity (WHSV) of ca. 1560 L_{STP}g⁻¹h⁻¹ composed of 4/1/5 H₂/CO₂/Ar and 3/1/6 H₂/CO/Ar for the CO₂ and CO methanation, respectively.

The simultaneous CO/CO₂ co-methanation experiments were conducted at 320 °C as this marked the upper limit of the stable operation regime in the CO methanation. The flowrate was set to 51.9 mL_{STP} min⁻¹. Initially, the inlet gas flow was composed of 4/1/6 H₂/CO₂/Ar, before CO₂ was replaced stepwise by CO maintaining a constant CO flow rate. The set ratios of CO₂/CO were 1.0 > 0.88/
0.12 > 0.65/0.35 > 0.44/0.56 > 0.12/0.88 > 0/1, afterwards the CO\textsubscript{2}/CO ratio was increased in reverse order. The hydrogen to carbon ratio remained fixed at 4/1 during the experiments. Each step was kept for at least 15 min. The conversion and selectivity are averaged over a time period of 10 min and the standard deviation was calculated from the respective data.

For the CO\textsubscript{2} methanation, the effluent gases were analyzed after passing through a cold trap (operated at 1°C) with an on-line compact gas chromatograph (Global Analyser Solution) equipped with a thermal conductivity sensor. A RT-Molsieve 5 Å column (15 m) was used to separate CO and CH\textsubscript{4}, whereas CO\textsubscript{2} was separated on a RT-Porabond column (30 m). In pre-experiments no C\textsubscript{2}H\textsubscript{4} hydrocarbons were detected.

The CO methanation and CO/CO\textsubscript{2} co-methanation measurements were conducted analogously, however instead of the compact GC, a quadrupole mass spectrometer (Hiden Analytical, USA) with SEM multiplier was used to achieve a higher temporal resolution. The mass spectrometer was calibrated for CO (28 amu), CO\textsubscript{2} (44 amu), CH\textsubscript{4} (15 amu) and Ar (40 amu), of which Ar was used as the internal standard. The contribution of the fragmentation of CO\textsubscript{2} to the CO signal was accounted for during calibration. Furthermore, the intensities of H\textsubscript{2}O (18 amu), as well as of C\textsubscript{2}H\textsubscript{4} (30 amu) and C\textsubscript{3}H\textsubscript{8} (41 amu), as qualitative criteria for higher hydrocarbons, were recorded, although, no higher hydrocarbons were detected at any time. The molar flow rate of H\textsubscript{2}O was calculated from the stoichiometry of the occurring reactions (Equations 1–3).

Results and Discussion

Catalyst Characterization

Representative TEM images of material A and B are given in Figure 2 (III, IV), which are in good agreement with our previous results,\textsuperscript{[35]} and thus, prove the reproducibility of the presented preparation method. The first batch of material A used for the synthesis of the core-shell catalysts forms aggregates with a modal size of about 44 nm consisting of primary particles of 12 nm (Figure 2-I, left). The second batch of material A, used to be supported on silica for the reference material, shows a comparable modal size of about 39 nm (Figure 2-I, right).

Material B exhibits uniform spherical particles with a modal size of ca. 150 nm, consisting of individually encapsulated cobalt oxide cores inside a silica shell (Figure 2-II, left). The core particles preserved their size from material A and the silica shell thickness is about 50 nm. The silica support material shows a much broader particle size distribution with a mean size of ca. 290 nm (Figure 2-II, right).

The successful deposition of the Co\textsubscript{3}O\textsubscript{4} particles on the silica spheres for material D is shown in Figure 2(V). The size distribution of the supported Co\textsubscript{3}O\textsubscript{4} aggregates of about 39 nm, as mentioned above, is in good agreement with material A of the respective batch and confirms the absence of sintering during the removal of PVP. The pore size of the support in the order of 2.5 nm hinders the Co\textsubscript{3}O\textsubscript{4} particles to enter and, thus, ensures the deposition at the external surface only. The
The SEM investigation of material C reveals crystals with a size of about 1 to 2 μm (see Figure S2-I in SI). Some cobalt oxide particles are located at the external surface of the silicalite-1 crystals, as can be seen by the small particles in the respective size range on the smooth crystal surface, indicating only partial encapsulation of the metal oxide particles. Slices of 80 nm thickness were also studied via TEM, after embedding material C in an epoxy resin (see Figure S2-II in SI). The crystals appear disrupted, due to the mechanical cutting procedure. However, the results clearly reveal cobalt oxide particles located inside the silicalite-1 crystals, as well as on the outer zeolite surface. In contrast to material B and D two cobalt species with respect to their location in the support matrix are thus present in material C, which probably possess different chemical environments regarding the gas composition during the syngas reaction.

The nitrogen sorption isotherms and the pore size distribution of the encapsulated catalyst materials and the silica support are given in Figure S3 (see SI). Material B reveals a high specific surface area and mesopores of 2.7 nm. The pure silica material used as support for material D shows results in the same range. Material C exhibits half of the specific surface area of material B as well as micro pores with an average pore width of 6.3 Å, which corresponds to the desired size of 6 Å for a zeolitic material of MFI type. Representative X-ray diffraction patterns of material B and C are shown in Figure S4 (see SI). The results confirm the successful transformation from an amorphous, mesoporous silica shell to a crystalline, microporous silicalite-1 matrix, as well as the presence of cobalt oxide.

The reduction behavior was studied by H\textsubscript{2}-TPR (Figure 3). The profiles of material B and C are similar and show significant H\textsubscript{2} consumption in a rather broad range between 230 °C and 400 °C. A closer look at the profile of material B reveals a first distinctive peak at 270 °C, which can be assigned to the reduction of Co\textsubscript{3}O\textsubscript{4} to CoO followed by a second broad peak with a maximum at 310 °C accounting for the reduction of CoO to metallic Co\textsubscript{0} [37]. In comparison, the reduction profile of material C is shifted to slightly higher temperatures. The first reduction step occurs at 280 °C, while for the second reduction step a shoulder at 325 °C and a maximum at 375 °C are observed. The differences in reduction temperatures can be explained by the different pore size distributions of the support materials, creating a higher diffusion barrier for the microporous structure, leading to higher reduction temperatures. This conclusion is supported by the profile of material B, which provides freely accessible Co\textsubscript{3}O\textsubscript{4} nanoparticles and shows a sharp reduction maximum at 275 °C. Obviously, the reduction behavior is influenced by the spatial arrangement of the active and support materials as well as the accessibility.

The quantitative analysis of the nanostructured core-shell materials reveals a cobalt content of 9.6 wt% for material B and of 10.6 wt% material C, respectively. The slight difference is due to Si losses during the synthesis procedure. For material D a cobalt content of 1.3 wt% was detected, which is in accordance with the calculated fraction of 1 wt%.

**Effect of the Carbon Oxide Source**

**CO\textsubscript{2} Methanation**

The catalysts were tested for the CO\textsubscript{2} methanation to prove their activity as well as to gain insights into the effect of the core-shell structure. The measured CO\textsubscript{2} conversion, CH\textsubscript{4} selectivity as well as the corresponding consumption (negative sign) and formation (positive sign) rates at different temperatures are given in Table 1. The catalyst stability and reproducibility of the results were confirmed by conducting three successive runs (see Figure S6 in SI). Here, we report the averaged values with standard deviation of the first run.

All catalysts are active for CO\textsubscript{2} methanation and reach their onset temperature at around 300 °C, however, the CO\textsubscript{2} consumption as well as the CO and CH\textsubscript{4} formation rates differ widely between the various catalysts. Particle size effects can be excluded due to the bottom-up synthesis approach and the resulting uniform size distribution of the primary Co\textsubscript{3}O\textsubscript{4} nanoparticles for all materials studied. The comparability of the H\textsubscript{2}-TPR experiments for material B and C indicates the sufficient reduction temperature and a similar chemical environment within the material. The stability against significant deactivation can be supported by the reproducibility of the three runs performed successively. Therefore, a different reduction and deactivation behavior, strong metal support interactions and
Thus, we attribute the observed differences in the activity and selectivity to the core-shell architecture.

Compared, since all materials consist of cobalt nanoparticles supported on SiO₂, synthesized based on the same procedure. Thus, we attribute the observed differences in the activity and selectivity to the core-shell architecture.

The most pronounced differences can be observed when comparing the core-shell material B with reference material D, especially if considering that the size distribution of the primary Co₉O₆ nanoparticles is comparable. Material B shows a high selectivity towards methane, while material D is mostly active for the reverse water-gas shift reaction (RWGS) as the CO₂ formation rate is around four times higher than the CH₄ formation rate. In addition to this, the CO₂ consumption rate for the encapsulated catalyst is higher, even though the reactants have to diffuse through the mesoporous matrix for this structure, while the active nanoparticles are exposed to the surface for material D.

For the interpretation of these findings the concentration of the reactive species in close environment of the active nanoparticle is decisive, since the reaction network is strongly interlinked by chemical equilibrium. However, the composition at the reaction locus is depending on the diffusive transport of reactants and products through the porous shell for material B. Consequently, the diffusion rates governed by the molecular diffusion coefficients and the pore size, as well as the effective diffusion length given by the spatial arrangement of the active nanoparticles inside the supporting shell is important. For Co@SiO₂ catalysts Pang et al. examined the influence of the shell structure on the activity and selectivity in the dry reforming of methane. They conclude that the shell thickness, as well as the size distribution of the core-shell interaction considerably influences the activity, selectivity and stability but they do not elaborate on the influence of the pore size. We believe that the pore size plays a major role for the core-shell architecture, rather than the diffusion length. This hypothesis becomes evident, if one considers the effect of the pore size on the diffusion mechanism, in particular for the meso- and microporous materials studied in this work. While Knudsen diffusion occurs in mesoporous structures, configurational diffusion dominates in microporous zeolites. The latter mechanism depends strongly on the size ratio of the pore and the diffusing molecule, as well as on the interaction between wall and molecule, among other factors. Thus, a tremendously different composition in the close proximity of the shell encapsulated cobalt core compared to the gas bulk and to the surface exposed Co particles in material D is very likely, owing to the size difference between the pores and the involved molecules.

Material C shows a CO₂ consumption and CH₄ formation rate between material B and D, which we attribute to the partial embedment of Co particles within the zeolite matrix (see Figure S2-I in SI). Obviously, material C hosts equal sized Co particles both embedded within a matrix as well as those exposed to the external surface of the crystal, which is associated with two different chemical environments. While the embedded particles probably behave similarly to those of material B, the exposed ones possess a comparable environment as for material D. Since the degree of encapsulation is hard to
We consequently attribute the observed differences in conversion and selectivity to the confinement effect inside the core-shell nanoreactor, as has been reported for hollow metal nanoparticles[39] but also other systems[11,40,41] Recently, Le et al.[42] reported that the confinement effect facilitates the CH4 formation in silica nanopores for the equilibrium composition during CO2 methanation. One possible explanation for the observations reported in the present paper is based on the restricted exit of product molecules through the silica shell encapsulating the Co nanoparticles. Considering that CO2 does not adsorb at the SiO2 surface, as reported for a Ni/SiO2 catalyst,[43,44] the reaction proceeds solely over the cobalt surface, where CO2 adsorbs dissociatively,[45,46] leading to the desorption of CO as a byproduct. The restricted exit effect in the confined environment might increase the probability for adsorption of CO on cobalt as compared to the supported reference catalyst. Thus, the methanation of the CO intermediate is favored for the core-shell structure, which explains the higher CH4 selectivity observed.

**CO Methanation**

The catalytic results for CO methanation using material B show stable operation up to 300 °C and rapid deactivation for higher temperatures (Figure 4). Since conversion and selectivity are intensively discussed in the following section on co-methanation of CO/CO2 mixtures, we focus the discussion on the deactivation behavior here. In literature, two deactivation reasons are most frequently considered - coking and sintering. Because TEM images (see Figure S9 in SI) of the spent catalyst prove the thermal stability of the core-shell particles even after 10 h at 400 °C, coking appears to be the most probable deactivation mechanism. Carbon deposition induced by the Boudouard reaction (Equation 4), as frequently reported for similar systems,[19,47,48] is underlined by the significant CO2 formation. According to the mechanistic study of Chen et al.[18] on a Co/SiO2 catalyst, the CO methanation proceeds by the direct dissociation of CO to atomic C and O, which is subsequently hydrogenated to CH4 and H2O. The overall reaction is rate-controlled by the CH4 hydrogenation. Following that reasoning, coking could also be a consequence of the reaction mechanism, as the dissociation of CO occurs faster than the hydrogenation leading to an accumulation of C on the surface. Comparing the CO with the CO2 consumption rate shows similar values, which is in line with the assumption that the CO2 methanation proceeds by the dissociation of CO2 to CO and O2, followed by the CO methanation.[49] Therefore, an accumulation of C on the cobalt surface can also be expected for the CO2 methanation, causing deactivation by coking. We, indeed, observed decreasing activity in the CO2 methanation at 400 °C over 7 h, though to a much lesser extent (see Figure S11 in SI), probably due to differences in the rate determining step in CO and CO2 methanation.

To confirm coking as a deactivation cause, we applied Raman spectroscopy on material B after a long-term CO methanation experiment at 400 °C. Figure 5 shows the Raman spectra measured at two different spots in the same catalyst sample in the region of 800 to 2200 cm−1 where information regarding carbon are expected. In the first microscope image a large black region is visible in the middle of the spot, indicative for the presence of carbon on the catalyst. The corresponding Raman spectrum (red) shows two distinctive peaks at 1347 and 1587 cm−1 belonging to the disordered graphitic lattice (D-band at ~1350 cm−1) and the ideal graphitic lattice (G-band at ~1590 cm−1).[49,50] The same peaks were detected with significantly less intensity in the second spot (blue), although no carbon is explicitly visible in the corresponding microscope image. Thus, the carbon distribution appears to be rather...
inhomogeneous within the volume of the catalyst bed. The intensity ratio $I_y/I_x$ of 1.5 in both cases confirms a high degree of graphitization and thus coking as the main deactivation mechanism in CO methanation. The coke formation might also lead to pore blockage, which aggravates the deactivation process. In comparison, material C and D are significantly less active but also suffer from a rapid deactivation (see Figure S7 and S8 in SI). In case of material D, sintering is an additional, however, minor issue as the mean Co particle size increased by 5 nm during a long-term run (see Figure S10 in SI for TEM images), justifying the encapsulation of the Co core in material B and C for enhanced thermal stability.

**Effect of Carbon Oxide Mixtures**

When replacing CO$_2$ stepwise with 0.12 and 0.35 CO both carbon sources are converted simultaneously, indicated by the negative sign of the rate. However, the CO$_2$ consumption rate decreases, while the methane formation rate increases. Obviously, the addition of CO inhibits the CO$_2$ conversion, as has also been observed by Weatherbee and Bartholomew under very similar reaction conditions.\cite{43} On the one hand the strong competitive adsorption of CO on the cobalt surface blocks sites for CO$_2$ adsorption and its subsequent conversion. On the other hand, the CO hydrogenation appears to be faster than that of CO$_2$ at moderate CO feed fractions, which is indicated by the associated increasing methane formation rate. Further, the simultaneous conversion of CO and CO$_2$ contradicts the literature on the selective methanation of CO (SMET), which usually reports a CO$_2$ conversion once CO has been fully converted.\cite{26,32,33,51} However, these studies consider mostly non-inert supports, such as CeO$_2$, which provides different adsorption sites for CO and CO$_2$ and thus less pronounced competition between both species.

Under a nearly balanced CO$_2$/CO feed, the CO$_2$ consumption rate becomes nearly zero. Hence, the only net reaction occurring is the methanation of CO. When the CO$_2$/CO ratio decreases further to 0.12/0.88, the only net reactions taking place are the CO methanation and the CO$_2$ formation by WGS as the CO$_2$ reaction rate is positive. Interestingly, the addition of 12% CO$_2$ does not affect the consumption rate of CO. Similar findings have been observed by Kopyscinski et al. for a Ni/Al$_2$O$_3$ catalyst,\cite{52} who found no retarding effect on the methane formation rate with 10 vol% CO$_2$ in the feed. Unfortunately, the authors do not elaborate in detail on the selectivity.

The comparison to material C and D exhibits a similar qualitative behavior (see Figure S12 and S13 in SI). However, the maximum methane formation rate is significantly smaller by a factor of more than five. In addition, the CO$_2$/CO-ratio for being the CO methanation the only net reaction varies in the range between 0.88/0.12 and 0.12/0.88.

In summary, the presence of both reactants leads to a shift in the kinetic regime of the reaction and suppresses the side reaction (RIWGS), which results in a weakly pronounced maximum in the CH$_4$ formation rate at almost equimolar CO/CO$_2$ feed ratio. For an increasing CO$_2$ share in the feed, CO$_2$ is converted to methane at a significant rate, while for smaller CO$_2$ fractions the CO methanation is the predominant reaction and CO$_2$ is produced via the WGS. We assume a change in the underlying mechanism induced by the presence of both CO and CO$_2$, whose identification is still a matter of debate.\cite{18,19} since only little is known for CO$_2$ hydrogenation on cobalt as active material thus far beyond Fischer-Tropsch synthesis.\cite{28–30}

On the other hand, our results also confirm a rather broad flexibility of the catalyst with respect to the carbon oxide source, particularly for over-stoichiometric availability of H$_2$. In addition, no pronounced deactivation was found under the reaction conditions in this study, neither by sintering of the cobalt nanoparticles (see SI) nor by severe coke deposition.

![Figure 6. Material B - Individual net reaction rates (positive sign: formation, negative sign: consumption) for the carbonaceous species vs. CO$_2$ fraction in CO$_2$ feed; left pointing arrows indicate increasing and right pointing arrows decreasing CO$_2$ content in the feed; averaged data and standard deviation for 10 min time on stream; reaction conditions: temperature 320 °C, pressure 1 bar, total flow rate 51.9 mL STP h$^{-1}$, molar feed composition 4/1/6.4 H$_2$/CO$_2$/Ar, 2.88 mg Co, WHSV 1080 h$^{-1}$, GRW $^{-1}$ h$^{-1}$].

reproducibility has been ensured by multiple runs and different starting compositions, though, only the results of the first run are shown here (for reproducibility see Figure S14 and S15 in SI). Equilibrium constraints can be excluded, as confirmed by calculating the respective equilibrium composition. No deactivation or hysteresis effect is observed over the measurement period as the rates do not differ significantly for the two half cycles of the CO$_2$/CO-hysteresis. Furthermore, the consumption and formation rates under pure CO$_2$ and CO methanation conditions fit well to the results from the previous sections, when considering the differences in WHSV.
Conclusions

Two nanostructured catalyst materials - Co@mSiO₂ and Co@silicalite-1 - were prepared via a bottom-up approach, fully characterized and subsequently applied for the CO, CO₂, and CO methanation. Our findings show that both catalysts are comparably active and selective for CO₂ hydrogenation towards methane. By comparing the Co@mSiO₂ core-shell material with a supported reference catalyst, a significantly higher methane selectivity was obtained with the core-shell catalyst. We attribute this surprising observation to the confinement effect and the associated higher chance of readсорption and subsequent hydrogenation of the CO intermediate. CO methanation experiments reveal a rapid temperature-dependent deactivation for temperatures above 300 °C which is caused by coking. As anticipated, the thermal stability of core-shell catalyst is high in comparison to the supported reference catalyst, which suffers from sintering. Furthermore, as evidenced in the simultaneous CO/CO₂ methanation experiments, the catalyst can react flexibly on changing feed gas compositions. In fact, the co-presence of CO and CO₂ leads to a shift in the kinetic regime, resulting in a weakly pronounced maximum in the methane yield while suppressing unwanted side reactions under an almost equi- molar CO/CO₂ feed. The Co@silicalite-1 catalyst exhibits reaction rates between those of the materials with encapsulated and non-encapsulated cobalt particles during CO₂ methanation, which is attributed to the partial embedment of the cores inside the zeolite matrix. For a more reliable analysis of the influence of the pore size on the confinement effect, the degree of encapsulation and the structure of the micropore network will be analyzed quantitatively via electron tomography in future. Future research should be also directed to unraveling the influence of the mass transport through the pore structure as well as the mechanistic implications of the co-presence of CO and CO₂. Therefore, operando techniques are required to identify the adsorbed species. Further, the transferability of our results to related reactions, such as the Fischer-Tropsch synthesis should be tested.

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Conflict of Interest

The authors declare no conflict of interest.
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