Comparing Co-catalytic Effects of ZrO$_x$, SmO$_x$, and Pt on CO$_x$ Methanation over Co-based Catalysts Prepared by Double Flame Spray Pyrolysis

Jakob Stahl$^+$, Jan Ilsemann$^+$, Suman Pokhrel$^{[a,c]}$, Marco Schowalter$^{[d]}$, Christian Tessarek$^{[d]}$, Andreas Rosenauer$^{[d,e]}$, Martin Eickhoff$^{[d,e]}$, Marcus Bäumer$^{[b,e]}$ and Lutz Mädler$^{[a,c,e]}$

The impact of different co-catalytically acting promoters (Pt, ZrO$_x$, and SmO$_x$) during CO$_x$ methanation was investigated on alumina supported Co-based model catalysts. To obtain samples with identical structure and morphology independent of the presence and the type of promoter added, double flame spray pyrolysis was employed for the synthesis, which, in contrast to classical catalyst preparation techniques, allows controlling and separating the particle formation processes of the different catalyst components. In this way, differently promoted and unpromoted catalysts with identical size distributions and dispersions could be synthesized to study co-catalytic effects in isolation. For CO$_2$ methanation, all promoters led to improved methanation yields and long-term activities within the whole temperature range as compared to the unpromoted catalyst. Among them, zirconia and platinum performed best. In case of CO methanation, a beneficial influence of the studied promoters could also be verified – with Pt showing the best results. Yet, all catalysts deactivated rapidly above 310°C, limiting their usability to lower temperatures.

Introduction

Climate change caused by rising CO$_2$ emissions render a paradigm shift in the energy sector away from fossil fuels towards “green” energy sources inevitable. The power-to-gas technology (PTG) is a promising process in this context which is based on the reaction of carbon oxides – in particular, CO$_2$ – with electrochemically produced H$_2$ to yield synthetic natural gas (CH$_4$) according to eq. (1) and (2). In this way, fluctuations in the power generation by solar or wind energy can be accommodated using the process to chemically store excess energy in form of methane, which then can be fed into the gas grid. As unwanted side reactions, the (reverse) water-gas shift and Boudouard reaction commonly occur (eq. (3) and (4)).\(^{[1]}\)

For renewable energy storage applications, both CO and CO$_2$ methanation are of interest since both educts are reported to be used as feed stock, stemming for example from steel production or biomass gasification.\(^{[10]}\) Even though both methanation reactions are exothermic, they are connected with high kinetic barriers and consequently require the presence of a catalyst to be economically feasible. Usually, supported transition metals, such as Ni, Co, Fe and Ru are employed as active components, while also bimetallic catalysts, i.e. NiFe alloys, recently have started to garner high interest.\(^{[11,2]}\) Among the potential active components, Ni is the most often investigated metal owing to its low price.\(^{[2,4]}\) In contrast, the higher price of Co has limited its application as a CO$_2$ methanation catalyst so far, although its successful use as a Fischer-Tropsch catalyst renders Co also promising for CO$_2$ methanation prospectively providing higher CH$_4$ yields compared to Ni.\(^{[3]}\)

In all cases, high surface area oxides, e.g. Al$_2$O$_3$ serve as support materials to ensure high dispersions and optimal particle sizes of the active metal, where highest activities can be expected (<10 nm).\(^{[4]}\) To further improve activity, selectivity and/or stability, suitable promoters can be added.\(^{[2a,3c]}\) Generally, promoters are distinguished into structural and chemical promoters.\(^{[5]}\) In case of Co catalysts, structural promoters, such as MgO or CrO$_x$, have been shown to stabilize the supported Co particles and prevent their sintering, whereas chemical pro-
moters directly enhance the catalytic performance either by electronic or co-catalytic effects.\(^{[5b]}\) Electronic promoters, such as Na, Li or K, affect the electronic structure of the active component, thus influencing, for instance, the surface coverage and binding strength of reactants or reaction intermediates positively on the metal.\(^{[6]}\) On the contrary, co-catalytic promoters directly impact the catalytic mechanism, e.g. by providing new or additional adsorption or reaction sites.

\[
\begin{align*}
CO + 3H_2 & \rightarrow CH_4 + H_2O \\
CO_2 + 4H_2 & \rightarrow CH_4 + 2H_2O \\
CO_2 + H_2 & \rightarrow CO + H_2O \\
2CO & \rightarrow CO_2 + C
\end{align*}
\]

In case of CO\(_2\) methanation over supported Co catalysts, it is generally accepted that CO\(_2\) adsorption and conversion occurs at metal-support perimeter sites by reacting with hydrogen that stems from H\(_2\) adsorption and dissociation on metallic Co sites.\(^{[14,7]}\) On the contrary, for Co methanation it is assumed that all reaction steps take place on the Co nanoparticles alone via hydrogenation of C and O atoms, immediately formed by dissociation of adsorbed CO.\(^{[15]}\) In case of basic oxide supports, however, an involvement of CO or CO\(_2\) adsorbed on the support in form of carbonates is also conceivable.

In view of these mechanistic considerations, (Lewis) basic metal oxides as well as noble metals, such as Pt, appear to be promising promoters. While in the first case the surface concentration of CO or CO\(_2\) can be increased by their fixation as carbonates, Pt is expected to improve the availability of hydrogen on the catalyst surface by providing additional H\(_2\) adsorption and dissociation sites.\(^{[16,8]}\) Although the potential benefits of co-catalysts for CO\(_2\) methanation are widely accepted, studies comparing different co-catalytic promoters and their relative effectiveness are missing so far. To contribute to a progress in this direction, we studied the Lewis basic oxides zirconia and samaria, as well as Pt as promoters for Co/Al\(_2\)O\(_3\) methanation catalysts.

As far as Pt is concerned, Schubert et al.\(^{[30]}\) already found that Pt promoted Co-Al\(_2\)O\(_3\) catalysts show a significantly higher reactivity for CO\(_2\) methanation and attributed the effect to an additional supply of hydrogen by spillover from finely dispersed Pt. Also in case of CO methanation, a beneficial impact of an added Pt promoter can be expected, as Chen \emph{et al.}\(^{[38]}\) for example, reported a reaction order for H\(_2\) that is higher than for CO over a Pt promoted Co-SiO\(_2\) catalyst. Turning to oxide promoters, zirconia is a good choice since its potential as a promoter for CO\(_2\) methanation and Fischer-Tropsch synthesis was already demonstrated – in accordance with its ability to form oxygen vacancies that, as Lewis basic centers, can efficiently adsorb and activate both CO and CO\(_2\).\(^{[14,9]}\) Similarly, samaria revealed a high potential when using it as a support or as a promoter for CO\(_2\) hydrogenation catalysts.\(^{[10]}\) In analogy to zirconia, its virtue results from its suitable surface basicity, resulting from surface OH groups and lattice O\(^+\) adsorption sites which interact with and bind the mildly acidic CO\(_2\) neither too strongly nor too weakly at the temperatures where the catalytic conversion is carried out.\(^{[11]}\)

Aiming at a reliable comparison of different promoters, an identical dispersion and particle size distribution of Co as the active component is pivotal as differences in this respect can easily obscure promoter effects due to the pronounced structure-sensitivity of the CO\(_2\) methanation reactions.\(^{[6,12]}\) Synthesizing differently promoted catalysts which are otherwise structurally identical with classical impregnation techniques is difficult or even impossible due to the poor control over the particle and the phase formation during the process.\(^{[13]}\) In contrast, flame spray pyrolysis (FSP) is a versatile, single-step technique allowing a continuous, highly reproducible and scalable\(^{[14]}\) synthesis of nanostructured multi-component materials.\(^{[15]}\) The process is based on the combustion of metal-organic precursor solutions that are continuously atomized in an oxygen gas stream, leading to the formation of nanoparticles by evaporation, nucleation, aggregation and agglomeration in the flame.\(^{[14]}\) When using a single flame set-up, the particle sizes and phase compositions obtained for multi-component materials depend highly on the kinetic and thermodynamic conditions in the flame.\(^{[16]}\) Due to the limited measures to control the relevant parameters, complete phase segregation, encapsulations or solid mixtures cannot always be avoided.\(^{[15b]}\) For some applications a phase separation leads to highly desired multiphase materials though. Teoh \emph{et al.} showed that finely dispersed 1–2 nm Co particles dispersed in a zirconia matrix can be synthesized this way, exhibiting highly competitive activity as CO hydrogenation catalysts.\(^{[17]}\)

In contrast, the use of two flames in the process allows a higher degree of control taking advantage of the possibility to preform nanoparticles of different components by separating the formation processes.\(^{[18]}\) Here, solutions of the respective precursors are fed independently to the two FSP nozzles. Adjusting the arrangement of the flames properly, the point where the flames intersect, and the particles meet, and aggregate can be varied. In this way, nanostructured materials comprising both components in form of individual phases or in form of mixed phases can be obtained and properties, such as chemical composition, phase composition, metal dispersion, specific surface area or the surface chemistry, tuned.\(^{[19]}\)

The capabilities of single and double flame FSP were documented in various studies dealing with the synthesis of novel materials with optimized properties for energy applications, such as catalysts\(^{[17,20]}\) or battery materials, for instance.\(^{[21]}\) To illustrate the advantages of double flame FSP, we would like to refer to a study of Minnermann \emph{et al.}, who described for Co/Al\(_2\)O\(_3\) catalysts – i.e. the type of catalyst of interest here – how flame distance and angle affect their structure and, in turn, the catalytic properties regarding Fischer-Tropsch synthesis.\(^{[18a]}\) While single flame FSP exclusively led to the formation of a thermally stable, but hardly reducible and thus catalytically inactive Co-Al\(_2\)O\(_3\) phase, its formation could be suppressed by double flame FSP.

Therefore, the double flame approach was also used in the present study. In an attempt to achieve an identical Co
dispersion and size distribution for all catalysts, we separated the nanoparticle formation of the active Co component from that of the promoted alumina (support) component. This was achieved by independently combusting a solution containing the precursors of the promoters and the Al₂O₃ precursor in one nozzle, and a solution with the precursor of the active component (Co) in a second nozzle. A flame arrangement was chosen which ensured that the formation of both types of nanoparticles was completed before meeting at the intersection point of the flames and forming joined aggregates. In all cases, a promoter loading of 2 wt.% by element was targeted as a compromise between economic interests (i.e., low Pt loading) on the one hand, and significant catalytic improvements on the other hand.

All as-prepared catalyst powders – an unpromoted as well as the three promoted Co/Al₂O₃ catalysts (platinum, zirconia, samaria) – were thoroughly characterized, using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and N₂ physisorption. To probe the surface properties, CO₂ and H₂ temperature-programmed desorption (CO₂-TPD, H₂-TPR) as well as pulsed H₂ and CO oxidation experiments were carried out – the latter to determine the density of metallic sites (H₂) as well as the density of basic CO₂ adsorption sites. All materials were tested as catalysts for CO and CO₂ methanation.

Results and Discussion

Structural and chemical characterization of the catalysts

The elementary analysis of the four catalysts using XPS is given in Table 3 and confirmed the targeted material composition given in Table 1. Additional data for EDX quantification is given in Table S4. The specific surface areas (SSA) of all as-prepared catalysts – the unpromoted one as well as the catalysts promoted with Pt, zirconia and samaria - were determined by BET measurements and ranged between 121 and 125 m²·g⁻¹, i.e., were very similar (see Table 2). Based on these values, BET particle diameters d_BET between 10.6 and 11.2 nm were calculated using eq. 5 (also given in Table 2). For comparison purposes, also pure Co₃O₄ and pure alumina samples were prepared by single flame FSP. For the Co oxide powder a specific surface area of 122 m²·g⁻¹ and a BET particle diameter d_BET of 8.0 nm were found, whereas the corresponding values for the alumina powder amounted to 124 m²·g⁻¹ and 12.3 nm, respectively. Averaging the d_BET values of these two samples according to the weight fractions of the two components in the catalysts (neglecting the small weight fraction of the promoters) (see Table 1), the results basically reflect the BET particle sizes of the catalysts. This similarity provides first evidence that, by virtue of the chosen arrangement of the two flames in the FSP process, the particle formation of each catalyst component was finished before the particles met at the intersection point of the flames. In this case the catalysts should comprise both components in form of individual particles, resembling in size the ones found for the single flame FSP samples. This conclusion will be corroborated by XRD and TEM in the following.

Turning first to the XRD measurements, the diffraction patterns of all catalysts (promoted and unpromoted) as well as...
the patterns of the individual (pure) components prepared by single flame FSP are presented in Figure 1. In the latter case, the Rietveld refinement of the XRD pattern revealed for Co that the pure material consists of Co$_3$O$_4$ particles (ICSD: 97004, space group Fd3m). The average crystallite size determined (8.6 nm) is in good agreement with the one derived from the BET measurements (d$_{BET}$). The flat background of the diffractogram, moreover, suggests a high crystallinity of the material. As far as the pure alumina material is concerned, it is worth noting that for the structural description of flame made alumina, such as industrial γ-Al$_2$O$_3$, no consensus exists in literature. A defect spinel with an idealized formula Al$_{21+1/3}$□$_{2+2/3}$O$_{32}$ is assumed, where □ denotes a vacancy. These metastable alumina phases are traditionally denoted by Greek letters such as η, γ or δ and were described as being intrinsically deformed spinels. In case of the FSP Al$_2$O$_3$ material in this study, the XRD patterns are best described by a combination of tetragonal γ-Al$_2$O$_3$ (ICSD: 99836, space group I4$_1$/amd) and cubic η-Al$_2$O$_3$ (ICSD: 66558, space group Fd3m). Unfortunately, a comparison of XRD derived crystallite sizes with d$_{BET}$ or mean values determined by TEM for the particle sizes is impossible due to their multiphase composition.

In agreement with an individual formation of the Co$_3$O$_4$ and alumina particles in both flames of the double flame FSP setup,

![Figure 1](image_url)

**Figure 1.** A) XRD patterns of all four, as prepared double flame (DF) catalysts and of the pure Co$_3$O$_4$ and Al$_2$O$_3$ powders prepared by single flames (SF). All major diffraction peaks are assigned to the occurring components and their crystallographic phase. B) Rietveld refinement of the unpromoted as prepared catalysts revealing the presence of Co$_3$O$_4$ (blue) as well as of a γ-Al$_2$O$_3$ (green) and η-Al$_2$O$_3$ (purple) phase. Blue dots represent the measured XRD intensities, the black line the background, the red line the calculated diffractogram according to the Rietveld refinement and the grey line shows the difference between the observed and calculated data. Refinements of the promoted catalysts are presented in Figure S2.
the XRD patterns of all four catalysts (unpromoted, Pt, zirconia and samaria promoted) can be explained with a superposition of the patterns observed for the pure components. This is exemplarily shown for the unpromoted catalyst by a Rietveld refinement of the corresponding diffractogram depicted in Figure 1B. The analysis reveals a CoO crystal size of 9.1 nm, in good agreement with the crystallite size determined for the pure material (see Table 2). The derived weight fraction (26 wt.% CoO, see Table S2) is in line with the composition targeted in the synthesis. Also, in case of the promoted catalysts, the Rietveld refinement provided very similar CoO crystallite sizes, ranging between 8.9 and 9.1 nm. Here, the calculated CoO weight fractions are somewhat higher than predetermined by the synthesis. Since only the crystalline parts of the samples contribute to the diffraction peaks, of course, some X-ray amorphous areas resulting from the presence of the promoters in the formation process of the alumina component could be responsible for these deviations. Due to the low concentration of the promoters (2 wt.%), separate XRD peaks indicating individual crystalline phases of the promoters were absent.

Micrographs of the catalysts acquired in TEM and STEM mode at various magnifications are presented in Figure 2. According to the images taken at larger magnification all samples exhibit the same morphology consisting of aggregated, interconnected nanoparticles. Consistent with the conclusions drawn so far, their size distribution is very similar and appears to be bimodal in all cases. The smaller particles are likely to represent CoO nanoparticles and the larger ones the alumina particles (with or without the promoter), as confirmed by EDX in the following.

First turning to the Pt promoted catalyst, it is known from previous studies that the Pt precursor sprayed together with the alumina precursor in one FSP flame results in the formation of individual Pt deposits on top of Al2O3.[26] An analogous behavior was observed for TiO2 if used as the oxide component.[19c,27] This finding was explained by hetero- or homogenous nucleation processes in the flame, leading to the formation of Al2O3 nanoparticles (or TiO2, respectively) prior to the deposition of Pt on their surface.[25] Ding et al. performed XAS and CO adsorption DRIFTS experiments on FSP catalysts with 0.2 wt.% Pt added to various supports. In TEM micrographs separate 1.3 nm Pt particles were reported on the Al2O3 support and XAS suggested that the Pt was in metallic form.[26b] Consistently, such Pt deposits were also discovered in the STEM images of the Pt promoted catalyst synthesized in the present study (see Figure 2H and L). After Fourier filtering of the micrographs to reduce noise, lattice distances of favorably oriented Pt crystals (0.226 and 0.237 nm, see insets in Figure 2H) were identified which are in good agreement with the d-values determined by XPS. The targeted fraction for the promoters was 2 wt.% and for the Co 18.5 wt.%. Data for oxygen is given in Table S3.

In contrast, the face of the added promoter was more difficult to clarify in case of the zirconia and samaria promoted catalysts. Individual promoter nanoparticles were hardly detectable in the TEM or STEM images of these samples, even though EDX and XPS measurements confirmed their presence (see Table 3 and S4). We will come back to this point later and first dwell in more detail on the spatial distribution of the two main components, CoO, and alumina, in the catalysts.

To this end, further analysis using energy filtered transmission electron microscopy (EFTEM) and STEM EDX were carried out. In Figure 3, representative results for the unpromoted and the platinum promoted catalyst are shown. The zero loss (ZL) filtered TEM images as well as Co and O elemental maps corroborate that the Co particles are evenly distributed within the aggregates. To determine the chemical composition of individual particles, EDX spectra were taken in STEM mode within corresponding regions (Figure 3 E and J). The data confirm that the larger particles appearing darker in the STEM images can indeed be attributed to Al2O3, whereas the smaller particles appearing brighter correspond to CoO. The average particle sizes dSTEM derived from the evaluation of TEM micrographs of the four as prepared catalysts ranged between 10.3 and 11.6 nm. In case of the unpromoted catalyst a clear maximum at ~8 nm and a weakly pronounced second maximum at ~12–13 nm can be discerned, matching the average particle sizes dBET of the pure CoO and Al2O3 samples (Table 2). Full particle size distributions are presented in Figure S5 and Table S5.

In view of this morphology, it is noteworthy that it somewhat differs from the usual morphology of supported catalysts, where nanoparticles of the active component are typically distributed on the surface of larger particles of the oxide support. Yet, a close proximity and contact between both components – i.e., Co (formed after reduction prior to the catalytic use) and alumina - is also given for the FSP catalysts. A comparison of TEM micrographs of the unpromoted, as prepared catalyst and the spent catalyst after reduction and CO2 methanation confirms the morphological stability of the aggregated and interconnected nanoparticles of both components (see Figure S13).

| Catalyst          | Composition of the as prepared catalysts by element |
|-------------------|-----------------------------------------------------|
|                   | Co [wt.%] | Al [wt.%] | Pt [wt.%] | Sm [wt.%] | Zr [wt.%] |
| Co/Al2O3          | 16.9(1)   | 39.2(1)   |           |           |           |
| Co/SmO2-Al2O3     | 15.2(1)   | 38.5(1)   |           |           | 2.3(1)    |
| Co/ZrO2-Al2O3     | 16.9(1)   | 37.1(1)   |           |           | 2.1(1)    |
| Co/Pt-Al2O3       | 16.4(1)   | 38.5(1)   |           |           | 2.1(1)    |

Table 3. Metal composition of the as prepared catalysts as oxides determined by XPS. The targeted fraction for the promoters was 2 wt.% and for the Co 18.5 wt.%. Data for oxygen is given in Table S3.
Coming back to the oxide promoted catalysts, samples with a higher content of the promoter (10 wt.% Zr or Sm loading on Al\(_2\)O\(_3\)) were additionally synthesized using single flame FSP (i.e., without the Co component), assuming that the formation of individual phases or deposits of these promoters (in analogy to Pt) is easier detectable then. For zirconia, TEM and STEM measurements indeed provided evidence for ZrO\(_2\) crystallites deposited on the surface of the Al\(_2\)O\(_3\) particles (see Figure S9). Also, in the XRD pattern of this sample diffraction peaks attributable to tetragonal ZrO\(_2\) with the space group \(P_{42/nmc}\) could be identified, whereas indications for the formation of mixed oxide phases were absent (see Figure S7).\(^{29}\) Yet, the diffraction peaks of Al\(_2\)O\(_3\) were slightly broadened for the 10 wt.% sample when compared to the pure Al\(_2\)O\(_3\) material. Since TEM (see Figure S6) proves that the larger half widths do not originate from smaller particle sizes obtained in this case, the finding points to a decreased crystallinity, i.e., some amorphous areas within the alumina particles. These are likely to be caused by the partial formation of non-crystalline mixed zirconia/alumina during the FSP process when increasing the

![Figure 2. Representative TEM images of the as prepared catalysts at lower (A–D) and at medium magnification (E–H) as well as images acquired in STEM mode (I–L) and SAED data (M–P). The insets in image H show HRTEM images of two platinum particles analyzed after Fourier filtering (see Figure S4).](image)
promoter concentration. However, at lower loadings/concentrations (2 wt.%) a comparable broadening of the diffraction peaks was absent (data not shown) so that such amorphous phases apparently do form to a lesser extent. In Electron Energy Loss Spectroscopy (EELS) experiments the white line positions of the Zr L-edge and the L3/L2 ratios suggested a similar valency and chemical environment of 2 wt.% zirconia with alumina compared to pure zirconia (see Figure 12). Thus, it is not surprising that in STEM images of the single flame alumina sample with 2 wt.% zirconia small ZrO$_2$ deposits or finely dispersed zirconia layers deposited on the Al$_2$O$_3$ surface were observed (see Figure S6).

Also, in case of samaria neither an own crystalline phase nor the formation of crystalline mixed oxide phases was detected by XRD for a 10 wt.% reference sample analogously prepared with single flame FSP (see Figure S7). A broadening of the Al$_2$O$_3$ diffraction peaks observed here as well again suggests an interference with the crystallinity of the Al$_2$O$_3$ matrix. Consistently, in TEM and STEM images acquired for this sample (see Figure S6), amorphous areas were discernible in this case, whereas lattice fringes indicating crystalline Sm$_2$O$_3$ could be recognized only sporadically. In a sample containing only 2 wt.% samaria as in the support of the catalyst discussed in this paper no such separate SmO$_x$ deposits were observed in TEM micrographs. An advanced characterization using the

Figure 3. A and F show zero loss (ZL) filtered TEM images acquired for the unpromoted and Pt promoted catalyst showing representative aggregates and C, D, H and I corresponding EFTEM data revealing the local distribution of cobalt and oxygen, respectively. In B and G STEM images for both samples are shown, which were used to further analyze the chemical composition in selected areas by EDX measurements (E and J). The insets in E and J show magnified views of the areas in the STEM images (B and G), within which EDX spectra were recorded inside the colored circles.
techniques Photoluminescence (PL), UV-Visible and EELS Spectroscopy show an altered chemical environment of Sm in 2 and 10 wt.% Sm doped Al₂O₃ compared to Sm₃O₉, while a trivalent oxidation state was detected in all samples (see Figure S10-S12). In summary, the results of the various structural characterizations for this catalyst are inconclusive in clarifying the form in which the samaria promoter occurs and is spatially distributed. Nevertheless, the CO₂ chemisorption experiments and TPD data, discussed in the following, will reveal its distinct influence on the surface chemistry.

The surface properties, including the surface basicity, as well as the reducibility of the catalysts were characterized by H₂ TPR, CO₂ TPD as well as by H₂, CO and CO₂ chemisorption experiments.

The reducibility of the materials is an important feature, as the Co₃O₄ component (catalytically inactive) needs to be reduced to metallic Co prior to their use as catalysts for CO methanation. In the H₂-TPR spectra, presented in Figure 4 A, two reduction peaks are visible for all samples which can be attributed to the reduction of Co₃O₄ to CoO and its further reduction to metallic Co.

In case of the unpromoted catalyst, the corresponding temperatures (360 °C and 580 °C) agree well with previously published results for Co/Al₂O₃ catalysts also prepared by double flame FSP.

The tailing visible at higher temperatures points to species which are more difficult to reduce. While in HRTEM and XRD hints for a stoichiometric CoAl₂O₄ spinel phase were missing, the aggregation of the Co₃O₄ and the alumina particles at the intersection point of the flames may, however, lead to the formation of a mixed oxide phase at their interface at the high temperatures. Such an interface reaction leading to strong adhesion between the particles explains the morphological stability of the aggregates and renders an exchange of adsorbed species possible, as manifested by the influence of the promoter (associated with the alumina component) on the reducibility (of the Co component) and also the catalytic performance (as will be discussed in the next section).

With Pt as a promoter, the former effect becomes obvious when noticing that both reduction peaks drastically shift to lower temperatures (to 200 °C for the first and 400 °C for the second step). The improved reducibility of this catalyst is in agreement with the ability of Pt to dissociate H₂ and supply H atoms which, after spill-over to adjacent Co₃O₄ particles, are able to facilitate their reduction. As expected, the ZrO₂ and SmO₂ promoted and unpromoted catalysts exhibit very similar reduction profiles.

A key figure for the catalytic activity is the metallic surface area accessible after the reduction of the catalysts which can be determined by pulsed H₂ chemisorption experiments. The H₂ adsorption capacities measured in this way after reducing the catalysts (in analogy to their pre-treatment prior to the catalytic tests) are summarized in Table 4 along with the derived surface areas and calculated metal dispersions. Considering the similar sizes of the Co oxide particles in all as-prepared catalysts, it was to be expected that the metallic surface areas and metal dispersion of the reduced unpromoted catalyst and the reduced SmO₂ and ZrO₂ promoted catalysts are very similar. Yet, a significantly larger metallic surface area was detected for the reduced Pt promoted catalyst, as expected in view of the additional adsorption sites on the metallic Pt deposits. Yet also an increase of metallic Co sites could contribute to this effect taking the improved reducibility of this catalyst into account. To clarify this point, we prepared a reference sample with the same Pt content (2 wt.%) but without Co by using single flame FSP. Interestingly, the metallic surface area determined by H₂ chemisorption in this case was ~2.6 m²g⁻¹, a value exceeding the difference between the metallic surface areas of the Co/
Al₂O₃ and the Co/Pt-Al₂O₃ catalyst (1.2 m² g⁻¹). Apparently, the Pt promoted catalyst exhibits more rather than less metallic surface than the reference material without Co. This result not only renders an increased number of metallic Co sites unlikely, but also suggests a significant loss of metallic Pt sites. The most likely reason is that a part of the Pt deposits on the alumina particles gets inaccessible after aggregation with the Co₂O₃ particles, as the particles are buried at the interface.

The higher metallic surface area of the Pt promoted catalyst is also reflected by an increased CO adsorption capacity as determined by pulsed CO chemisorption experiments. Opposed to H₂ adsorbing only on metallic (Pt and Co) sites, however, CO can also adsorb on basic oxide sites. These are supposed to be augmented by the ZrO₂ and the SmO₂ promoters, possibly enhancing the catalytic performance for CO methanation in this way.[31] Yet, the results of the chemisorption experiments are divergent for both oxides, as demonstrated by the results presented in Table 4. While for the zirconia promoted catalyst an CO adsorption capacity almost twice as high as compared to the unpromoted catalyst was detected, in case of the samaria promoted catalyst no increased CO uptake could be found. The reason is unclear but might be connected to the lack of an own (crystalline) samaria phase as evidenced by TEM and XRD in contrast to the zirconia promoter.

To further analyze basic site properties available on the surface of the various catalysts, also pulsed chemisorption experiments were carried out for CO. The measurements revealed that the unpromoted Co/Al₂O₃ catalyst exhibits the lowest CO₂ adsorption capacity of all catalysts (Table 4) (which, also in comparison to values reported for other Co/Al₂O₃ catalysts in the literature,[32] is quite low). The addition of Pt as a promoter, hardly affects the CO₂ uptake, whereas promoting the catalyst with zirconia significantly increases the CO₂ uptake by about 100% (rel.), thus indicating even a gain of basic surface sites binding CO₂. Also, in case of the samaria promoted catalyst, an increase is observed – yet amounting to only 50%.

To clarify whether the carbonates formed after CO₂ adsorption are neither too stable nor too labile at the applied methanation reaction temperatures (200°C–400°C), temperature-programmed desorption spectra (presented in Figure 4B) were recorded, after completing the chemisorption runs. In all four cases, their shape generally matched the CO₂ desorption profiles reported for other alumina supported catalysts in the literature.[32] In addition to overlapping desorption features below 400°C consisting of two or possibly three (in case of the zirconia promoted catalyst) individual peaks, a continuously rising signal appears at higher temperatures. The carbonates leading to this high temperature desorption are too strongly bound to be catalytically relevant (spectator species), whereas the peaks at lower temperatures indicate carbonates of intermediate stability that can potentially participate in the catalytic turnovers. Even though a part of them exhibits desorption temperatures below 200°C, i.e., below the lower limit of the reaction window, the surface concentrations achieved under reaction conditions (i.e., in the presence of CO₂ in the gas phase) could be sufficiently high to be catalytically relevant.

As anticipated, the spectra of the unpromoted and the Pt promoted catalyst resemble each other at low temperatures, as the Pt promoter is supposed to leave the basicity of the alumina surface unaltered. The samaria and zirconia promoted catalysts, however, clearly deviate in their CO₂ desorption behavior – in comparison to the other two catalysts and with respect to each other – revealing an increased but slightly diverting surface basicity. Integrating the low and high temperature desorption peak features and putting them into relation, however, shows that the promotion of the catalyst with both oxides increases the share of CO₂ adsorption sites with intermediate strength (~0.26 as opposed to 0.16 for the Co-Al₂O₃ catalyst, see Table S7).

### Catalytic results

To understand the influence of the different promoters on the catalytic performance, all DFSP catalysts were evaluated in CO₂ and CO methanation experiments. The methanation performance was compared relative to each other and to an industrial methanation reference catalyst (Ni-Al₂O₃).

Turning first to CO₂ methanation, the results are summarized in Figure S5 showing CO₂ conversion and CH₄ selectivity as a function of temperature as well as the on-stream stability of both criteria at 400°C (see Figure S14 for the reproduction experiments). All catalysts were already active at 200°C, i.e., at the lowest temperature, and showed increasing conversions and selectivities with rising temperature. Clearly, all studied promoters improve the activity and selectivity (except for the Pt promoted catalyst exhibiting a lower selectivity at temperatures below 250°C) compared to the unpromoted catalyst. Interestingly, higher CO₂ turnovers could be achieved with all FSP catalysts up to 330°C, in comparison to the industrial, Ni based catalyst; only at 400°C, i.e., the highest temperature studied here, the reference catalyst outperformed them.

As far as the methane selectivity is concerned, however, the industrial catalyst is superior to our Co/alumina catalysts, although the differences become smaller with increasing temperature. Among the latter, the highest activity and

| Catalyst | Chemisorption capacities [μmol g⁻¹] | Metallic surface area [m² g⁻¹] | Co Dispersion [%] |
|----------|-------------------------------------|-------------------------------|------------------|
| Co/Al₂O₃ | 51(3) 24(2) 22(2) 4.2(2)            | 3.0(2)                        |
| Co/Pt-Al₂O₃ | 67(3) 27(2) 95(2) 5.5(2)         | –                             |
| Al₂O₃    | 50(3) 46(2) 42(2) 4.2(2)          | 3.0(2)                        |
| Co/ZrO₂  | 52(3) 37(2) 25(2) 4.3(2)          | 3.1(2)                        |
| Al₂O₃    |                                    |                               |
selectivity are observed for the zirconia promoted catalyst within the whole investigated temperature range followed by Pt and samaria, which perform fairly similar above 300 °C as promoters. At lower reaction temperatures, the higher CO₂ conversion of the Pt promoted catalyst is balanced by the higher CH₄ selectivity achieved with the samaria promoter so that similar CH₄ yields are obtained in both cases.

Assuming a Langmuir-Hougen-Hinshelwood-Watson (LHHW) mechanism for the CO₂ methanation reaction, increased surface concentrations of the active surface species are expected to result in higher rates. In case of the Pt promoted system, the H₂ uptake and, correspondingly, the metallic surface area are markedly increased, whereas the CO₂ adsorption capacity is similar to the value for the unpromoted Co catalyst. Based on the excellent ability of Pt to adsorb and dissociate H₂, a higher H/CO₂ ratio is therefore expected on the catalyst surface under reaction conditions. Although Pt is deposited on the alumina component of the catalyst, already Schubert et al. demonstrated that the impact on rate at which CO₂ is converted is negligible. They attributed this finding to a fast hydrogen spillover, facilitated by the Pt deposits, to reaction sites located at the Co/alumina interface, where then hydrogenation of CO₂.
In comparison to the other promoters, the addition of Pt leads to an inferior CH₄ selectivity – at least below 330 °C where the Pt promoted catalyst reaches the value of the samaria promoted one. This downside is probably due to the fact that Pt can act as a (reverse) water-gas shift catalyst leading to stronger contributions of the unwanted reverse water-gas shift reaction, i.e. CO formation.\(^{[34]}\)

In contrast, the superiority of the zirconia promoted catalyst as compared to the unpromoted can be directly attributed to its higher CO\(_2\) adsorption capacity and, in particular, to the proven presence of CO\(_2\) adsorption sites with a suitable intermediate basicity. Apart from its strength, also the location of these basic sites needs to be factored in. In order to contribute, these sites must also be easily accessible for hydrogen atoms spilling over from the Co nanoparticle. However, taking into account that hydrogen spillover occurs slow and is limited to short distances on Al\(_2\)O\(_3\),\(^{[35]}\) only those sites located at the Co perimeter can be considered as active. The higher catalytical impact of such sites as compared to metallic sites enhancing H\(_2\) adsorption and dissociation sites becomes obvious when considering that the increase of the respective chemisorption capacities is similar upon promoting the catalyst with the same amount (wt.\%) of either Pt or zirconia (+16 \(\mu\)mol g\(^{-1}\) H\(_2\) = +32 \(\mu\)mol g\(^{-1}\) H for Pt compared to +22 \(\mu\)mol g\(^{-1}\) CO\(_2\) for zirconia). As conversion and selectivity (thus the CH\(_4\) yield) for the zirconia promoted system clearly excel the gain achieved when using Pt as a promoter, the former represents the economically much more favorable option (comparing identical weight fractions), in particular because Pt is much more expensive than zirconia.

For the samaria promoted catalyst, the situation seems to be different. Even though this oxide promoter also provides sites on its surface exhibiting a suitable basicity according to the CO\(_2\) chemisorption and TPD results, their density is lower so that the CO\(_2\) surface concentration is less enhanced. Moreover, clear evidence of a distinct samaria phase or of discrete samaria deposits on the surface of the alumina component in the XRD and TEM data provided is missing. Thus, the improved catalytic performance also found for this catalyst (as compared to the unpromoted one) cannot unambiguously associated with a specific co-catalytic effect of samaria, i.e., providing additional CO\(_2\) adsorption sites on O\(^{2-}\) ions in the SmO\(_2\) lattice. Since both characterization methods pointed to a reduced crystallinity of the alumina component, Sm presumably forms mixed oxide phases with the alumina component and thus acts here rather as a dopant, i.e., it diffuses in and alters the electronic properties of the Al\(_2\)O\(_3\) host matrix, than as a (classical) co-catalyst. Nevertheless, also in this form it exerts beneficial influence on the catalytic performance to a similar extent than Pt.

Apart from improving activity and selectivity, also an advancement regarding the catalytic long-term stability of the promoted catalysts was observed. Whereas time-on-stream experiments carried over 950 min at 400 °C (Figure 5C) revealed an activity loss of about 11% (rel.) – accompanied by a similarly distinct decrease in CH\(_4\) selectivity – for the unpromoted catalyst, especially the Pt and ZrO\(_2\) promoters obviously prevent such a deactivation. Here, stable operation was achieved after ~400 min with a minimal loss of activity and selectivity up to this point in time.

CO methanation was performed applying the same reaction conditions as for the CO\(_2\) methanation experiments, using a stoichiometric ratio of CO and H\(_2\) here as well while keeping the volumetric flow rate identical (50 mL min\(^{-1}\)). In analogy to Figure 5, Figure 6 shows the CO conversion and CH\(_4\) selectivity for all investigated catalysts, including the results for the industrial Ni reference catalyst.

In contrast to CO\(_2\) methanation, both, the zirconia and the samaria promoter, are clearly outperformed by Pt in terms of activity and CH\(_4\) selectivity. The Pt promoted catalyst, moreover, is superior to the Ni reference catalyst up to temperatures of 270 °C. Considering that the CO hydrogenation is supposed to occur on Co sites alone and assuming fast hydrogen spillover from the Pt deposits on the alumina component to the reaction sites on Co (as in case of CO\(_2\) methanation), this result corroborates the co-catalytic effect of Pt as an efficient hydro- gen supplier also in this case. The increased hydrogen availability also improves the CH\(_4\) selectivity and less CO\(_2\) is formed as a by-product stemming from the simultaneously occurring water-gas shift reaction.

Zirconia and samaria promote the methanation of CO to a lesser extent. While the selectivities rather closely mimic the behavior of the unpromoted catalyst in the investigated temperature range, the CO conversions are somewhat higher and fall between those achieved for the unpromoted and the Pt promoted sample. The performance-enhancing influence of the zirconia promoter, although small and much less pronounced as compared to CO\(_2\) methanation, is in line with the increased CO adsorption capacity. Assuming spillover to Co, the higher CO supply is expected to raise the rate. In case of the samaria promoter, though, this explanation is not reflected by the CO chemisorption experiments providing no evidence for a promoter induced increase of CO adsorption sites.

In contrast to CO\(_2\) methanation, all catalysts exhibited major stability issues at temperatures above 300 °C. The unpromoted as well as the zirconia and samaria promoted catalyst deactivated rapidly, when exceeding this limit and lost their entire activity irreversibly within minutes. Similarly, the Pt promoted catalyst showed no stable operation at temperatures above 310 °C; yet it deactivated at a significantly slower rate than the other catalysts. The concomitant decline in CH\(_4\) selectivity (corresponding to an increased CO\(_2\) formation) detected in all cases points towards the Boudouard reaction (CO disproportionation to C and CO\(_2\)) as the origin, disrupting the methanation reaction as a consequence of accumulating carbon deposition on the catalyst surfaces.\(^{[36]}\) This hypothesis was confirmed by XRD, Raman and TEM measurements performed for the spent catalysts. The XRD patterns exhibit broad d\(_{002}\) reflections of graphitic carbon at 26.6°.\(^{[36]}\) TEM images presented in Figure 7B and C, moreover, revealed that the carbon deposits grow in layers around the catalysts, with a layer distance of 0.35 nm that is characteristic of graphite (for further TEM images of all catalysts after methanation see Figure S13). In addition, strong Raman bands observed at 1367
and 1600 cm\(^{-1}\) corroborate the deposition of graphitic carbon as the reason for the rapid deactivation above 300 °C–310 °C. They are related to sp\(^3\) and sp\(^2\) hybridization of carbon atoms and are known as D and G bands, respectively.\(^{[37]}\) The peak intensity ratio I(D)/I(G) of 1.3 and the G peak position suggest that the carbon, indeed, is mainly present in form of nanocrystalline graphite.\(^{[37a]}\) (For a more detailed discussion of the data presented in Figure 7 see the supporting information.) Numerous studies report a high stability of graphitic carbon deposits, rendering catalyst reactivation difficult to achieve.\(^{[38]}\) In line with those reports, our efforts to regenerate the catalyst via hydrogenation of the graphitic carbon at elevated temperatures (up to 600 °C) unfortunately proved unsuccessful.

Post catalysis investigations were also conducted for all catalysts used for CO\(_2\) methanation in time-on-stream experiments at 400 °C. In agreement with the good long-term stability of the promoted catalysts, TEM micrographs (see Figure S13 and S15) show no major sintering of particles within the aggregates after use if compared to the as-prepared materials (see Figure 2). Yet, as major morphological changes, in particular Co sintering, were discerned for the unpromoted catalyst neither, these cannot be the cause for the noticeable deactivation detected in this case. Coking could be excluded as well, based on the absence of associated features in the XRD pattern and Raman spectra shown in Figure 7A and Figure 7D, respectively. Thus, the reason for the deactivation remains unclear here.

Conclusion

In the present study, we demonstrated the potential of double flame spray pyrolysis as a tool to prepare structurally well-defined Co-alumina catalysts for CO and CO\(_2\) methanation. The distance and angle of the two flames in the set up were set to ensure independent particle formation of the two components. When meeting at the intersection point of the flames, both types of nanoparticles meet and aggregate to larger composites. The approach was successfully employed to prepare differently promoted Co-alumina catalysts, each with a 2 wt.% loading of the promoter, along with an unpromoted catalyst for comparison. To this end, suitable promoter precursors were added to the precursor solution of the alumina component combusted in one flame while the other flame remained reserved for the nanoparticle formation of the Co component in all cases.

Three different promoters – ZrO\(_2\), SmO\(_2\), and Pt – were chosen since they were expected to contribute different co-catalytic effects by either enhancing the concentration of hydrogen or of the carbon oxides on the surface. Whereas Pt as a noble metal is able to adsorb and dissociate H\(_2\), the two oxide promoters expose additional adsorption sites for CO\(_2\) and CO.

A thorough structural characterization of the FSP materials proved that all prepared catalysts exhibited the same morphology represented by interconnected chains of ~12 nm sized alumina-promoter particles and ~8 nm cobalt oxide particles. Based on Rietveld refinements, XRD clarified the crystallographic phases of the two constituents - a mixture of γ-Al\(_2\)O\(_3\) and η-Al\(_2\)O\(_3\) in the first case and cubic CoO\(_{2n}\) in the second case. According to N\(_2\) physisorption measurements, all catalysts
did exhibit very similar SSA and BET derived particle diameters, the latter corresponding to the composition weighted mean particle sizes of the two individual components.

As far as the promoter is concerned, only in the case of Pt TEM clearly revealed its presence in form of an individual phase, which occurred in the form of small 1–2 nm Pt nanoparticles homogeneously distributed on the alumina particles. In XRD diffractograms and TEM images which were acquired for Al₂O₃ samples prepared by single flame FSP (that is without Co) with higher loadings of the oxide promoters (10 wt.%), crystalline deposits of the promoter on the alumina surface could be detected for zirconia, whereas for samaria indications of that kind were missing, rendering an incorporation of the promoter into the alumina lattice likely.

When using the FSP materials as catalysts for the methanation of CO₂, an enhanced performance of the promoted systems was observed compared to the unpromoted catalyst. This improvement was attributed to the presence of the promoter, which favored the conversion of CO₂ to CH₄.

Figure 7. (A) XRD data of the 4 spent catalysts and the unpromoted as prepared catalyst (see Figure 1) shown for comparison. (B) and (C) TEM image indicating carbon formation that occurs during CO methanation over the unpromoted sample. The determined d₀₀₂ lattice distance corresponds to interlayer spacing of graphitic carbon and is in agreement with the 2θ diffraction angle of 26.6° in the XRD data. (D) Raman spectra of the catalysts after using them for CO and CO₂ methanation. A deconvolution of the Raman modes characteristic of nanocrystalline graphite is shown in the Figure S13.
was found in all cases. Since all catalysts exhibited the same structure and morphology thanks to the well-controllable FSP process, particle size effects could be excluded as a contributing factor to the observed differences, meaning that the improvements are ascribable to co-catalytic effects exerted by the added promoters. Pt and zirconia turned out to be the best choice to enhance the methane yield - in agreement with an increased H₂ adsorption and dissociation ability in case of Pt and a higher CO₂ adsorption capacity due to oxide sites with medium basicity in case of zirconia. Comparing the impact of both promoters on the catalytic performance, our results indicate that zirconia represents the economically more favorable variant, considering that comparable catalytic advancements could be achieved using the same (2 wt.%) loading but that the oxide is much cheaper than the noble metal.

As far as CO methanation is concerned, Pt was found to be the best promoter outperforming all other systems, in line with an increased availability of hydrogen on the catalyst. The inferior effectiveness of both oxide promoters was coconant with a distinctly lower ability to increase the CO adsorption capacity as compared to CO₂. For zirconia, the density of basic surface sites binding CO in form of carbonates was only half as large as for CO₂, whereas the samaria promoter led to no increase at all. In contrast to an industrial Ni catalyst included in the catalytic tests for comparison, all FSP catalysts suffered from fast deactivation during CO methanation at reaction temperatures higher than ~300 °C. Characterization of the spent catalysts by TEM, Raman and XRD revealed that graphitic carbon deposits formed covering the surface of the Co particles because of the Boudouard reaction. Thus, the operation of neither DFSP Co catalysts was possible in this temperature regime.

To improve the capabilities of the FSP process to tailor the structural properties of such multi-component catalysts even further, the inclusion of quenching options for the flames seems promising, as reported by Schulz et al. in case of single flame FSP. In this way, the temperatures in the flames which are known to strongly influence the particle formation process can be adjusted enhancing the options to vary and optimize catalytic properties. Since a gradual variation of the promoter concentration is easily achieved by FSP, solubility and loading effects of various promoters in the support matrix will be studied this way. Furthermore, we plan in future work to evaluate the potential of a triple flame setup in order to spray and combust the precursor solution of the promoter independently, possibly opening ways to avoid the formation of mixed oxides and to control distribution, form, and size of the promoter deposits.

**Experimental Section**

**Catalyst synthesis**

The catalysts were synthesized as nanopowders, using a double flame FSP setup as described by Schubert et al., where the solution containing the cobalt precursor and a solution containing precursors for alumina and the promoters (see below) were separately sprayed and combusted in the two flames. The spray nozzles were fixed at a distance of 15 cm and an inclination angle of 20° so that the two aerosol streams mixed 21.9 cm above them (see Figure S1). Both liquid precursor solutions were delivered by a Legato 210 syringe pump (KD Scientific Inc., USA), using 100 ml Hamilton 1000 syringes (Hamilton, USA). The oxygen dispersion gas (99.95 vol.%, Westfalen) was supplied at a rate of 5 L min⁻¹, applying a constant pressure drop of 1.5 bar. The support flame was fed with 3.2 L min⁻¹ oxygen (99.95 vol.%, Westfalen) and 1.5 L min⁻¹ methane (99.5 vol.%, Westfalen). Gas flows were controlled by Bronkhorst mass flow controllers. The synthesized materials were collected 60 cm above the nozzles, using circular grade GF/F Whatman glass microfiber filters with a diameter of 25.7 cm. All samples were passed through a 25 μm mesh sieve to achieve homogenous agglomerate sizes and to remove filter fibers.

The precursors were prepared by diluting cobalt naphthenate solution (6 wt.% Co naphthenate in mineral spirits, Sigma-Aldrich) and aluminum-tri-sec-butoxide (97 wt.%, Sigma Aldrich) each with xylene (99.9% pure, VWR). The final cobalt precursor solution used for the FSP process had a concentration of 0.107 M. In case of the non-promoted catalyst, the concentration of aluminum precursor solution was adjusted to 0.5 M. To achieve a 2 wt.% promoter loading by element in the as prepared powder for each promoted catalyst, the aluminum concentration of the solution was correspondingly reduced, ensuring the same weight fraction of cobalt in all catalysts. Platinum acetylacetonate (purity ≥ 99.98%, Sigma Aldrich), samarium naphthenate solution (9.16 wt.% Sm in naphthenic acid, Strem) and zirconium n-propoxide solution (70 wt.% zirconium n-propoxide in 1-propanol, Sigma-Aldrich) in the required amounts were added to the aluminum precursor solution. Two 100 ml batches were prepared consecutively for each sample, using the same precursor solution (see Table 1 regarding their composition).

For comparative purposes also pure Co₃O₄ and Al₂O₃ samples were prepared by single flame FSP using the same precursor solutions and double flame settings as during catalyst synthesis with the second flame combusting pure Xylene. Moreover, pure Sm₂O₃ and ZrO₂ samples (using 0.3 M precursor solutions) as well as samples consisting of alumina promoted with 10 wt.% of Sm and Zr, i.e., containing no Co, were synthesized using single flame FSP to check in more detail the possible formation of mixed alumina-samaria and zirconia-alumina phases, respectively. In addition, for zirconia and samaria also samples with a 2 wt.% loading (in analogy to the catalysts) were produced for this purpose.

**Characterization**

**N₂ physisorption.** Brunauer-Emmett-Teller (BET) measurements were performed to determine the specific surface areas (SSA) of the synthesized materials. To this end, N₂ physisorption was carried out with a Quantachrome Nova 4000e (Quantachrome, USA) instrument, using five pressure points between 0.05 and 0.15 p/p₀. For the experiments, 100 mg of the samples were placed in the glass cell of the instrument and outgassed for 2 h at 200 °C to remove moisture. Based on the measured SSA, the BET particle diameter d_BET was calculated using eq. (5) with p being the mass density of the as-prepared nanoparticles taken from literature. For double flame samples an average density was assumed based on the theoretical powder composition in Table 1:

\[
d_{\text{BET}} = \frac{6}{\rho \times \text{SSA}}
\]
Powder X-ray diffraction (XRD). Powder diffraction patterns were recorded using a Bruker D8 Discover diffractometer (Bruker, USA), operated in a Bragg-Brentano geometry. The samples were placed on circular Si single crystal sample holders. Monochromatized CuKα radiation (λ = 0.154 nm) was used to record the diffractograms in the 2θ range between 5° to 135° in 0.015° steps (acquisition time: 1.5 s) with a total aperture of 3°. A LynxEye XE–T linear position sensitive detector with 192 channels was employed to collect the signals while suppressing photons originating from cobalt fluorescence. The recorded XRD patterns of the catalysts were subsequently analyzed by Rietveld refinement using the software BRASS (Version 2.4.0) and phase models taken from the Inorganic Crystal Structure Database (ICSD).[40]

Transmission Electron Microscopy (TEM). A FEI Titan 80–300ST with imaging corrector and operated at 300 kV was employed for the microscopic characterization of the samples. The instrument is equipped with a Gatan Imaging Filter (GIF), that can be used for Energy Filtered TEM (EFTEM) or electron energy loss spectroscopy (EELS) and an Energy Dispersive X-ray (EDX) detector for EDX spectroscopy as well as with a Fischione High Angle Annular Dark Field (HAADF) detector for Scanning Transmission Electron Microscopy (STEM). Selected Electron Area Diffraction (SAED) data and TEM images were collected using a Gatan UltraScan CCD camera. Fourier filtering to determine lattice distances from High Resolution TEM (HRTEM) images was performed using the software Gatan DigitalMicrograph (Version 3.11.1) and, for the EDX data analysis, the TEM imaging and analysis (TIA) program of FEI was employed. EELS was done in image coupled mode with a nearly parallel illumination and an entrance aperture diameter of 5 mm. Spectra were evaluated using written matlab scripts. For the measurements, the as-prepared FSP materials were dispersed in pure ethanol (Sigma-Aldrich, purity 99.5%) followed by ultrasonification for 5 min. Afterwards, 2 drops of the liquid were deposited onto amorphous carbon coated Cu grids and dried. Particle size distributions were determined by evaluating TEM images with the software ImageJ (NIH, USA).

Raman, Photoluminescence and UV-vis spectroscopy. Raman spectra were recorded at room temperature and under ambient conditions in a Horiba LabRAM HR Evolution (Horioba, Japan) instrument. A 441.6 nm HeCd laser was used for excitation. The laser was focused on the sample with a 20x objective lens, exhibiting a numerical aperture (NA) of 0.4. For the measurements, the laser power was set to 0.15 mW to avoid artefacts by laser illumination and an entrance aperture diameter of 5 mm. Spectra were evaluated using written matlab scripts. For the measurements, the as-prepared FSP materials were dispersed in pure ethanol (Sigma-Aldrich, purity 99.5%) followed by ultrasonification for 5 min. Afterwards, 2 drops of the liquid were deposited onto amorphous carbon coated Cu grids and dried. Particle size distributions were determined by evaluating TEM images with the software ImageJ (NIH, USA).

CO2-Temperature-Programmed Desorption. Directly after the pulsed CO2 chemisorption experiments, a temperature-programmed desorption spectrum (CO2-TPD) was recorded in the same instrument to get insight into the strength of CO2 adsorption sites present on the catalyst surfaces. Once the pulsed chemisorption was ended, the reactor was flushed with pure He for 30 min to remove loosely adsorbed CO2 from the catalyst’s surface. The desorption spectra were then recorded in He, applying a linear heating ramp of 20 °C·min⁻¹ up to the maximum temperature of 800 °C and detecting the desorbing species with the TCD detector.

Catalytic set-up and experiments

All catalytic experiments were carried out in a fixed-bed reactor (quartz glass tube, 6 mm inner diameter), operated at atmospheric conditions.
pressure. A custom-made coil-heater (Hotset, Germany) was used for reactor heating and controlled with a thermocouple placed at the end of the catalyst bed inside the reactor. Gas flow rates were set using mass-flow controllers (Bronkhorst). The stainless steel tubings of the set-up were heated to at least 120 °C to preheat the reaction gases flowing into the reactor and to avoid condensation of reaction water in the tubing at the reactor outlet.

For a typical experiment, 25 mg of the catalyst powders (used as synthesized) were diluted with 500 mg quartz (size fraction: 150–200 μm) and fixed in the middle of the reactor with two quartz wool plugs. Apart from the various Co catalysts, an industrial methanation catalyst (9 wt.% Ni-Al2O3, size fraction: 150–200 μm, supplier is known but does not want to be disclosed) was used as a reference catalyst.

Prior to the catalytic experiments, the catalysts were reduced in-situ at 450 °C for 10 h (heating ramp: 1 °C min−1) in pure H2 and subsequently cooled down to 200 °C in an Ar atmosphere. Subsequently, the catalysts were exposed to the reactant mixture composed of H2/CO2/Ar in a molar ratio of 4/1/5 at a total flow rate of 50 mL min−1 and thus the weight hourly space velocity (WHSV) for all experiments was 120 L g−1 h−1. CO2 and CO conversions and CH4 selectivities were determined in the temperature range between 200 °C to 400 °C. Each temperature was kept for 30 min.

The effluent gas was passed through a cold trap (operated at −1 °C) to remove water from the product stream and was subsequently analyzed using an online process gas analyzer equipped with a non-dispersive infrared detector (GMS810 with a non-dispersive infrared detector (GMS810 with a non-dispersive infrared detector (GMS810 with a non-dispersive infrared detector (GMS810) to quantify the concentrations (vol.%)) of CO2, CO and CH4. Pre-experiments confirmed the absence of any higher hydrocarbons as reaction products, thus allowing the calculation of the CO2 conversion XCO2, the CH4 yield YCH4, and the CH4 selectivity SCH4 according to eq. (8)-(10):

\[
X_{CO_2} = 1 - \frac{c_{CO_2}}{c_{CO_2_0} + c_{CO} + c_{CH_4}}, \quad (8)
\]

\[
Y_{CH_4} = \frac{c_{CH_4}}{c_{CO_2} + c_{CO} + c_{CH_4}}, \quad (9)
\]

\[
S_{CH_4} = \frac{Y_{CH_4}}{X_{CO_2}}. \quad (10)
\]

### Associated Content

In the Supporting Information additional XRD, EDX, XPS, EELS HRTEM/(S)TEM, Raman, UV-vis and PL data referred to in this paper is shown.

### Acknowledgements

Ji J, MB and LM thank the German Research Foundation (DFG) for funding through the priority program SPP 2080 DynaKat. The authors thank Oliver Thüringer and Jan Treumann for assistance with the experimental work. JS thanks the Geology Department of the University Bremen for XRD measuring time and especially Johannes Birkenstock for his helpful comments on the Rietveld refinements. The authors thank Dr. Martin Wiesing for contributing elementary quantifications by XPS performed at the Fraunhofer Institute for Manufacturing Technology and Advanced Materials (IFAM). CT thanks the Central Research Development Fund (CRDF) of the University of Bremen for funding. Open access funding enabled and organized by Projekt DEAL.

### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

Double flame spray pyrolysis · CO2 methanation · CO methanation · Cobalt catalysts · promoter

---

1. K. Ghaib, F.-Z. Ben-Fares, Renewable Sustainable Energy Rev. 2018, 81, 433; b) M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable Energy 2016, 85, 1371; c) M. Younas, L. Loong Kong, J. M. K. Bashir, H. Nadeem, A. Shehzad, S. Sethupathi, Energy Fuel 2016, 30, 8815.
2. a) B. Mutz, M. Belimov, W. Wang, P. Sprenger, M.-A. Serrar, D. Wang, P. Pfeifer, W. Kleist, J.-D. Grunwaldt, ACS Catal. 2017, 7, 6802; b) M. P. Andersson, T. Biliaird, A. Kustov, K. E. Larsen, J. Greeley, T. Johannessen, C. H. Christensen, J. K. Narskov, J. Catal. 2015, 339, 501; c) J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong, F. Su, RSC Adv. 2015, 5, 22759; d) M. A. A. Aziz, A. A. Jalil, S. Triwahyono, A. Ahmad, Green Chem. 2015, 17, 2647.
3. a) T. Biliaird, J. K. Narskov, S. Dahl, J. Matthesien, C. H. Christensen, J. Sehested, J. Catal. 2004, 224, 206; b) W. Chen, R. Pestman, B. Zijlstra, I. A. W. Pilot, E. J. M. Hensen, ACS Catal. 2017, 7, 8050; c) J. Iollomann, A. Strahl-Effert, J. Friedland, L. Kiewitz, J. Thöming, M. Bäumer, R. Güttel, ChemCatChem 2019, 11, 4884; d) W. Li, X. Nie, X. Jiang, A. Zhang, F. Ding, M. Liu, Z. Liu, X. Guo, C. Song, Appl. Catal. B 2018, 220, 397; e) S. Rönsch, J. Schneider, M. Mattischke, M. Schlüter, M. Götz, J. Pfeifer, M. W. Bächmuysen, Appl. Catal. B 2017, 433; b) M. Krämer, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable Energy 2016, 85, 1371; c) M. Younas, L. Loong Kong, J. M. K. Bashir, H. Nadeem, A. Shehzad, S. Sethupathi, Energy Fuel 2016, 30, 8815.
