Promoted cobalt metal catalysts suitable for the production of lower olefins from natural gas

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Due to the surge of natural gas production, feedstocks for chemicals shift towards lighter hydrocarbons, particularly methane. The success of a Gas-to-Chemicals process via synthesis gas (CO and H2) depends on the ability of catalysts to suppress methane and carbon dioxide formation. We designed a Co/Mn/Na/S catalyst, which gives rise to negligible Water-Gas-Shift activity and a hydrocarbon product spectrum deviating from the Anderson–Schulz–Flory distribution. At 240 °C and 1 bar, it shows a C2-C4 olefins selectivity of 54%. At 10 bar, it displays 30% and 59% selectivities towards lower olefins and fuels, respectively. The spent catalyst consists of 10 nm Co nanoparticles with hcp Co metal phase. We propose a synergistic effect of Na plus S, which act as electronic promoters on the Co surface, thus improving selectivities towards lower olefins and fuels while largely reducing methane and carbon dioxide formation.
The abundant availability of methane feedstock due to the shale gas revolution decreases the dependence on crude oil, however new technologies have to be developed to utilize its potential. Methane may be converted to synthesis gas (syngas, a mixture of H₂ and CO), which can then be used to produce chemicals and fuels via the Fischer-Tropsch synthesis (FTS) process. FTS is a surface polymerization reaction so the product selectivity is governed by the Anderson–Schulz–Flory (ASF) distribution. Deviation of the ASF distribution to suppress methane formation is critical to attain high fractions of lower olefins (ethylene, propylene, and butylenes), and this is possible with promoted Fe-carbide-based and promoted Co-carbide-based catalysts. However, most carbide-based catalysts are also active for the water-gas-shift (WGS) reaction, thereby producing CO₂ and rendering them inefficient for methane-derived H₂-rich syngas. Similarly, the bifunctional oxide-zeolite catalysts, which convert syngas directly to lower olefins, showed high activity for WGS and are thus only suitable for Co-rich syngas. The importance of decreasing CO₂ production during the FT step was recently highlighted by Wang et al. in their development of phase pure, stable and low-CO₂ production during the FT step. Preliminary DFT calculations indicate the importance of the counter-ion for sodium and the consequences to catalysis. The approach of dispersing metallic Co nanoparticles on the MnO support, and utilizing alkali metal Na and its counter-ion S as electronic promoters is effective in reducing CO₂ and methane formation, hence creating new opportunities in gas-to-chemicals processes.

Results
Catalysts. Co₃Mn₃ catalysts with an atomic ratio Co/Mn = 1/3 were synthesized via co-precipitation, and the calcined catalysts were impregnated with Na₂CO₃, (NH₄)₂SO₄, Na₂S₄O₃ or Na₂S precursors followed by another calcination step. These catalysts were named Co₁Mn₃−Na₂O, Co₁Mn₃−SO₄²⁻, Co₁Mn₃−Na₂S₄O₃ and Co₁Mn₃−Na₂S, respectively. As a comparison, Co₃Mn₃ catalysts were also synthesized and named in a similar fashion. An overview of calcined catalysts and their elemental loadings of Mn, Co, Na and S are included in Supplementary Table 1. The XRD pattern of calcined Co₁Mn₃−Na₂S (Supplementary Figure 1) consisted of Mn₂O₃, MnO₂ and CoMnO₃ phases, and the addition of promoters did not result in change of crystalline phases. An SEM image (Supplementary Figure 2) of calcined Co₁Mn₃−Na₂S showed its morphology and the homogeneity of Co and Mn elemental loadings was confirmed by scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX, Supplementary Table 2). Scanning transmission electron microscopy-energy-dispersive X-ray spectroscopy (STEM-EDX) mapping (Supplementary Figure 3) also showed mixing of Co and Mn, and no isolated Co nanoparticles were observed.

Catalytic performance. Catalytic performance was evaluated at a range of reaction conditions (240–280 °C, 1–10 bar, H₂/CO = 2). At mild conditions of 240 °C, 1 bar, H₂/CO = 2, 1% CO conversion, Co₁Mn₃−Na₂S displayed a high C₂–C₄ olefins selectivity of 54% with a C₂–C₄ olefin/paraffin ratio of 17. Moreover, methane selectivity at 17% was lower than what was predicted by the ASF distribution (Supplementary Figure 4 and Supplementary Table 3). While the addition of Na₂S improved selectivity, it also decreased activity which is in agreement with literature that S is detrimental to activity of metallic Co catalysts. In a control experiment, addition of sulfur only (without Na) was shown to decrease activity, while increasing methane selectivity (Supplementary Figure 4 and Supplementary Table 3).

The effects of reaction pressures and temperatures on the catalytic performance of Co₁Mn₃−Na₂S are shown in Fig. 1 and detailed information can be found in Supplementary Tables 4–7. From Fig. 1a, at 10 bar, H₂/CO = 2, 13–30% CO conversion, an increase in temperature from 240 to 280 °C corresponded to a decrease in C₂–C₄ olefins and C₃+, selectivities, but increase in methane and C₂–C₄ paraffins selectivities. For Co₁Mn₃−Na₂S 21% CO₂ selectivity was attained at 280 °C and 10 bar. From Fig. 1b, at 240 °C, H₂/CO = 2, 10–18% CO conversion, an increase in pressure from 3 to 10 bar corresponded to an increase in C₅+, selectivity together with a decrease of selectivity towards C₁–C₄ hydrocarbon products. For Co₁Mn₃−Na₂S, no CO₂ production was detected at 3–10 bar, 240 °C, H₂/CO = 2. The increase in chain growth probability, α, due to increase in pressure was confirmed by the ASF distribution plot in Supplementary Figure 5. Notably, the methane fraction was always lower than expected from the ASF distribution for Co₁Mn₃−Na₂S. Since a high olefin/paraffin ratio was attained and no C₁ olefin exists, a lowered C₁ fraction is to be expected. Nonetheless, only with Na₂S promotion this is actually achieved, while in literature catalysts always produce more methane than expected.
Catalytic stability is an important consideration hence the catalytic performance of Co1Mn3–Na2S over 70 h is shown in Fig. 2a. The activity of Co1Mn3–Na2S showed an initial increase and remained then constant over 70 h. Methane selectivity remained stable over time, while C5+ (all products except CO2 and C1–C4 hydrocarbons) and C2–C4 olefin selectivities also stabilized after 10 h. The activity and stability of Co1Mn3–Na2S were also compared with other Co-based catalysts in Fig. 2b. As shown in Fig. 2b, the addition of Mn increased activity for Co-based catalysts, which is in agreement with literature. Catalysts with Co/Mn = 0.3 showed highest activity per gram Co (cobalt-time-yield, CTY), and the addition of Na2O, Na2S2O3 or Na2S decreased activity. Nonetheless, the activity of Co1Mn3–Na2S was still higher than the remaining Co-based catalysts. In terms of stability, Co1Mn3, Co1Mn3–Na2O, Co1Mn3–Na2S2O3 and Co1Mn3 showed deactivation but all other catalysts remained stable over 70 h.

At more industrially relevant conditions of 240 °C, 10 bar, H2/CO = 2, 18–30% CO conversion, the catalytic performance of Co1Mn3–Na2S was compared to other Co-based catalysts (Table 1). Co1Mn3–Na2S displayed the highest selectivity towards lower olefins and lowest selectivities towards undesired methane and lower paraffins (C2–C4 olefin/paraffin ratio = 4.2). Remarkably, CO2 selectivity was below 3% (below detection limit, see Supplementary Figure 6 for chromatograms), suggesting the absence of WGS activity and making it an attractive catalyst for H2-rich syngas. CO2 selectivity was consistently below detection limit for all catalysts except where less Mn is present, i.e. Co3Mn1–Na2O and Co3Mn1–Na2S. Even so, the suppression of WGS activity by Na2S compared to Co1Mn3–Na2S, i.e. 13 versus 28%, respectively. The precursor of Na/S and loading of Na were varied (Na2S and Na2S2O3) and the favourable effects on selectivity remain (Supplementary Table 1 and Table 1). Further optimization of precursor and loadings of the promoters is however outside the scope of this study.

Bulk Co catalyst had the highest α, therefore its main product was C4 hydrocarbons. The addition of Mn–Co resulted in a lower α, and the addition of Na2O or Na2S further decreased α. Bulk Co catalyst showed typical ASF distribution deviation,
whereby the C1 fraction is higher and the C2 fraction is lower than predicted. The addition of Na2O suppressed the C1 fraction, but this suppression was most prominent with the addition of Na2S (Supplementary Figure 5).

To obtain further mechanistic insights into the various catalytic systems, the detailed C product flow of 1-olefin and n-paraffin for each C number product is shown in Fig. 3. The mechanistic considerations of metallic Co FT catalysts include chain growth, chain branching, primary olefin/paraffin formation and olefin secondary reactions, such as secondary hydrogenation and isomerization36. From Fig. 3, Co1Mn3–Na2S produced significantly more primary olefins than linear paraffins for each C containing hydrocarbon product. This suggests that β-H elimination was the dominant termination pathway for Co1Mn3–Na2S and secondary hydrogenation of olefins was also suppressed. Besides, the lower fraction of 2-butene in the C4 hydrocarbon product spectrum of Co1Mn3–Na2S implied the suppression of secondary isomerization of olefins (Supplementary Table 9 and Supplementary Figure 7). This is in agreement with the presumption that secondary hydrogenation and isomerization of olefins take place at identical sites36. In addition, the low methane and C2 hydrocarbon products from Co1Mn3–Na2S point to the blocking of sites for surface methyl, methylene and H species37.

Table 1 Catalytic performance at 240 °C, 10 bar, H2/CO = 2, 18-30% CO conversion

| CO conv., X (%) | CTY (10^-4 mol_CO \_ \_ \_gCo\_1 \_s\_1) | C1 S (%) | C2–C4 olefins, S (%) | C2–C4 paraffins, S (%) | C5+, S (%) | CO2, S (%) | O/P | α |
|----------------|----------------------------------|----------|----------------------|-----------------------|------------|-------------|------|----|
| Co             | 32                               | 0.13     | 12                   | 6                     | 7          | 75          | <2  | 0.8| 0.69|
| Co2Mn1         | 31                               | 0.14     | 11                   | 17                    | 10         | 62          | <2  | 1.8| 0.63|
| Co2Mn1–Na2O    | 20                               | 0.09     | 9                    | 14                    | 7          | 42          | 28   | 1.9| 0.53|
| Co3Mn1–Na2S    | 25                               | 0.12     | 5                    | 20                    | 7          | 56          | 13   | 2.9| 0.56|
| Co3Mn1         | 31                               | 0.56     | 15                   | 12                    | 13         | 61          | <2  | 0.9| 0.67|
| Co3Mn1–Na2O    | 27                               | 0.46     | 14                   | 11                    | 12         | 63          | <2  | 0.9| 0.65|
| Co3Mn1–Na2S    | 18                               | 0.40     | 4                    | 30                    | 18         | 59          | <3   | 4.2| 0.53|
| Co3Mn1–Na2S2O3 | 22                               | 0.42     | 7                    | 25                    | 12         | 56          | <3   | 2.1| 0.50|

CO conversion (X, %), activity per gram of Co (CTY), product selectivity (S, %). The detection limit of CO2 selectivity is 0.5% yield, equivalent to 3% CO2 selectivity at 18% CO conversion.

Fig. 3 Distribution of 1-olefins and n-paraffins of C1–C8 hydrocarbon products. Reaction conditions: 240 °C, 10 bar, H2/CO = 2, 18–30% CO conversion. 

a Co1Mn3–Na2S, b Co3Mn1–Na2O, c Co3Mn1 and d Co. Red bar corresponds to olefin product flow and light red bar corresponds to paraffin product flow.
Structure analysis of spent catalysts. In order to understand the catalytic performance, the spent catalysts after being exposed to industrially relevant FTS conditions were characterized. Fig. 4a compares the XRD patterns of spent Co$_1$Mn$_3$, Co$_1$Mn$_3$–Na$_2$S and Co$_3$Mn$_1$–Na$_2$O and their crystalline phase compositions are summarized in Fig. 4b. Additional Rietveld QPA results for the spent catalysts are given in Supplementary Table 10. The diffraction patterns of crystallized wax were observed in Fig. 4a, and the wax present on the spent catalysts served to prevent oxidation of the spent catalysts. Co$_1$Mn$_3$ and Co$_1$Mn$_3$–Na$_2$S consisted predominantly of a Mn$_{0.95}$O phase, and a mixed Mn$_x$Co$_y$O$_4$ phase was observed which both contributed most likely not to any form of FT activity. Crucially, the hexagonal (hcp) metallic Co phase was present in both spent Co$_1$Mn$_3$ and Co$_1$Mn$_3$–Na$_2$S. The average crystallite size for the hcp Co phase was 9.2 nm with a standard deviation of 1.9 nm. Small contributions from a MnCO$_3$ phase were also noted in both spent Co$_1$Mn$_3$ and Co$_3$Mn$_1$–Na$_2$O. In addition to the Mn$_{0.95}$O, Mn$_x$Co$_y$O$_4$, Co (hcp), MnCO$_3$ phases, a Co$_2$C phase was present in spent Co$_3$Mn$_1$–Na$_2$O in line with the work of Sun et al.

Fig. 5 shows the electron microscopy images and particle size distribution of spent Co$_1$Mn$_3$–Na$_2$S after industrially relevant conditions (240–280 °C, 10 bar, and H$_2$/CO = 2), and STEM-EDX mappings were carried out to differentiate Co and Mn. From Fig. 5a, wax/amorphous carbon (indicated with arrows) was observed, which is in agreement with the XRD analysis in Fig. 4a. The Co particle size distribution from TEM revealed the average Co particle size to be 9.6 nm with a standard deviation of 4.4 nm,

![Fig. 4 XRD analysis of spent Co$_1$Mn$_3$, Co$_1$Mn$_3$–Na$_2$S, Co$_3$Mn$_1$–Na$_2$O. Reaction conditions: 240–280 °C, 10 bar, and H$_2$/CO = 2. a Background corrected XRD patterns and b Rietveld QPA-based crystalline phase compositions, which shows the Mn$_x$Co$_y$O$_4$ phase (blue), Mn$_{0.95}$O (cyan), MnCO$_3$ (green), hcp Co (violet) and Co$_2$C (brown)](https://DOI.org/10.1038/s41467-018-08019-7)
in agreement with the Co crystallite size of 9.2 nm with a standard deviation of 1.9 nm from XRD analysis. The elemental maps of Co and Mn in Fig. 5f confirmed that spent Co1Mn3–Na2S consisted of Co nanoparticles well dispersed on the MnO support.

**Theoretical calculations on Na2S vs. Na2O.** To gain further understanding of the difference in Na2S and Na2O, DFT calculations of both species on metallic Co (0001) surface were performed. Please note that these calculations are of a preliminary nature and further work is needed to arrive at full reaction pathway analysis which is outside the scope of this work. Pederson et al. recently performed DFT calculations on CoMnO systems for the production of light olefins and they found that selectivities can be attributed to an inhibited hydrogenation activity demonstrated by the increased barriers for CH3 and CH4 formation. Strømsheim et al. recently showed that the restructuring of Co surface under CO exposure with K pre-adsorbed proceeded on the terraces rather than from the step edges. Other notable theoretical studies on multiple elemental surfaces include ZnO/Cu, Co2C/Co, Cu/Co. While these studies are highly relevant, they are insufficient to explain current findings. As it is shown that the combination of Na2S is critical for product selectivity, the theoretical calculations were focused on Na2S and Na2O promotion. The function of the sodium promoter, as any alkali metal promoter, is to donate charge to the cobalt metal. For the manganese-containing catalysts studied here, this turns out to increase olefin formation. However, for good effect another counter-ion is needed, i.e., sulfur. As shown by DFT calculations (Fig. 6), the function of the sulfur promoter is to increase the charge donation from the Na promoter ions to the cobalt surface. When no specific counter-ions are added, sodium binds in the form of Na2O and a considerable part of the sodium charge donation is taken up by the oxygen atom. With sulfur it is suggested to form Na2S instead, resulting in a higher charge donation to the cobalt surface. The DFT calculations show that every Na2O moiety donates a total charge of −0.51 to the cobalt surface (Na becomes +0.39 and O becomes −0.28), whereas Na2S donates a total charge of −0.62 (Na becomes +0.36 and S becomes −0.10). We tentatively interpret these results of higher charge donation to coincide with lower hydrogen coverages thus leading to lower methane selectivity in FTS similar to what we have reported for iron carbide.

**Structure-performance relations of metallic Co vs. Co2C.** In Table 1, CO2 selectivity was negligible for most catalysts except Co3Mn1–Na2O and Co3Mn1–Na2S. From detailed XRD structural analysis of the spent catalysts, it was revealed that the active Co phase in Co3Mn1 and Co3Mn1–Na2S was metallic Co, but Co2C was present as an active phase in Co3Mn1–Na2O. For classic Co-based FT catalysts (i.e. bulk Co and CoMn) with appropriate reduction/activation procedure and reaction conditions, metallic Co is widely accepted to be the active phase. As metallic Co catalysts are not active for WGS, it was expected that no CO2 selectivity was observed for these catalysts. Upon the addition of Na2O or Na2S, the ratio of Co/Mn apparently played a critical role in influencing the crystal structure of the Co phase during FT as CO2 selectivities were significantly higher for Co3Mn1 than Co1Mn3. Li et al. recently concluded that Mn has a controlling effect on Co2C morphology and the formation of Co2C nanoprism or nanospheres was dependent on the synthesis method. In this study, the results of Co3Mn1–Na2O and Co3Mn1–Na2S were in agreement with Li et al. as Co content was higher than Mn in both cases. However, for catalysts with more Mn than Co, Co2C was not formed and Co remained in metallic phase. It is believed that when Co/Mn = 0.3, MnOx served as a support for the metallic Co nanoparticles thereby ensuring a good dispersion and stabilization of these nanoparticles (Fig. 5). MnO is also known to act as an electronic and structural promoter and the promoting effects of MnO are strongly dependent on its location and amount. For instance, Morales et al. showed that CO preferentially bonded linearly to surface metal sites when MnO loading was increased. It is noted, however, that in mentioned literature, the MnO loading was much lower than the Co loading.
and the promoting effects of using MnO as a support are not yet clear. These findings are illustrated in Fig. 7.

While similar hydrocarbon product selectivities were reported earlier by Sun et al. for Na-promoted Co2Mn1 catalytic systems, it is noteworthy to point out that in their work CO2 selectivity was almost 50% of CO converted due to high WGS activity. The addition of Na (most likely in Na2O state) served as a structural promoter and appeared to facilitate the formation of Co2C nanoprisms, which displayed high C2–C4 olefin selectivity and CO2 selectivities. In our Co1Mn3–Na2S catalytic system, the active phase appeared to be metallic Co and Na2S seemed to be an electronic promoter for product selectivity. Sun et al. showed the effect of Na2O loading on Co2Mn1 catalytic systems, and here we presented the importance of the counter-ion for Na (Fig. 6) using theoretical DFT calculations.

Besides the loadings and counter-ions for Na, the activation procedure is an important parameter for catalytic performance and structure-performance relations. For instance, de Smit et al. demonstrated that different Fe-carbide phases may be synthesized during catalyst pretreatment by controlling carbon chemical potential. Claeyts et al. concluded that while cobalt carbide is relatively stable at typical reaction conditions, it would decompose rapidly into hcp Co with hydrogen at 150 °C. Davis et al. also showed that reaction conditions played a significant role in formation of cobalt carbide or metallic cobalt. To induce the formation of metallic Co, calcined catalysts in our study were reduced at 350 °C and 1 bar under diluted H2 flow for 8 h, followed by introduction of syngas at a temperature of 180 °C and a pressure of 10 bar. This activation procedure to form metallic Co is different from that of Sun et al. to form Co2C. To show the effect of activation procedure on catalytic performance, the same catalysts were reduced at 300 °C and 1 bar under diluted H2 flow for 5 h, followed by introduction of syngas at 250 °C and 10 bar. With this activation procedure, CO2 selectivity increased to 6% (Supplementary Table 13) possibly related to cobalt carbide formation. Nonetheless, Na2S was still the most effective promoter (Supplementary Tables 11–13).

In summary, we have designed a catalytic system Co1Mn3–Na2S, which showed negligible WGS activity and
suppression of methane formation in FTS. Structure analysis of the spent catalyst revealed 10 nm metallic Co nanoparticles as the active phase supported on MnO during reaction. Theoretical calculations revealed the importance of counter-ion S for Na and Na₂S was more efficient in tuning hydrocarbon product selectivity than Na₂O. Tentatively the addition of Na₂S to Co₃Mn₁ was proposed to deactivate sites for secondary olefin production. A Na₂O addition on the reaction to GC was heated to at least 150 °C to prevent hydrocarbon condensation. Activities and product selectivities were calculated on a carbon atom basis. Activity is reported as moles of CO converted per gram Co per second, and moles of CO converted is based on moles of C in the hydrocarbon product stream. Product selectivity was calculated as equivalent of carbon atoms in a product with respect to the total carbon atoms present in the hydrocarbons produced (% C).

Catalytic tests at industrially relevant conditions. Medium pressure tests were performed using a high throughput 16 parallel fixed-bed reactors set-up (Flowrence, Avantium). Each reactor was loaded with 50 mg catalyst (75–150 μm) and 100 mL (212–425 μm) as diluent. The catalysts were first dried at 100 °C (5 °C/min) under He flow for 2 h and subsequently reduced at 350 °C (1 °C/min) under H₂ flow (25 vol.% H₂, 75 vol.% He) for 8 h. After reduction, temperature was decreased to 180 °C (1 °C/min) and pressure was increased to 10 bar under H₂ flow. At 180 °C and 10 bar, the feed flow was switched to syngas mixture (H₂/CO/He = 60/30/10, 6.6 mL/min total flow per reactor) and subsequently the temperature was raised to 240 °C (1 °C/min). The product stream was analysed using online gas chromatography (Agilent 7890A) with Ar as carrier gas. Hydrocarbons (C₁–C₅) were separated on an Agilent J&W PoraBond Q column, detected using a FID detector and quantified against the TCD signal of the internal standard He. The permanent gases (CO, H₂, He, CO₂, and CH₄) were also analyzed on a ShinChrom ST (910943) column and quantified against He as an internal standard using a TCD detector. CO₂ was also measured and the detection limit of CO₂ was determined to 0.5% yield, which was 3% CO₂ selectivity and 18% CO conversion (Supplementary Figure 5 and Supplementary Table 8). Catalytic activity and product selectivities were measured at 240–280 °C, 10 bar, H₂/CO = 2, 10–70% CO conversion. To show the effect of activation procedure on catalytic performance, the same catalysts were reduced at 300 °C and 1 bar under diluted H₂ flow for 5 h, followed by introduction of syngas at 250 °C and 10 bar. Definitions of the selectivity and activity, expressed as CO conversion and cobalt-time-yield (CTV) are included as Supplementary Methods.

DFT calculations. DFT modelling was performed with the ADF-BAND package (version 2016.102)⁴⁹,⁵⁰, using the rPBE functional⁵¹ and Grimme D3 corrections⁵². A TZP basis set with small frozen cores, a “good” k-space, and otherwise “normal” settings were used for efficiency, the SCF was converged to only 5 × 10⁻⁶ Hartree. Gradients were converged to 0.001 Hartree/Å. The bulk cobalt unit cell vectors were reoptimized, giving a = 2.43 Å (experimental 2.51 Å) and c = 3.91 Å (experimental 4.07 Å). The (0001) surface was modelled with 6 atomic layers, giving a slab of 12 Å thick, of which the bottom two layers were frozen and calculated at minimal settings (SZ basis set with large frozen core, orbital con­finement to 4 bohr, and “basic” settings for the Becke grid and znm-fit parameters). The surface unit cell consisted of 4 x 4 atoms. Since ADF-BAND uses true 2D periodicity, no vacuum spacing nor dipole corrections were needed. Atomic charges were calculated with Hirshfeld’s method⁵³.

Data availability. The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Received: 18 August 2018 Accepted: 7 December 2018
Published online: 11 January 2019

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