Enhanced C3+ alcohol synthesis from syngas using KCoMoSx catalysts: effect of the Co-Mo ratio on catalyst performance

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\section{1. Introduction}

The depletion of fossil resources together with a strong drive to limit greenhouse gas emissions has led to an increasing effort in the development of sustainable and green transportation fuels. Well known examples are ethanol from sugars using fermentative approaches \cite{1} and biodiesel from vegetable oils \cite{2}, which have both been commercialized in the last decades. When considering ethanol, some disadvantages have been identified, including a low energy density, high vapor pressure and high water solubility, which cause corrosion issues when using ethanol-rich ethanol-gasoline blends \cite{3}. These disadvantages may be alleviated by using C3+ alcohols, which have superior fuel properties, such as higher energy density, lower volatility and better solubility in hydrocarbons (HC), while at the same time possessing comparable octane numbers as found for gasoline \cite{4}.

When considering chemo-catalytic routes to higher alcohols, syngas appears an interesting feed \cite{5}. Various catalytic systems have been identified for this purpose \cite{6}. Among them, molybdenum sulfide-based catalysts are of particular interest due to their low cost, high water-gas shift activity and high resistance to sulfur poisoning \cite{7}, thus avoiding the need for water separation and deep desulfurization units. MoS\textsubscript{2} alone mainly produces CO\textsubscript{2} and hydrocarbons (HC) from syngas, while alkali metals, especially potassium (K) modified MoS\textsubscript{2} catalysts are commonly used to achieve good selectivity for alcohols \cite{8}. K promotion suppresses hydrogenation of metal-alkyl species to HCs and enhances the rate of CO insertion in the M-alkyl bond to form metal-acyl species, which are subsequently converted to alcohols \cite{9}. It is proposed that KMoS\textsubscript{2} phases, formed by the intercalation of K into the MoS\textsubscript{2} structure, are responsible for the higher selectivity to alcohols when compared to MoS\textsubscript{2} alone \cite{10-13}. However, K modified MoS\textsubscript{2} catalysts normally suffer from low activity \cite{6}, leading to relatively low CO conversion and thus a low yield of alcohols. Efforts have been undertaken on tailoring the structure of the K modified MoS\textsubscript{2} catalysts to enhance the selectivity to C3+ alcohols \cite{14,15}. In previous work from our groups, we prepared multilayer K modified MoS\textsubscript{2} catalysts with well-contacted MoS\textsubscript{2} and KMoS\textsubscript{2} phases and showed that these catalysts lead to improved alcohol selectivities \cite{16}. Another approach involves promotion by group VIII metals, such as rhodium (Rh) to improve the selectivity to alcohols and to enhance the activity \cite{17}.
as Co and Ni [7,17–19]. Especially cobalt is known to promote carbon chain growth, leading to higher selectivities to higher alcohols [20,21], though often ethanol is the major product.

Co promoted MoS2 catalysts are widely used in hydrodesulfurization (HDS) reactions and the promoting effect of Co is attributed to the formation of a Co-Mo-S phase [22], formed by partial substitution of Mo atoms at the edge of MoS2 slabs by Co atoms [23]. This particular phase has also been observed in K modified, Co promoted MoS2 catalysts for alcohol synthesis [18,20,24–27]. To elucidate the function of cobalt, Mo free, K modified cobalt sulfide catalysts were employed for the reaction. In this case, the amount of higher alcohols was low and Cl-C4 alkanes were prevailing [20], indicating that K-CoS phases are not suitable for higher alcohol synthesis. It also has been shown that, the number of active Co-Mo-S species decreases at high Co loadings due to the formation of Co3S8 phases, which are stable under typical reaction conditions and have a low activity for higher alcohols [28–31].

Thus, literature data imply that a Co-Mo-S phase in Co promoted MoS2 catalysts is the active phase, [20,28–33], though the exact mechanism to promote carbon chain growth is still under debate. However, the role of both K and Co in K modified CoMoSx catalysts has not been explored in detail. We therefore performed a systematic investigation on the effect of these promoters on the performance of MoS2 catalysts for higher alcohol synthesis from syngas. For this purpose, a series of K modified Co promoted molybdenum sulfide catalysts with different Co contents and a fixed K content were prepared, characterized in detail and tested for the conversion of syngas to higher alcohols. The results were compared with a Mo free catalyst in the form of K-CoS2 and a K-free catalyst (CoMo0.13). In addition, for the optimized catalyst regarding Co content, the effect of process conditions, such as temperature (T), pressure (P), gas hourly space velocity (GHSV) and H2/CO ratio was explored. The results were quantified using statistical approaches allowing determination of the optimal process conditions for higher alcohol selectivity and yield.

2. Experimental Section

2.1. Catalyst preparation

The cobalt-molybdenum sulfide was prepared by sulfidization of the cobalt-molybdenum oxide precursor with KSCN according to a method reported in the literature [34] with some modifications. The cobalt-molybdenum oxide precursor was typically synthesized by mixing Co(NO3)2·6H2O and (NH4)6Mo7O24·4H2O (20g in total, Sigma-Aldrich) in 50 mL of deionized water. The resulting suspension was heated and maintained at 120 °C for 3 h, during which most of the water evaporated. The resulting mixture was calcined in air at 500 °C for 3 h to form the cobalt-molybdenum oxide. The amount of Co(NO3)2·6H2O and (NH4)6MoO24·4H2O was varied to adjust the atomic ratio Co/(Co + Mo) between 0 and 0.7.

For sulfidization, the cobalt-molybdenum oxide (0.648 g), KSCN (0.875 g, Sigma-Aldrich), and deionized water (35 mL) were mixed in a autoclave, which was kept at 200 °C for 24 h. Then the autoclave was rapidly cooled with ice, and the resulting precipitate was filtered and washed with deionized water (total 500 mL). The product was obtained after drying at ambient conditions overnight. The molybdenum sulfide is labelled as MoSx and the mixed metal sulfide catalysts are labelled as Co-MoSx-R, where R represents the actual Co/(Co + Mo) ratio as obtained from ICP-OES. The elemental composition of the sulfidized catalysts is shown in Table 1.

| Catalyst                  | Co/(Co+Mo) | BET (m² g⁻¹) | V pore (cm³ g⁻¹) | D mean (Å) |
|---------------------------|------------|--------------|-----------------|------------|
| MoSx                      | 0          | 9.7          | 0.05            | 155        |
| Co-MoSx-0.13              | 0.13       | 11.5         | 0.07            | 184        |
| Co-MoSx-0.37              | 0.37       | 8.2          | 0.04            | 163        |
| Co-MoSx-0.53              | 0.53       | 7.2          | 0.03            | 164        |
| Co-MoSx-0.63              | 0.63       | 7.7          | 0.03            | 158        |

Table 1 Physical and chemical properties of the sulfidized catalysts.

2.2. Catalyst characterization

The cobalt-molybdenum sulfide samples were characterized with ICP-OES (Spectroblue, Germany) to quantify the elemental composition.

The specific surface area and pore parameter were determined using N2 physisorption, which was conducted at 77 K using an ASAP 2420 system (Micromeritics, USA). Prior to analysis, the samples were degassed at 150 °C under vacuum for 12 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method in the P/P0 range of 0.05–0.25. The total pore volume was estimated from the single point desorption data at P/P0 = 0.97. The pore diameter was obtained from the desorption branch according to the Barrett-Joyner-Halenda (BJH) method.

X-ray diffraction (XRD) patterns of the sulfurized samples were collected for a 2θ scan range of 5–80° on a D8 Advance powder diffractometer (Bruker, Germany) with CuKα radiation (λ = 1.5418 Å) operated at 40 kV and 40 mA. XRD spectra of the K modified sample (K-Co-MoSx-0.13) were recorded in the same way.

H2-TPR measurements were conducted using 10 vol.% H2 in He (30 ml min⁻¹) and the samples were heated from room temperature to 900 °C at a temperature ramp of 10 °C/min using an AutoChem system (Micromeritics, USA) equipped with a thermal conductivity detector (TCD). Raman spectroscopy was measured using a WITec Alpha 300R microscope with a 532 nm excitation laser.

The micro-structure of the sulfurized samples was examined with high-resolution transmission electron microscopy (HRTEM, JEOL 2010 FEG, Japan) operated at 200 kV. The samples were first ultrasonically dispersed in ethanol and then deposited on a carbon-coated copper grid. Processing of the HRTEM images was accomplished using DigitalMicrograph software.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of the K-Co-MoSx-0.13 sample were obtained using a probe and image aberration corrected Themis Z microscope (Thermo Fisher Scientific) operating at 300 kV in STEM mode with a convergence semi-angle of 21 mrad and a probe current of 50 pA. Energy dispersive X-ray spectroscopy (EDS mapping) results were achieved with a Dual X EDS system (Bruker) with a probe current of 250 pA. Data acquisition and analysis were done using Velox software (version 2.8.0).

2.3. Catalytic testing in a continuous fixed-bed reactor

Reactions were performed in a continuous fixed-bed reactor (stainless steel) with an internal diameter of 10 mm. Typically, the cobalt-molybdenum sulfide catalyst (0.35 g) was physically mixed with K2CO3 (0.05 g, Sigma-Aldrich) and SiC (2.0 g, Sigma-Aldrich) and then loaded to the reactor. Before reaction, the catalyst was reduced in situ using a flow of H2 (50 ml min⁻¹) at 400 °C for 8 h. After cooling to room temperature under a N2 stream, the reaction was started by switching to a gas mixture of H2/CO (molar ratio ranging from 1.0 to 2.0) with 6%
N₂ (internal standard). Typical reaction conditions are pressures between 8.7 and 14.7 MPa and temperatures between 340 and 380 °C. The gas hourly space velocity (GHSV) was varied from 4500 to 27000 mL g⁻¹ h⁻¹ by adjusting the flow rate of the feed gas. The reactor effluent was cooled and the liquid product was separated from the gas phase by using a double walled condenser at −5 °C. Details regarding product analysis are described in a previous publication from our groups [16]. The CO conversion (X_CO), the product selectivity (S_i) and yield (Y_i) were calculated using Eqs. (1)–(3).

\[
X_CO = \frac{\text{moles of CO_{influent} - moles of CO_{effluent}}}{\text{moles of CO_{influent}}} \times 100\%
\]  
\[
S_i = \frac{\text{moles of product } i \times \text{number of carbons in product } i}{\text{moles of CO_{influent} - moles of CO_{effluent}}} \times 100\%
\]  
\[
Y_i = X_CO \times S_i
\]  

The activity data given in this study are the average for at least 6 h runtime and collected after 20 h, to ensure stable operation of the reactor. The selectivity of all products is carbon based and only data with carbon balances higher than 95% are reported here.

The chain growth probability \( \alpha \) was determined from the experimental data assuming an ASF distribution for the alcohols (Eq. (4)).

\[
\frac{S_i}{n} = \alpha^i \times \left(1 - \frac{\alpha}{n}\right)^{n-i}
\]

Here, \( S_i \) is the selectivity of the alcohols with a carbon number of \( n \), \( n \) is the carbon number, and \( \alpha \) is the chain growth probability. The value of \( \alpha \) was determined by plotting \( \ln\left(\frac{S_i}{n}\right) \) against \( n \).

2.4. Statistical modeling

Multivariable regression was used to quantify the effect of process conditions (T, P, GHSV and H₂/CO ratio) on catalytic performance (Eq. (5)).

\[
Y = a_0 + \sum a_i x_i + \sum a_{ij} x_i x_j
\]

Here \( x \) is independent variable (T, P, GHSV and H₂/CO ratio) and \( Y \) is a dependent variable (selectivity and yield of C₃+ alcohol), \( a_0, a_i \) and \( a_{ij} \) are the regression coefficients and \( a_0 \) is the intercept. The regression coefficients were determined using the Design-Expert (Version 7) software by backward elimination of statistically non-significant parameters. The significant factors were selected based on their p-value in the analysis of variance (ANOVA). A parameter with a p-value less than 0.05 is considered significant and is included in the response model.

3. Results and discussion

3.1. Characterization of the cobalt-molybdenum sulfide catalysts

The cobalt-molybdenum sulfide catalysts with different Co contents were prepared by sulfurization of the corresponding cobalt-molybdenum oxide precursors using KSCN. The actual Co/(Co + Mo) molar ratio was determined by ICP-OES and ranged from 0 to 0.63 (Table 1). The textural properties of the sulfurized catalysts (without K addition) are depending on the Co content, see Table 1 for details. When considering the specific surface area, a maximum was found for Co-MoSₓ-0.13, with a value of 11.5 m²/g. This value is in the broad range reported in the literature for Co-MoSₓ catalysts (from single digit values to several hundred square meters per gram [35]), rationalized by differences in the Co and Mo precursors used and synthesis conditions. The observed reduction at higher Co amounts may be due to the formation of a segregated Co sulfide phase [36]. Similar trends were observed for the pore volume and pore diameters of the catalysts, viz. the highest value was found for catalyst Co-MoSₓ-0.13.

The XRD patterns of the catalyst (without K addition) are shown in Fig. 1. The MoSₓ catalyst shows broad diffractions at 2θ values of about 14°, 33°, 36° and 58°, which are associated with the (0 0 2), (1 0 0), (1 0 2) and (1 1 0) planes, respectively, of the 2H-MoS₂ phase (JCPDS card No. 00-037-1492). Upon the addition of Co, the reflexes of the crystalline MoS₂ phase disappear and new signals arise. These were identified as cobalt-containing species like CoS₂ (JCPDS card No. 01-089-3056), CoMoS₃.₁₃ (JCPDS card No. 00-016-0439) and CoMoO₄ (JCPDS card No. 00-021-0866). Of interest is the presence the CoMoS₃.₁₃ phase, which is known to be formed by partial substitution of Mo atoms at the edges of MoS₂ sheets by Co. Mixed Co-Mo-S phases are generally thought to be active for higher alcohol synthesis by promoting carbon chain growth [6]. At high Co loadings, sharp reflexes from crystalline CoS₂ and CoMoO₄ are present, suggesting a higher abundance and larger nanoparticle sizes. Reflexes attributed to a CoS₂ phase, reported to be present at higher Co loadings, were not detected [30].

H₂-TPR measurements were performed for all sulfided Co-Mo catalysts and the profiles are given in Fig. 2. The Co free MoSₓ catalyst displays two H₂ peaks, a small one at 310 °C and a larger one at about 720 °C. The first peak is ascribed either to the presence of over-stoichiometric Sₓ species or to weakly bonded sulfur anions along MoS₂ edges [37]. The high temperature peak is associated with more strongly bound sulfur anions located at the edges [38]. Another possibility is a
phase formed by desulfurization of the MoS₂ phase by elimination of basal sulfur, though not likely as temperatures higher than 830–1030 °C are required for this transition [39]. Upon the addition of Co, additional peaks become visible. The low temperature peak is shifted to lower temperatures (about 220 °C), indicating that the presence of Co leads to a weakening of the Mo-S bond [40]. A similar low temperature peak was also observed during H₂-TPR measurements on supported Co-MoS₂/Al₂O₃ catalysts for HDS reactions and associated with the presence of a Co-Mo-S phase [41]. The area of the first peak is reduced when adding more Co in the catalyst formulation. Besides, a new peak at an intermediate temperature (370–470 °C) appears, which is ascribed to a cobalt sulfide phase [41]. In line with this explanation is the observation that the area of this particular peak increases with increasing Co content. This suggests that for low Co/(Co + Mo) ratios, the Co atoms are dispersed at the edge of a MoS₂ phase to form a Co-Mo-S phase, whereas higher Co amounts lead to the formation of Co sulfide species. These may be present as a single phase or closely interact with Co-Mo-S and MoS₂ phases.

The Raman spectra of the sulfided Co-Mo catalysts (without K) are shown in Fig. 3. The unpromoted MoSₓ catalyst exhibits two peaks at 380 cm⁻¹ and 405 cm⁻¹, which are ascribed to the in-plane E₂g and out-of-plane A₁g vibration mode of the MoS₂ layer structure [42]. These two bands are also detected in Co-MoSₓ-0.13, and the distance between the two bands, which is an indicator for the interlayer distance between the MoS₂ stacked layers [15,43], is similar to that for the unpromoted MoS₂ catalyst. This suggests that, different with K [12], Co is not intercalated in the interlayer space of MoS₂ phase, which is consistent with the H₂-TPR result. For the catalysts with high Co contents, the two peaks disappear, and a new peak at 931 cm⁻¹ emerges, associated with the formation of a β-CoMoO₄ phase, which is in consistent with the XRD results. The intensity of the peak increases with increasing Co content.

HRTEM was used to determine the morphology and microstructure of the catalysts. Representative images are displayed in Fig. 4. The MoS₂ catalyst without Co shows a multilayer structure with a lattice spacing of 0.63 nm, corresponding to the (0 0 2) plane of the MoS₂ phase (Fig. 4a) [44]. After the addition of Co, various Co-containing species were identified based on their specific lattice fringes. Examples are Co-MoSₓ, CoSₓ, and CoMoO₄ phases (Fig. 4b–f). The lattice fringe with a lattice spacing of 0.25 nm corresponds to the (2 1 0) plane of CoS₂.

Of interest is the observation of close contacts between the CoS₂ and MoS₂ phase for Co-MoSₓ-0.13 (Fig. 4b–c), indicating the presence of a CoS₂/MoS₂ interface. The presence of this interface has been reported to be beneficial for higher alcohol formation [45]. The phase with a lattice spacing of 0.63 nm may be either from MoS₂ or a CoMoSₓ₋₀.₁₃ species. For catalysts with a higher Co content (e.g. Co-MoSₓ₋₀.₃₇), a CoMoO₄ phase is present (lattice fringe with a spacing of 0.68 nm (Fig. 4d)), consistent with the XRD analysis.

With the catalyst characterization data available, the effect of the amount of Co on catalyst structure may be assessed. Unpromoted MoSₐ reveals a multilayer structure with long-range ordered MoS₂ domains, in line with the literature data. After promotion with Co, Co-MoS₂ and CoS₂ phases are formed, which are considered possible active phases for higher alcohol synthesis (Co-MoSₓ₋₀.₁₃). At higher Co contents, higher amounts of CoS₂ and CoMoO₄ species are present, which may have a negative effect on catalyst performance (vide infra).

Finally, the K promoted version of Co-MoSₓ₋₀.₁₃ (K-Co-MoSₓ₋₀.₁₃), which is the best catalyst in terms of performance for higher alcohol synthesis (vide infra), was characterized in detail using XRD, HRTEM and STEM with EDS mapping to gain insights in changes in the structure upon the addition of K. The sample was prepared by physically mixing Co-MoSₓ₋₀.₁₃ with K₂CO₃ followed by reduction with hydrogen and passivation (see experimental section).

XRD spectra of K-Co-MoSₓ₋₀.₁₃, together with MoSₓ and Co-MoSₓ₋₀.₁₃ for comparison, are given in Fig. 5a. The (002) reflex of K-Co-MoSₓ₋₀.₁₃ at 13.3° is slightly shifted downfield compared to that of MoSₓ (14.1°), indicating an expanded interlayer spacing due to the incorporation of K. A HRTEM image (Fig. 5b) of K-Co-MoSₓ₋₀.₁₃ confirms the expanded interlayer spacing (0.77–0.81 nm vs 0.63 nm for Co-MoSₓ₋₀.₁₃, Fig. 4c) after K addition. The intercalation of K into the MoS₂ structure leads to the formation of a KMoS₂ phase, which was discussed in detail in our previous work [16] and is suggested to be essential for alcohol synthesis.

The reflexes of CoS₂, clearly visible in Co-MoSₓ₋₀.₁₃, are absent in the XRD spectrum of K-Co-MoSₓ₋₀.₁₃. New reflexes at 30.1°, 31.2° and 39.7°, identified as CoS₂ species (JCPDS card No. 00-003-0631) are present. The CoS₂ species are likely formed by reduction of CoS₂, which is consistent with the H₂-TPR results (Fig. 2). Representative reflexes of crystalline CoMoSₓ₋₀.₁₃ are also present in K-Co-MoSₓ₋₀.₁₃. The presence of both CoSₓ and CoMoSₓ₋₀.₁₃ species in K-Co-MoSₓ₋₀.₁₃ is confirmed by HRTEM images (Fig. 5c–d). Close contacts between the CoSₓ and K promoted (Co)MoSₓ phase were observed (Fig. 5b–d), in agreement with the observation of CoSₓ/(Co)MoSₓ interfaces in the unpromoted Co-MoSₓ₋₀.₁₃ catalyst (Fig. 4b–c).

A STEM dark field image combined with EDS mapping (Fig. S1) of K-Co-MoSₓ₋₀.₁₃ shows that K, Co, Mo and S are uniformly dispersed in the catalyst. Such a homogeneous distribution is indicative for the presence of abundant CoSₓ/K-(Co)MoSₓ interfaces in K-Co-MoSₓ₋₀.₁₃.

### 3.2. Higher alcohol synthesis using K promoted Co-MoSₓ catalysts with different Co contents

Benchmark experiments with all catalysts were performed at 360 °C, 8.7 MPa, a GHSV of 4500 mL g⁻¹ h⁻¹ and a H₂/CO ratio of 1 in a continuous packed bed reactor set-up. These conditions were selected based on previous experience in our group on the use of MoS₂ catalysts for higher alcohol synthesis [16]. Prior to reaction, the catalysts were promoted with K using a physical mixing method followed by an in situ treatment with H₂. The same amount of K was used for all catalyst formulations. The experiments were performed for at least 6 h and the performance of the catalyst was the average over the time period from 20 h to final runtime and thus taken at steady state conditions in the reactor (Table 2).

A typical example of the product selectivity and CO conversion versus the runtime is given in Fig. 6 (340 °C, 11.7 MPa, GHSV of 4500 mL g⁻¹ h⁻¹ and H₂/CO ratio of 1.5 using the K-Co-MoSₓ₋₀.₁₃ catalyst). It also shows the catalyst is stable for at least 100 h without co-feeding of sulfur.

Typical reactions products are alcohols (methanol, ethanol, and C₃+ alcohol), hydrocarbons (methane and higher ones) and CO₂. The latter is formed by the water-gas shift reaction involving CO and water. The unpromoted K-MoSₓ catalyst provides a selectivity of 40.8% to alcohols and 24.8% to hydrocarbons at a CO conversion level of 25.6%.
Upon the addition of Co to the catalyst formulation, the CO conversion decreases, which may be due to the reduced availability of the active sulfided Mo-Co species by coverage with inactive CoMoO₄ species and/or the presence of less active CoS₂ species, as observed from XRD and HRTEM results. The selectivity is a clear function of the Co content. Alcohol selectivity reaches a maximum (47.1%) for the K-Co-MoSₓ-0.13 catalyst and decreases with higher Co loadings, see Fig. 7 for details. The selectivity to hydrocarbons (mainly CH₄), shows a reverse trend, whereas the CO₂ selectivity is about constant. The product selectivity at two other temperatures (340 and 380 °C) also shows a similar trend regarding the Co content in the catalyst formulation (Table S2).

The effect of Co addition on the carbon distribution of the alcohols is given in Fig. 8a. It shows that the amount of C₃+ alcohols reaches a maximum at 59.0% for the K-Co-MoSₓ-0.13 catalyst and decreases at higher Co amounts. The individual distribution of alcohols for the unpromoted K-MoSₓ, K-Co-MoSₓ-0.13 and K-Co-MoSₓ-0.63 catalyst are depicted in Fig. 8b (the distributions for other catalysts are shown in Fig. S2) as Anderson-Schulz-Flory (ASF) plots. The unpromoted K-MoSₓ catalyst shows a large deviation for particularly methanol when considering an ideal linear ASF distribution. This is in line with previous findings of our group, rationalized by assuming an enhanced chain growth mechanism for C₃+ alcohol using these types of catalysts [16]. After loading with Co, an even larger deviation for methanol and also for ethanol is observed for the K-Co-MoSₓ-0.13 catalyst. However, the deviation is less pronounced when further increasing the Co content.
(Fig. S2) and the K-Co-MoSx-0.63 catalyst shows an almost perfect linear distribution for the mixed alcohols including methanol. The carbon chain growth probability was calculated for the C2+ alcohols, showing a volcano-shaped curve with a peak for the K-Co-MoSx-0.13 catalyst (Fig. S3). Thus, alcohol selectivity and carbon chain growth are best for the K-Co-MoSx-0.13 catalyst, whereas higher Co contents lead to a higher hydrocarbon selectivity and a lower carbon chain growth for the alcohols.

For comparison, and also to determine the role of Mo in the catalyst formulation, the catalytic performance of a K promoted CoS2 catalyst was also investigated. We first attempted to prepare the CoS2 catalyst by a similar procedure as used for the Co-MoSx samples (viz. sulfurization of the cobalt-oxide precursors using KSCN). However, Co3O4 instead of CoS2 was obtained (Fig. S4), indicating that Co-oxides are difficult to sulfurize using KSCN at the prevailing conditions. Therefore, CoS2 (Sigma-Aldrich) was used as the catalyst precursor, and after K addition and pretreatment (in situ reduction with H2 at 400°C for 8h) tested for higher alcohol synthesis (360°C, 8.7MPa, GHSV of 4500mL g-1 h-1 and H2/CO molar ratio of 1). A very high hydrocarbon selectivity of 63.1% was achieved at a CO conversion of 1.3% (Table S3). Higher alcohols could not be detected in the liquid phase. The low CO conversion might be due to the presence of large crystallites (76nm, from Fig. 5.)

![XRD patterns of MoSx, CoMoSx-0.13 and K-CoMoSx-0.13 catalyst. b-c) HRTEM images of K-Co-MoSx-0.13. d) is the close-view of the marked area in b.](image)

Table 2
Catalytic performance of K-MoSx and K-Co-MoSx catalysts for the conversion of syngas to mixed alcohols.\(^a\)

| Catalyst         | XCO (%) | Selectivity (%) | Alcohol distribution (%) |
|------------------|---------|-----------------|--------------------------|
|                  | CH4     | HC  | CO2 | Alcohols | Others\(^b\) | Methanol | Ethanol | C3+OH\(^c\) |
| K-MoSx           | 25.6    | 17.7 | 24.8 | 31.8     | 40.8 | 2.6   | 19.3 | 32.3 | 42.5 |
| K-Co-MoSx-0.13   | 18.7    | 16.8 | 19.9 | 29.5     | 47.1 | 3.5   | 11.3 | 26.9 | 54.9 |
| K-Co-MoSx-0.37   | 17.4    | 19.0 | 21.6 | 29.1     | 47.0 | 2.3   | 17.3 | 38.4 | 39.6 |
| K-Co-MoSx-0.53   | 12.3    | 19.1 | 22.1 | 28.4     | 46.0 | 3.5   | 22.7 | 41.6 | 28.6 |
| K-Co-MoSx-0.63   | 8.8     | 22.2 | 25.9 | 32.0     | 41.5 | 0.6   | 33.6 | 42.6 | 22.4 |

\(^{a}\) Reaction conditions: 360 °C, 8.7 MPa, GHSV = 4500 mL g\(^{-1}\) h\(^{-1}\), H\(_2\)/CO = 1.

\(^{b}\) CO conversion.

\(^{c}\) Hydrocarbons.

\(^{d}\) Other liquid oxygenates except alcohols; \(^{e}\) C3+ alcohol.
XRD data using Scherrer equation) and the lack of structural defects (Fig. S5). These findings are in line with experiments by Li et al., who reported that only C1-C4 alkanes and no alcohols were formed when using a K-CoSx on activated carbon catalyst (in which Co is present in the form of CoSx crystallites) [20]. CoSx species, formed by reduction of CoS2 were indeed detected after reaction (Fig. S5), in line with literature data [20].

3.3. Mechanistic implications

The unpromoted Co-MoSx-0.13 catalyst (without K) showed high CO conversion and very low selectivity for alcohols (<2%) in comparison with that of K-Co-MoSx-0.13 (Table S4), indicating the important role of K for alcohol synthesis. Specifically, the presence of a KMoS2 phase (Fig. 5) is considered to be essential for alcohol synthesis, see also previous work from our group [16]. This is also in agreement with literature data revealing that the addition of K in MoS2 catalysts leads to lower hydrogenation rates while maintaining good CO insertion rates [8,9,46]. The obtained higher alcohols over the K modified catalysts are mainly composed of linear primary alcohols as well as branched alcohols like 2-methyl-1-propanol, 2-methyl-1-butanol, and 2-methyl-1-pentanol (Figs. S6–9). These branched alcohols were suggested to be formed via a β-addition process [47,48]. We have recently proposed that the linear primary alcohols are formed through CO insertion, while the branched alcohols are formed by CO insertion and CHx β-addition [16,49], see Schema 1 for details. n-Propanol is formed through both routes, supported by the high amount (>97%) of n-propanol in total propanol fraction (Fig. S6) (Scheme 1).

In the current investigation, the role of Co on product selectivity was investigated. Upon Co addition, the CH4 selectivity is lowered slightly from 17.7% for K-MoSx to 16.8% for the K-Co-MoSx-0.13 catalyst. A further increase in Co in the catalyst formulation leads to a gradual increase in CH4 selectivity (Fig. 7), suggesting a somewhat higher hydrogenation ability. The latter may be due to the presence of higher amounts of (K promoted) CoSx species (Figs. 1, 2 and 4) in the catalysts at higher Co contents.

The selectivity to alcohols in general and C3+ alcohols in particular shows an optimum for the K-Co-MoSx-0.13 catalyst and decreases with higher Co loadings (Figs. 7 and 9). These findings are rationalized by considering that the amounts of Co-Mo-S and CoSx phases in the Co-MoSx-0.13 catalyst are highest and that these are preferred for higher alcohol synthesis. At higher Co contents, considerable amounts of CoMoO4 species are present which result in lower higher alcohol selectivity.
The trend as given in Fig. 9 holds for the unpromoted (no K) catalysts. Analyses of a K-promoted catalyst (K-Co-MoSx-0.13) by XRD and HRTEM shows that the CoS2 phase, is reduced to Co9S8 (Fig. 5). Based on these findings, we propose that the catalytic performance of the K-MoSx catalyst is enhanced by the addition of Co due to the formation of cobalt sulfides (mainly Co9S8) and a K-promoted (Co)MoSx phase in close proximity. This assembly is given in Scheme 2 and shows a (K promoted) Co9S8 phase sandwiched between two K-promoted (Co)MoSx phases. The (K)Co9S8 phase gives mainly hydrocarbons for syngas conversions, see results for the Mo free K-Co, provided in this manuscript and literature data [20]. This implies the presence of significant amounts of adsorbed CHx* (and higher carbon number analogs) on the surface of the Co9S8 phase. We assume that efficient transfer of such CHx* species from the Co9S8 phase to adsorbed CH3CH2CH2O* species on the K-(Co)MoSx phase occurs, leading to branched alcohols (CHx β-addition mechanism). In addition, linear alcohols are formed by transfer of adsorbed CH3CH2CH2* on the Co9S8 phase to adsorbed CO on the K-(Co)MoSx phase.

3.4. Statistical modeling of process variables on alcohol selectivity using the best catalyst in this study (K-Co-MoSx-0.13)

To determine the effects of process conditions on CO conversion and product selectivity (particularly C3+ alcohols), a total of 44 experiments were performed in the continuous set-up at a range of 340–380 °C, 8.7–14.7 MPa, GHSV of 4500–27000 mL g\(^{-1}\) h\(^{-1}\), \(\text{H}_2/\text{CO}\) of 1.0–2.0 for the best catalyst (K-Co-MoSx-0.13) based on the benchmark experiments. In the initial stage, one variable was changed within the range while the other variables were kept constant (Figs. S10–18). This allows for determination of the individual effects of a variable on the CO conversion and product selectivity. In a later stage all experimental data (Table 3) were used simultaneously to develop multivariable nonlinear regression models of the form given in Eq. (5).
The yield (%) and selectivity (%) of C3+ alcohol as a function of temperature (°C), GHSV and H2/CO ratio. The models also predict that interactions between parameters are significant (e.g. P × GHSV and GHSV × Ratio). The predicted values of C3+ alcohol yield and selectivity match well with the experiment data (Fig. S19–20, R² = 0.92 for yield and R² = 0.91 for selectivity).

The effect of the pressure and GHSV on C3+ alcohol yield (Fig. 10) and selectivity (Fig. S21) are represented in response surface plots. It shows that intermediate pressure and GHSV are best for highest C3+ alcohol yield. This is confirmed by experiments in this regime, viz. a C3+ alcohol yield of 9.2% at 11.7 MPa, GHSV of 13500 mL g⁻¹ h⁻¹ (380 °C, H2/CO ratio of 1, Table 3, entry 11). The model also predicts that a relatively high temperature and low H2/CO ratio are also best for higher alcohol synthesis (surface plots not shown for brevity).

3.5. Comparison of catalyst performance with literature data for Mo-based catalysts

The experimentally obtained C3+ alcohol selectivity at different CO conversion over the best catalyst (K-Co-MoSx-0.13) in this study is given in Fig. 11, together with literature data for other Mo-based catalysts. Details regarding reaction conditions are shown in Table S7. Literature sources providing alcohol selectivity only on a CO₂-free basis were excluded since this leads to an overestimation of the actual C3+ alcohol selectivity and thus does not enable a fair comparison. The majority of the KMoS₂-based catalyst reported in the literature are promoted by Co or Ni and are supported on activated carbon (AC), carbon nanotubes (CNT), mixed metal oxides (MMO) and Al₂O₃.

It is clear that the best catalysts identified in this work (K-Co-MoSx-0.13) outperforms all existing Mo-based catalysts. In comparison with the Co free K-MoS₂ catalyst reported previously by our groups (Table S7, entry 5), promotion with the appropriate amount of Co leads to higher selectivity and yield for C3+ alcohol.

4. Conclusions

We have prepared a series of K-Co-MoSₓ catalyst with different Co contents to investigate the effect of Co promotion on product selectivity and particularly C3+ alcohol formation from syngas. The preparation of the Co-MoSₓ samples through sulfurization of cobalt-molybdenum oxide precursors leads to among others the formation of Co-Mo-S and Co₉S₈ phases, the actual amounts being dependent on the Co amount in the catalyst formulation. The best performance was obtained using the K-Co-MoSₓ-0.13 catalyst. This catalyst contains the highest amounts of Co-MoS and Co₉S₈ phases, implying that these are preferred for higher alcohol synthesis. It is speculated that close contact between a potassium modified Co₉S₈ phase and a Co promoted Mo₉S₈ phases is beneficial for higher alcohol synthesis due to facile transfer of adsorbed CH₃CH₂CH₂⁺ on the Co₉S₈ phase to adsorbed CH₃CH₂CH₂⁺ on the Co₉S₈ phase to adsorbed CO on the (K-Co)MoS₉ phase to give alcohols. Reaction conditions (T, P, GHSV and H₂/CO ratio) were varied to study the effect on catalytic performance and models with high significance were developed. Highest C₃+ alcohol yields of 7.3–9.2% and selectivities between 31.0–37.6% were obtained at a temperature of 380 °C, a pressure of 11.7 MPa, a GHSV of 13500–27000 mL g⁻¹ h⁻¹ and H₂/CO ratio of 1 over the optimized K-Co-MoSₓ-0.13 catalyst. These results are the highest reported in the literature so far, and indicate the potential of such catalysts for further scale up studies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

This approach allowed the identification of interactions between the variables (T, P, GHSV and H₂/CO ratio) on the selectivity and yield of C₃+ alcohol.

The yield (%) and selectivity (%) of C₃+ alcohol as a function of reaction conditions were successfully modeled and the results are given in Eqs. (6) and (7), respectively.

**Yield**  = 2.05 × P + 0.13 × T + 0.00034 × GHSV - 1.27 × Ratio - 0.000021 × P × GHSV - 0.088 × P² - 3.91 × 10⁻⁶ × GHSV² - 51.51

**Selectivity**  = -11.45 × P + 0.20 × T + 0.0037 × GHSV - 5.14 × Ratio - 0.00017 × P × GHSV - 0.00029 × GHSV × Ratio + 0.41 × P² - 1.86 × 10⁻⁸ × GHSV² + 20.77

The high F-value of both models (Tables S5–6) implies that the models are significant and adequate to represent the actual relationship between the response and the variables [50]. The models also reveal
CRediT authorship contribution statement

Xiaoying Xi: Investigation, Data curation, Formal analysis, Writing - original draft. Feng Zeng: Investigation, Data curation, Formal analysis, Writing - original draft. Huatang Cao: Investigation, Data curation, Formal analysis. Catia Cannilla: Investigation, Data curation, Formal analysis, Writing - review & editing. Timo Bisswanger: Data curation, Formal analysis, Writing - review & editing. Sytze de Graaf: Investigation, Data curation, Formal analysis. Yutao Pei: Supervision, Validation, Writing - review & editing. Francesco Frusteri: Supervision, Validation, Writing - review & editing. Christoph Stampfer: Data curation, Formal analysis. Regina Palkovits: Conceptualization, Supervision, Validation, Writing - review & editing. Hero Jan Heeres: Conceptualization, Funding acquisition, Supervision, Validation, Writing - review & editing.

Acknowledgement

Xiaoying Xi and Feng Zeng acknowledge the China Scholarship Council (CSC) for financial support.
Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2020.118950.

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