Synthesis of mixed alcohols with enhanced C3+ alcohol production by CO hydrogenation over potassium promoted molybdenum sulfide

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ABSTRACT

Alcohol mixtures with high C3+ alcohols content can enhance the performance of alcohol mixtures as a blend component in gasoline. Sulfur-resistant potassium promoted molybdenum sulfide (K-MoS2) catalysts enabled synthesizing mixed alcohols through CO hydrogenation. However, the liquid oxygenate selectivity and yield of K-MoS2 catalysts are usually low, and the alcohols follow the Anderson-Schulz-Flory (ASF) distribution, which means methanol and ethanol present the main liquid oxygenates. To achieve high liquid oxygenate selectivity and yield enhancing C3+ alcohol production, we designed multilayer K-MoS2 catalysts possessing a well-contacted MoS2 and KMoS2 phase, respectively. The reduced rim site exposure and the well-contacted MoS2-KMoS2 dual site induced by the multilayer structure enhance the chain growth through CHxβ-addition and CO insertion. Accordingly, the observed higher alcohol formation deviates from the ASF distribution. By tailoring the K/Mo ratio, catalysts with varying composition of MoS2 and KMoS2 phases were obtained for suppressing the formation of hydrocarbons and CO2 effectively. An optimized production of liquid oxygenates with enhanced C3+ alcohol production under appropriate reaction temperature became possible. The optimized catalysts have liquid oxygenate selectivity and yield of 29.1–32.7% and 7.9–10.6%, respectively, yet with good stability. C3+ alcohols take up more than 46% (carbon atom fraction) in the liquid oxygenate. The C3+ alcohol yield reaches 3.6–5.1%.

1. Introduction

Since world’s crude oil reserves are quickly consumed, alternatives for gasoline like alcohols, natural gas, and hydrogen are indispensable for a sustainable society [1–6]. Alcohols including methanol and ethanol have been intensively studied and used as gasoline blend components [6–8]. However, methanol and ethanol hold low energy density, high vapor pressure, and high affinity to water leaving room for further improvement [9,10]. Compared with methanol and ethanol, C3+ alcohols generally possess higher energy density and lower vapor pressure, and C3+ alcohols like butanol exhibit a lower affinity to water. The octane number of C3+ alcohols is also comparable to gasoline [9,10]. Thus alcohol mixtures with high C3+ alcohol content may help to improve the performance as a gasoline blend component.

Alcohols can be synthesized by the catalytic conversion of syngas, the fermentation of sugars, and the hydration of petroleum-derived alkenes [11–13]. Since syngas could be produced through various routes and feedstock such as biomass gasification, natural gas reforming, and CO2 reduction, the direct catalytic conversion of syngas provides high sustainability and is very appealing for the direct mixed alcohols production [14–17]. The catalytic conversion of syngas to mixed alcohols comprehends alcohol formation as the major reaction, together with hydrocarbon formation and the water-gas-shift reaction as main side reactions [18].

Alcohol formation: nCO + 2nH2 ⇌ CnH2n + nOH + (n - 1)H2O (1)

Hydrocarbon formation: nCO + (2n + 1)H2 ⇌ CnH2n + 2 + nH2O (2)

Water-gas-shift: CO + H2O ⇌ CO2 + H2 (3)

The most intensively studied catalysts for mixed alcohols’ synthesis from syngas include rhodium-based catalysts, molybdenum-based systems, modified Fischer-Tropsch synthesis catalysts, and modified...
methanol synthesis catalysts [13]. Among them, molybdenum sulfide-based materials exhibit promising performance and significant sulfur-resistance avoiding the costly deep desulfurization of syngas [19,20]. Even though sole MoS₂ produces mainly hydrocarbons, alkali metal promoted molybdenum disulfide enables increasing selectivity for alcohols [21]. Alkali metals, for example potassium (K), are relevant for the formation of alcohols [13,22]. A dual site model is proposed for the conversion of syngas to mixed alcohols over transition metal promoted potassium-doped molybdenum sulfide (K-MoS₂) catalysts. CO dissociative adsorption, H₄O dissociative adsorption, and CH₄ formation take place on the transition metal sulfide phase (MSₐ, M = Fe, Co, or Ni), and methane is formed by direct hydrogenation of CH₄ species. Non-dissociative CO adsorption, chain growth, and alcohol formation take place on the potassium promoted metal sulfide phase (KMMoS) [18,23]. The carbon chain growth comprises CO insertion and C₁ intermediate addition. Linear primary alcohols are formed through CO insertion, while branched alcohols form via C₁ intermediate addition [18,24].

Even though alkali metal promotion shifts the product selectivity from hydrocarbons to alcohols, the selectivity and yield of alcohols are usually low and hinder the successful commercialization of mixed alcohol synthesis from syngas [25]. Besides, the alcohol product possesses a selectivity order of methanol > ethanol > propanol obeying Anderson-Schulz-Flory (ASF) distribution [19,26]. Accordingly, C₃+ alcohols take up less than 30% (carbon atom fraction) of the alcohols [20,24,26–28]. Nickle, cobalt, and lanthanum are reported as promoters to enhance the chain growth over K-MoS₂ catalysts allowing to deviate from the ASF distribution [24,26–28]. Therewith, the C₃+ alcohol content reaches about 50% (carbon atom fraction) of the alcohol product. Except for promoters, the structure of MoS₂ is also of significant importance to enhance chain growth to boost C₃+ alcohols production. Dorokhov et al. propose that the active centers for mixed alcohols synthesis are located on the edges of two adjacent K-MoS₂ layers [29]. The adsorbed methyl fragment can participate in chain growth with other adsorbed species on the adjacent layers. Therefore, edge sites of multilayer K-MoS₂ are more favorable for chain growth with methyl fragment participation than rim sites or fewer stacked K-MoS₂, which hold less adjacent layers. The C₃+ alcohol selectivity can also be enhanced by tailoring the MoS₂ double layer structure [30]. Even though C₃+ alcohol content reaches about 50% (carbon atom fraction) in the alcohols product, the overall yield of C₃+ alcohols accounts for less than 2%, clearly leaving space for further improvement [30].

Herein we report a method to prepare multilayer K-MoS₂ catalysts for converting syngas to mixed alcohols with high selectivity and yield together with an enhanced C₃+ alcohol production. Thermal treatment of a mixture of amorphous molybdenum sulfide precursor with K₂CO₃ leads to the formation of a multilayer K-MoS₂ structure with well-contacted MoS₂ phase and KMoS₂ phase, which are the bifunctional active centers for mixed alcohols synthesis. The reduced rim site exposure and well-contacted MoS₂–KMoS₂ dual site due to the multilayer structure boost C₃+ alcohol formation and allow deviating from ASF distribution of the alcohols through enhanced CO insertion and CH₄ β-addition. The potassium loading is optimized to obtain K-MoS₂ with varying content of MoS₂ and KMoS₂ to inhibit hydrocarbons and CO₂ formation, and enhance alcohols formation with enhanced C₃+ alcohol production under appropriate reaction temperature to reach high liquid oxygenate selectivity and yield. The optimized catalysts enable high liquid oxygenate selectivity and yield, together with an enhanced C₃+ alcohol yield reaching 29.1–32.7%, 7.9–10.6%, and 3.6–5.1%, respectively. C₃+ alcohols take up more than 46% (carbon atom fraction) in the liquid oxygenate. We therewith contribute a new method to deviate from the ASF distribution of alcohols with high C₃+ alcohol yield over MoS₂ based catalyst by designing the structure of K-MoS₂ catalyst without nickel, cobalt, or lanthanum promoter.

2. Experimental

2.1. Catalyst preparation

The amorphous molybdenum sulfide precursor was prepared by the method reported in [31]. Generally, molybdenum sulfide was precipitated by mixing 5 mL 15.0% (NH₄)₂MoO₄·4H₂O (Fluka) solution with 5 mL 34.6% Na₂S·9H₂O (Sigma-Aldrich) solution in 88 mL 4.0% hydrochloric acid (Fluka) solution. The obtained dark brown slurry was kept under 80 °C with stirring and reflux. 0.7 g HONH₂·HCl (Sigma-Aldrich) was added to the mixture after half an hour. The slurry was filtered and washed with deionized water after one more hour, followed by drying in atmospheric condition. Thereby the amorphous molybdenum sulfide precursor was obtained with less than 0.08 wt% sodium impurity (inductively coupled plasma optical emission spectrometry). Potassium was incorporated into the catalyst by physical mixing of the amorphous molybdenum sulfide precursor with K₂CO₃ (Sigma-Aldrich) in a mortar with a pestle followed by treatment at 500 °C in hydrogen atmosphere for 3 h with a heating rate of 5°C/min. The amount of K₂CO₃ was varied to adjust the K/Mo mole ratio from 0 to 0.52.

2.2. Catalyst characterization

N₂-physisorption was used to measure the surface area, the pore volume, the pore diameter, and the pore diameter distribution of the catalyst. The measurement was performed on an ASAP 2420 analyzer. The specific surface area was calculated with Brunauer–Emmett–Teller (BET) method. The pore volume was calculated using single point desorption data at P/P₀ = 0.97. The pore diameter and pore diameter distribution were calculated with Barrett-Joyner-Halenda (BJH) method using the desorption branch. X-ray diffraction (XRD) analyses were performed on a D8 Advance Bruker diffractometer with a CuKα₁ radiation (λ = 1.5418 Å). The XRD patterns were collected under 40 kV and 40 mA in the 2θ range of 5°–80°. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were collected on a Bruker VERTEX 70 spectrometer equipped with an ATR geometry, in the wave number range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹. SPECTROBLUE ICP-OES (inductively coupled plasma optical emission spectrometry) was used to determine the potassium/molybdenum ratio. Electron probe microanalysis (EPMA) was carried out on a JEOL JXA-8530 F electron probe microanalyzer to study the distribution of potassium promoter. Raman spectroscopy was performed on a WITec Alpha 300R microscope with a 532 nm excitation laser. High resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM-2100F microscope operating at 200 kV. The X-ray photoelectron spectra (XPS) were obtained by a SSX-100 (Surface Science Instruments) photoelectron spectrometer using a monochromatic Al Kα X-ray source (hν = 1486.6 eV).

2.3. Catalytic reaction test

To evaluate the catalytic performance in the conversion of syngas to mixed alcohols, the catalysts were tested using a high-pressure fixed bed reactor (10 mm inner diameter) setup. The gas mixture with a H₂/CO/N₂ volume ratio of 47:47:6 was mixed and pressurized by a high-pressure compressor before entering the reactor. The flow rate of gas mixture was controlled by a high-pressure mass flow controller. The reactor was located in an oven to keep the reaction temperature. The exit stream from the reactor was cooled and separated by a double walled condenser at -5°C. The gas products were analyzed by an online gas chromatograph (Compact GC, Interscience BV). The liquid products were collected during steady operation and were analyzed by an offline gas chromatograph (Finnigan TRACE GC Ultra, Thermo Scientific). Typically, the reactor was loaded with a layer of SiC (Sigma-Aldrich) at the bottom of the reactor, then a layer of the catalyst (0.40 g), and again...
a layer of SiC on the top of the catalyst. The reactions were investigated under a gas hourly space velocity (GHSV) of 4500 mL g\(^{-1}\) h\(^{-1}\), a reaction pressure of 8.7 MPa, and at three temperatures of 300, 340 and 380 °C, respectively. External and internal mass transfer were excluded according to the methods reported in references [32,33]. The CO conversion, the product selectivity and yield were calculated with the following formulas. All the data reported in this article hold a carbon balance of higher than 95%. Methanol and ethanol loss was estimated by the online gas chromatograph. The identification and quantification of methanol and ethanol in gas phase were performed by passing nitrogen through a gas-washing bottle, which is filled with methanol or ethanol, and through the gas chromatograph at fixed flow rate. The carbon selectivity of methanol and ethanol in gas phase was calculated by formula (5).

\[ X_{\text{CO}} = \frac{\text{mole of CO}_{\text{influent}} - \text{mole of CO}_{\text{effluent}}}{\text{mole of CO}_{\text{influent}}} \times 100\% \]  
\[ S_{i} = \left( \frac{\text{mole of product} \times \text{number of carbons in product}}{\text{mole of CO}_{\text{influent}} - \text{mole of CO}_{\text{effluent}}} \right) \times 100\% \]  
\[ Y = X_{\text{CO}} \times S_{\text{liquid oxygenate}} \]  
\[ \frac{S_{i}}{n} = \alpha^{n-1} \times (1 - \alpha) \]

3. Results and discussion
3.1. Synthesis of potassium promoted MoS\(_{2}\) catalysts

The catalysts were prepared by thermal treatment of a mixture of MoS\(_{3.7}\) (ICP-OES) precursor with K\(_{2}\)CO\(_{3}\), and a series of K-MoS\(_{2}\) catalysts were obtained by varying the weight ratio of K\(_{2}\)CO\(_{3}/\)MoS\(_{3.7}\). Table 1 summarizes the physical and chemical properties of the catalysts. The catalysts (M0, M1, M2, M3, M4, and M5) possess K/Mo mole ratios ranging from 0 to 0.52 (S/Mo mole ratio is shown in Table S1). With increasing K/Mo ratio, the BET specific surface area and the pore volume decrease, while all the catalysts possess similar pore diameters of about 230 Å and similar pore size distributions (Fig. S1). The decrease of the specific surface area and the pore volume may be ascribed to partial blockage of the pores by potassium with increasing K/Mo ratio.

Fig. 1 presents the XRD patterns of the as-precipitated catalyst precursor and thermal treated catalysts with varying K/Mo ratio. K/Mo ratios of M0, M1, M2, M3, M4, and M5 are 0, 0.08, 0.15, 0.22, 0.38, and 0.52, respectively.

Table 1 summarizes the physical and chemical properties of the catalysts. The as-precipitated catalyst precursor, MoS\(_{3.7}\), shows only one broadened 002 reflex of 2H-MoS\(_{2}\) (JCPDS card No. 01-073-1508) at 2θ of about 14°, indicating an amorphous structure. After treatment at 500 °C in H\(_{2}\) atmosphere, the obtained M0 possesses identical reflexes of crystalized 2H-MoS\(_{2}\). The addition of potassium leads to the formation of potassium-containing species like KMoS\(_{2}\) (JCPDS card No. 00-018-1064), K\(_{2}\)SO\(_{4}\) (JCPDS card No. 01-070-1488) and K\(_{2}\)S\(_{2}\)O\(_{7}\) (JCPDS card No. 00-001-0717). The KMoS\(_{2}\) phase is essential for the formation of mixed alcohols; however, no corresponding reflexes occur for low K/Mo ratios (M1 and M2), maybe due to very small and therewith X-ray amorphous KMoS\(_{2}\) crystallites. The characteristic reflex of KMoS\(_{2}\) at 2θ of 10° appears for a K/Mo ratio of 0.22 (M3). The down shift of the 002 reflex from 14° to 10° indicates an expanded interlayer space and the insertion of potassium into the interlayer space of MoS\(_{2}\), while the in-plane lattice parameter of pristine MoS\(_{2}\) is maintained [34–36]. With increasing K/Mo ratio, the formation of KMoS\(_{2}\) increases, while the amount of MoS\(_{2}\) phase decreases. Thus, a mixture with adjacent MoS\(_{2}\) and KMoS\(_{2}\) layer structure could be obtained. Other potassium-containing species like K\(_{2}\)SO\(_{4}\) and K\(_{2}\)S\(_{2}\)O\(_{7}\), which may cover the active MoS\(_{2}\) and KMoS\(_{2}\) sites, are found with increasing K/Mo ratio. The existence of K\(_{2}\)SO\(_{4}\) and K\(_{2}\)S\(_{2}\)O\(_{7}\) is further confirmed by ATR-FTIR spectra (Fig. S2). Even though the unpromoted catalyst (M0) exhibits no bands in ATR-FTIR spectra, because MoS\(_{2}\) is black, the promoted catalysts (M1, M2, M3, M4, and M5) possess bands of K\(_{2}\)SO\(_{4}\) and K\(_{2}\)S\(_{2}\)O\(_{7}\). With increasing K/Mo ratio, the bands get stronger, indicating more K\(_{2}\)SO\(_{4}\) and K\(_{2}\)S\(_{2}\)O\(_{7}\). The formation MoO\(_{3}\) was also detected by ATR-FTIR with high K/Mo ratio (M4 and M5).

Fig. 2 shows SEM images and elemental mappings of molybdenum, sulfur, and potassium for potassium promoted catalysts obtained by EPMA. With low K/Mo ratio (M1 and M2), potassium distributes homogeneously. Obvious aggregation of potassium is observed with a K/Mo ratio of 0.22 (M3). With higher K/Mo ratio (M4 and M5), more intensive aggregation of potassium is found. The excessive addition of potassium leads to the formation of inactive K\(_{2}\)SO\(_{4}\) and K\(_{2}\)S\(_{2}\)O\(_{7}\) as inferred by XRD and ATR-FTIR results, and the aggregation of inactive potassium-containing species, which may block the catalyst pore structure and cover the active sites.

Fig. 3 shows TEM images of the as-precipitated catalyst precursor and the thermal treated catalysts. The as-precipitated molybdenum sulfide precursor is amorphous consisting of short-range disordered chains (Fig. 3a), consistent with XRD result. After thermal treatment, long-range ordered multilayer structures are formed (Fig. 3b-e). The multilayer structure reduces the exposure of rim sites, which are located on the rim of the two ends of MoS\(_{2}\) along 002 direction (Fig. S3). The unpromoted catalyst (M0) possesses an interlayer distance of about
0.65 nm, which corresponds to the d spacing of the MoS\textsubscript{2} 002 plane. Fig. S4 presents the interlayer distance distribution of the catalysts. With increasing K ratio, the average interlayer distance of the catalysts increases from 0.65 nm (M0) to 0.81 nm (M5), due to the insertion of potassium-containing species and formation of the KMoS\textsubscript{2} phase as indicated by the existence of the reflex at 2\theta of 10° in XRD patterns \cite{35}. Interlayer distances of about 0.64 and 0.79 nm were found between adjacent layers in M3 (Fig. 3f), confirming the existence of well-contacted MoS\textsubscript{2} and KMoS\textsubscript{2} phases.

Fig. 4 illustrates the Raman spectra of the catalysts. The unpromoted catalyst (M0) shows two bands at 380.8 cm\textsuperscript{-1} and 406.5 cm\textsuperscript{-1}, which are ascribed to the in-plane E\textsubscript{1g} and out-of-plane A\textsubscript{1g} vibration mode of the MoS\textsubscript{2} layer structure \cite{37,38}. These two bands are also found in potassium promoted catalysts (M1, M2, M3, M4, and M5); however, the A\textsubscript{1g} vibration mode shifts to lower frequency compared to M0, suggesting a bigger interlayer distance compared to M0 due to the insertion of potassium into MoS\textsubscript{2} interlayer space \cite{30}.

The oxidation states of potassium promoted MoS\textsubscript{2} depend on the precursor, the sulfurization method, and the way to incorporate potassium \cite{39}. We studied the oxidation states of the multilayer MoS\textsubscript{2}-KMoS\textsubscript{2} catalysts by XPS. XPS spectra of S 2p and Mo 3d are presented in Fig. S5. The doublet located at binding energies of about 161.8 eV and 163.0 eV is assigned to S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2} of S\textsuperscript{2-} and/or terminal S\textsuperscript{2-}. The doublet located at about 163.4 eV and 164.6 eV is ascribed to S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2} of bridge S\textsuperscript{2-} and/or sulfur in oxysulfide. Moreover, the peak located at 169.0 eV relates to sulfate species, which are formed due to exposure of MoS\textsubscript{2} to air and water \cite{40}. The doublets at about 229.2 eV and 232.3 eV, 230.2 eV and 233.4 eV, 232.4 eV and 235.6 eV are assigned to Mo 3d\textsubscript{5/2} and Mo 3d\textsubscript{3/2} of Mo\textsuperscript{4+} (MoS\textsubscript{2}), Mo\textsuperscript{5+} (MoO\textsubscript{x}S\textsubscript{y}), and Mo\textsuperscript{6+} (MoO\textsubscript{3}), respectively \cite{22,40,41}. Table 2 summarizes the mole percentage of Mo\textsuperscript{4+}, Mo\textsuperscript{5+}, and Mo\textsuperscript{6+} obtained by XPS fitting. With increasing K/Mo ratio, the percentage of the more active Mo\textsuperscript{4+} decreases \cite{42}, while that of Mo\textsuperscript{5+} increases, which is consistent with ATR-FTIR results showing MoO\textsubscript{x} bands at high K/Mo ratio. Under mixed alcohols synthesis conditions, only a minor portion of Mo\textsuperscript{6+} is reduced to Mo\textsuperscript{4+}, and the major portion is reduced to Mo\textsuperscript{5+} \cite{43}.

Summarizing the characterization results, we propose a possible formation and evolution route of potassium promoted molybdenum sulfide catalysts. The as-precipitated molybdenum sulfide precursor possesses an amorphous structure with short-range disordered molybdenum sulfide domains. Thermal treatment of the amorphous molybdenum sulfide precursor with potassium addition on one hand enables the formation of a multilayer long-range ordered structure with reduced exposure of rim sites, on the other hand it leads to the formation of well-contacted MoS\textsubscript{2} and KMoS\textsubscript{2} phases. While the sole MoS\textsubscript{2} produces mainly hydrocarbons (Scheme 1, left), the potassium promoted MoS\textsubscript{2} can shift the products from hydrocarbons to alcohols due to the enhanced formation of C\textsubscript{x}H\textsubscript{y}O\textsuperscript{*} intermediates on the KMoS\textsubscript{2} phase (Scheme 1, middle). With increasing K/Mo ratio, the amount of MoS\textsubscript{2} phase reduces, while that of KMoS\textsubscript{2} phase increases. At the same time, the increasing K/Mo ratio leads to the formation of inactive species such as K\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}S\textsubscript{2}O\textsubscript{7}, and MoO\textsubscript{3}, which may block the active species (Scheme 1, right). With this method, a series of multilayer bifunctional MoS\textsubscript{2}-KMoS\textsubscript{2} catalysts with reduced rim site exposure, varying composition of MoS\textsubscript{2}/KMoS\textsubscript{2}, and different active sites...
Fig. 3. TEM images of the as precipitated catalyst precursor (a) and thermal treated catalysts with varying K/Mo ratio (b–f). K/Mo ratios of M0 (b), M1 (c), M3 (d), and M5 (e) are 0, 0.08, 0.22, and 0.52, respectively. (f) is the close-view of the marked area in (d).
exposure were obtained for studying the conversion of syngas to mixed alcohols aiming for enhanced C3+ alcohols production.

### 3.2. Catalytic conversion of syngas to mixed alcohols

The obtained catalysts were tested in the catalytic conversion of syngas to mixed alcohols using a fixed bed reactor at 300, 340, and 380 °C, under a pressure of 8.7 MPa and a GHSV of 4500 mL g⁻¹ h⁻¹, with a H₂/CO ratio of 1. Fig. 5 shows the time on stream CO conversion and selectivity for M3 at 340 °C. In the first 20 h, the CO conversion and liquid oxygenates selectivity decrease, while the selectivity of hydrocarbons and CO₂ increases. Stable conversion and selectivity are obtained after 20 h, and the catalyst is stable for at least 100 h without the addition of a sulfidation agent in the feed. The 20-hour induction period, which may be due to surface sulfur loss of the catalyst and potassium-containing species redistribution during CO hydrogenation [44], is found for all the catalysts and under the different reaction conditions. However, the S/Mo ratio remains at 1.90 after 100 h catalytic test, which is almost the same as 1.89 of the fresh catalyst, indicating no significant sulfur loss and suggesting the reason for the induction period to be the redistribution of potassium containing species. To obtain reliable and comparable catalytic results, we collected all the data after the induction period at a stable reaction state.

The catalytic performance of the potassium promoted catalysts is summarized in Table 3. Fig. 6 presents the CO conversion of the K-MoS₂ catalysts under different reaction temperatures. The CO conversion ranges from 7.8% to 50.1%, and increases with increasing reaction temperature and decreasing K/Mo ratio. With increasing K/Mo ratio, the reduced availability of molybdenum, blockage of active sites by the inactive potassium-containing species, and the formation of inactive Mo⁶⁺ lead to decreased CO conversion. The unpromoted catalyst (M0) shows a low liquid oxygenate selectivity of less than 3.2% (Table S2), hindering collection of liquid product during catalytic tests for analysis and further discussion. The promoted catalysts (M1, M2, M3, M4, and M5) enable high liquid oxygenate selectivity and yields ranging from 14.2 to 46.0% and from 3.6 to 10.6%. The C3+ alcohol selectivity and yield range from 6.0 to 20.7% and from 1.6 to 5.1%, respectively.

The catalytic performance of the K-MoS₂ catalysts is further analyzed. The hydrocarbon selectivity of the catalysts under varying reaction temperature is plotted as a function of CO conversion (Fig. 7). At the same reaction temperature, the hydrocarbon selectivity decreases with increasing K/Mo ratio. As suggested by XRD, the addition of potassium leads to the formation of KMoS₂ and a decreased content of MoS₂. The latter is active for H₂ dissociation, while potassium promotion may decrease its hydrogenation ability. The reduced availability of active H and hydrogenation ability due to the decreasing MoS₂ content and potassium promotion are suggested to lead to a lower hydrocarbon selectivity [21,45]. For the same catalyst, hydrocarbon selectivity increases with increasing reaction temperature, because high reaction temperature favors H₂ dissociation facilitating higher hydrocarbon selectivity [46].

The CO₂ selectivity of the catalysts at varying reaction temperature is plotted as a function of CO conversion (Fig. 8). The effect of potassium and reaction temperature on the water-gas-shift reaction and CO₂ selectivity hasn’t reached a consensus yet. Potassium promotion...
was described to either enhance or weaken the water-gas-shift reaction depending on the catalyst synthesis procedure [19, 21, 47, 48]. The water-gas-shift reaction is favored at low reaction temperature, because the equilibrium constant of the equilibrium-controlled water-gas-shift reaction decreases with increasing temperature; however, higher reaction temperatures are usually required to achieve a sufficient reaction rate [49]. Thus, inverted influences of temperature on water-gas-shift reaction are reported. Lower equilibrium CO content is found at lower reaction temperature for the water-gas-shift reaction, while an increased CO₂ selectivity with raising reaction temperature is found for mixed alcohols synthesis [47, 49]. In this work, a high K/Mo ratio leads to low CO₂ selectivity, and CO₂ selectivity increases with increasing reaction temperature. A nearly linear relation of CO₂ selectivity and CO conversion occurs. The formation of alcohols and hydrocarbons consumes H₂ and CO with a ratio of higher than 2, indicating H₂ is consumed faster with increasing CO conversion. Also H₂O is formed as a side product of these two reactions. With increasing CO conversion, the consumption of H₂ and the formation of H₂O drive the water-gas-shift reaction to the formation of CO₂ and H₂.

Table 3
Catalytic performance of K-MoS₂ catalysts in the conversion of syngas to mixed alcohols.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T/°C</th>
<th>(X_{\text{CO}})/%</th>
<th>CH₂</th>
<th>CO₂</th>
<th>Oxy</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>(\text{C}_3+\text{OH})</th>
<th>Others</th>
<th>Yield/%</th>
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<td>26.7</td>
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* Reaction pressure = 8.7 MPa, GHSV = 4500 mL g⁻¹ h⁻¹, H₂/CO = 1.
* K/Mo ratios of M1, M2, M3, M4, and M5 are 0.08, 0.15, 0.22, 0.38, and 0.52, respectively.
* Reaction temperature.
* CO conversion.
* Hydrocarbons.
* Liquid oxygenate.
* \(\text{C}_3+\text{} \) alcohols.
* Other liquid oxygenate except alcohols.
selectivity are obtained by M3 at 340 °C and M5 at 380 °C located in the rectangle in Fig.10. M3 and M5 provide liquid oxygenate yields of 7.9 and 10.6% as well as a selectivity of 32.7 and 29.1%, respectively.

Fig. 8. CO₂ selectivity as a function of CO conversion. K/Mo ratios of M1, M2, M3, M4, and M5 are 0.08, 0.15, 0.22, 0.38, and 0.52, respectively. Reaction pressure = 8.7 MPa, GHSV = 4500 mL g⁻¹ h⁻¹, H₂/CO = 1.

Fig. 9. Liquid oxygenate selectivity as a function of CO conversion. K/Mo ratios of M1, M2, M3, M4, and M5 are 0.08, 0.15, 0.22, 0.38, and 0.52, respectively. Reaction pressure = 8.7 MPa, GHSV = 4500 mL g⁻¹ h⁻¹, H₂/CO = 1.

Fig. 10. Liquid oxygenate yield as a function of liquid oxygenate selectivity. K/Mo ratios of M1, M2, M3, M4, and M5 are 0.08, 0.15, 0.22, 0.38, and 0.52, respectively. Reaction pressure = 8.7 MPa, GHSV = 4500 mL g⁻¹ h⁻¹, H₂/CO = 1.

Fig. 11. C3+ alcohol yield as a function of liquid oxygenate selectivity. K/Mo ratios of M1, M2, M3, M4, and M5 are 0.08, 0.15, 0.22, 0.38, and 0.52, respectively. Reaction pressure = 8.7 MPa, GHSV = 4500 mL g⁻¹ h⁻¹, H₂/CO = 1.

Fig. 12. ASF distributions of alcohols over M3 (K/Mo = 0.22). Reaction temperature = 340 °C, reaction pressure = 8.7 MPa, GHSV = 4500 mL g⁻¹ h⁻¹, H₂/CO = 1. The points are measure data, and the dash lines are ASF fittings for C3+ alcohols.
and fluctuates slightly from M3 to M5 as indicated by the angle between the fitting line of methanol and ethanol, and C3+ alcohols (Fig. S6). The deviation implies a different chain growth mechanism of C3+ alcohols compared to that of ethanol [24,50,51]. The two possible chain growth mechanisms are CO insertion and CH₄ addition. The chain growth probabilities calculated with C3+ alcohols range from 0.2 to 0.3 (Table S4).

To further study the chain growth mechanism, the composition of the produced alcohols is analyzed. Fig. S7 summarizes the mole ratio of isomeric alcohols to the respective linear primary alcohols over different catalysts, and Scheme 2 presents the formation of the main products through CO insertion and CH₄ β-addition. The main isomeric alcohols are 2-methyl-1-propanol, 2-methyl-1-butanol, and 2-methyl-1-pentanol. As shown in Scheme 2, the linear primary alcohols are formed through CO insertion, while the branched alcohols, 2-methyl-1-propanol, 2-methyl-1-butanol, and 2-methyl-1-pentanol, are formed by joint CO insertion and CH₄ β-addition, which is responsible for the growth of the branched chain [24]. Propanol may be formed through both routes. The two chain growth mechanisms, CO insertion for ethanol, and joint CO insertion and CH₄ β-addition for C3+ alcohols are consistent with the deviation from ASF distribution. At a low K/Mo ratio, M1 shows a low branched alcohols/linear primary alcohols ratio of less than 0.4. With increasing K/Mo ratio, the branched alcohols/linear primary alcohols ratios increase and reach a maximum of about 0.9 with M3. The branched alcohols/linear primary alcohols ratios decrease slightly with further increasing K/Mo ratio (M4 and M5). Since CH₄ is formed on MoS₂ [52], and CO adsorption happens on KMoS₂, a good contact and balance between these two phases are of great importance for the chain growth through CH₄ β-addition and CO insertion. The multilayer structure of the catalyst with potassium located in the interlayer space enables good contact between the two phases. With low K/Mo ratio, the CH₄ tends to form CH₄, however the availability of CH₄ decreases with increasing K/Mo. Thus, the formation of branched alcohols reaches a maximum with medium potassium promotion, too high or too low K/Mo ratio weakens the branched alcohols formation. By tailoring the K/Mo ratio, the chain growth through CO insertion and CH₄ β-addition is optimized enabling an enhanced C3+ alcohol production with high liquid oxygenate yield and selectivity.

4. Conclusion

We report a method for tailoring the structure of potassium promoted MoS₂ catalysts to produce mixed alcohols with enhanced C3+ alcohol production. The preparation of potassium promoted MoS₂ by thermal treatment of a mixture of amorphous MoS₂ and K₂CO₃ leads to the formation of a multilayer structure with MoS₂ and K₂MoS₂ mixed phases. The multilayer structure with reduced exposure of rim sites and well-contacted MoS₂ and KMOS₂ phase fosters carbon chain growth and C3+ alcohol production, and allows deviating from the ASF distribution of the alcohols through enhanced CO insertion and CH₄ β-addition. By tailoring the K/Mo ratio, catalysts with different relative ratio of KMoS₂ and MoS₂ phases were obtained to optimize the formation of liquid oxygenates with enhance C3+ alcohol production under appropriate reaction temperature. High liquid oxygenate selectivity and yield of 29.1–32.7% and 7.9–10.6%, and high C3+ alcohols content in the liquid oxygenates and a high C3+ alcohol yield of 46% and 3.6–5.1%, respectively, as well as good stability are obtained by catalyst design and optimizing the reaction condition.

Conflicts of interest

The authors declare that they have no conflicts of interest.

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