The critical role of solvent polarity in the preparation of tube-like Co–Mo sulfide catalysts for the hydrodeoxygenation of stearic acid†

Kai Guo, Zhengting Xiao, Di Liu, Cong Zhang, Guangci Li, Xuebing Li and Song Chen†

Co–Mo sulfides with tube-like structures were prepared through a low-temperature pre-sulfurization process using rod-like CoMoO₄ as the precursor. Pre-sulfurization solvents with different polarities markedly affected the textural properties, the concentration and microstructure of the active components, and the catalytic deoxygenation activity. The increased solvent polarity can promote the formation of hollow structures and the degree of sulfurization of the precursor, and the appropriate polarity of pre-sulfurization solvents is helpful for the sulfurization of CoMoO₄ to form CoMoS₂ slabs with shorter lengths and greater stacking numbers, which means more coordinatively unsaturated sites, especially corner sites. The results of the hydrodeoxygenation reaction of stearic acid suggested that a higher f₁/f₆ resulted in a greater reaction rate of stearic acid, and the yields of the liquid products were highly dependent on the number of surface-active sites, which mainly originated from type II CoMoS species. Moreover, increasing the reaction temperature favored the direct hydrodeoxygenation pathway.

Introduction

Due to the CO₂ emission issue and the nonrenewable nature of fossil energy, researchers are committed to identifying renewable energy alternatives (e.g., biomass). Biodiesel (fatty acid methyl ester, FAME) produced from natural lipids can alleviate the shortage of fossil energy and environmental pollution and thus has gained much attention. Nevertheless, unsaturated C—C double bonds and oxygenated components in biodiesel lead to poor stability, high corrosivity, and easy deterioration during storage. Therefore, hydrogenation and deoxygenation treatments are beneficial for improving the quality of biodiesel.

The catalytic hydrodeoxygenation (HDO) process offers a possible solution for eliminating C—C double bonds and oxygen atoms with H₂. This process is very similar to conventional hydrorefining processes for the upgrading of petroleum fractions. The development of efficient HDO catalysts is highly important. Currently, supported transition metal (Co, Mo, Ni, and W) sulfides, such as CoMo/γ-Al₂O₃ and NiMo/γ-Al₂O₃, are commonly used in HDO reactions. Nevertheless, the metal content of supported catalysts is limited because of the pore structure of the supports, and thus, it is difficult to meet the demand of high-activity catalysts for HDO reactions. At the same time, the non-negligible metal–support interactions cause the active components to exist in the low-activity single phase (i.e., Co₆S₈ and MoS₆) rather than in the high-activity CoMoS₈ phase. In comparison, unsupported catalysts without any support will supply more active components and exhibit better catalytic performance. The NEBULA™ catalyst family of the Albemarle Catalyst Company is regarded as a representative of unsupported hydropprocessing catalysts, which exhibit at least three times higher HDS activity than traditional CoMoS₈-supported CoMo and NiMo catalysts. The unprecedented activity was thought to originate from the abundant metal components, which provide more active sites for the activation of the substrate and H₂.

The unsupported catalysts show the desired hydrogenation activity; however, the relatively low surface area affects the dispersion and utilization of active components. Therefore, many efforts have been devoted to improving the utilization of active components. Wang et al. prepared unsupported NiMoW sulfide HDO catalysts with different nickel concentrations using a mechanical activation method, which showed high HDO activity toward 4-methylphenol. They found that...
the addition of surfactants not only increased the specific surface area but also changed the microstructure of MoS₂ and subsequently enhanced the HDO activity. Li et al. prepared unsupported Co–Mo sulfide catalysts with different molybdenum disulfide plate-like morphologies through ion exchange. This method improved the dispersion of Mo species in Co–Mo oxides, and thus, the unsupported catalysts showed better activity and selectivity in HDS than did the reference catalysts.¹⁴

Recently, our work revealed that Co–Mo oxides with rod-like structures can be sulfurized into corresponding sulfides with tube-like structures under mild pre-sulfurization conditions,¹⁵,¹⁶ resulting in a higher catalytic desulfurization capacity. This work provided a feasible approach to improve the utilization of active metals inside unsupported catalyst particles. Compared to the conventional pre-sulfurization process, the most notable difference was that we used polar ethanol instead of nonpolar solvents (i.e., dodecane, decalin, and fraction oils) as a pre-sulfurization solvent. Coincidentally, Chen et al. reported that the polarity of the impregnating solution altered the shell layer thickness of Cu-based catalysts, leading to improvements in the surface composition and pore structure.¹⁷ Therefore, it was thought that the polarity of the pre-sulfurization solvents may have similar effects on the microstructure of the Co–Mo sulfides, which subsequently affects the HDO activity of the catalyst. According to our previous experimental results, it was preliminarily deduced that the polar solvent promoted the formation of pores inside the particles, which made these active sites more accessible and efficient. However, detailed investigations are still lacking.

In this work, different unsupported Co–Mo sulfides were prepared through a low-temperature sulfurization process with different solvents. The effects of solvent polarity on the physical characteristics of sulfides and on hydrodeoxygenation reactions were investigated systematically. It was found that CH₃OH was favorable for obtaining catalysts with a moderate pore volume and higher utilization of active components, leading to higher HDO activity and alkane selectivity.

**Experimental section**

**Chemicals**

Ammonium molybdate, cobalt acetate, methanol, ethanol, n-propanol, n-butanol, carbon disulfide, n-dodecane, and stearic acid were purchased from Sinopharm. All of them were of AR standard grade and were used as received without further purification.

**Preparation of the Co–Mo precursor**

Typically, a certain amount of cobalt acetate (8.0 mmol) was dissolved in 50 mL of anhydrous ethanol, and ammonium molybdate (1.1 mmol) was dissolved in 50 mL of deionized water to form two clear solutions. Then, the two solutions were mixed and heated at 95 °C at a stirring rate of 600 rpm to evaporate the solvent. After 2 h, a viscous purple precipitate was obtained. Finally, it was air-dried at 80 °C overnight to remove the remaining water.

**Preparation of the Co–Mo sulfide catalyst**

Co–Mo sulfide was prepared via a low-temperature sulfurization process reported in our previous work.¹⁶ Typically, 0.4 g of the precursor and 30.0 g of the sulfiding agent containing 2.0 wt% CS₂ were added to a 100 mL stainless steel autoclave with mechanical stirring. Then, the reactor was sealed and purged with H₂ to displace the air inside. After that, the reactor was pressurized to 2.0 MPa H₂ at room temperature, heated to 165 °C, and maintained for 6 h with a stirring rate of 600 rpm. After naturally cooling, the sulfide was collected by filtration, washed with ethanol, and then dried at 60 °C for 8 h under vacuum. Before the activity test, the dried sulfide was activated in a tube furnace with H₂ at 350 °C for 2 h and then passivated in 1.0 vol% O₂/Ar at room temperature for 30 min.

See the ESI† for characterization and activity evaluation of materials.

Different solvents, such as H₂O, CH₃OH, CH₃CH₂OH, CH₃(CH₂)₂OH, and CH₃(CH₂)₃OH, were used as sulfiding agents to investigate the effects of the solvent. The obtained Co–Mo sulfide catalysts were labeled Cat-W, Cat-M, Cat-E, Cat-P, and Cat-B, in that order.

**Characterization**

The crystalline structure of the samples was characterized via X-ray diffraction on a Bruker AXS-D8 Advance powder diffractometer. The textural properties were measured by N₂ physical adsorption on a Micromeritics ASAP 2020 system. The morphology and microstructure were observed by scanning electron microscopy (SEM, FEI Quanta200) and high-resolution transmission electron microscopy (HRTEM, JEM-2100). The surface chemical compositions of the sulfides were detected by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific ESCALAB 250Xi spectrometer. For details of the characterization methods, see the ESL†

**Catalytic activity evaluation**

The catalytic activity was evaluated in a 100 mL batch reactor. Typically, 30.0 g of n-dodecane, 2.0 g of SA, and 0.1 g of catalyst were transferred to the reactor. After the air inside the reactor was exchanged with high-purity H₂, the reactor was pressurized to 3.0 MPa at room temperature and then heated to 280 °C with a stirring speed of 700 rpm. The reactor was cooled to room temperature after 4 h, and the liquid product was collected and analyzed using a GC–MS instrument (Agilent 7890A-5975C) equipped with an HP-INNOWAX (30 m × 0.25 mm, 0.25 μm), a DB-HT-SIMDIS (5 m × 0.53 mm, 0.15 μm) and a flame ionization detector (FID). Each activity evaluation was conducted three times to ensure reliability.

The SA conversion was used to describe the HDO activity of the as-prepared catalysts, which can be calculated using the following equation:

\[
δSA (\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]
where $x_{SA}$ is the SA conversion (%), $C_0$ is the SA content in the feedstock (wt%), and $C_t$ is the SA content in the product (wt%).

The apparent reaction rate was calculated using the following equation:

$$r = \frac{W}{m \times t} \times x_{SA}$$

where $r$ is the apparent reaction rate (mol g cat$^{-1}$ s$^{-1}$), $W$ is the number of moles of reactants (mol), $m$ is the catalyst weight (g), and $t$ is the reaction duration (s).

The reaction activation energy was calculated using the following equations:

$$\ln \left( \frac{1}{1-x_{SA}} \right) = k \tau$$

$$k = A e^{E_a / RT}$$

where $k$ is the reaction rate constant, $\tau$ is the contact time (s), $A$ is the prefactor, $E_a$ is the apparent activation energy (kJ mol$^{-1}$), $T$ is the reaction temperature (K), and $R$ is the gas constant (kJ mol$^{-1}$ K$^{-1}$).

Results and discussion

Crystalline structures

The XRD pattern of the Co–Mo precursors in Fig. 1A shows that most diffraction peaks were attributed to the diffraction peaks of CoMoO$_6 \cdot 0.9$H$_2$O (JCPDS No. 14-0086), while some weak diffraction peaks were assigned to CoMoO$_4$ (JCPDS No. 15-0493). No diffraction signals from other substances were observed, indicating that the precursor was composed of cobalt molybdate salt.

The XRD patterns of each sulfide catalyst are shown in Fig. 1B. The diffraction peaks of CoMoO$_4$ disappeared, indicating that the oxide precursor was well transformed to sulfide. All sulfides had similar crystal structures, consisting mainly of the MoS$_2$ phase (JCPDS No. 74-0932) and Co$_9$S$_8$ phase (JCPDS No. 86-2273). The diffraction peak intensity of Co$_9$S$_8$ gradually increased with increasing solvent polarity (Table S1, ESI†), which to some extent indicates that increasing the solvent polarity promoted the growth of the Co$_9$S$_8$ crystallites.

Morphology and structure analysis

Fig. 2A shows the SEM image of the Co–Mo oxide precursor, which consisted of rod-like particles with a cross-section close to a square, and the rod-like particles were composed of smaller particles. During the pre-sulfurization process, the precursors were converted from oxides to sulfides, and the pre-sulfurization solvent had a significant effect on the morphology and structure. As shown in Fig. 2B, when $n$-butanol, a weakly polar solvent, was used, the rod-like particles remained basically unchanged, and there was no hollow structure inside the particles, although the surface became rough. As the solvent polarity increased, the particle surface became rougher, and a hollow structure gradually formed (see Fig. 2C–E). These changes indicate that the higher polarity of the solvent favors the formation of sulfide particles with tube-like structures. The formation of hollow structures is closely related to the dissolution of metal components and the etching of polar solvents. During pre-sulfurization, as the polarity of the solvent increased, the precursor particles were more easily dissolved and etched, and these dissolved nanoparticles were easier to sulfurize than large particles, which allowed the precursor to achieve a higher degree of sulfurization even at lower operating temperatures ($<200 \, ^\circ C$). Thus, Co–Mo sulfides prepared with more polar methanol have obvious and desirable hollow structures. However, when water, a solvent with higher polarity, was used, a tube-like structure was not formed. This is probably because the excellent solubility of water completely destroyed the original rod-like structure, which was replaced by irregular aggregates of nanoparticles.

Textural properties

The N$_2$ physisorption isotherms of different sulfide catalysts are shown in Fig. 3. The isotherms of all catalysts are type II, suggesting the presence of large mesopores and macropores. At higher relative pressures ($>0.8$), the hysteresis loops are small and narrow for all catalysts, indicating larger pore sizes...
and lower specific surface areas. No significant absorption appeared at low relative pressures (<0.1), suggesting that there were no micropores. In addition, all hysteresis loops are of type H3, indicating that the pores were formed by particle aggregation or accumulation.

The specific surface area (SSA) and pore volume (PV) of the prepared catalysts are shown in Fig. 4. Among them, the catalyst Cat-B had the lowest SSA and PV. During pre-sulfurization, the SSA and PV increase and then decrease with increasing solvent polarity. As mentioned above, increasing the solvent polarity not only enhanced the sulfurization of CoMoO₄ but also improved the ability of the solvent to dissolve, etc., the metal components, and both effects facilitated the formation of the internal space of the sulfide particles. The SSA and PV decreased when more polar water was used as the pre-sulfurization solvent because the excessive polarity caused the disappearance of the hollow structure. These results are in agreement with the TEM characterization and showed that the sulfides prepared with methanol have a higher SSA and PV.

**Active phase compositions and microstructures**

XPS data for different sulfide catalysts are shown in Fig. 5. In Fig. 5A, the Mo 3d bands of all the catalysts were deconvoluted into three peaks at 224.0–238.0 eV, which were assigned to MoS₂ 3d⁵/₂, MoS₂ 3d³/₂, and other molybdenum sulfides (Mo⁶⁺/Mo⁵⁺), respectively. In Fig. 5B, the Co 2p⁵/₂ bands were also deconvoluted into three peaks at 776.0–784.0 eV, which were assigned to Co₉S₈, CoMoS phase, and Co²⁺, respectively, according to previous reports.²⁵⁻²⁷ The results suggested that pre-sulfurization solvents with different polarities did not markedly change the surface composition of the catalysts during pre-sulfurization but affected their relative contents to a certain extent. Furthermore, Co²⁺ in the oxidation state was found in the Co 2p spectra of each sulfide but not in the XRD pattern, which indicates that the surface oxide was attributed to the passivation of Co–Mo sulfide catalysts.²⁸⁻²⁹

The composition distribution in Table 1 shows that the concentration of oxides gradually decreased while that of sulfides gradually increased with increasing polarity of the pre-sulfurization solvent. A higher polarity indicates greater solvation, which can promote the dissolution and etching of Co–Mo oxides. Therefore, the crystalline structure of the precursor particles was destroyed, and the particles became more easily sulfurized. During this stage, an increasing number of pores were produced, which further accelerated the diffusion of hydrogen sulfide inside the precursor and ultimately facilitated the sulfurization of the metal oxides. However, further
increasing the polarity of the pre-sulfurization solvent decreased the concentration of the CoMoS phase. Indeed, the pre-sulfurization process is a complex solvothermal process because of the presence of polar solvents. During this process, both the sulfurization of the oxides and the particle growth of the sulfides occurred, and they were enhanced simultaneously as the solvent polarity increased. As a result, the Co atoms tended to form an isolated Co$_9$S$_8$ phase rather than interacting with MoS$_2$ to form CoMoS species in the presence of water. H. Topošek et al.\textsuperscript{30} reported the existence of CoMoS species, which are regarded as highly active species and exhibit excellent catalytic activity in the HDO of triglycerides and their derivatives. Thus, a catalyst (Cat-M) with more CoMoS will have higher activity.

Based on the experimental results and theoretical calculations, the morphology of the (Co)MoS$_2$ slabs, including the length and stacking number, was verified to significantly affect the rate of the HDO reaction and product selectivity.\textsuperscript{31,32} Therefore, the slab lengths and stacking numbers of all the catalysts were measured by HRTEM (see Fig. S1, ESI†), and the calculation results are shown in Fig. 6. During pre-sulfurization, the slab length decreases as the polarity of the alcohol solvent increases but becomes longer when water, a more polar solvent, is used. For the alcohol solvents, as the polarity increased, the dissolution of metal atoms accelerated, inducing the destruction of the CoMoO$_4$ particles into small ones. Nevertheless, the rod-like structure of the CoMoO$_4$ precursor was not completely destroyed. Due to the different polarities of the alcohol solvents, the CoMoO$_4$ structure was preserved to varying degrees; as shown in Fig. 2, the structure of Cat-M was tube-like, while that of Cat-B was still rod-like. Although the pre-sulfurization

![Figure 5](image_url)  
**Fig. 5** (A) The Mo 3d spectra of Cat-W, Cat-M, Cat-E, Cat-P, and Cat-B and (B) Co 2p spectra of Cat-W, Cat-M, Cat-E, Cat-P, and Cat-B.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>MoS$_2$</th>
<th>Mo$^{6+}$/Mo$^{5+}$</th>
<th>Co$_9$S$_8$</th>
<th>CoMoS</th>
<th>Co$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-W</td>
<td>75.9</td>
<td>24.1</td>
<td>33.1</td>
<td>26.9</td>
<td>40.0</td>
</tr>
<tr>
<td>Cat-M</td>
<td>71.5</td>
<td>28.5</td>
<td>18.1</td>
<td>31.8</td>
<td>50.1</td>
</tr>
<tr>
<td>Cat-E</td>
<td>69.3</td>
<td>30.7</td>
<td>17.6</td>
<td>29.4</td>
<td>53.0</td>
</tr>
<tr>
<td>Cat-P</td>
<td>63.5</td>
<td>36.5</td>
<td>16.1</td>
<td>26.4</td>
<td>57.5</td>
</tr>
<tr>
<td>Cat-B</td>
<td>61.3</td>
<td>38.7</td>
<td>15.5</td>
<td>23.3</td>
<td>61.2</td>
</tr>
</tbody>
</table>

![Figure 6](image_url)  
**Fig. 6** Layer length (A) and stacking number (B) of the (Co)MoS$_2$ slabs in various Co–Mo sulfide catalysts.
process also destroyed the structure of the CoMoO₄ precursor because metal–O bond cleavage and S–O exchange reactions occurred, relatively complete CoMoO₄ particles were not easily sulfurized and thus tended to generate longer (Co)MoS₂ slabs. When a strongly polar solvent, water, was used instead of alcohol, the rod-like structure of the CoMoO₄ precursor was completely destroyed during pre-sulfurization (see Fig. 2F), and then, the sulfide crystallites generated in situ underwent a hydrothermal growth process, resulting in longer (Co)MoS₂ slabs.

A sulfide consisting of shorter (Co)MoS₂ slabs corresponds to a greater proportion of Mo atoms at corner sites. According to DFT calculations, the corner sites of the (Co)MoS₂ slabs preferred to create coordinatively unsaturated sites (CUSs) rather than edges, which may promote the adsorption of oxygen atoms to lipids and their derivatives. Therefore, increasing the polarity of the pre-sulfurization solvent improved the HDO performance of the sulfurization catalyst. In Fig. 6b, the stacking number of the slabs for the as-prepared catalysts was mainly distributed in 3–5 layers, which was not significantly affected by the solvent polarity in comparison with the slab length. It was found that the CoMoS species in supported Co–Mo catalysts have two microstructures: monolayered slabs (so-called type I) and multilayered slabs (so-called type II). and the latter were much more active because they had a higher degree of sulfurization and more accessible active sites. Herein, all of the catalysts did not have oxide supports; thus, a monolayered (Co)MoS₂ slab was not found, and only a highly active multilayered slab appeared in the TEM images.

Based on the results shown in Fig. 6, the average length and stacking number of (Co)MoS₂ slabs and the distribution of Mo atoms on edge/corner sites were calculated (see Table 2). Since the average length is the shortest, the Cat-M catalyst has the highest fc/fc ratio, indicating a relatively large number of Mo atoms at the corner sites of the (Co)MoS₂ slabs. fc is usually calculated without considering the stacking number, while the parameter, especially the number of accessible Mo atoms, directly affects the number of active sites. Thus, the ratios of N/L were used to describe the relationship between the morphology of the (Co)MoS₂ slabs and the number of corner sites. A higher ratio suggests that the catalyst may offer more Mo atoms at the corner sites; thus, the Cat-M catalyst will possess a higher HDO activity.

### HDO activity tests

Considering that the reaction was performed in a batch reactor, and the conversion will be greatly affected by the stirring rate because of the external diffusion of reactant molecules, the suitable stirring rate should be determined before activity tests to eliminate the effect of external diffusion. As shown in Fig. S2 (ESI†), the conversion of stearic acid (SA) first increased with the stirring rate and then became stable beyond 600 rpm. Therefore, the stirring rate was set at 700 rpm.

Stearic acid was used as the model reactant to evaluate the HDO activity of the as-prepared Co–Mo sulfides, and the reaction results are shown in Table 3. The seven liquid products heptadecane (C₁₇), heptadecene (C₁₇=), octadecane (C₁₈), octadecene (C₁₈=), octadecenal (C₁₈=CHO), and C₃₆–ester (C₃₆=) were detected by GC–MS, where C₃₆–ester was the main deoxygenation product intermediate for each catalyst. The conversion of SA over Cat-M had the highest reaction rate (7.3 × 10⁻⁷ mol g_cat⁻¹ s⁻¹) and selectivity for completely deoxygenated products (10.1 wt%). Zhang et al. showed that cobalt promoted hydrogen adsorption at the sulfur site to produce stable hydrogen bonds and that the (Co–)SH group had the most stable H on the Co-decorated S-edge. The weak bonding between the S and Co atoms favored a strong interaction between the terminal S and H atoms. The formed –SH group was highly nucleophilic and attracted to electrophilic C atoms with or near carboxyl groups. Then, the C–C bond was cleaved to form C₁₇ or C₁₇=, C₁₈, C₁₇=CHO, and C₁₈=OH were produced by direct hydrodeoxygenation (direct-HDO), referred to as the removal of O atoms in the form of H₂O. DFT calculations of electronic effects confirmed that the promotion effect of Co arose from electron transfer from Co to MoS₂, which can weaken the Mo–S bond energy to produce more CUS vacancies and thus increase the cleavage rate of the C–S bond and promote the hydrodesulfurization reaction. This mechanism is also applicable to hydrodeoxygenation reactions. SA was first converted by C–O hydrolysis, and one molecule of water was released to form C₁₇=CHO as the primary product. Subsequent hydrogenation converted C₁₇=CHO into C₁₈=OH, which was then deoxygenated by an elimination reaction to C₁₈=. Followed by hydrogenation to produce C₁₈. C₃₆–e was produced via esterification reaction between SA and in situ-generated C₁₈=OH.

The effect of reaction temperature on the hydrodeoxygenation of SA was investigated at 240 °C, 260 °C, and 280 °C using five sulfides as catalysts, and the reaction results are shown in Table 3 and Tables S2 and S3 (ESI†). The conversion of SA for the five catalysts increased as the reaction temperature increased from 240 °C to 280 °C. As the reaction temperature increased, the yields of C₁₇= (the total decarbonylation products, including C₁₇ and C₁₇=) and C₁₈= (the total deoxygenation products, including C₁₈ and C₁₈=) showed a noticeable temperature dependence, the C₁₈/C₁₇= ratios gradually increased with increasing SA conversion for all catalysts. For the Cat-M catalyst, the C₁₈/C₁₇= ratios were 1.3, 1.4, and 1.6 at different temperatures, suggesting that elevated temperature was more favorable for direct-HDO.

The results in Fig. 7 show that the activity of the catalysts gradually increased with increasing polarity of the presulfurization solvents but decreased when water was used as the solvent. According to the XPS analysis results, the catalytic
activity of the Co–Mo catalysts was dependent on the number of CoMoS species. In addition, the reaction rate of SA was closely related to the ratio of the Mo atoms at the corner and edge sites (Fig. S3, ESI†). It is generally accepted that the CUS located at the edge and corner of MoS$_2$ slabs are the active sites for the HDO reaction. Before the conversion, SA molecules were preferentially adsorbed on the CUS by the O atom in the carbonyl group (C$\equiv$O) because of their highly nucleophilic character.\textsuperscript{39} DFT calculations revealed that those active CUS were more easily formed at corner sites than at edge sites under hydrogenation reaction conditions, both for MoS$_2$ and Co-promoted MoS$_2$.\textsuperscript{37} A higher f$_c$/f$_e$ ratio indicated that there were more Mo atoms at the corner sites for the adsorption and activation of the carboxyl groups in SA. Thus, compared with the other catalysts, Cat-M exhibited a greater SA reaction rate. Notably, the reaction rate was affected by two reactions, namely, (1) SA hydrogenation to C$_{17}$–CHO and (2) SA esterification to C$_{36}$–e. Since the C$_{18}$–OH for reaction (2) was produced by the continuous hydrogenation of SA, reaction (2) progress was directly controlled by reaction (1). Thus, it was concluded that the total conversion of SA was dependent on the hydrogenation activity of CUS on the (Co)MoS$_2$ slabs, although reaction (2) may also be catalyzed simultaneously because of the Lewis acid nature of CUS.

In addition, based on the experimental results, the reaction rate constants of SA at different temperatures were calculated and the relationship of ln $k$ versus $1/T$ was plotted, and the apparent activation energies ($E_a$) for the hydrodeoxygenation of SA were obtained from the slopes of the best-fit straight lines ($R^2 > 0.99$). The results in Fig. 8 show that the energy increased in turn: Cat-M (77.7 kJ mol$^{-1}$) < Cat-E (79.1 kJ mol$^{-1}$) < Cat-W (80.3 kJ mol$^{-1}$) < Cat-P (81.1 kJ mol$^{-1}$) < Cat-B (104.4 kJ mol$^{-1}$), further indicating that catalyst Cat-M has the highest hydrogenation activity.

Fig. 9 shows the conversion of SA over Cat-M at 280 °C with different contact times. The main products at the beginning of the reaction were C$_{18}$–OH and C$_{36}$–e, and the latter was generated by rapid esterification of C$_{18}$–OH with SA. While the content of C$_{17}$–CHO was always lower than that of C$_{18}$–OH because the hydrogenation rate of C$_{17}$–CHO was much faster. C$_{18}$Q production and consumption were observed, indicating that C$_{18}$Q arose from C$_{18}$–OH dehydration, which was subsequently hydrogenated to C$_{18}$. In addition to the HDO route, C$_{17}$–CHO can also be decarboxylated to C$_{17}$Q, and then was hydrogenated to C$_{17}$. Note that when SA conversion was below 80%, the yields of C$_{17}$Q and C$_{18}$Q increased with the conversion, and were higher than that of C$_{17}$ and C$_{18}$ accordingly, indicating that alkene hydrogenation to alkane was slower than SA hydrogenation under the set reaction conditions. This is because the competitive adsorption of SA on the active sites inhibited the alkene hydrogenation reaction.\textsuperscript{40,41} The C$_{36}$–e

![Fig. 7](image-url) Effect of the reaction temperature on the conversion of SA over various sulfide catalysts.

![Fig. 8](image-url) Arrhenius plots of various Co–Mo sulfide catalysts in SA conversion.

### Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>C$_{17}$</th>
<th>C$_{17}$–CHO</th>
<th>C$_{18}$</th>
<th>C$_{18}$–OH</th>
<th>C$_{36}$–e</th>
<th>Rate ($\times 10^{-7}$ mol g$_{cat}$$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-W</td>
<td>12.0</td>
<td>0.9</td>
<td>2.5</td>
<td>1.8</td>
<td>3.4</td>
<td>14.4</td>
<td>22.9</td>
</tr>
<tr>
<td>Cat-M</td>
<td>14.9</td>
<td>1.0</td>
<td>3.3</td>
<td>1.8</td>
<td>4.0</td>
<td>6.7</td>
<td>21.7</td>
</tr>
<tr>
<td>Cat-E</td>
<td>13.6</td>
<td>1.1</td>
<td>3.6</td>
<td>1.4</td>
<td>3.4</td>
<td>6.5</td>
<td>21.6</td>
</tr>
<tr>
<td>Cat-P</td>
<td>11.8</td>
<td>1.2</td>
<td>3.5</td>
<td>1.4</td>
<td>3.3</td>
<td>6.8</td>
<td>17.9</td>
</tr>
<tr>
<td>Cat-B</td>
<td>7.6</td>
<td>1.2</td>
<td>4.9</td>
<td>1.5</td>
<td>3.8</td>
<td>8.1</td>
<td>20.4</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial H$_2$ pressure (3.0 MPa), reaction temperature (240 °C), stirring rate (700 rpm), reaction duration (4 h). $^b$ To accurately calculate the reaction rate, the conversion was controlled at a low level (<15%) to eliminate concentration gradient effects.
deoxygenation was slower probably because its large molecule size inhibited the contact of the ester functional groups with the active sites and further activation.42 Thus, the reaction temperature can be increased to degrade the C_{36}^{–e} to octadecanol and octadecane, which was further hydrogenated and deoxygenated directly to obtain hydrocarbons.43

It is well known that sulfide catalysts, such as the NEXBTL technology from the Neste Oil Company and the Ecofining\textsuperscript{TM} process from the ENI/Honeywell-UOP,44 are used for the commercial production of second-generation biodiesel, and the reaction temperature is usually in the range of 280–350 °C. Therefore, the effect of reaction temperature on the hydrodeoxygenation of stearic acid was further investigated, and the results are shown in Table 4. When the reaction temperature increased from 280 °C to 300 °C, the SA conversion further increased, and C_{36}^{–e} disappeared. The main products were alkane compounds, and the ratio of C_{18}/C_{17} was approximately 3.4, suggesting that direct HDO was the major reaction route. Further increasing the temperature to 320 °C did not markedly change the selectivity for alkanes. In addition, a small amount of alkane isomerization products was produced during the reaction, indicating the Cat-M catalyst exhibited a certain degree of isomerization/cracking. Comparative experiments were also conducted for the hydrodeoxygenation of SA under the same reaction conditions using rod-like sulfide (r-CoMoS) (see Fig. S4, ESI\textsuperscript{†}) and supported sulfide (CoMoS/γ-Al_{2}O_{3}) as catalysts (see Table S4, ESI\textsuperscript{†}). The results show that the selectivity of C_{16}^{–e} reached 23.2 wt% when r-CoMoS was used as the catalyst, indicating that the solid structure was not favorable for the conversion of macromolecular esters. Compared with those of Cat-M, both r-CoMoS and CoMoS/γ-Al_{2}O_{3} exhibited greater selectivity for $C_{17}^{=}$ and $C_{18}^{=}$, suggesting that the two catalysts are relatively ineffective for hydrogenation.

In addition, the reusability of the Cat-M catalyst was evaluated. Before each reuse, the used catalyst was washed three times with hexane and dried in a vacuum oven at 50 °C. Moreover, a small amount of fresh catalyst would be supplemented based on the loss of catalyst in the recovery process (loss rate not exceeding 10 wt%). As shown in Table S5 (ESI\textsuperscript{†}), the conversion of stearic acid and the selectivity of the fully deoxygenated product remained almost unchanged after five cycles, indicating good active stability of the Cat-M catalyst. Furthermore, the Cat-M catalyst after reaction for 30 h was characterized by XRD (see Fig. S5, ESI\textsuperscript{†}) and XPS (see Fig. S6, ESI\textsuperscript{†}), and the distribution of the surface-active species was calculated (see Table S6, ESI\textsuperscript{†}). The results show that the crystal structure and active phase composition of the Cat-M catalyst remained basically unchanged, indicating good chemical stability.

**Table 4** Effects of the reaction temperature on SA conversion and product selectivity over the Cat-M catalyst\textsuperscript{a}

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Conv. (%)</th>
<th>Selectivity (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{17}$</td>
<td>$C_{17}^{=}$</td>
</tr>
<tr>
<td>280</td>
<td>94.2</td>
<td>3.6</td>
</tr>
<tr>
<td>300</td>
<td>98.0</td>
<td>22.0</td>
</tr>
<tr>
<td>320</td>
<td>100.0</td>
<td>20.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: catalyst (0.1 g), SA (2.0 g), dodecane (30.0 g), initial H\textsubscript{2} pressure (3.0 MPa), stirring rate (700 rpm), reaction duration (12 h). \textsuperscript{b} Includes alkane isomerization and cracking products.

**Conclusions**

In this work, porous tubular Co–Mo sulfide particles were prepared via a low-temperature pre-sulfurization method. The polarity of the pre-sulfurization solvent plays a key role in the hydrodeoxygenation activity of the catalyst. In a certain range, the higher polarity of the pre-sulfurization solvent can promote the diffusion effect of the active metal ions and enhance the solvent's ability to dissolve and etch the Co–Mo oxide precursor, which is conducive to the formation of hollow structures with higher specific surface areas. In addition, the higher polarity of the pre-sulfurization solvent promoted the sulfuration of the CoMoO\textsubscript{4} precursor and the formation of type II (Co)MoS\textsubscript{2} active slabs with shorter lengths and greater stacking numbers, leading to more Mo atoms at the corner positions. The HDO reaction rate and complete deoxygenation product yield for the Cat-M catalyst were greater than those of the other catalysts due to its larger specific surface area, higher CoMoS surface concentration and greater number of Mo atoms at the corner sites.

**Author contributions**

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is financially supported by the Shandong Provincial Natural Science Foundation of China (Grant No. ZR2020MB029) and the Shandong Energy Institute (SEI) (Grant No. SEI I202103).

References