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Highly efficient unsupported Co-doped nano- MoS_2 catalysts for *p*-cresol hydrodeoxygenation

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ABSTRACT

To prepare catalyst with high activity, high selectivity and good stability remains the biggest challenge in the hydrodeoxygenation (HDO) of phenols by adopting MoS_2 -based sulfides as catalysts. Herein, we report a simple hydrothermal method to synthesize highly-dispersed nano- MoS_2 with abundant defects and some curved slabs. All these advantages enable nano- MoS_2 to provide a large number of coordination unsaturated sites to anchor Co atoms. The unsupported Co-doped catalyst with an optimal Co/(Co + Mo) molar ratio of 0.3 exhibited excellent performance in the HDO of *p*-cresol with conversion of 98.7 % and toluene selectivity of 98.9 % at 220 °C. Moreover, the optimized Co/MoS_2-0.3 catalyst had a good stability after reaction of 72 h. The excellent HDO performance was attributed to the formation of abundant Co-Mo-S active sites which optimize the electrical structure of nano-MoS_2 by Co promoter.

1. Introduction

In recent years, bio-oil derived from biomass has become a green, alternative and promising liquid fuel due to the depletion of petrochemical resources and the enforcement of stricter environmental regulations [1–4]. However, bio-oil resulted from fast-pyrolysis of lignocellulosic materials contains a high content of oxygenated compounds, which hinders its direct application because of some disadvantages such as poor thermal stability, low heating value and corrosivity [5,6]. As recently reported, hydrodeoxygenation (HDO) was considered as a potential method for upgrading of bio-oil [7–9]. The biggest challenge in producing high quality bio-oil is how to efficiently reduce the oxygen content while minimizing the hydrogen consumption. To achieve this goal, it is necessary to develop HDO catalysts with high activity, high selectivity and good stability.

A variety of catalytic systems have been reported for the HDO of biooil including noble metal catalysts [10–12], Ni-based catalysts [13–15], phosphides [16,17] and sulfides catalysts [18,19]. Compared with the high price of noble metals and the low activity of phosphide catalysts, MoS_2 -based sulfides have been proposed as promising candidates due to the low cost and high efficiency for the HDO of phenol compounds. However, for traditional CoMoS/Al₂O₃ or NiMoS/Al₂O₃ supported catalysts, the reaction temperature is usually higher than 300 °C and the HDO activity is not particularly ideal [20]. It was reported that unsupported MoS₂-based catalysts exhibited better HDS and HDO performance than supported catalysts due to their higher active site density [21–25]. Hence, the preparation of highly dispersed MoS₂-based catalysts is of great importance for developing highly efficient unsupported HDO catalysts and reducing the catalyst manufacturing costs for industrial applications.

Nano-MoS₂ could be synthesized by a lot of methods such as hydrothermal [26,27], thermal decomposition [28,29], ball-milling [30, 31] and solution method [32,33]. Because of its simple operation and controllable morphology, hydrothermal method is considered to be the most promising synthesis method. For example, Song et al. synthesized CoMoS nanosulfides by surface engineering and achieved a 100 % conversion in the HDO of *p*-cresol at 300 °C and 4 MPa [23]. Wang at al. also reported a 100 % *p*-cresol conversion at 275 °C and 4 MPa utilizing unsupported Co-Mo-S catalyst prepared by a one-step hydrothermal method [21]. However, the HDO activity was decreased to 94.6 % after recycling for 5 times due to the harsh reaction conditions. Therefore, the HDO activity of unsupported Co-Mo-S catalysts still need to be enhanced

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to make the reaction take place under milder conditions to improve the stability.

Herein, we report a facile hydrothermal method to prepare highly dispersed nano- MoS_2 with slab length of 10-20 nm and layer number of 2-4 layer. Abundant defects and some curved structures were also found on the as-prepared nano- MoS_2 catalyst. After doped with a series amount of Co, the unsupported MoS_2 and Co-promoted MoS_2 catalysts were evaluated in the HDO of a model bio-oil containing *p*-cresol as probe. Afterwards, the corresponding catalysts were characterized by XRD, N₂-physisorption, SEM, HRTEM, XPS and TPR in detail. Then, the structure-HDO performance correlation of Co-promoted MoS_2 catalysts was revealed. Finally, the stability of optimized catalyst was investigated, and comparison of its HDO performance along with other Co-doped MoS_2 unsupported catalysts was conducted.

2. Experimental section

2.1. Materials

All the chemicals and reagents were used without further purification. Molybdenum trioxide (MoO₃, 99.9%), sodium sulfide nonahydrate (Na₂S·9H₂O, 98.0%), dodecane (99.5%), *p*-cresol (99.0%), *n*-octane (99.0%) and cobalt(II) acetate tetrahydrate (Co(CH₃COO)₂·4H₂O, 99.9%) were purchased from Aladdin Chemical Reagent Co., Ltd. Absolute ethanol (AR) and hydrochloric acid (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Catalyst preparation

Nano-sized MoS₂ was synthesized by a one-pot hydrothermal method. Typically, MoO₃ (1.4496 g) and Na₂S·9H₂O (9.0638 g) were dissolved in 80 mL deionized water firstly. Then, HCl (11.5 mL, 4 M) was added and stirred for 15–20 min furtherly. Finally, the solution was transferred into a 150 mL high-pressure stainless steel autoclave and heated at 320 °C for 2 h. The obtained black products were washed with deionized water and absolute ethanol for several times, dried at 60 °C under vacuum.

Co-promoted catalysts were prepared by impregnating the asprepared MoS₂ with different amount of Co(CH₃COO)₂·4H₂O. The obtained catalysts were denoted as Co/MoS₂-*x*, where *x* represents the molar ratio of Co/(Co + Mo). All the catalysts were pelleted and crushed to 20–40 mesh before catalytic evaluation.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker diffractometer with Cu Ka radiation. Nitrogen physisorption isotherms were obtained on a Micromeritics ASAP 2020 instrument. Metal content of Co/MoS_2 -x samples were determined by an ICPS-8100 spectrometer. The carbon and sulfur content were determined by a Thermo FLASH 2000 CHNS analyzer. Raman spectra was obtained on a Renishaw instrument (532 nm). The morphology of catalysts was observed on a JSM-6330f field emission scanning electronic microscopy (FESEM). Highresolution transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2100 electron microscope at the accelerating voltage of 200 kV. Temperature programmed reduction (TPR) analysis was conducted on a home-made instrument. Typically, 30 mg samples were pretreated under Ar atmosphere at 130 °C for 1 h and cooled down to room temperature. Then, the samples were heated to 600 $^\circ C$ under 5 vol.% $\mathrm{H_{2}/Ar}$ and the signal was detected with a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) characterization was carried out on a Thermo ESCALAB 250Xi spectrometer using an Al K α radiation (1486.6 eV). It should be noted that all Co/MoS₂-x samples were freshly sulfided at 400 $^\circ C$ for 2 h under 10 vol.% H_2S/H_2 (60 mL/min) before characterization.



Fig. 1. (a) p-cresol conversion and (b) toluene selectivity over $\rm MoS_2$ and Co/ $\rm MoS_2\text{-}x$ catalysts versus reaction time.

2.4. Catalytic performance evaluation

The hydrodeoxygenation performance tests of catalysts were carried out on a high pressure fixed-bed reactor with a catalyst loading of 0.5 g (20–40 mesh). A model bio-oil consists of *p*-cresol (3.0 wt.%), dodecane (solvent, 96.0 wt.%) and *n*-octane (internal standard, 1.0 wt.%) was utilized as feedstock. The catalytic tests were carried out at conditions: 180–220 °C, 3 MPa, a liquid hourly space velocity (LHSV) of 10 h⁻¹ and H₂/feed volumetric ratio of 300 Ncm³/cm³. Before measurements, the Co-promoted catalysts were pre-sulfided at 400 °C for 2 h under a gas flow of 10 vol.% H₂S/H₂ (60 mL/min). The liquid products after reaction were analyzed by an Agilent 7890B gas chromatograph equipped with a flame ionization detector (FID) and HP-1 capillary column (100 m). The kinetic rate constant was calculated by the following equation and assuming the reaction as a pseudo-first-order reaction.

$\ln\left(1 - x\right) = -kt$

where *x* represents the conversion of *p*-cresol, *t* is the reaction time (1/LHSV) and *k* is the pseudo-first-order rate constant (h^{-1}). All the rate constants were calculated at a low HDO conversion (< 40 %). Besides, all the reaction data were repeated two times to ensure the accuracy.

3. Results and discussions

3.1. HDO performance of p-cresol on MoS₂ and Co/MoS₂-x catalysts

The unsupported MoS₂ and Co/MoS₂-x catalysts were evaluated by

Table 1

	$O/MoS_2 - x$ catalysts.
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	MoS_2		$Co/MoS_2-0.$	1	Co/MoS ₂ -0.3	3	Co/MoS ₂ -0.5	5
Temperature (°C)	180	220	180	220	180	220	180	220
Conversion (%)	3.8	16.9	17.7	85.6	37.1	98.7	22.3	88.6
$k (h^{-1})$	0.39	/	1.95	/	4.64	/	2.52	/
Products selectivity (%)								
Toluene	62.4	65.0	91.2	93.4	96.0	98.9	92.9	95.3
3-Methylcyclohexene	12.8	4.2	1.0	0.7	0.3	0	1.0	0.5
Methylcyclohexane	24.8	30.8	7.8	5.9	3.7	1.1	6.1	4.2
HYD/DDO	0.60	0.54	0.10	0.07	0.04	0.01	0.08	0.05

Reaction conditions: 180 and 220 °C, 0.5 g catalysts, 3 MPa, LHSV of 10 h^{-1} and H_2 /feed volumetric ratio of 300 Ncm³/cm³. HYD/DDO = (Methylcyclohexane + 3-Methylcyclohexene)/Toluene.

Table 2

Effect of H₂ pressure on the HDO performance of Co/MoS₂-0.3.

Catalyst	Co/MoS ₂ -0.3			
Pressure	1 MPa	2 MPa	3 MPa	
Conversion (%)	49.2	77.7	98.7	
Products selectivity (%)				
Toluene	100	99.5	98.9	
3-Methylcyclohexene	0	0	0	
Methylcyclohexane	0	0.5	1.1	

Reaction conditions: 220 $^\circ C$, 0.5 g catalysts, 1–3 MPa, LHSV of 10 h^{-1} and $H_2/$ feed volumetric ratio of 300 Ncm^3/cm^3 .

employing the HDO of *p*-cresol as probe reaction. As shown in Fig. 1, all the catalysts kept steady conversion and toluene selectivity under 10 h reaction. The detailed catalytic performance data of MoS_2 and Co/MoS_2 -*x* catalysts was listed in Table 1. For non-promoted MoS_2 catalyst, the conversion was rather low (only 16.9 %) at 220 °C and 3 MPa. However, a significantly improved conversion of 85.6 % was achieved for Co/ MoS_2 -0.1, which suggests a small amount of cobalt can effectively enhance the performance of MoS_2 catalyst. As the Co content continues to increase, the conversion reached a peak value of 98.7 % for Co/ MoS_2 -0.3 and then showed a decrease to 88.6 % for Co/ MoS_2 -0.5. This activity trend indicates that a reasonable amount of Co incorporation can optimize the catalytic performance of MoS_2 , while excessive amount of Co will contrary result in a decrease of catalytic activity.

As for the product distribution, three products including toluene, 3methylcyclohexene and methylcyclohexane for the HDO of p-cresol were detected. It is widely accepted that hydrodeoxygenation of phenols proceeds along with two main routes: namely direct deoxygenation (DDO) and hydrogenation-dehydration (HYD) [34]. The product of former path is toluene, which is beneficial for minimizing the hydrogen consumption (Fig. S1). The toluene selectivity was increased following the same order with conversion: MoS_2 (65.0 %) $< Co/MoS_2$ -0.1 (93.4 %) < Co/MoS_2-0.5 (95.3 %) < Co/MoS_2-0.3 (98.9 %). This indicates that all Co-doped catalysts are dominated by DDO path, and Co addition into MoS₂ is helpful to enhance the activity of DDO route. The rate constants of all catalysts were also calculated at a low conversion to compare their intrinsic activity. It is clearly seen that Co/MoS₂-0.3 had a reaction rate of 4.64 h⁻¹ and was much higher than non-promoted MoS₂ catalyst (nearly 12 times), which implies the efficient Co incorporation to form a high content of active phase. This result is also much better than the previously reported Co-doped MoS_2 nanoflowers (0.68 h⁻¹) [22].

The effect of reaction parameters such as temperature and H₂ pressure on the catalytic performance was also investigated. As shown in Table 1, all the catalysts exhibited improved HDO conversion and toluene selectivity with reaction temperature increased from 180 °C to 220 °C. This indicates high temperature is more conducive to the direct deoxygenation path, which was explained by the higher activation energy of DDO route than HYD route. H₂ pressure also had an influence on the *p*-cresol conversion and product distribution. As listed in Table 2, with H₂ pressure increased from 1 MPa to 3 MPa, the HDO conversion of



Fig. 2. XRD patterns of MoS_2 and Co/MoS_2 -x catalysts.

Co/MoS₂-0.3 increased form 49.2% to 98.7% while the toluene selectivity showed a decrease from 100 % to 98.9 %. This phenomenon was consistent with previous study and explained by the improved hydrogen solubility in liquid phase at high H₂ pressure [35]. Although high hydrogen pressure is favorable for the HYD pathway, the toluene selectivity of 98.9 % also proves the high direct deoxygenation activity of Co/MoS₂-0.3 catalyst which helps to reduce the hydrogen consumption.

3.2. Characterization of MoS₂ and Co/MoS₂-x catalysts

Fig. 2 shows the XRD patterns of unsupported MoS₂ and Copromoted catalysts. The MoS_2 sample exhibited four broad peaks at 2θ $= 14^{\circ}, 33^{\circ}, 39^{\circ}$ and 59° corresponding to (002), (100), (103) and (110) crystal planes of 2H-MoS₂, which suggests a poor crystallite structure. Besides, stacking height of MoS₂ materials along the *c*-axis direction could be obtained utilizing the full width at half-maximum intensity (FWHM) of the (002) diffraction peak by Scherrer equation. The calculated layer number of MoS2 was 2.8 which indicates a few layer structure. With the addition of Co, the diffraction peaks of MoS2 become broaden gradually, suggesting a decreased MoS₂ crystallinity caused by the formation of Co-Mo-S phase. For Co/MoS₂-0.1, the Co species were well incorporated and highly dispersed on the surface of MoS₂ because no separated $Co_x S_y$ phase was observed. With the increase of Co amount, some other peaks at $2\theta = 30^{\circ}$, 31° , 48° and 52° assigned to Co_9S_8 [36] were found. Additionally, large Co₉S₈ aggregates were formed on Co/MoS₂-0.5, resulting in a marked reduced crystallinity degree of MoS₂ support.

Fig. 3 shows the nitrogen adsorption-desorption isotherms and pore size distribution curves of MoS₂ and Co/MoS₂-x catalysts. All the samples had typical type IV isotherms and H3 hysteresis loops which are characteristics of slit-shape mesoporous materials. The surface area and



Fig. 3. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of MoS_2 and Co/MoS_2 -x catalysts.

 Table 3

 Physical properties of MoS₂ and Co/MoS₂-x catalysts.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	n(Co)/n (Co + Mo) ^a	MoS ₂ size (nm) ^b
MoS ₂	131	0.55	2.5, 9.4	/	13.1
Co/	98	0.30	2.5, 6.7	0.1	14.2
MoS ₂ -					
0.1	77	0.24	22.06	0.2	12.0
MoS	//	0.24	2.3, 8.0	0.3	13.8
0.3					
0.3 Co/	32	0.11	2.3	0.5	13.5
MoS ₂ -					
0.5					

^a Determined by ICP analysis.

^b Determined by HRTEM statistical analysis.

pore volume of MoS_2 are $131 \text{ m}^2/\text{g}$ and $0.55 \text{ cm}^3/\text{g}$, which are relatively high values for reported unsupported MoS_2 materials synthesized by hydrothermal method. With the introduction and increase of Co, the specific surface area and pore volume of catalysts decreased gradually, indicating that Co species had successfully filled the pore channels (Table 3). Moreover, the bimodal pore structure of MoS_2 catalyst gradually changed into single small pores after adding a large amount of Co, which was probably caused by the pore blockage of large Co_9S_8 particles.

The morphologies of MoS_2 and Co/MoS_2 -*x* catalysts were observed by SEM and HRTEM characterization. As shown in Fig. 4a and b, MoS_2 and Co/MoS_2 -x showed a typical flower structure with size about 150-200 nm. These nanoflowers are aggregated by MoS₂ nanosheets in order to reduce the total surface energy. By increasing Co content, the surface of MoS₂ nanosheets gradually becomes rough due to the interaction between Co and MoS₂, thus resulting in a weakened flower-like structure (Fig. 4c). For Co/MoS₂-0.5, Co₉S₈ particles with large size were found to deposit on the MoS2 surface because of excessive Co addition (Fig. 4d). HRTEM images of MoS₂ catalyst show a typical lamellar structure with layer spacing of 0.65 nm (Fig. 5a and Fig. S2a). In addition, it is obvious that most MoS2 particles have slab length of 10-20 nm and layer number of 2-4 layer. A statistic distribution was conducted by counting 200 MoS₂ particles and the result is shown in Fig. S3. The calculated average slab length and layer number is 13.1 nm and 2.87 layer. This indicates the MoS₂ catalyst is high dispersed, which is advantageous to expose more active sites. Meanwhile, some irregular fringes such as basal curvature and defects were also found. It has been previously reported that the curved or defect-rich MoS₂ slabs could generate new active sites on the original inert basal planes, which is beneficial to improve its catalytic performance in hyrodesulfurization, hydrodeoxygenation and electro-catalysis [24,37,38]. For Co-doped catalysts, the statistical MoS₂ average size of Co/MoS₂-0.1, Co/MoS₂-0.3 and Co/MoS₂-0.5 was 14.2, 13.8 and 13.5 nm, respectively (Table 3). The decreased size was caused by the inhibition effect of Co to the growth of MoS₂ crystallites during the high temperature sulfidation process. Besides, no lattice fringes assigned to any Co_xS_y phase could be observed for Co/MoS₂-0.1 and Co/MoS₂-0.3. Although the diffraction peaks of Co₉S₈ appears on the XRD pattern of Co/MoS₂-0.3, the particles are too small to be observed. However, another group of lattice fringes with interlayer spacing of 0.58 nm corresponding to (111) planes of Co₉S₈ were observed for Co/MoS₂-0.5 (Fig. 5d and Fig. S2b). The approximate size of Co₉S₈ particles is 8–10 nm, which is consistent with the results of large particles observed by XRD and SEM. Elemental analysis results of Co/MoS₂-0.3 catalyst in Fig. S4 display a homogeneously distribution of cobalt, molybdenum and sulfur elements, which further proves the formation of "Co-Mo-S" active phase.

The surface valence states and species distribution of the catalysts were analyzed by XPS. Fig. 6a and b show the Mo3d and S2p spectra of MoS₂ catalyst. Two main peaks located at binding energy of 229.0 and 232.2 eV are attributed to Mo3d_{5/2} and Mo3d_{3/2} of Mo(IV) species [39]. Besides, very few amount of Mo(V) and Mo(VI) species at 233.3 eV and 235.2 eV were found after carefully deconvoluting the Mo3d spectra. This means that the Mo precursors are highly sulfided and most of the Mo species exist in Mo(IV) active phase. As for the sulfur species, the doublet at 161.9 eV and 163.0 eV are ascribed to S2p3/2 and 2p1/2 orbitals of S^{2-} . No corresponding peaks of S_2^{2-} species were detected on the surface of MoS₂. For Co-doped catalysts, Fig. 6c exhibits that a small amount of Mo⁵⁺ and Mo⁶⁺ species still exists after the Co incorporation and sulfidation process. Detailed fitting of Co2p_{3/2} envelope can be conducted as follows: Co₉S₈ (778.0 eV), Co-Mo-S (778.7 eV), CoO_x (781.6 eV) and their corresponding satellite peaks (Fig. 6d) [40]. The presence of CoO_x for all Co-doped catalysts indicates not all of the Co^{2+} has been sulfided to cobalt sulfides. Only one major peak assigned to Co-Mo-S was observed for Co/MoS₂-0.1, while another cobalt sulfide attributed to Co₉S₈ besides Co-Mo-S was found for Co/MoS₂-0.3 and Co/MoS₂-0.5. This phenomenon is the same as XRD results and could be understood as follows. When a small amount of Co is introduced, the Co atoms are preferentially located at the edge site of ${\rm MoS}_2$ catalyst to form the Co-Mo-S phase [41]. With the Co content reaching a threshold, the edge sites of MoS₂ particles are fully covered by Co. If further increasing the Co content, the excess Co species will aggregate to form separated Co₉S₈ particles.

Fig. 7 shows the TPR profiles of MoS_2 and Co/MoS_2 -x catalysts, which is important to well comprehend the information about active centers. For non-promoted MoS_2 , a sharp peak at 285 °C was attributed to the reduction of non-stoichiometric sulfur at edge planes [42], thus producing coordinative unsaturated sites (CUS). The broad reduction



Fig. 4. SEM images of (a) MoS₂, (b) Co/MoS₂-0.1, (c) Co/MoS₂-0.3 and (d) Co/MoS₂-0.5.

signal with low intensity in the high temperature region was assigned to the partial reduction of MoS₂ bulk phase. When adding Co to form a certain amount of Co-Mo-S active phase, the temperature for CUS formation is remarkably lowered to 235 °C for Co/MoS₂-0.1 due to the electrical structure optimization of MoS₂ by Co promoter. This result is a pretty good explanation of why the introduction of Co or Ni into MoS₂ catalyst can greatly improve the catalytic performance. With the further increase of Co-Mo-S content for Co/MoS₂-0.3, the reduction temperature is decreased to 224 °C which promotes the continuous improvement of catalytic activity. The formation of large Co₃S₈ particles on Co/MoS₂-0.5 will cover the MoS₂ surface and block the pores, thus resulting in decreased amount of catalytic active sites.

3.3. Structure-performance relationship

From Fig.5 and Fig. S3, it is shown the as-prepared unsupported MoS₂ catalyst has a high dispersion, rich defects and some curved slabs. Therefore, a large amount of edge sites and additional CUS are available for accommodating Co to form active phase. However, the nonpromoted MoS₂ catalyst is not efficient enough because it only shows HDO conversion of 16.9 % and toluene selectivity of 65.0 % at 220 $^\circ\text{C}.$ After incorporating a certain amount of Co promoters, the Co atoms prefer to locate in the CUS of edge planes to form Co-Mo-S active phase. Besides, no separated $\mathrm{Co}_9\mathrm{S}_8$ phase was checked by XRD and XPS when the Co/(Co + Mo) molar ratio is 0.1. Although the MoS₂ size was increased and the surface area was decreased after Co incorporation, the Co doping resulted in the great decreased reduction temperature for sulfur vacancy formation (Fig. 7). Thus, the HDO activity was improved about 5 folds from MoS_2 to Co/MoS_2 -0.1. Meanwhile, the toluene selectivity was increased from 65.0% to 93.4% because Co promotion mainly promoted the reaction rate of DDO route. By further increasing

the Co/(Co + Mo) molar ratio to 0.3, the edge planes were fully occupied by Co and the Co-Mo-S content reached the maximum. Besides, a small amount of Co₉S₈ phase was formed which plays the role to provide spillover hydrogen in the HDO process. Thus, Co/MoS₂-0.3 catalyst showed the highest HDO conversion of 98.7 % and toluene selectivity of 98.9 %. However, when excessive Co was introduced, a large number of large Co₉S₈ particles will deposit on the surface of catalyst, thus blocking the pores and covering the active sites (Table 3 and Fig. 7). Consequently, decreased HDO activity and toluene selectivity were observed for Co/MoS₂-0.5 catalyst. The catalytic performance-structure volcano curve is well illustrated in Scheme 1.

3.4. Stability performance of Co/MoS₂-0.3

The stability of Co/MoS₂-0.3 in the HDO of p-cresol was evaluated at 220 °C and 3 MPa for 72 h. As shown in Fig. 8, the HDO activity and toluene selectivity were only decreased by 1.4 % and 1.0 % respectively, demonstrating a relative good stability of Co/MoS₂-0.3. Fig. 9 shows the Raman spectra of fresh and spent Co/MoS₂-0.3 catalysts. It could be clearly seen that the MoS2 structure was well preserved while graphitic carbon was formed on the spent Co/MoS2-0.3 catalyst after reaction. As listed in Table S1, the carbon content on spent Co/MoS₂-0.3 was 2.3% g_{carbon}/g_{catalyst}, and the Co amount was unchanged while the sulfur content showed a 0.4 wt.% loss after reaction. Hence, coke deposition and sulfur loss were supposed to be the reasons for the slight deactivation of Co/MoS₂-0.3 catalyst. Actually, maintaining the catalyst stability is a great challenge for the application of sulfides in HDO reactions due to the sulfur loss under harsh reaction conditions. Some methods have been reported in the literatures to improve the stability by enhancing the hydrophobicity of catalyst [43,44] or adding sulfur-containing compounds [45]. However, these methods are either too complex or



Fig. 5. HRTEM images of (a) MoS₂, (b) Co/MoS₂-0.1, (c) Co/MoS₂-0.3 and (d) Co/MoS₂-0.5.

introduce sulfur contamination into the products. Recently, Liu et al. reported the Co-doped monolayer MoS_2 could be recycled for 7 times without deactivation by lowering the reaction temperature to 180 °C [46]. In the present work, we also proves that by preparing highly efficient sulfide catalysts to make the HDO reaction progressing under mild reaction conditions is crucially important for maintaining the stability.

3.5. Comparison of Co/MoS_2-0.3 and other reported MoS_2-based sulfide catalysts

The catalytic performance in the HDO of *p*-cresol between Co/MoS₂-0.3 and other reported MoS₂-based sulfide catalysts is compared. As listed in Table 4, Co/MoS₂-0.3 displays a much better performance than CoMo/Al₂O₃ supported catalyst which achieved conversion of 95 % and toluene selectivity of 18 % at 360 °C and 7 MPa. In addition, most of the unsupported catalysts obtained satisfactory HDO performance at reaction temperature of 250–300 °C. However, Co/MoS₂-0.3 realized an excellent HDO performance of 98.7 % conversion and 98.9 % toluene selectivity under a mild reaction condition of 220 °C and 3 MPa. Although the HDO activity of Co/MoS₂-0.3 is lower than Co-doped monolayer MoS₂ (Co-^SMoS₂) and Co nanoparticles supported on defect MoS_{2-x} (Co/MoS_{2-x}), the procedure to prepare Co-^SMoS₂ is too complicated and difficult to achieve mass production. Moreover, our catalysts are evaluated using a fixed-bed reactor and much closer to industrial conditions.

4. Conclusions

Unsupported nano-MoS₂ was synthesized by hydrothermal method using MoO₃ and Na₂S as precursors. The as-prepared MoS₂ was highly dispersed with slab length of 10–20 nm and stacking number of 2–4 layer. Defect and curved structure was interestingly formed on the nano-MoS₂ slabs. Therefore, a large amount of coordination unsaturated sites was provided for accommodation of Co atoms to form abundant Co-Mo-S active phase. With varying different molar ratio of Co/(Co + Mo), Co/ MoS₂-0.3 displayed the highest activity and toluene selectivity under mild reaction conditions in the HDO of *p*-cresol. Good stability was also observed under continuous reaction of 72 h. The present work provides a highly efficient unsupported Co-doped MoS₂ catalyst with minimum hydrogen consumption for the HDO process of biomass conversion.

CRediT authorship contribution statement

Jing Cao: Investigation, Writing - original draft. An Li: Investigation, Writing - original draft. Yicen Zhang: Investigation. Linchao Mu: Formal analysis. Xi Huang: Validation. Yankun Li: Validation. Tao Yang: Formal analysis. Cen Zhang: Conceptualization, Methodology, Writing - review & editing. Congshan Zhou: Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no competing financial interests



Fig. 6. XPS spectra of (a) Mo3d and (b) S2p for MoS_{2} , (c) Mo3d and (d) $Co2p_{3/2}$ for Co/MoS_{2} -x.



Fig. 7. TPR profiles of (a) $\rm MoS_2,$ (b) Co/MoS_2-0.1, (c) Co/MoS_2-0.3 and (d) Co/ MoS_2-0.5.



Scheme 1. Structure-performance relation of Co-promoted \mbox{MoS}_2 catalysts in the HDO reaction.



Fig. 8. Stability test for HDO of *p*-cresol over Co/MoS₂-0.3 after 72 h. (Reaction conditions: 220 $^{\circ}$ C, 3 MPa).



Fig. 9. Raman spectra of fresh and spent Co/MoS₂-0.3 catalysts in the region of (a) $360-430 \text{ cm}^{-1}$ and (b) $1200-1800 \text{ cm}^{-1}$.

Table 4

Comparison of HDO performance between Co/MoS_2 -0.3 and other reported sulfided catalysts.

		Conditions			Catalytic		
Entry	Catalyst	T (°C)	P (MPa)	t (h)	Conv. (%)	Toluene Select. (%)	Ref.
1	Co/nano- MoS ₂	220	3.0	Λ.	98.7	98.9	This work
2	Co-Mo-S	275	4.0	4	100	92.2	[21]
3	CoS ₂ / MoS ₂ Flower-	250	4.0	1	98	99	[47]
4	like Co-doped MoS ₂	300	4.0	4	99.8	97.9	[22]
5	CoMoS Flower-	300	4.0	3	100	100	[23]
6	like Co-Mo-S	275	4.0	5	85.6	97.5	[48]
7	CoMo/ Al ₂ O ₃	360	7.0	1	95	18	[20]
8	CoMoS	300	3.0	6	99.1	94.4	[25]
9	Co- ^S MoS ₂	180	3.0	8	97.6	98.4	[<mark>46</mark>]
10	Co-MoS _{2-x}	120	3.0	6	97.4	99.5	[24]
11	NiMoWS	300	3.0	5	97.8	87.2	[49]
12	Ni-Mo-S	300	4.0	6	99.9	28.8	[35]
13	NiS ₂ // MoS ₂	275	4.0	4	95.8	35.6	[50]
14	Ni-Mo-W-S	300	4.0	6	97.9	30.1	[51]

Note: Except for the fixed-bed reactor used in our study, the batch reactor was used in other reports.

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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.mcat.2021.111507.

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J. Cao et al.

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