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Short Communication

Hydrodeoxygenation of p-cresol on unsupported Ni–W–Mo–S catalysts prepared by one step hydrothermal method



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ABSTRACT

Unsupported Ni–Mo–W sulfide catalysts were prepared by one step hydrothermal method using ammonium heptamolybdate and thiocarbamide in water, and characterized by X-ray diffraction (XRD), nitrogen physisorption and transmission electron microscopy (TEM). The effect of W/Mo molar ratio on the catalytic performance was studied using the HDO of p-cresol as a probe. The results showed that the Ni–Mo–W–S catalyst with an appropriate W/Mo molar ratio possesses the short slab length of MoS₂ or WS₂ structure and many active sites, leading to the high HDO activity and HYD selectivity.

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1. Introduction

With the depletion of non-renewable fossil fuels and the growing greenhouse effect, many countries have given great efforts on the exploitation of biomass to the bio-oil in the past few decades [1–3]. Compared with the conventional petroleum, the main characteristic of the bio-oil obtained from biomass pyrolysis is the negligible sulfur content but high oxygen content, which leaded to the indirect utilization of bio-oil as supplements or replacements for gasoline or fossil diesel without any additional treatment due to its poor heating value, high viscosity, thermal and chemical instability as well as its tendency to the polymerization during storage and transportation [3,4]. Hence, it needs to remove the oxygen from bio-oil to decrease its oxygen content.

Catalytic hydrodeoxygenation (HDO), an efficient and direct technology for the elimination of oxygen atom in the presence of hydrogen, has been investigated extensively. The key for this technology is to develop a high active catalyst. Noble metal catalysts possess high hydrogenation activity, favoring mild required reaction conditions and a low aromatic content in the final product [5,6], but the high cost prevents their wide application. We had designed and prepared Ni–W–B amorphous catalysts, which also exhibit very high HDO activity, but the thermal unstability is its intrinsic drawback [7,8]. Conventional molybdenum sulfide catalysts promoted by cobalt (Co) or nickel (Ni), conducted over classical catalysts originally developed for hydrodesulfurization (HDS)

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reactions in petroleum refining processes, were investigated extensively in the HDO of model compounds [9–14]. In recent years, Ni– W–Mo trimetallic unsupported catalysts, called NEBULA®, were developed and showed much greater HDS activity than that observed for the commonly used industrial catalysts [15]. This arouses a wide research concerning Ni–Mo–W ternary catalysts. For example, R. Huirache-Acuña et al. have synthesized trimetallic Ni–Mo– W sulfides by sulfidization of the corresponding trimetallic oxide precursors [16]. Nava et al. have prepared Ni(Co)–Mo–W catalysts by in-situ decomposition of alkylthiomolybdotungstates, and reported interesting morphological properties and an enhancement in HDS activity [17]. Wang et al. have prepared unsupported Ni– Mo–W sulfide catalysts by mechanical activation method and found Ni_{0.33}MoW catalyst presented the highest HDO activity in the HDO of 4-methylphenol [18].

The effects of nickel content for unsupported trimetallic Ni–Mo–W sulfide catalysts had been investigated, which influenced the surface area, pore size distribution and catalytic activity of the sulfides [18–20]. Adding a low content of nickel in Mo–W–S give a positive effect on the catalytic performance, but excess nickel content results in a decrease of activity due to the formation of nickel sulfides. However, to our best knowledge, very few literatures have reported the HDO properties of Ni–Mo–W–S catalyst and the optimal W/Mo molar ratio that made the HDO activity to be the maximum. Among many oxygen containing compounds in the bio-oil, phenolic hydroxyl oxygen is considered as the most difficult one to remove because the C–O σ -bond is attached to the aromatic ring that delocalizes the out-of plane oxygen lone-pair orbital. In this work, therefore, we prepare unsupported Ni–Mo–W sulfide

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catalysts by one step hydrothermal method and select p-cresol as a model compound to determine the effect of W/Mo molar ratio on the structure and catalytic performance.

2. Experimental

2.1. Catalyst preparation

All solvents and reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. in high purity (\geq 99%) and used without further purification. Unsupported Ni-W-Mo-S catalysts were synthesized by using one step hydrothermal method. The catalyst synthesis was carried out in quartz reactor with a volume of 300 mL. Nickel nitrate, ammonium heptamolybdate, sodium tungstate and thiourea (3.0 g) were dissolved in 250 mL ultra-pure water. The Ni/(Mo + W) molar ratio in the initial solution was fixed to 0.12 in each case while the W/Mo molar ratio was adjusted from 0 to 0.7. The reactor was sealed, and then heated to 200 °C. After 24 h, the resulting catalysts were separated and washed with absolute ethanol several times to remove the residual water and water-soluble impurities. Finally, the resulting product was dried under vacuum at 323 K for 8 h and stored in nitrogen environment. All the catalyst synthesis experiments were repeated to ensure repeatability of the data. The prepared catalysts were denoted as W-Mo-X, where X represented the molar ratio of W/Mo in the initial solution. The unsupported Ni-Mo-S catalyst without W was also prepared by the same procedure as described above.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried on a D/max2550 18KW Rotating Anode X-ray Diffractometer with monochromatic Cu K α radiation ($\lambda = 1.5418$ Å) radiation at voltage and current of 40 kV and 300 mA. The specific surface area was measured by a Quantachrome's NOVA-2100e Surface Area instrument by physisorption of nitrogen at 77 K. The morphologies of catalysts were determined by transmission electron microscopy (TEM) on a JEOL JEM-2100 transmission electron microscope with a lattice resolution of 0.19 nm and an accelerating voltage of 200 kV.

2.3. Catalyst activity measurement

The HDO activity tests were carried out in a 100-mL sealed autoclave. The prepared catalyst (0.20 g) without any further treatment, p-cresol (4.50 g) and dodecane (28.73 g) were placed into the autoclave. Air in the autoclave was evacuated by pressurization–depressurization cycles with nitrogen and subsequently with hydrogen. The system was heated to 300 °C, then pressurized with hydrogen to 4.0 MPa and adjusted the stirring speed to 700 rpm. During the reaction, liquid samples were withdrawn from the reactor and analyzed by Agilent 6890/5973N GC–MS and 7890 gas chromatography using a flame ionization detector (FID) with a 30 m AT-5 capillary column. The experiments have been repeated twice at least and the results showed that the conversion and selectivity were within 3.0% of the average values. The carbon balance across the reactor was shown to be >95%. The HYD/DDO and deoxygenation rate for each experiment were calculated as follows:

HYD/DDO =	total selectivity of methylcyclohexane and 4-methylcyclohexene
	selectivity of toluene

deoxygen	ation rate(wt.%)
/	ovugen content in the final organic compounds)

$$= \left(1 - \frac{\text{oxygen content in the initial organic compounds}}{\text{total oxygen content in the initial material}}\right) \times 100\%.$$



Fig. 1. XRD patterns of the fresh Ni-Mo-S and Ni-W-Mo-S unsupported catalysts.

3. Results and discussion

3.1. Characterization of the unsupported catalysts

The XRD patterns of the prepared Ni-Mo-S and Ni-W-Mo-S catalysts are shown in Fig. 1. All the prepared sulfide catalysts showed some broad diffraction peaks at $2\theta = 14^{\circ}$, 33° , 39° and 59° , corresponding to the (002), (100), (103), (110) basal planes of crystalline MoS₂ (JCPDS Card No. 65-1951) [21,22], respectively, which indicated a very poorly crystallized MoS_2 structure. The presence of the (0 0 2) peak at $2\theta = 14^{\circ}$ is representative for the multi-stacked slabs along the c direction, while the presence of the (1 1 0) peak at $2\theta = 59^{\circ}$ is representative of the slab layer [20,21]. As revealed by the XRD patterns (Fig. 1), the intensity of the peak at $2\theta = 14^{\circ}$ gradually became weak and then increased as the W/Mo molar ratio was increased from 0 to 0.7. W-Mo-0.5 showed the lowest (0 0 2) peak intensity, indicating that W-Mo-0.5 possesses the lowest stacking slabs along the c direction. No any obvious peak for separated Ni sulfides was observed. This might be resulted from the synergistic effect of W and Mo. An optimum W/Mo molar ratio facilitates the high dispersion of Ni sulfides on MoS₂/WS₂ or formation of small particles [21]. For these prepared sulfide catalysts, the ternary Ni-Mo-S or Ni-W-S phase did not appear clearly. It is probably due to the fact that these phases are possibly presented as very small nanocrystallites or there is overlapping of diffraction peaks from MoS₂/WS₂ phase and Ni-Mo(W)-S phase, which cannot be detected by X-ray diffraction method [23,24].

The surface area and pore volume of Ni–W–Mo–S unsupported catalysts are summarized in Table 1. Unlike the report that Ni–Mo–S has a surface area in the range of 138–329 m²/g with a pore volume in the range of 0.6–0.8 cm³/g [10], in this study, the specific surface area of the Ni–Mo–S is only 38.7 m²/g with a pore volume of 0.2 cm³/g because of the different prepared conditions and raw material. With the increase of W/Mo molar ratio from 0 to 0.7, the specific surface area increases from 38.7 m²/g to 49.5 m²/g, which might be attributed to the reductive block of nickel sulfide in the pore channels due to the synergistic effect of W and Mo [20].

Fig. 2 presents the HRTEM images of Ni–Mo–S and Ni–Mo–W–S unsupported catalysts. Some groups of parallel dark thread-like fringes

Table 1	
Physical properties of Ni-Mo-S and Ni-W-Mo-S unsupported catalysts.	

Catalysts	W/(Mo)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Slab length (nm)
Ni-Mo-S	0	38.7	0.2	23.9
W-Mo-0.1	0.1	42.2	0.2	18.3
W-Mo-0.3	0.3	45.8	0.2	10.4
W-Mo-0.5	0.5	46.3	0.2	6.3
W-Mo-0.7	0.7	49.5	0.2	9.2

can be clearly seen from the HRTEM images, characterizing of the (002) basal planes of MoS₂ or WS₂ structure [25,26]. According to the literature, the average number of MoS₂ stacking layers was calculated by

examining more than 200 slabs on several HRTEM pictures taken from different parts of the same sample dispersed on the microscope grid and the statistical results are shown in Table 1. The HRTEM images



Fig. 2. HRTEM images of Ni-Mo-S and Ni-Mo-W-S unsupported catalysts.



Fig. 3. Concentrations of p-cresol and product versus reaction time on (a) Ni-Mo-S, (b) W-Mo-0.1, (c) W-Mo-0.2, (d) W-Mo-0.3, (e) W-Mo-0.5 and (f) W-Mo-0.7 catalysts at 300 °C.

clearly show that the Ni–Mo–S has many long slabs with the average slab length of 23.9 nm. This length is decreased to 6.3 nm when the W/Mo molar ratio increases to 0.5, and then increases with the further increase of W/Mo molar ratio. In other words, adjusting W/Mo molar ratio to an optimum value can obtain Ni–Mo–W–S with the shortest average slab length.

3.2. Hydrodeoxygenation of p-cresol

The catalytic performances of Ni–Mo–S and Ni–Mo–W–S unsupported catalysts were tested using the HDO of p-cresol as the probe reaction. The concentrations of p-cresol and products versus reaction time on Ni–Mo–S and Ni–Mo–W–S unsupported catalysts are shown in

Table 2

Activity and selectivity of Ni-Mo-S and Ni-Mo-W-S unsupported catalysts for the HDO of p-cresol at 300 °C for 6 h.

Catalyst	Ni-Mo-S	W-Mo-0.1	W-Mo-0.2	W-Mo-0.3	W-Mo-0.5	W-Mo-0.7
Conversion (mol%) $k \times 10^2$, mL/(s·g catalyst)	80.3 1.64	91.8 2.09	93.5 2.30	94.6 2.57	97.9 2.75	85.1 2.09
Methylcyclohexane	62.1 1 7	65.2 3.2	64.9 4 5	65.3 4 2	66.7 3 2	62.1
Toluene HYD/DDO D. P. (ut %)	36.2 1.77 78.22	31.7 2.16	30.6 2.27	30.3 2.29	30.1 2.32 07.56	35.4 1.82

Fig. 3. The products in the HDO of p-cresol on Ni-Mo-S or Ni-Mo-W-S at 300 °C were toluene, 4-methylcyclohexene and methylcyclohexane, and no oxygen-containing compound was detected. Fig. 3e showed that the toluene concentration remained relatively constant in the last 2 h where the p-cresol conversion has been higher than 99.0%, indicating that the hydrogenation of toluene was very hard on this catalyst. However, Fig. 3 showed that p-cresol concentration decreased gradually while both the methylcyclohexane concentration and toluene concentration continuously increased. Hence, it can conclude that the HDO of p-cresol on these catalysts proceeds with two parallel reaction paths: direct deoxygenating route (DDO) and hydrogenation-dehydration route (HYD). For the HYD route, p-cresol was hydrogenated to 4methylcyclohexanol at first and then deoxygenation to methylcyclohexane. This is a consecutive reaction, in which 4-methylcyclohexanol acted as an intermediate. It has been reported that some intermediates such as cyclohexanol or cyclohexanone analogues via hydrogenation of the corresponding aromatic ring before the C–O σ -bond scission were found during the reaction [27], but we did not detect any 4-methylcyclohexanol or 4-methylcyclohexanone in the liquid sample. The appearance of 3-methylcyclohexene with a little amount demonstrated that the hydrogenation of aromatic ring before deoxygenation was occurred. The sum concentration of methylcyclohexane and methylcyclohexene was much higher than that of toluene, suggesting that the HYD route was the primary route for the HDO of p-cresol on Ni-Mo-S catalyst. Therefore, the rate-limiting step of p-cresol reaction on unsupported Ni-Mo-S and Ni-W-Mo-S catalysts is the reaction step prior to the deoxygenation step.

As reviewed in the previous literature [28], the conversion of p-cresol was modeled assuming a pseudo-first-order reaction: $-\ln(1 - x) =$ $k \cdot C_{cat} \cdot t$, where k is the pseudo-first-order rate constant (mL·s⁻¹·g⁻¹ catalyst). The conversion of p-cresol, initial rate constants (k) and product selectivity on Ni-Mo-S and Ni-Mo-W-S unsupported catalysts were calculated and listed in Table 2. After 6 h of reaction, the conversion of p-cresol increased in the order of Ni-Mo-S (80.3%) < W-Mo-0.7 (85.1%) < W-Mo-0.1 (91.8%) < W-Mo-0.2 (93.5%) < W-Mo-0.3(94.6%) < W-Mo-0.5 (97.9%), and the HYD/DDO exhibited the same order as the p-cresol conversion, suggesting that the HDO activity progressively increases with the W/Mo molar ratio to reach the maximum value and then decreases, which might be resulted from the following reason. Addition of W in Ni-Mo-S catalyst changes the already existing interaction between Ni and Mo and creates new interaction between W and existing metals [29]. This in turn increased the adsorption of phenol on coordinatively unsaturated sites (CUS) through its oxygen atom so as to improve the HDO activity. The reaction rate constants (k)for Ni-Mo-S, W-Mo-0.1, W-Mo-0.2, W-Mo-0.3, W-Mo-0.5 and W-Mo-0.7 are 1.64, 2.09, 2.30, 2.57 and 2.09 mL/(s·g catalyst), respectively. The above results indicated that W had a positive effect for improving the HDO activity of Ni-Mo-S catalyst and the optimum W/Mo molar ratio was 0.5. Compared with other catalysts such as MoO₃, MoO₂, MoS₂ and MoP in the literatures [14,30-32], W-Mo-0.5 unsupported catalyst prepared in this study had a higher activity in p-cresol HDO.

B. Subramaniam et al. [33] had reported that the main difference between HYD and DDO routes is attributed to the adsorption mode of the oxygenated molecule on the active site, which suggested that two kinds of active sites are required in these catalysts: One (edge site) for hydrogenolysis of C–O σ -bond and the other one (corner site) for hydrogenation of aromatic ring [34]. According to the "Co-Mo-S" phase model [35], Ni is located at the edge of the MoS₂ or WS₂ slabs, but it is important to note that the plane of the MoS₂ or WS₂ slabs is inactive. These allow a better understanding of the influence of the slab length and slab stacking layers of Mo/W sulfide catalysts. In other word, the HYD/DDO ratio essentially depends on the catalyst morphology. As shown in Fig. 2, adjusting the W/Mo molar ratio could modify the morphological characteristics of the MoS₂ and WS₂ slabs, leading to a better dispersion of the active phases and higher number of active sites than that of Ni-Mo-S. The higher dispersion of the active components resulted to shorter slab length and, consequently, to a higher proportion of corner sites. It also showed that the number of MoS₂/WS₂ slab was increased with the increase of W/Mo molar ratio to 0.5, and then decreased. The increase of the stacking layers suggests the increase of the corner site and edge site of the MoS₂ or WS₂ slabs, namely, more active sites. Therefore, based on the TEM and activity test results, it is reasonable that the highest conversion and the largest HYD/DDO ratio value in the HDO of p-cresol on W-Mo-0.5 can be attributed to the most active sites and the highest proportion of corner sites of the catalyst, respectively.

4. Conclusions

Adjusting the W/Mo molar ratio in the Ni-Mo-W-S catalysts can promote the dispersion of the active phases, leading to a high number of active site, and shorten the slab length of MoS₂ structure, producing a high proportion of corner site. Among these catalyst, W-Mo-0.5 exhibited the highest activity in the HDO of p-cresol: the conversion was high to 97.9% with a deoxygenation rate of 97.56% at 300 °C for 4 h and the corresponding reaction rate constant (k) was 0.0275 mL/($s \cdot g$ catalyst). The HDO activity and HYD selectivity of Ni-Mo-W-S catalysts depended on their active sites and the proportion of corner sites, respectively.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2014.06.024. This data include MOL files and InChiKeys of the most important compounds described in this article.

References

- [1] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, Renew. Sustain. Energy Rev. 21 (2013) 506-523
- [2] A.V. Bridgwater, Biomass Bioenergy 38 (2012) 68-94.
- E. Furimsky, Catal. Today 217 (2013) 13-56.
- J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev. 110 (2010) 3552-3599.
- P.T.M. Do, A.J. Foster, J. Chen, R.F. Lobo, Green Chem. 14 (2012) 1388-1397.
- [6] C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, Angew. Chem. Int. Ed. 48 (2009) 3987-3990.
- [7] W. Wang, Y. Yang, H. Luo, H. Peng, F. Wang, Ind. Eng. Chem. Res. 50 (2011) 10936-10942.
- [8] W. Wang, Y. Yang, H. Luo, H. Peng, B. He, W. Liu, Catal. Commun. 12 (2011) 1275-1279
- [9] A. Popov, E. Kondratieva, L. Mariey, J.M. Goupil, J. El Fallah, J.-P. Gilson, A. Travert, F. Maugé, J. Catal. 297 (2013) 176-186.
- [10] B. Yoosuk, D. Tumnantong, P. Prasassarakich, Fuel 91 (2012) 246-252.
- [11] P.E. Ruiz, B.G. Frederick, W.J. De Sisto, R.N. Austin, L.R. Radovic, K. Leiva, R. García, N.
- Escalona, M.C. Wheeler, Catal. Commun. 27 (2012) 44-48. [12] M. Ruinart de Brimont, C. Dupont, A. Daudin, C. Geantet, P. Raybaud, J. Catal. 286 (2012) 153-164
- [13] V.N. Bui, D. Laurenti, P. Afanasiev, C. Geantet, Appl. Catal. B Environ. 101 (2011) 239-245
- Y.Q. Yang, C.T. Tye, K.J. Smith, Catal. Commun. 9 (2008) 1364-1368.
- [15] F.L. Plantenga, R.G. Leliveld, Appl. Catal. A Gen. 248 (2003) 1-7
- R. Huirache-Acuña, B. Pawelec, C.V. Loricera, E.M. Rivera-Muñoz, R. Nava, B. Torres, J.L.G. [16] Fierro, Appl. Catal. B Environ. 125 (2012) 473-485.
- [17] H. Nava, F. Pedraza, G. Alonso, Catal. Lett. 99 (2005) 65-71.
- C. Wang, Z. Wu, C. Tang, L. Li, D. Wang, Catal. Commun. 32 (2013) 76-80. [18] [19] J. Bocarando, R. Huirache-Acuña, W. Bensch, Z.D. Huang, V. Petranovskii, S. Fuentes,
- G. Alonso-Núñez, Appl. Catal, A Gen. 363 (2009) 45-51. Y. Yi, B. Zhang, X. Jin, L. Wang, C.T. Williams, G. Xiong, D. Su, C. Liang, J. Mol. Catal. A [20]
- Chem. 351 (2011) 120-127. [21] Y. Yi, X. Jin, L. Wang, Q. Zhang, G. Xiong, C. Liang, Catal. Today 175 (2011) 460-466.
- [22] P. Afanasiev, J. Catal. 269 (2010) 269-280.

- [23] L.S. Byskov, B. Hammer, J.K. Nørskov, B.S. Clausen, H. Topsøe, Catal. Lett. 47 (1997) 177–182.
- [24] B. Yoosuk, C. Song, J.H. Kim, C. Ngamcharussrivichai, P. Prasassarakich, Catal. Today 149 (2010) 52–61.
- [25] N. Berntsen, T. Gutjahr, L. Loeffler, J.R. Gomm, R. Seshadri, W. Tremel, Chem. Mater. 15 (2003) 4498-4502.
- [26] N.A. Dhas, A. Ekhtiarzadeh, K.S. Suslick, J. Am. Chem. Soc. 123 (2001) 8310–8316.
 [27] O.I. Senol, E.M. Ryymin, T.R. Viljava, A.O.I. Krause, J. Mol. Catal. A Chem. 277 (2007) 107–112.

- [28] E. Furimsky, Appl. Catal. A Gen. 199 (2000) 147–190.
 [29] Y.-C. Park, E.-S. Oh, H.-K. Rhee, Ind. Eng. Chem. Res. 36 (1997) 5083–5089.
 [30] W. Wang, K. Zhang, H. Liu, Z. Qiao, Y. Yang, K. Ren, Catal. Commun. 41 (2013) 41-46.
- 41-46.
 V.L. Whiffen, K. Smith, Top. Catal. 55 (2012) 981–990.
 V.M.L. Whiffen, K.J. Smith, Energy Fuels 24 (2010) 4728–4737.
 H. Wan, R. Chaudhari, B. Subramaniam, Top. Catal. 55 (2012) 129–139.
 M. Daage, R.R. Chianelli, J. Catal. 149 (1994) 414–427.
 H. Topsøe, B.S. Clausen, Catal. Rev. 26 (1984) 395–420.