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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 MoS_2 or WS_2 structure and many active sites, leading to the high HDO activity and HYD selectivity.

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) 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 (≥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 Kα 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:

$$\mathrm{HYD/DDO} = \frac{\text{total selectivity of methylcyclohexane and 4-methylcyclohexene}}{\text{selectivity of toluene}}$$

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

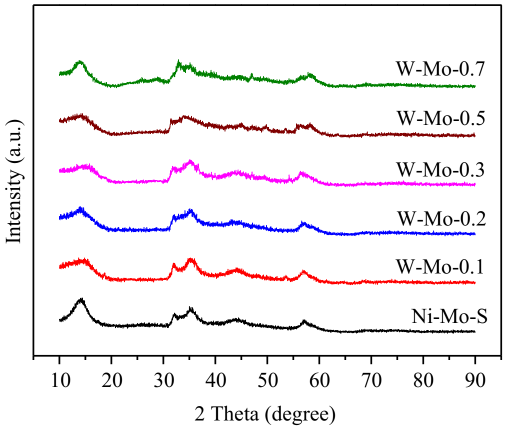

Fig. 1. XRD patterns of the fresh Ni–Mo–S and Ni–W–Mo–S unsupported catalysts.

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 $2\theta = 14°$, 33°, 39° and 59°, corresponding to the (0 0 2), (1 0 0), (1 0 3), (1 1 0) basal planes of crystalline MoS_2 (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 $2\theta = 14°$ is representative for the multi-stacked slabs along the c direction, while the presence of the (1 1 0) peak at $2\theta = 59°$ is representative of the slab layer [20,21]. As revealed by the XRD patterns (Fig. 1), the intensity of the peak at $2\theta = 14°$ 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 MoS_2/WS_2 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 MoS_2/WS_2 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 m^2/g with a pore volume in the range of 0.6–0.8 cm^3/g [10], in this study, the specific surface area of the Ni–Mo–S is only 38.7 m^2/g with a pore volume of 0.2 cm^3/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 m^2/g to 49.5 m^2/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