Preparation of Ni–Mo–S catalysts by hydrothermal method and their hydrodeoxygenation properties

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ABSTRACT

Unsupported Ni–Mo–S catalysts with different $Ni/(Ni+Mo)$ molar ratio were prepared by hydrothermal method using ammonium heptamolybdate and thiocarbamide as materials. The resultant catalysts were characterized by X-ray diffraction, nitrogen physisorption and transmission electron microscopy, and their activities were measured using the hydrodeoxygenation (HDO) of *p*-cresol as a probe reaction. The addition of Ni promoter caused a reduction in the surface area. The peaks attributed to NiS_2 on catalyst surface became noticeable as the Ni content increased in the catalyst. The catalyst with an optimal $Ni/(Ni+Mo)$ molar ratio (0.3) exhibited the highest activity (99.8% deoxgenation degree at 300 °C and 4.0 MPa hydrogen pressure for 6 h). The HDO of *p*-cresol on these prepared Ni–Mo–S catalysts proceeded with two parallel routes: hydrogenation-dehydration (HYD) and direct deoxygenation (DDO), and HYD/DDO closely related to the $Ni/(Ni+Mo)$ molar ratio in the catalyst, the HDO reaction temperature and H_2 pressure. The comparison of Ni–Mo–S with MoS_2–NiS_2 (prepared by two hydrothermal method) and $MoS_2 + NiS_2$ (prepared by physically mixing separately MoS_2 and NiS_2) indicated that the high HDO activity of Ni promoted MoS_2 catalyst was attributed to the synergistic effect of MoS_2 and NiS_2 rather than the formation of Ni–Mo–S phase, which could be well explained by the remote control model.

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1. Introduction

The continuous decrease in fossil fuels reserves, rapid growth in global energy consumption and stringent environmental regulations in greenhouse gases emissions have attracted much attention in the development of renewable energy resource in the last ten years [1,2]. Bio-oil, derived from biomass by fast pyrolysis, is a promising substituted fuel because of the CO_2-neutral and free of SOx emission during its combustion. Unfortunately, this bio-oil contains a considerable amount of oxygenated compounds such as phenols, aldehydes, ketones and furans, contributing to its high oxygen content, which leads to some deleterious properties and prevents its direct utilization as a supplement or replacement for gasoline or fossil diesel [3,4]. Consequently, upgrading bio-oil to liquid hydrocarbon via catalytic hydrodeoxygenation (HDO) becomes a challenge for obtaining renewable, sustainable and environment friendly liquid fuel, and the key to this technology is how to prepare HDO catalysts with high activity.

Some investigators had studied the HDO of the biomass-derived oils on sulfides and noble metal catalysts [5,6]. Because of the intermolecular interaction and adsorption-site competition in a complex mixture such as bio-oils, detailed study with model compound is of significance for understanding the different reaction paths and reaction mechanism [7]. Phenols are widely selected as model compounds to investigate the HDO activity of various catalysts under different conditions [8–22] since they take a considerable quantity in bio-oil (66.9%) [23] and possess a high C—O bond dissociation energy [2,24]. The HDO of these phenols usually occurs via two main pathways: direct deoxygenation (DDO) with aromatic C—O bond scission and hydrogenation-dehydration (HYD) that starts with ring hydrogenation followed by dehydration reactions. Among these catalysts that applied in the HDO of phenols, noble metals and amorphous Mo(W) based borides exhibit high activities, but the high cost or insufficient stability at high temperature inhibit their widely practical application. Ni or Co promoted Mo- or W-based sulfide catalysts are usually prepared by sulfidation of oxide precursors at high temperature (about 400 °C) with H_2/H_2S or organic sulfur compound [20]. This method requires H_2S or releases poisonous gas and causes

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some agglomeration. To overcome these disadvantages on the synthesis of sulfide catalyst, several new methods such as thermal decomposition method [25], mechanical activation method [26] and hydrothermal method [17] had appeared. As we known, the synthesis method has a great effect for the performance of catalyst. For instance, Smith et al. [22] had prepared MoS₂ catalysts by different methods and compared their activities based on kinetic study. They found that exfoliated MoS₂ had the highest activity in the HDO of phenols. Wang et al. [26] had adopted mechanical activation method to prepare Ni–Mo–W sulfide catalysts and confirmed that these catalysts had high catalytic activity for the HDO of 4-methylphenol. Hydrothermal method, an important technique for producing highly homogeneous nano-composite materials, has become one of the most efficient processes for the preparation of nano-catalyst. Adopting the isolation effect of the organic solvent for the precursor molecules, Yoosuk et al. [27] had prepared unsupported Mo based sulfide catalyst with a surface area in the range of 138–368 m²/g and found that MoS₂ catalyst prepared by the hydrothermal method showed 2.4-fold higher conversion than commercial crystalline MoS₂ in the HDO of phenol [17].

To explain the active sites for Ni(Co) promoted MoS₂ catalysts, there had proposed several models. Two generally accepted models are Co(Ni)–Mo–S model and remote control (RC) model. Co(Ni)–Mo–S model claims that the effect of Co or Ni in Mo sulfide catalyst is attributed to the location of promoter atom on the edges of MoS₂ layers [28]. RC model supposes that the spillover hydrogen migrates from a donor phase (such as Co₉S₈ and NiSₓ) to an acceptor phase (such as MoS₂, WS₂ and ReS₂) and modifies the latter. Gil-Llambías et al. [29–31] had provided a direct proof of the role of a remote control in the hydrodesulfurization using a reactor with physically separated and layered catalyst beds. As we known, all of literatures reported that the high activity of Co(Ni)MoS₂ catalysts in the HDO is attributed to the formation of Co(Ni)–Mo–S phase [17,27]. However, the stability of the so-called Co(Ni)–Mo–S phase decreases if the reaction temperature increases [32], and this phase will decompose during the reaction [33,34], suggesting that Co(Ni)–Mo–S phase is only a 'precursor' of the real catalyst system [30]. Hence, the explanation of the exact nature of active sites by Co(Ni)–Mo–S model is still a subject of debate. In this work, we prepare unsupported Ni–Mo sulfide catalysts by hydrothermal method used ammonium heptamolybdate and thiocarbamide as initial materials. The first aim is to obtain the maximum deoxygenation degree in the HDO of p-cresol by studying the effects of Ni content on the catalytic activity and the HDO reaction conditions on the conversion and product distribution in detail. The additional one is to reveal the HDO reaction mechanism by comparing the HDO activity of different Ni–Mo–S catalysts with the same Ni–Mo molar ratio.

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–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 (2.3 g) and thiourea (3.0 g) were dissolved in 250 mL ultra-pure water. The composition of the samples was adjusted by changing the initial Ni/Mo molar ratio in the solution. The mixed solution was added into a reactor, and then sealed and 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 50 °C for 8 h and stored in nitrogen environment. The prepared catalysts were denoted as Ni–Mo–X, where X represented the molar ratio of Ni/(Ni + Mo) in the initial solution.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried on a D/max2550 18 kW Rotating anode X-ray Diffractometer with monochromatic Cu Kα radiation (λ = 1.5418 Å) radiation at voltage and current of 40 kV and 300 mA. The 2θ was scanned over the range of 10–90° at a rate of 10°/min. The specific surface area was measured by a Quantachrome's NOVA-2100e Surface Area instrument by physisorption of nitrogen at −196 °C. The samples were dehydrated at 300 °C using vacuum degassing for 12 h before physical absorption experiments. 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. The samples for the TEM study were prepared by the ultrasonic dispersing in ethanol and consequent deposition of the suspension upon a "holey" carbon film supported on a copper grid. The samples were kept under inert atmosphere until the last process.

2.3. Catalyst activity measurement

The HDO activity tests were carried out in a 300-mL sealed autoclave with the inner diameter of 50 mm, height of 185 mm and vessel walls thickness of 7 mm. The prepared catalyst without any further treatment (0.60 g), p-cresol (13.50 g) and dodecane (86.50 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 the required temperature with a heat-up rate of 10 °C/min and kept constant, then pressurized with hydrogen to 4.0 MPa and adjusted the stirring speed to 900 rpm. During the reaction, liquid samples were withdrawn from the reactor and analyzed by Agilent 6890/5973 N GC–MS and 7890 gas chromatography using a flame ionization detector (FID) with a 30 m AT-5 capillary column. To separate the reaction products, the temperature in the GC oven was heated from 40 °C to 85 °C with the ramp of 20 °C/min, held at 85 °C for 4.0 min, then heated to 200 °C at a rate of 20 °C/min and kept at 200 °C for 5.0 min. Internal standards (i.e., octane for methylcyclohexane, toluene and decane for p-cresol) were used to determine the product distribution and carbon balance. 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 in the sample for each of experiment was better than 95.0 ± 3.0%. The conversion, selectivity, deoxygenation degree and HYD/DDO for each experiment were calculated as follows:

$$\text{Conversion(mol\%)} = \left(1 - \frac{\text{moles of residual reactant}}{\text{moles of initial reactant}}\right) \times 100\%$$

$$\text{Selectivity(A, mol\%)} = \frac{\text{moles of product(A)}}{\text{moles of reacted reactant}} \times 100\%$$

Deoxygenation degree(D.D.,wt%)

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

$$\frac{\text{HYD}}{\text{DDO}}$$

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