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Performance of Ni-rich bimetallic phosphides on simultaneous quinoline hydrodenitrogenation and dibenzothiophene hydrodesulfurization

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ABSTRACT

A series of Ni-rich bimetallic phosphides incorporating different metals were successfully prepared by initial wetness impregnation, followed by temperature-programmed reduction. Catalyst characterization indicates that the bulk structure and physical properties maintained after adding 2.5 mol% another metal on Ni_2P. Electron transfer from the second metal to Ni was found on $Mo_{0.05}Ni_{1.95}P$, $Co_{0.05}Ni_{1.95}P$, and $Fe_{0.05}Ni_{1.95}P$, except on $W_{0.05}Ni_{1.95}P$. Simultaneous hydrodenitrogenation (HDN) of quinoline and hydrodesulfurization (HDS) of dibenzothiophene (DBT) over phosphides and a commercial metal sulfide were studied at 320–380 °C, 3 MPa, weight hourly space velocity of 6 h^{-1}, and H_2/feed ratio of 500:1. Metal phosphides show higher HDN of quinoline and the same HDS of dibenzothiophene activities than that of a commercial catalyst at 380 °C. $Mo_{0.05}Ni_{1.95}P$ shows the best performance and lowest N and S content adsorbed on the catalyst, due to the active M(2) sites. HDS conversion and product selectivities are seriously impacted by the adsorption of N-containing compounds on active sites of catalysts. Increasing temperature to 360 °C or/and decreasing N content to less than 1000 ppm quinoline in the feed are suggested to obtain simultaneous efficient removal of N and S.

1. Introduction

The energy supply in China will be seriously dependent on rich coal resources in the next few decades. Poly-generation technology based on coal pyrolysis coupled with downstream coal chemical industry has gained wide attention for its production of chemical and liquid fuel, high efficiency and availability on coal utilization. Millions of tons of low temperature coal tar, one of the main products from coal pyrolysis, are obtained every year and hard to treat [1]. Therefore, researches have been conducted on the transformation from coal tar to gasoline and diesel oil by hydrotreating and hydrocracking [2–8].

Heteroatoms, like O, N, and S are eliminated with the help of catalyst during the hydrotreating process [9]. Traditionally, transition metal sulfides have been used as the catalyst in the crude oil hydrotreating process for years because of its excellent hydrodesulfurization (HDS) performance. However, the hydrodenitrogenation (HDN) activity of metal sulfide is not satisfactory [10]. The content of N is about 2 wt.% in coal tar fraction, much higher than that in the feedstock from petroleum. Thus, the catalysts with higher activity on both HDS and HDN are eagerly required.

Among all the catalyst candidates, transition metal phosphide is considered as a promising one [11,12]. The effects of metal loading [13], the ratio of metal and phosphorus [14], metal types [15,16], and preparation methods [17,18] on the activity of metal phosphides have been sufficiently investigated. Different from bimetallic sulfides, carbides, and nitrides, early study showed that no synergistic effect was observed on bimetallic phosphides [20]. However, recently, Burns [19] and Abu and Smith [20,21] and their coworkers revealed that adding less than 5 mol% of Co in Ni_2P promoted the thiophene HDS activity. In contrast against the previous work which showed poor activity on bimetallic phosphides, much lower content of the second metal was incorporated into Ni_2P in their studies. The quite high selectivity to direct desulfurization was also discovered on FeNi bimetallic phosphide by Oyama et al. [22]. Bimetallic phosphides had different catalytic performance from monometallic phosphides. Further researches revealed that on these bimetallic phosphides, Ni atom led to preferential occupation for the square pyramidal M(2) site, which is the active site for hydrogenation [19,23]. Consequently, the activity was remarkably improved after adding small amount of Co or Fe in Ni_2P. The results above confirmed the synergistic effect between Co, Fe and Ni on bimetallic phosphides. However, whether this synergistic effect exists on other transition metals such as Mo and W, needs to be investigated.

Besides HDS, HDN was crucial to the upgrading of oil as well. Compared with sulfides, higher HDN activity on phosphides has been reported [24]. Abu and Smith [25] employed bimetallic phosphides on HDN to probe the effect of different supports on activity. The results showed that MCM-41 had stronger acidity than Al_2O_3, leading to higher HDN activity. MCM-41 has much high surface area, guaranteeing a high dispersion of the active phases, which could improve the activity of catalysts. Lu et al. [26] found that the HDN activity of Ni_2P/MCM-41 dramatically decreased when the content of carbon disulfide or DBT in the feed was

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0.5 wt.%. Thus, hydrotreatment activity of single model compound and complex feed could be different, due to the competitive adsorption on the active site over catalysts. Although bimetallic phosphides showed good HDS performance, simultaneous HDN and HDS activities of such catalysts were not well known.

This work focused on the effect of the adding several different transition metals in Ni_2P on the activity of simultaneous HDN and HDS. The effect of quinoline on DBT HDS conversion was also studied by keeping constant S concentration and changing the content of quinoline in the feedstock.

2. Experiment

2.1. Catalyst preparation

A Ni_2P precursor was prepared on a commercial MCM-41 by incipient wetness impregnation. Typically, 3.525 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.281 g of $(NH_4)_2HPO_4$ were dissolved in 20 ml de-ionized water. Nitric acid was used for clear aqueous solution. 4 g of MCM-41 dried at 110 °C for 2 h in advance was impregnated with the solution at room temperature for 10 h and dried at 120 °C overnight. So, the molar ratio of Ni/P, and the Ni loading on the support MCM-41 were 1.25 and 15%, respectively. The obtained material was calcined at 550 °C for 4 h.

As to bimetallic phosphides, the preparation procedure is the same as that of Ni_2P, except that another appropriate metal was added in the solution for impregnating. For example, a $Co_{0.05}Ni_{1.95}P$/MCM-41 precursor was prepared by dissolving 0.088 g of $Co(NO_3)_2 \cdot 6H_2O$ together with 3.437 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.281 g of $(NH_4)_2HPO_4$ for the co-impregnating. All catalysts are prepared with the molar ratio M/Ni = 0.05:1.95 (M = Co, Mo, Fe, W) and Me/P = 2:1.6 (Me = Ni + M). $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $Fe(NO_3)_2 \cdot 9H_2O$ and $(NH_4)_6H_2W_{12}O_{40}$ were used as the precursors of the second metal with the catalysts named as $Co_{0.05}Ni_{1.95}P$, $Mo_{0.05}Ni_{1.95}P$, $Fe_{0.05}Ni_{1.95}P$, and $W_{0.05}Ni_{1.95}P$, respectively.

As comparison, an oxide precursor of commercial sulfide catalyst with the composition of Mo, Ni, W, and P on support γ-Al_2O_3 was bought and named as MoNiW/Al_2O_3. The loading of Mo, Ni, W, and P was 5.5 wt.%, 1.5 wt.%, 10 wt.%, and 1.8 wt.%, respectively.

2.2. Catalyst characterization

The characterization of Ni_2P and $M_{0.05}Ni_{1.95}P$ (M = Co, Mo, Fe, W) was conducted after the programmed-temperature reduction of the precursor. The flow rate of H_2 for reduction was 150 ml/min. High H_2 flow rate was in favor of the removal of water, which was negative to the formulation of Ni_2P [17]. The heating rate from room temperature to 120 °C was 5 °C/min. The temperature was kept at 120 °C for 1 h, then 3 °C/min to 400 °C, keeping for 0.5 h, and finally at 1 °C/min to 550 °C, holding for 2 h. After reduction, catalyst was cooled down to room temperature followed by passivation with 0.5 vol.% O_2 in N_2 for 2 h.

N_2 adsorption–desorption isotherms of the catalysts were measured on Micromeritics TriStarII3020 apparatus. The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) equation. The desorption branch of the isotherm was used to calculate the average pore diameter according to the Barrett–Joyner–Halenda (BJH) method.

X-ray diffraction (XRD) of the catalysts was recorded by X'Pert PRO diffractometer (PANalytical), using monochromatic CuKα radiation ($\lambda = 1.541$ Å). The X-ray tube was set at 40 kV and 40 mA.

High resolution transmission electron microscope (HRTEM) images were obtained on a Tecnai G2 F20 S-Twin (FEI) operating on 200 kV. The samples were ultrasonic dissolved and placed on a 200-mesh copper grid coated with carbon.

CO chemisorption was measured on an Autosorb-IQ system (Quantachrome). Usually, passivated samples (0.1 g) were loaded into a quartz reactor and reduced at 500 °C for 2 h. After being cooled in He at room temperature, CO in a He carrier flowing was passed through at the same temperature. The total CO uptake was then calculated.

To determine the elemental composition on the surface of catalysts, X-ray photoelectron spectroscopy (XPS) was acquired with an Escalab 250Xi X-ray photoelectron spectroscopy (Thermo) using a AlK_α source. All binding energies were referenced to the C 1s peak at 284.6 eV.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to investigate the bulk element content of catalysts by an iCAP6300 instrument (Thermo). Samples were dissolved in a mixture of HF, HCl and HNO_3, and homogenized at 120 °C in a microwave oven.

2.3. Catalyst activity measurement

Simultaneous quinoline HDN and dibenzothiophene (DBT) HDS activity measurement was carried out in a fix-bed reactor with inner diameter of 8 mm. The precursors of the Ni_2P catalyst or the commercial MoNiW/Al_2O_3 catalyst of 1 g were pelleted, crushed, and sieved to 20–40 meshes (0.42–0.84 mm), and then packed into the fix-bed reactor with 9 ml quartz sand. Before reaction, Ni_2P and $M_{0.05}Ni_{1.95}P$ (M = Co, Mo, Fe, W) precursors were reduced in situ by the temperature-programmed reduction as the same as that before catalyst characterization except the passivation with 0.5 vol.% O_2 in N_2. On the other hand, the MoNiW/Al_2O_3 precursor was presulfided by 360 °C for 4 h at 3 MPa. The presulfiding solution was 5 wt.% carbon disulfide in cyclohexane. The flow rates of H_2 and presulfiding solution were 100 ml/min and 0.5 ml/min, respectively. After the reduction or presulfidation, temperature and pressure were adjusted to the reaction values. The liquid flow was switched to a solution of 2 wt.% quinoline (A.R. grade) and 1 wt.% DBT (A.R. grade) in decalin (A.R. grade). Quinoline and DBT were chosen as the model compounds because they were the main compounds of the N-containing and S-containing compounds in coal tar, respectively. The activities of simultaneous HDN and HDS were investigated under the condition as follows: temperature of 320–380 °C, total pressure of 3 MPa, weight hourly space velocity (WHSV) of 6 h^{-1}, and H_2/feed flow ratio of 500:1. Liquid products were sampled at 3 h after steady reaction condition had been achieved. Four samples in each run were collected with the interval of 1 h to ensure the accuracy of product analysis. The composition of both the feed and products was analyzed by a gas chromatography (Agilent 7890A) equipped with a flame ionization detector (FID) using a HP-5 capillary column. The compounds in liquid products were identified by gas chromatography–mass spectroscopy (GC–MS).

To investigate the effect of quinoline on HDS activity, the DBT concentration in the decalin solution was kept constant (1 wt.%) by varying quinoline content as 0, 1000 ppm, 5000 ppm, and 20,000 ppm. The feeds with different quinoline contents were pumped into the reactor and HDN and HDS activities were measured at 300–380 °C, 3 MPa, WHSV = 6 h^{-1}, and H_2/feed = 500.

In this paper, the HDN conversion, HDS conversion and compound selectivities are defined as follows:

$$\text{HDN conversion } (\%) = \frac{C_{Q0} - C_{Q1} - C_N}{C_{Q0}} \times 100\%$$

where C_{Q0} represents the concentration of quinoline in the feed, while C_{Q1} expresses quinoline concentration in liquid products and C_N is the concentration of other nitrogen-contained compounds in liquid products.

Similarly,

$$\text{HDS conversion } (\%) = \frac{C_{D0} - C_{D1} - C_S}{C_{D0}} \times 100\%$$