Preparation, characterization, and hydrodesulfurization properties of binary transition-metal sulfide catalysts

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HIGHLIGHTS

- Preparation of unsupported binary transition-metal sulfide catalyst.
- Benzylcyclopentane and cyclopentylmethylcyclohexane are observed from isomerization pathway.
- A CoMo catalyst showed a high direct desulfurization activity of dibenzothiophene.
- A NiMo catalyst had high hydrodesulfurization and hydrodenitrogenation abilities.

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ABSTRACT

Binary NiMo, CoMo, NiW, and CoW transition-metal oxide catalyst precursors, were synthesized through a hydrothermal reaction, and highly-loaded hydrodesulfurization (HDS) catalysts were prepared by mixing the precursors with an alumina gel, calcination and sulfidation. The transition-metal oxide catalyst precursors and highly-loaded sulfide catalysts were characterized by XRD, N_2 adsorption–desorption, XRF, and HRTEM. Dibenzothiophene and fluid catalytic cracking (FCC) diesel were employed to evaluate the HDS performance. The crystalline phases of ammonium nickel (or cobalt) molybdate were detected in the NiMo (or CoMo) oxide catalyst precursors, while quasi-amorphous phases were observed for the CoW and NiW oxide precursors. In the sulfided HDS catalysts, typical MoS_2 or WS_2 phases were observed by TEM, while XRD demonstrated that Ni and Co sulfides were present, in accordance with HRTEM results. The catalytic results showed that the binary transition-metal CoMo sulfide catalyst exhibited high direct desulfurization activity and that the NiMo sulfide catalyst had higher HDS and hydrodenitrogenation activities toward the FCC diesel than the other catalysts, with conversions of higher than 99.1% and 99.7%, respectively.

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1. Introduction

Hydrodesulfurization (HDS) plays a vital role in the production of clean fuels, because more stringent environmental legislations forces the sulfur content to an ultra-low level, which nowadays means no more than 10–15 µg/g. The HDS catalysts are considered as the core of HDS processes, and transition metal sulfide (TMS) catalysts have been the major HDS catalysts used in refineries [1]. These catalysts are composed of catalytically active Mo or W sulfides promoted by the sulfides of Co or Ni [1]. Extensive efforts have been devoted to the full usage of the TMS catalysts. For example, the optimal combination and the proper ratio of active component and promoter and the alternation and optimization of the support have received attention [2–5].

Molybdenum-based HDS catalysts have been widely investigated and reported in the literature, while fewer papers cover the applications of tungsten-based catalysts [1,6]. Although the structure of WS_2 is similar to that of MoS_2 [7], there are distinct differences. It is more difficult to convert tungsten oxide to its corresponding sulfide than molybdenum oxide to MoS_2 [7]. Co or Ni promoted Mo-based catalysts are supposed to be an order of magnitude more active in HDS reactions than unpromoted catalysts, predominantly due to the synergetic effect [1,8], while the addition of Co to W-based catalysts does not have such an effect [7,9]. On the other hand, the incorporation of Ni in W-based catalysts leads to catalysts with high hydrogenation ability [9,10].

Similar situations have also been found concerning the geometrical, electronic, and theoretical aspects of Co(Ni)MoS active phases [6]. Lauritsen et al. first observed the Co(Ni)MoS active phases using scanning tunneling microscopy (STM), and classified them into two types according to the degree of sulfidation and to

the interactions between the active metals and the support [6,8,11]. They also found that the Ni and Co promoters preferably substituted the molybdenum atoms at the S edges of single-layer MoS_2 nanoclusters and that the Mo atoms were fully substituted by the promoters at 50% sulfur coverage in the Co(Ni)–Mo–S (-1010) edges [8]. Various morphologies of MoS_2 nanoclusters induced by the promoters (Ni or Co) were also detected, which were attributed to the modified electronic effect [6,8]. Density functional theory (DFT) calculations performed by Sun et al. revealed that for Ni–W-based catalysts Ni replaced tungsten on the W edge, while for Co-promoted WS_2 catalysts, the preferable situation was to substitute tungsten at the S edge [7]. The variations among the preferable substitution of the active metal compound by the promoter might affect the geometrical or electronic aspects and the subsequent catalytic performances.

Apart from the theoretical studies of the HDS catalysts, nowadays more focus has been paid to bulk or unsupported HDS catalysts due to their high activities [1,12–14]. Among them NEBULA is a typical example, which could produce the clean diesel (S content $\ngtr$ 10 μg/g) in a traditional hydrotreating unit originally designed for 350 or 500 μg/g [1,12]. In our previous study, an ammonium nickel molybdate catalyst precursor was synthesized through hydrothermal reactions and it was found to have high activity in the HDS of fluid catalytic cracking (FCC) diesel [15]. In the search for HDS catalysts with high activity and specific selectivity, binary NiMo, CoMo, NiW and CoW transition-metal oxide catalyst precursors were synthesized through the hydrothermal reaction method and highly-loaded catalysts were prepared and tested in the HDS of the model compound dibenzothiophene (DBT) and of FCC diesel. Several characterizations, including XRD, N_2 adsorption–desorption, and HRTEM, were carried out and were used to correlate the physicochemical properties with the activities.

2. Experimental

2.1. Preparation of highly-loaded binary transition-metal oxide catalysts

The binary transition-metal oxide catalyst precursors were synthesized by the hydrothermal reaction method as described before [15]. The reagents used were purchased from Sinopharm Chemical Reagent Company (PR China) without any further purification (Grade AR). Nickel nitrate $(Ni(NO_3)_2 \cdot 6H_2O)$ or cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O)$ were mixed with ammonium heptamolybdate $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ or ammonium metatungstate $((NH_4)_6W_7O_{24} \cdot 6H_2O)$ in the molar ratio 1:1, then urea and polyethylene glycol additive were added and the mixture was stirred with a proper amount of deionized water. The liquid mixtures were transferred to an autoclave and after reacting at 150 °C for 5 h, precipitates were obtained. The products were washed several times with deionized water and isolated by vacuum filtration. To obtain highly-loaded HDS catalysts, the precursors were first mixed with an alumina gel (80/20 in weight) and then extruded into rods. The rods were dried at 110 °C for 12 h, then calcined at 350 °C for 4 h, and crushed into 20–40 mesh particles for catalytic reactions. According to the composition of as-synthesized precursor, the binary transition-metal oxide precursors, and corresponding highly-loaded sulfide catalysts were named NiMo, CoMo, NiW, and CoW.

2.2. Characterization of binary transition-metal oxide and sulfide catalysts

X-ray powder diffraction (XRD) characterizations were carried out on an X'Pert Pro MPD equipment (Panalytical). Nitrogen adsorption–desorption experiments were taken on a ChemBET 3000 workstation (Quantachrome). Elemental analysis of the binary precursors were performed on a X-ray fluorescent instrument (Axios, Panalytical). The dispersions of the sulfided binary transition-metal catalysts were investigated with a JEM 2100 microscope operated at 200 kV.

2.3. Catalytic evaluation of binary transition-metal sulfide catalysts

DBT desulfurization reactions were carried out in a high pressure fixed-bed down-flow microreactor, and 3 ml of the highly-loaded binary transition-metal oxide catalysts was loaded in the center. Before catalytic reaction, the catalysts were first in-situ sulfided at 320 °C for 10 h with a liquid stream containing 3.0 wt.% CS_2 in cyclohexane. Then 3 wt.% DBT–toluene solution was pumped into the reactor. In order to distinguish differences between the catalytic activities of the binary transition-metal sulfide catalysts, the conversions of DBT were kept at a low level, so the experiments were carried out in moderate conditions at a hydrogen pressure of 3.0 MPa, a temperature of 240, 260, and 280 °C, and a liquid hourly space velocity (LHSV) of 4.0 h^{-1}. The liquid product obtained from the high-pressure separator was analyzed by a Varian 3800 gas chromatograph (flame ionization detected, FID) coupled with a quadrupole mass spectrometer (Finnigan SSQ710) (GC–MS).

The rate constants of the pseudo first-order reactions for the conversion of DBT were determined using the equation [16]:

$$k_{TOT} = \frac{F_0}{w} \ln (1 - x_{DBT}) \tag{1}$$

In the HDS reactions, tetrahydro-dibenzothiophene (THDBT), hexahydro-dibenzothiophene (HHDBT), biphenyl (BP), cyclohexylbenzene (CHB), benzylcyclopentane (BCP), and cyclopentylmethylcyclohexane (CPMCH) were detected. The selectivities and rate constants of three pathways (DDS, HYD and ISO) were calculated as follows [17]:

$$S_{DDS} = \frac{BP \times 100\%}{THDBT + HHDBT + BP + CHB + BCH + BCP + CPMCH} \tag{2}$$

$$S_{HYD} = \frac{(THDBT + HHDBT + CHB + BCH) \times 100\%}{THDBT + HHDBT + BP + CHB + BCH + BCP + CPMCH} \tag{3}$$

$$S_{ISO} = \frac{(BCP + CPMCH) \times 100\%}{THDBT + HHDBT + BP + CHB + BCH + BCP + CPMCH} \tag{4}$$

$$k_{DDS} = k_{TOT} \times S_{DDS} \tag{5}$$

$$k_{HYD} = k_{TOT} \times S_{HYD} \tag{6}$$

$$k_{ISO} = k_{TOT} \times S_{ISO} \tag{7}$$

where k_{TOT}, k_{DDS}, k_{HYD}, and k_{ISO} are the pseudo first-order reaction constants of the total HDS, direct desulfurization (DDS), hydrogenation (HYD), and isomerization (ISO) reactions (mol g^{-1} s^{-1}), respectively. S_{DDS}, S_{HYD}, and S_{ISO} are the selectivities of the DDS, HYD, and ISO pathways, respectively. x_{DBT} is the conversion of DBT, F_{DBT} is flow rate of the DBT reactant (mol s^{-1}), while w is the weight of the catalyst (g).

The HDS reactions of the FCC diesel were carried out in the same microreactor, but 10 ml of the binary transition-metal sulfide catalysts was loaded in the reactor. After sulfidation as described above, the FCC diesel produced by Shenghua refinery was pumped into the reactor for HDS reactions. The catalytic reactions were carried out under a hydrogen pressure of 6.0 MPa, at a temperature of 340 °C, and with a H_2/oil volume ratio of 600 and a LHSV of 1.0 h^{-1} For comparison, an industrial NiMo/Al_2O_3 supported catalyst (22.5 wt.% MoO_3, 3.9 wt.% NiO, and BET surface area 235 m^2/g) was