



Synthesis, characterization and hydrodesulfurization properties of nickel–copper–molybdenum catalysts for the production of ultra-low sulfur diesel



Huan Liu, Changlong Yin^{*}, He Li, Bin Liu, Xuehui Li, Yongming Chai, Yanpeng Li, Chenguang Liu^{*}

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, CNPC, China University of Petroleum, Qingdao, Shandong 266555, China

HIGHLIGHTS

- A series of nickel–copper–molybdenum catalyst precursors was synthesized by chemical precipitation.
- The particle sizes of the MoS₂ nanoclusters and sulfided nickel-containing compounds varied with the introduction of copper.
- A Ni_{9.5}Cu_{0.5}Mo₁₀ catalyst exhibited high hydrodesulfurization activity.

ARTICLE INFO

Article history:

Received 17 February 2014

Received in revised form 18 March 2014

Accepted 25 March 2014

Available online 5 April 2014

Keywords:

Nickel–copper–molybdenum catalyst

Hydrodesulfurization

4,6-Dimethyldibenzothiophene

Ultra-low sulfur diesel

Chemical precipitation

ABSTRACT

A series of nickel–copper–molybdenum catalyst precursors was synthesized through chemical precipitation method, and highly loaded catalysts were prepared by mixing the precursors with alumina sol. The nickel–copper–molybdenum catalysts were tested in the hydrodesulfurization (HDS) of the model compound 4,6-dimethyldibenzothiophene (4,6-DMDBT) and fluid catalytic cracking (FCC) diesel. The catalysts were characterized by means of N₂-physisorption, XRD, FT-IR, SEM, TG–DSC–MS, TPR and HRTEM. The characterization results indicated that nickel–copper–molybdenum catalyst precursors could be synthesized due to the similarities of the lattice parameters and ionic radii of nickel and copper, and the HRTEM micrographs and XRD results of the sulfided nickel–copper–molybdenum catalysts revealed that the introduction of copper affected the particle sizes of the stacked MoS₂ and sulfided nickel-containing compounds. The catalytic results showed that the Ni_{9.5}Cu_{0.5}Mo₁₀ catalyst exhibited high catalytic activity in the HDS of 4,6-DMDBT and FCC diesel, and might be suitable for the production of ultra-low sulfur diesel.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrotreating is one of the most important reactions in petroleum refining processes for the removal of heteroatoms from feedstocks. Especially the removal of sulfur from sulfur-containing compounds, the contents of which typically ranges between 1 and 3 wt.% (10,000–30,000 ppmw) in middle distillates or raw distillates, is of importance [1,2]. The sulfur-containing compounds cause several severe problems, such as the pollution of the environment through the emission of SO₂, the corrosion of materials by acid rain, and the poisoning of most petrochemical catalysts [2–4]. In recent years, more stringent environmental legislations and growing concerns about the environment, coupled with the

dwindling fossil fuel reserves, have accelerated research of economically effective hydrodesulfurization (HDS) catalysts for producing cleaner fuels from feedstocks of progressively lower quality [2]. The industrial HDS process is carried out over sulfided Mo or W-based catalysts promoted by Ni or Co and supported on γ -Al₂O₃ [3,5–7]. To lower the sulfur content of fuels to 10–15 ppmw, the urgent need for a drastic improvement of the HDS catalyst activity motivated the search for novel and more efficient catalysts [1,8].

Significant and promising improvements in HDS catalysts have been achieved for the production of ultra-low sulfur diesel (ULSD). The introduction of organic additives during the preparation of HDS catalysts, like ethyleneglycol and triethyleneglycol [9,10], might promote the formation of the so-called “NiMoS phase” or “CoMoS phase”, which are supposed to be catalytically active in HDS [5,11]. Pt and Rh sulfides were more active than MoS₂ due to electronic effects [12,13], and were more suitable for the

^{*} Corresponding author. Tel.: +86 053286984686.

E-mail addresses: yincl@upc.edu.cn (C. Yin), cgliu.upc.edu.cn@gmail.com (C. Liu).

production of ULSD, because of the steric effects of the refractory sulfur-containing molecules, like dibenzothiophenes (DBTs) alkylated at the 4 and 4,6 positions. The concentration of these molecules can predominantly be reduced through hydrogenation [1,12,14]. Additives like fluoride or phosphate are also used to prepare highly active supported HDS catalysts. They modify and optimize the interactions between the active phase and support [8,9,15,16].

Copper-containing compounds are known to be catalytically active for hydrogenation processes such as methanol synthesis and selective hydrogenation [17–19], although few papers deal with copper in HDS catalysts. Harris and Chianelli found that the introduction of Cu in unsupported MoS₂ (through the reaction of CuCl₂ with (NH₄)₂MoS₄) acted as a poison, because Cu decreased the electron density on Mo, thus leading to oxidation of Mo in MoS₂ [20]. Recently, the formation of mixed-metal “Cu–Mo–S” – type structures shaped as single-layer hexagonally truncated triangular MoS₂-like nanoclusters was revealed by Kibsgaard et al. [5]. Also, Cu⁺ ions are efficient adsorbents for the removal of sulfur, because they can form π -complexes with thiophenic aromatic rings, as in DBT and its derivatives [21,22].

More recently, we reported the synthesis of novel crystalline ammonium nickel molybdate as efficient HDS catalyst precursor towards the production of ULSD, which was attributed to the efficient formation of the Ni–Mo–S structure [23]. As the lattice parameters as well as the ionic radii of nickel and copper are very close [24], it can be expected that nickel–copper–molybdenum compounds could be prepared, which might have novel physicochemical and catalytic properties. To explore if such compounds are efficient HDS catalysts, a series of nickel–copper–molybdenum catalysts was synthesized by chemical precipitation and evaluated in the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT), and fluid catalytic cracking (FCC) diesel.

2. Experimental

2.1. Preparation of nickel–copper–molybdenum catalyst precursors

Nickel–copper–molybdenum catalyst precursors were prepared by the chemical precipitation method in the following way. An amount of 0.10 mol ammonium heptamolybdate and the required amount of nickel nitrate and/or copper nitrate (Sinopharm Chemical Reagent Company, China, Grade AR) were dissolved in deionized water with the desired molar ratio (shown in Table 1). The solution was added to a flask, heated, and stirred at 90 °C. The addition of aqueous ammonia precipitated a light green solid that dissolved in excess ammonia, giving a solution with various colors (shown in Table 1 as “Color of dissolved precipitate”) depending on the composition and molar ratio. The solution was stirred and heated for 12 h, leading to the formation of a precipitate. The products were isolated by vacuum filtration, washed with deionized water, and dried overnight at 80 °C and atmospheric pressure.

2.2. Preparation of highly loaded catalyst

The preparation of a highly loaded catalyst has been described in detail elsewhere [23]. First, an alumina sol was made from

boehmite and nitric acid. Then the nickel–copper–molybdenum catalyst precursor was mixed with the alumina sol with the weight ratio of precursor/alumina 75/25, and extruded into rods 1.2 mm in diameter. The rods were dried at 100 °C for 12 h and then calcined at 350 °C for 4 h.

An industrial NiMo/Al₂O₃ catalyst containing 24 wt.% MoO₃ and 4 wt.% NiO supported on alumina (BET specific surface area of 225 m²/g) was used as reference catalyst in the HDS of FCC diesel.

2.3. Characterization of nickel–copper–molybdenum catalyst precursors

N₂ adsorption–desorption experiments were carried out on a ChemBET 3000 (Quantachrome, USA) instrument. X-ray powder diffraction (XRD) characterization was performed on a Rigaku D/max-IIA diffractometer using graphite-filtered Cu K α radiation. Combined thermogravimetry, differential scanning calorimetry, and mass spectrometry analysis (TG–DSC–MS) was carried out at a heating rate of 10 °C/min under high-purity nitrogen atmosphere. Fourier-transform infrared (FT-IR) spectra were collected on a Nexus spectrometer (Nicolet, USA) using KBr disks. Morphological information was collected on a FEI Quanta200 scanning electron microscope (SEM) instrument. Temperature-programmed reduction (TPR) analysis of nickel–copper–molybdenum catalyst precursors and sulfided catalysts was performed on a Micromeritics RS 232 instrument. The H₂ consumption of the catalyst precursor or sulfided catalyst reduction was recorded by a thermal conductivity detector (TCD). High-resolution transmission electron microscopy (HRTEM) was carried out on a JEM 2100 microscope operated at 200 kV. More detailed information about the characterization of the nickel–copper–molybdenum catalyst precursors can be found in Ref. [23].

2.4. Catalytic activity

2.4.1. HDS of 4,6-DMDBT using sulfided catalyst precursors

Catalytic activity measurements were carried out in a 500 mL micro-autoclave reactor. 4,6-DMDBT (purchased from Aladdin Co., purity 97%), was chosen as representative component for the HDS reaction. The sulfided catalyst was made from the precursor in the following way. The reactor was charged with 2.0 g nickel–copper–molybdenum catalyst precursor of 400–460 mesh size and 1.0 mL CS₂ in petroleum ether solvent (boiling ranging 90–120 °C). Before the sulfidation reaction, the reactor was flushed five times with high-purity hydrogen followed by adjusting the hydrogen pressure to 3.0 MPa at room temperature. The reactor was then heated at a ramping rate of 3 °C/min, and stirred at about 60 r/min, so that the catalytic reaction was inhibited until reaching the desired reaction conditions. When the temperature was approaching the evaluated temperature (320 °C for sulfidation), the stirring rate was set as 700 r/min. At that time, the catalytic reaction began. After 6 h sulfidation, the reactor was opened at room temperature and atmospheric pressure, then 0.10 g 4,6-DMDBT was added to the reactor, and the hydrodesulfurization reactions were carried out at 8.0 MPa and 315 °C during 3 h. Then the products were cooled to room temperature and analyzed with a Varian 3800

Table 1
Experimental conditions and textural properties.

Label	Ni/mol	Cu/mol	Color of dissolved precipitate	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Cu10Mo10	0	0.10	Dark blue	9	0.07	37.3
Ni5Cu5Mo10	0.05	0.05	Blackish green	38	0.10	7.7
Ni8Cu2Mo10	0.08	0.02	Dark blue	53	0.10	5.4
Ni9.5Cu0.5Mo10	0.095	0.005	Dark blue	28	0.09	8.6
Ni10Mo10	0.10	0	Dark blue	88	0.13	4.5

Download English Version:

<https://daneshyari.com/en/article/6637582>

Download Persian Version:

<https://daneshyari.com/article/6637582>

[Daneshyari.com](https://daneshyari.com)