Highly efficient NiMo/SiO$_2$-Al$_2$O$_3$ hydrodesulfurization catalyst prepared from gemini surfactant-dispersed Mo precursor

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ABSTRACT

This article proposes a novel gemini surfactant-assisted synthesis of Mo precursor for preparing NiMo/SiO$_2$-Al$_2$O$_3$ ultra-deep hydrodesulfurization (HDS) catalysts. The proposed method transforms polymolybdate anions into gemini surfactant-linked Mo precursor (GSMP), which facilitates the formation of highly dispersed MoS$_2$ phases with improved stacking and therefore produces a large number of accessible Ni-Mo-S phases after Ni incorporation. The GSMP-based NiMo/SiO$_2$-Al$_2$O$_3$ catalyst presents higher catalytic activity for the HDS of 4,6-dimethyldibenzothiophene and fluid catalytic cracking (FCC) diesel than its counterparts prepared via impregnation and the cetyltrimethylammonium bromide-assisted hydrothermal method.

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1. Introduction

Increasingly stringent environmental regulations and fuel standards impel refineries to produce clean diesel with ultra-low sulfur [1]. However, the presence of sterically hindered 4,6-dimethyldibenzothiophene (4,6-DMDBT) makes sulfur removal from diesel a critical challenge [2]. Hydrodesulfurization (HDS) is an important technique for diesel desulfurization [3]. The key to improving HDS performance lies in the fabrication of highly active catalysts.

Mo(W)-based sulfides as active components and Ni(Co) as promoters supported on alumina have been used as HDS catalysts for more than 80 years [4]. Extensive studies indicate that there are two Co(Ni)-Mo(W)-S phases in γ-Al$_2$O$_3$-supported Co(Ni)-Mo(W) sulfides [5–9]. The type I phase with poor sulfidation has strong Mo-O-Al linkages with γ-Al$_2$O$_3$ and presents poor HDS activity, whereas the type II phase with full sulfidation possesses weak van der Waals interactions with γ-Al$_2$O$_3$ and exhibits high HDS activity. Therefore, the key point for improving the HDS activity of Mo-based sulfides lies in increasing the amount of the type II phase. The strong metal-support interaction leads to excellent dispersion but poor sulfidation of Mo oxidic species, while the weak metal-support interaction brings about superior sulfidation but poor dispersion

of Mo oxidic species [10]. In conventional alumina-supported Mo-based catalysts, the strong Mo-support interaction results from the interaction between the Mo oxides and the basic hydroxyls of γ-Al$_2$O$_3$ [11–13]. The strong interaction can be reduced using mesoporous materials, such as SBA-15 [14,15], KIT-6 [16] and MCM-41 [17,18], but their poorer mechanical strength, thermal and hydrothermal stability restrict the industrial application of these materials. The surface modification of alumina is an efficient way to weaken the metal-support interaction. Felipe Sánchez-Minero et al. [19–21] showed that modifying the alumina surface with SiO$_2$ reduced the number of reactive hydroxyls on the γ-Al$_2$O$_3$ surface and therefore weakened the Mo-γ-Al$_2$O$_3$ interaction, promoting the sulfidation of supported Mo oxides. However, the weakened interaction produced the metal species with large particles, decreasing the number of active metal sites.

Several methods have been developed to obtain highly dispersed metal phases, such as equilibrium deposition filtration [22,23], deposition-precipitation [24], and the chemical vapor deposition and sonochemical method [25]. These methods enhance the dispersion of metal phases but decrease the stacking of active metal phases with strong metal-support interactions, blocking the adsorption and subsequent reaction of sterically hindered 4,6-DMDBT. To improve the stacking of active metal phases, chelated metal precursors were synthesized, such as Mo$_4$(Hcitrate)$_2$O$_{11}$$^{4-}$ complexes [26], (CoL)$_2$[Mo$_4$(C$_6$H$_5$O$_7$)$_2$O$_{11}$]·xH$_2$O complexes [27] and (NH$_4$)$_4$[Ni(OH)$_6$Mo$_6$O$_{18}$] [28]. However, the low stability of these complexes leads to their decomposition during the load-

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ing process and to an uneven distribution of active metal phases, reducing the activity of the corresponding catalysts. It is still a challenge for balancing the dispersion and stacking of supported metal phases to efficiently remove sterically hindered sulfur-containing compounds.

Herein, we prepare a novel $NiMo/SiO_2-Al_2O_3$ catalyst with the improved stacking and good dispersion of supported active phases via gemini surfactant-assisted synthesis. In this method, polymolybdate anions were transformed into gemini surfactant-linked Mo precursor (GSMP), dispersing Mo species well and weakening the strong Mo-support interaction. Meanwhile, a hydrothermal system was adopted to decrease the viscosity of solution and increase mass transfer for improving the dispersion of Mo precursor [29]. The above measures ensured the superior dispersion of the supported Mo species with improved stacking and thereby yielded highly efficient $NiMo/SiO_2-Al_2O_3$ catalyst for 4,6-DMDBT HDS.

2. Experimental

2.1. Synthesis of Mo precursors

Gemini-type quaternary ammonium surfactant ($C_{16}H_{33}$-N(CH_3)$_2$-C_6H_{12}-N(CH_3)$_2$-$C_{16}H_{33}$)Br_2 (abbreviated as 16-N_2-16Br_2) was synthesized according to the literatures [30,31]. The reaction of N,N,N′,N′-tetramethyl-1,6-hexanediamine ((CH_3)$_2$N-(CH_2)$_6$-N(CH_3)$_2$, 99 wt.%, J & K Scientific Ltd., Beijing) with 1-bromohexadecane ($C_{16}H_{33}Br$, 98 wt.%, J & K Scientific Ltd., Beijing) in isopropanol ((CH_3)$_2$CHOH, 99 wt.%, J & K Scientific Ltd., Beijing) under reflux at 85 °C for 48 h yielded the gemini surfactant 16-N_2-16Br_2, which was recrystallized from a mixture of acetone and ethanol. The products were detected by ^{1}HNMR in a $CDCl_3$ solution using a Bruker Avance apparatus (300 MHz).

A typical procedure for the synthesis of Mo-based precursor involved the following steps: firstly, 1.04 g of ammonium heptamolybdate tetrahydrate (AHT, (NH_4)$_6$$Mo_7O_{24}$·4$H_2O$, 99.99 wt.%, J & K Scientific Ltd., Beijing) was dissolved in 50 mL deionized water, and a hydrochloric acid solution (containing 37% HCl) was added to the aqueous solution until the pH reached 3.0. Then, at 50 °C, 20 mL of 0.074 M 16-N_2-16Br_2 solution was added to the above aqueous solution under vigorous stirring. The as-prepared mixture was acidulated to pH = 3.0 by adding hydrochloric acid solution and was then stirred for 2 h at 50 °C. Finally, the suspension was washed with deionized water, centrifuged, and dried at 100 °C for 6 h. The obtained product was considered gemini surfactant-linked Mo precursor (GSMP).

2.2. Preparation of catalysts

The $SiO_2-Al_2O_3$ support (Shandong Alumina Plant, P.R. China) contained 96.4 wt.% Al_2O_3 and 3.6 wt.% SiO_2, with a surface area of 316 m^2 g^{-1}, average diameter of 8.0 nm, and pore volume of 0.63 mL g^{-1}. The support was denoted by SA.

Three MoO_3/SA catalysts, designated as Mo-GSHD, Mo-CTHD and Mo-IM, were prepared by the gemini surfactant-assisted hydrothermal deposition (GSHD), the CTAB-assisted hydrothermal deposition (CTHD) and impregnation (IM).

The preparation of oxidic Mo-GSHD involved the following steps: 4.0 g of the above SA particles (20–40 meshes) was placed in a 100 mL autoclave containing 70 mL of GSMP suspension, and the autoclave was heated at 120 °C for 24 h under rotation. Next, the obtained GSMP/SA composite was filtered, and washed with deionized water. Last, the composite was dried at 120 °C for 2 h, and calcined at 500 °C for 4 h in N_2 atmosphere. As a result, the oxidic Mo-GSHD catalyst was obtained.

For comparison, oxidic Mo-CTHD was prepared as follows: first, a (NH_4)$_6$$Mo_7O_{24}$·4$H_2O$ aqueous solution was acidulated to pH = 3.0, and CTAB was added to obtain a suspension. Then, 4.0 g of the above SA particles (20–40 meshes) was added to a 100 mL autoclave containing 70 mL of the as-prepared suspension, and the autoclave was heated at 120 °C for 24 h under rotation; finally, the resulting composite was treated with the same procedures as those for the GSMP/SA composite. As a result, the oxidic Mo-CTHD catalyst was obtained.

Oxidic Mo-IM was prepared via impregnating 20–40 meshes SA particles with a (NH_4)$_6$$Mo_7O_{24}$·4$H_2O$ aqueous solution. Following the impregnation, the sample was dried and calcined with the same procedures as those for the GSMP/SA composite.

The MoO_3 loadings of the Mo-IM, Mo-CTHD and Mo-GSHD catalysts, detected by X-ray fluorescence spectroscopy (XRF) on an AxiosmAX instrument, were 16.7, 17.0 and 16.8 wt.%, respectively.

The loading of NiO on the three MoO_3/SA catalysts was carried out by impregnating Mo-GSHD, Mo-CTHD and Mo-IM with nickel nitrate (Ni(NO_3)$_2$·6H_2O, 98 wt.%) as the Ni precursor. After impregnation, the products were dried at 120 °C for 2 h and calcined at 500 °C for 4 h in N_2 to produce three oxidic NiMo/SA catalysts, denoted as NiMo-GSHD, NiMo-CTHD and NiMo-IM. According to the XRF results, the contents of MoO_3 in NiMo-IM, NiMo-CTHD and NiMo-GSHD were 16.3, 16.7 and 16.5 wt.%, respectively; the contents of NiO in NiMo-IM, NiMo-CTHD and NiMo-GSHD were 3.8, 3.5 and 3.6 wt.%, respectively.

2.3. Characterizations

Fourier transform infrared (FT-IR) experiments were measured on a Nicolet 6700 FT-IR spectrometer, and the spectra of samples were recorded in the wavenumber range of 650–4000 cm^{-1} at a 4 cm^{-1} resolution.

NO adsorption followed by FT-IR spectroscopy (Nicolet 6700 FT-IR spectrometer) was conducted using self-supported wafers (5–10 mg/cm^2) of the oxidic catalysts that were mounted in the FT-IR cell. The catalyst was sulfided in situ at 360 °C for 2 h in a flow of 15% H_2S/H_2 and then flushed with He at 360 °C for 1 h. After cooling to room temperature in a pure He flow, the cell was evacuated to 10^{-3} Pa. The sample was exposed to 6650 Pa of NO for 30 min, followed by flushing the gas phase NO with pure He, and subsequently the spectra were recorded. The background was subtracted in all reported spectra.

Laser Raman (LR) experiments were performed on a Bruker Raman spectrometer, and the spectra were recorded in 3600–100 cm^{-1}, using the Nd-YAG laser excited at 532 nm as the laser source. Elemental analyses were acquired through inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Perkin Elmer instrument combined with 2400 II CHN element analyzer.

N_2 adsorption-desorption experiments of the support SA and catalysts were conducted on a Micromeritics ASAP 2420 instrument. The samples were pretreated at 250 °C under a vacuum of 10^{-3} Pa for 15 h prior to the experiments, and subsequently transferred to the analysis station for adsorption-desorption at −196 °C.

X-ray diffraction (XRD) analyses were conducted on a Bruker D8 Advance instrument (40 kV and 30 mA), using Cu Kα radiation (λ = 1.54 Ao). The scanning range of 2θ was between 10 and 80° with a speed at 4°/min.

The hydrogen temperature-programmed reduction (H_2-TPR) experiments of the oxidic catalysts were carried out with a self-established device. First, 100 mg of each sample were heated at 450 °C for 2 h in an Ar atmosphere and subsequently the sample was cooled down to 60 °C. Subsequently, the sample was heated from 60 to 1050 °C with a rate of 10 °C/min and kept at 1050 °C for