

Short Communication

Structure and activity of NiMo/alumina hydrodesulfurization model catalyst with ordered opal-like pores

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ARTICLE INFO

Article history:

Received 28 September 2011

Received in revised form 30 November 2011

Accepted 7 December 2011

Available online 13 December 2011

Keywords:

Opal
Model catalyst
Ordered pores
Uniform pore size
Hydrodesulfurization

ABSTRACT

Ordered porous opal-like NiMo/alumina hydrodesulfurization model catalyst was prepared by loading NiMo oxides on alumina-coated silica opal, and the state of active metal oxides was investigated. The results showed that the pore size of the model catalyst is uniformly distributed. The catalyst pore structure is independent of NiMo loadings below five-fold the monolayer capacity. Due to the regular smooth surface of the catalyst, metal oxides on it can be easily observed with high resolution transmission electron microscopy. Subsequently, the activity of model catalysts was tested and correlated with the metal oxides species.

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1. Introduction

Al₂O₃-supported Co(Ni)-Mo sulfide catalysts have been widely used in hydrodesulfurization (HDS). However, commercial alumina-supported catalysts usually have a very broad pore size distribution and irregular pores. Therefore, it is unsatisfactory to investigate the surface nature of HDS catalyst correlated to the activity. Metal loadings usually impact the pore structure of catalyst due to small pores blocking [1], which more or less decreased the activity of catalyst by lowering the diffusion rate of sulfur-containing molecules and accessibility of active sites in small pores. This effect is more obvious for larger molecules system, such as heavy oil HDS [2]. Thus, to further understand the structure–activity relationship, a catalyst with narrow pore-size distribution, well-defined pore size and constant pore structure is needed. Meanwhile, to observe the surface active metals, the smooth and simple geometric surface of catalyst is favorable [3–5].

Opal is an ideal model support with very uniform-pore-size distribution due to its ordered pores from voids of the face-center cubic compact of mono-sized spherical SiO₂. It has been successfully used in the diffusion study of petroleum residue fractions in Chen's research group [6]. Spherical silica composing the opal is easily observed with electron microscopy [7]. The silica surface of opals is rich in H-bonded silanol groups [8], and can be modified readily through grafting these silanol groups with other metal oxides. Thus,

this support is versatile and can be applied to other heterogeneous catalytic systems.

In the present study, a NiMo/alumina HDS model catalyst with well-defined and uniform pore size was obtained by depositing Al₂O₃, MoO₃ and NiO on the internal surface of SiO₂ opal sequentially. Having ordered pore structure and regular surface, the model catalyst is suitable for the investigation of structure–activity relationship and the surface metal state of the catalyst.

2. Experimental

2.1. Preparation of alumina opal support

Monodisperse silica microspheres (100 nm) were prepared by dropwise adding a calculated quantity of tetraethoxysilane (TEOS) in ethanol solution with silica sol (0.3 wt.%), water (6 mol/L) and ammonia (2 mol/L) under 200 rpm agitation at 25 °C [9,10]. The particle size was monitored with laser granulometer (Zetasizer Nano ZS, Marvern, UK). Then 100 mL suspension of silica microspheres (5 wt.%) was put in a 500 mL beaker covered by a lid with 3 mm² hole. The silica microspheres were self-assembled into opal after drying the suspension at 50 °C for about one week. The as-prepared silica opal was then dried at 100 °C for 24 h in an air oven, calcined at 800 °C for 2 h, and hydrothermally treated in water at 220 °C for 10 h in an autoclave. Alumina was coated onto the internal surface of silica opal by depositing precursor Al(NO₃)₃ on the support surface with incipient wet impregnation method, hydrolyzing in ammonia/water vapor at 100 °C for 7 h [11] and calcining at 500 °C for 5 h. The amount of alumina coating was its monolayer capacity (1.38 wt.% Al₂O₃ or 4.26 wt.% Al(NO₃)₃·9H₂O) [12].

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2.2. Preparation of model catalyst

An aqueous $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solution was added to the support. The sample was then dried at 100 °C for 12 h and calcined at 500 °C for 5 h. And the calcined sample was re-impregnated with the aqueous $\text{Ni}(\text{NO}_3)_2$ solution, and dried, calcined as above. The metal loadings were multiples of their monolayer capacity on γ -alumina with atom molar ratio $\text{Ni}:\text{Mo}=1:2$ (0.6 wt.% NiO and 2.3 wt.% MoO_3) [13]. Model catalyst with different NiMo loadings (different quantity but constant atom molar ratio) was denoted as “CAT-Ni x Mo y ”, where x and y represent the weight percentage of NiO and MoO_3 . The treated silica opal and alumina-coated silica opal were denoted as “SLI-0” and “SUP-0”.

2.3. Characterization of model catalyst

The morphology of the samples was observed with HRTEM (High Resolution Transmission Electron Microscopy), using FEI F20 microscope (FEI, Oregon, USA) operated at 200 kV. The X-ray powder diffraction patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Bruker, Germany) using $\text{CuK}\alpha$ radiation of wavelength 0.154 nm with a scanning rate of 1°/min. The N_2 adsorption–desorption data were recorded with a Micromeritics ASAP 2010 automatic adsorption analyzer (Micromeritics, Norcross, GA). UV-Raman spectra were recorded on a HR800 UV-Raman spectrograph (Horiba Jobin Yvon Company, France). The 244.0 nm-line of He–Cd laser was used as the excitation source.

2.4. Activity test

HDS of dibenzothiophene (DBT) was performed in a trickle-bed reactor (stainless steel, 9 mm i.d., catalyst bed 20 mm) at 300 °C under 6.0 MPa on 1.0 g catalyst with a grain size 0.2–0.3 mm. Hydrogen was mixed with DBT-lube base oil (11.03 $\mu\text{mol}/\text{mL}$) and fed at the ratio of $\text{H}_2/\text{Oil}=600$ to the reactor. The total sulfur contents of products were analyzed by a micro-coulometer (LC-4, Shuangyang, China). Prior to

the HDS reaction, the catalyst was presulfided by stream of 3 wt.% $\text{CS}_2/\text{cyclohexane}$ (0.2 mL/min) and H_2 (30 mL/min) under 4.0 MPa at 300 °C for 4 h. The rate of HDS was normalized to moles of DBT conversion per mol of Mo and per m^2 of sulfided catalyst. Activities were calculated from the expression: $\text{HDS rate} = \text{FYC}/N$, where F is the flow rate of feed (mL/min); Y the fractional conversion; C the concentration of DBT in the feed (mol/mL) and N Mo content (mol) or surface area (m^2) of the catalyst.

3. Results and discussion

3.1. N_2 adsorption–desorption

The pore structure of catalysts with different NiMo loadings were measured by N_2 adsorption–desorption. Fig. 1A gives the hysteresis loops of catalysts with different NiMo loadings. These hysteresis loops are type IV isotherm, which is characteristic of mesoporous solids. Fig. 1B shows that the catalysts and the support have an identical uniform pore-size distribution centered at ca. 26 nm below five-fold the monolayer capacity of NiMo. The pore volume (PV) and specific surface area (SSA) of the model catalysts were all determined as 0.18–0.19 mL/g and about $28 \pm 2 \text{ m}^2/\text{g}$. More loadings decrease the pore size and pore volume.

3.2. X-ray diffraction (XRD)

XRD patterns of model catalysts with different NiMo loadings are shown in Fig. 2. The model catalyst with low NiMo loadings (CAT-Ni0.6Mo2.3) shows no noticeable diffraction peaks. XRD patterns of catalysts with higher NiMo loadings present the evidence of MoO_3 and NiMoO_4 crystalline phases. The bands at $2\theta = 12.8^\circ, 23.3^\circ, 25.7^\circ, 27.3^\circ$ and 33.7° correspond to crystalline orthorhombic $\alpha\text{-MoO}_3$ (JCPDS 47-1320) [14]. The weak peaks at $2\theta = 26.6^\circ$ and $28.8^\circ, 39.1^\circ, 49.3^\circ$ correspond to $\beta\text{-}$ and $\alpha\text{-NiMoO}_4$ phase, respectively

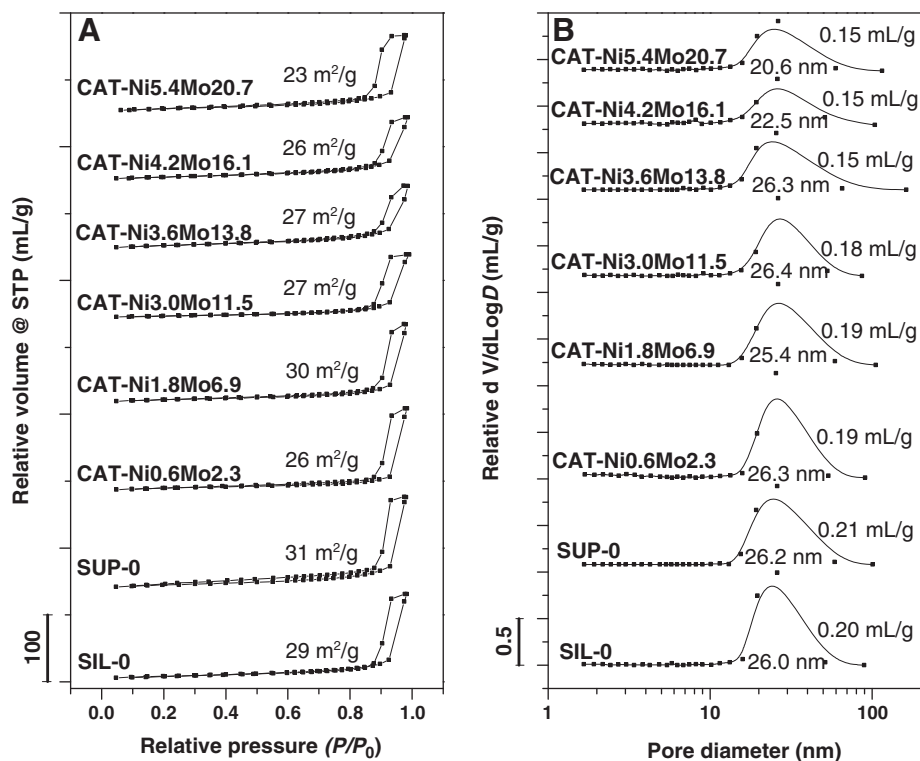


Fig. 1. Pore structure of the support and model catalysts with different NiMo loadings. (A) Hysteresis loops with specific surface areas; (B) pore-size distributions with average pore-sizes and pore volumes.

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