



Synthesis of hierarchically structured alumina support with adjustable nanocrystalline aggregation towards efficient hydrodesulfurization

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ABSTRACT

The development of highly active hydrodesulfurization (HDS) catalysts is still of great importance in hydro-processing of the heavy residue oils in industry. Herein, hierarchically structured alumina hollow microspheres with high specific surface area were successfully prepared via a citric-acid-modulated hydrothermal method. With different dosages of citric acid applied, alumina microspheres were assembled with different specific surface areas, pore volumes and acidity. After the loading of the MoNi active components, a series of HDS catalysts were characterized systematically by various relevant techniques; and their catalytic activity and selectivity towards hydrodesulfurization of dibenzothiophene (DBT) were evaluated and compared. It is revealed that, the catalytic efficiency of the catalyst highly depends on the factors including the specific surface area and the acidity, the sulfidity and the dispersion of the active metal components. On this basis, we have established a facile method for preparation of hierarchically structured alumina supports with desirable physicochemical properties and high HDS catalytic efficiency. This work could also provide theoretical guidance for rational design of highly active HDS catalysts.

1. Introduction

In recent decades, with increasing global concern on environment protection, strict regulations have been made to control the sulfur contents in gasoline and diesel in many countries, which accelerates the demand for high-quality petroleum products and also set high requirements for the industrial capacity of hydrodesulfurization (HDS) [1–4]. Therefore, highly active HDS catalysts are urgently required. Conventionally, the HDS catalyst generally uses Ni (Co)-Mo (W) as the active component [5–7], with alumina or alumina composite oxide containing silica, titanium dioxide or zeolite used as the catalyst carrier [1,2,8–10]. To meet the increasing demand, new HDS catalysts have also been exploited, which mainly explore novel active components (such as NiP, MoP and WP) [11–14]. However, the commercialization of these new catalysts is often limited by the high cost, the harsh preparation conditions and/or the poor catalyst stability. In this respect, exploitation of approaches towards highly efficient and stable Ni (Co)-Mo (W) catalysts is still necessary to upgrade the present HDS technologies.

Towards this end, it is crucial to develop desirable support materials

because the HDS performance strongly depends on the physical properties (e.g., the specific surface area, the pore volume, and the pore size) and chemical properties (e.g., acidity) of the catalyst supports. The higher specific surface area facilitates the dispersion of the metal active component on the surface of the support. Until now, γ -Al₂O₃ support is the most widely used support for HDS catalysts [15]. However, the conventional alumina supports usually have an unimodal pore size distribution curve, most of which have only mesopores. As such, the reactions over such catalysts are susceptible to diffusion control; and the catalyst support could suffer from pore plugging easily, which leads to catalytic activity decline and short cycle life. In view of the above issues, hierarchically porous alumina materials, especially those with macro-meso-porosities, have aroused the interest of many scholars. The macropores can facilitate the diffusion of reactants with large molecule sizes from the outer surface of the catalyst to the active sites, whereas the mesopores provide the large surface area for the homogeneous dispersion of active sites, both of which work together to support high catalytic activity and durability.

To produce such hierarchical catalysts, template agents, such as carbon black [16], polystyrene (PS) [17], poly-(methyl methacrylate)

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(PMMA) [18], have been most commonly used. Pore size and volume of such prepared samples closely depend on the amount and/or the size of the templates. Maity et al. reported that the 10% carbon modified-alumina-supported P-containing CoMo catalysts (105 m²/g) which had larger pore diameter and higher pore volume exhibited higher HDS and HDM activities than the control samples [16]. Han et al. found that the coprecipitated Co–Mo/Al₂O₃ catalyst with both macro- and meso-pores whose surface area is 79 m²/g exhibited a superior durability for hydrodesulfurization of dibenzothiophene (DBT) compared to those without macropores [18]. However, it shall also be noted that, compared with the conventional mesoporous alumina, the macro-mesoporous alumina generally has relatively small specific surface area. Moreover, the acidity of the surface of the support which affects the interaction between the active metal components and the support also influence the dispersion and the active composition of the metal oxide [19–21]. Alumina carriers with suitable acidity are favorable for the hydrodesulfurization process. P, B and other elements were employed to further regulate the acidity of the catalytic support [16,22–24]. Therefore, the development of an ideal macro-mesoporous alumina carrier material with both high specific surface area and moderate acid sites is essentially important.

Herein, we reported citric-acid-mediated preparations of macro-mesoporous alumina with adjustable large specific surface area and moderate acid sites via a simple hydrothermal method without using any templates, and the role of citric acid on the formation of such hierarchical alumina was attempted. Thus-prepared alumina supports were loaded with Ni–Mo active components and tested for hydrodesulfurization reaction of DBT, which showed superior catalytic activity, clearly confirming their structural merits. On this basis, the properties of the alumina support, especially their mesoporous structure and acidic property which play a key role in improving the HDS catalytic efficiency, were characterized and discussed in detail.

2. Experimental section

2.1. Materials

Dibenzothiophene (DBT) was purchased from Aldrich. Al₂(SO₄)₃·18H₂O, urea, citric acid, (NH₄)₆Mo₇O₂₄·24H₂O and Ni(NO₃)₂·6H₂O were purchased from Sinopharm Chemical Reagent Co. All of these reagents were of analytical purity and were used without further purification. In addition, commercial alumina was purchased from Fushun Research Institute of Petroleum and Petrochemical, SINOPEC, Fushun, China.

2.2. Synthesis of macro-mesoporous alumina supports

The alumina precursors were synthesized by a hydrothermal method. Aluminum sulfate (5.1 g), urea (1.2 g) and a certain amount of citric acid were added to the deionized water (70 mL) and stirred for 60 min. Then, the above mixture solution was transferred into a 100 mL Teflon-lined autoclave reactor and heated at 180 °C for 10 h. After cooling down to room temperature naturally, the samples were collected by washing with water and ethanol, which after drying in air for 24 h at 60 °C was then calcined at 800 °C for 4 h. The obtained samples were referred to as Al₂O₃-xCA where x denotes the gram of citric acid (CA) added in each synthesis ranging from 0 to 0.6 g.

2.3. Preparation of the MoNi/Al₂O₃-xCA catalysts

The active components Ni and Mo were loaded on the Al₂O₃-xCA support via the simultaneous incipient wetness impregnation method, forming a series of MoNi/Al₂O₃-xCA catalysts. In brief, the as-prepared alumina support and the precursor salts (NH₄)₆Mo₇O₂₄·24H₂O and Ni(NO₃)₂·6H₂O were well mixed and dispersed in deionized water. The samples were then dried at 120 °C for 12 h and calcined in air at 500 °C

for 3 h. In all of these catalysts the loading of the active components are controlled to be the same, with 12.0 wt. % of MoO₃ and 3.0 wt. % of NiO. Meanwhile, a control catalyst was also prepared by employing the commercial alumina as the support, which was denoted as MoNi/cAl₂O₃.

2.4. Characterization of the supports and the catalysts

The wide-angle XRD patterns were measured on Rigaku Ultima IV X-ray diffractometer (35 kV, 15 mA) using Cu-K α radiation ($\lambda = 0.15418$ nm) and with a scanning rate of 10 °C/min.

N₂ physisorption tests were performed on a Micromeritics Tristar 3020 instrument. The samples were degassed in the preparation station at 300 °C under vacuum, and were then switched to the analysis station for adsorption–desorption at –196 °C. The Brunauer–Emmett–Teller (BET) method was used for calculating the specific surface areas of the samples. The pore sizes and the pore volumes of the materials were calculated via the adsorption and desorption branches of the N₂-sorption isotherms, respectively, according to the Barrett–Joyner–Halenda (BJH) method.

SEM images were obtained from a Zeiss Sigma SEM microscope with an operating voltage of 5 kV. HRTEM was conducted on a Tecnai F30 instrument with an acceleration voltage of 300 kV.

The Raman spectra of the catalysts were collected by a Raman spectrometer (Renishaw) with a laser wavelength of 532 nm and 8 mW power used.

FT-IR pyridine adsorption was performed on a Bruker Fourier transform infrared spectrometer to determine the types of surface acid sites of the catalysts. Before analysis, the samples were degassed in vacuum at 400 °C for 1 h, which then were cooled and exposed to a saturated pyridine atmosphere at 100 °C for 30 min. After adsorption, the infrared spectrum was recorded with a resolution of 4 cm^{–1} at 150 °C for degassing.

NH₃-TPD was performed on a Micromeritics AutoChem II 2920 instrument. The sample (100 mg) was pretreated at 400 °C in He for 1 h, which was then cooled down to 120 °C and further saturated with NH₃ for 1 h. After being purged with 10 mL/min of He for 30 min to remove the loosely bonded ammonia, the sample was subjected to desorption test from 120 to 800 °C at a ramping rate of 10 °C/min in a He stream (20 mL/min).

H₂-TPR of the sample was performed on a GC-TPR apparatus. The sample (50 mg) was pretreated in an Ar stream at 300 °C for 1 h and then cooled to 50 °C. Subsequently, a 5% H₂/Ar atmosphere was applied, and the catalyst sample was heated to 900 °C with a ramping rate of 10 °C/min.

XPS analysis of the sulfided catalysts were conducted on a MultiLab 2000 spectrometer using Mg K α radiation under vacuum (< 10^{–9} mbar). Before the test, the oxide catalysts were sulfurized in a 15% H₂S/H₂ stream at 400 °C for 2 h and then cooled to RT in a nitrogen flow. All binding energies (BE) were calibrated based on C1s of adventitious carbon (284.6 eV). The XPSPEAK software with the version 4.1 was employed to quantify the contents of Mo and Ni species.

2.5. Evaluation of HDS catalytic activity

Dibenzothiophene hydrodesulfurization activity of the catalysts was evaluated in a high-pressure fixed-bed continuous-flow stainless steel reactor, using 2.0 wt. % DBT in cyclohexane as a model compound. Before loading into the reactor, 100 mg of the catalyst (20–40 mesh particle size), which was diluted with 400 mg quartz pellets, was pre-sulfided at 400 °C at a flow rate of 40 mL/min of 15% H₂S/H₂ under atmospheric pressure. The tests were stabilized at 260 °C, with a total pressure of 1.5 MPa, a liquid hour space velocity (LHSV) of 4 h^{–1} and an H₂/oil ratio of 600/1 (v/v). The liquid product was collected and analyzed by a gas chromatograph (GC-9560) equipped with FID detector and SE-30 capillary column. The reaction products were

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