



Synthesis of hierarchically porous L-KIT-6 silica–alumina material and the super catalytic performances for hydrodesulfurization of benzothiophene

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ABSTRACT

A novel micro/mesoporous composite material L-KIT-6 (LK) was successfully synthesized from zeolite L nano-crystals using low cost solid silica–alumina microsphere via two-step hydrothermal crystallization method. LK was used as catalyst support to prepare the hydrodesulfurization (HDS) catalyst. LK micro/mesoporous material and its corresponding catalyst CoMo/LK were characterized using XRD, FTIR, SEM, TEM, N₂-adsorption, ²⁷Al MAS NMR, Pyridine-FTIR, H₂-TPR, XPS and HRTEM techniques. The physicochemical properties of CoMo/LK were compared with the reference catalysts with different support materials including zeolite L, KIT-6 and γ -Al₂O₃. The characterization results demonstrated that the textural and acidic properties of the LK composite were dramatically improved comparing with that of zeolite L and mesoporous silica KIT-6. Furthermore, LK had a positive effect on the formation of moderate MoS₂ stacking morphology and more “edge” active centers. The catalyst CoMo/LK exhibited a superior catalytic performance for HDS of BT, which could be attributed to the synergistic effects of open porous structure, excellent textural property, appropriate acidity, and MoS₂ stacking morphology of CoMo/LK. Moreover, a possible reaction network for BT HDS over CoMo/LK catalyst was proposed.

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1. Introduction

With the growing concerns about environmental problems, more stringent fuel specifications have been carried out in numerous countries to constraint sulfur contents in gasoline (<10 ppm) [1]. To reach this ultra low sulfur content, highly refractory sulfur compounds in gasoline fraction, such as alkylthiophene and benzothiophene (BT) must be desulfurized [2]. Conventional alumina-supported Co(Ni)Mo industrial hydrodesulfurization (HDS) catalysts fail to achieve the ultra-low sulfur standard due to the single Lewis acid sites distribution and amorphous pore structures of Al₂O₃. In order to develop high-efficiency HDS catalysts, several approaches including preparation method, selection of supports and active components have been pursued

among which the development of novel catalyst support materials is of great importance.

A wide variety of support materials such as zeolite NaY [3], basic magnesium oxides [4], amphoteric carbon [5] and mesoporous materials [6–8] have been employed as candidate supports for the partial or complete substitution of conventional support γ -Al₂O₃. Due to strong acidity, high stability and shape selectivity, acidic zeolites are widely used as the supports for HDS catalysts. The synergistic effect of different acid sites not only accelerates the direct cleavage of the C–S bond but also promotes alternative pathways to remove the sulfur atom attached to the aromatic rings. Zeolite L possesses a LTL type framework topology with one-dimension pore channels and shows excellent catalytic performances in the selective hydrogenation [9] and HDS [10]. However, similar to other zeolites, the small pore size (0.71 nm × 0.71 nm) of zeolite L strongly hinders the diffusion of bulky molecules after loading of MoS₂ active phase [11].

Mesoporous materials with outstanding textural characteristics including large specific area and open porosity are considered to be an ideal catalyst supports for catalytic conversion of bulky molecules. KIT-6, a type of bicontinuous cubic *la3d* mesoporous

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material, possesses large specific surface area and large pores sizes which could enhance the dispersion and the accessibility of active centers [12]. Soni et al. [13] used KIT-6 material as CoMo catalyst support for the HDS of thiophene and the corresponding catalyst exhibited a higher activity than SBA-15 and γ -Al₂O₃-supported catalysts. Larger pore size and excellent interconnected framework structure of KIT-6 might be the reasons for its high activity. Nevertheless, the weak acidity and stability restrict its applications in catalytic area.

In order to combine the advantages of microporous zeolites and mesoporous silica materials, many considerable efforts have been devoted to synthesizing novel zeolite with mesostructure. Various mesoporous zeolites were synthesized and applied in the catalytic processes. Sirvastava et al. [14] reported that MFI zeolite with a hierarchical porous structure (MeMFI) exhibited relatively high activities in the catalytic synthesis of bulky molecules and improved the catalytic stability in reactions involving small molecules. The high activities of these catalysts were related to the mesoporous/microporous structure and mild acidity of MeMFI. Di [15] firstly synthesized ordered mesoporous aluminosilicates of MAS-3 and MAS-8 from L precursors, which retained the similar structures to MCM-41 and SBA-15, respectively. MAS-8 showed a higher conversion than the mesoporous aluminosilicates Al-MCM-41 and Al-SBA-15 in the cumene cracking process, which was ascribed to the improvement of acidity derived from L precursors.

Due to the desired properties, micro/mesoporous composite materials have become the focus of HDS catalysts. Sun [16] reported a high activity in the HDS of 4, 6-dimethyldibenzothiophene (4,6-DMDBT) over noble metals supported on mesoporous ZSM-5 zeolite. Fu [17] prepared mesoporous zeolite Y catalysts (Pd/HY-M), and this catalyst showed a very high activity in the HDS of 4, 6-DMDBT compared with Pd/HZSM-5-M, Pd/HBeta-M and Pd/ γ -Al₂O₃. This high activity could be attributed to the combination of the advantages for the mesoporosity and large pore size in HY-M. In our previous works [18,19], zeolite Beta and L-based composite materials with the characteristic mesostructures of KIT-6 and MCM-41 were prepared, respectively. The corresponding catalysts exhibited better HDS efficiency than their counterpart catalysts using single zeolites and mesoporous materials as supports. It can be concluded that the supports with open porous structure and appropriate acidic properties would make positive effects on enhancing HDS activities of catalysts.

In the present work, a novel micro/mesoporous composite material L-KIT-6(LK) was firstly synthesized by a two-step hydrothermal crystallization method using low-cost solid silica–alumina microspheres. The corresponding CoMo supported catalyst CoMo/LK was prepared and evaluated in the HDS of benzothiophene. To investigate the effects of textural and acidity of supports on the catalytic performances, other catalysts with different support materials including zeolite L, KIT-6 and γ -Al₂O₃ were also evaluated for comparison. Various techniques were employed to characterize both physicochemical properties of supports and corresponding catalysts. The main factors affecting the catalytic performance of LK composite supported CoMo catalyst for the HDS of benzothiophene were discussed. Furthermore, a possible reaction network of benzothiophene HDS over the CoMo/LK catalyst was proposed.

2. Experimental

2.1. Synthesis of materials

The micro/mesoporous composite material L-KIT-6 (LK) was hydrothermally synthesized from the in-situ assembly of EO₂₀PO₇₀EO₂₀ (Pluronic P123, M_{av} = 5800, Aldrich) with a

preformed L microcrystal solution. First, zeolite L nanocrystal clusters were prepared with the molar ratio of 1.0 SiO₂:0.1 Al₂O₃:0.15 K₂O:25-H₂O. A kind of low-cost silica–alumina microsphere (Fushun Catalyst Company, SiO₂ 69.4 wt%, Al₂O₃ 11.8 wt%) was used as the silica and aluminum sources, then it was mixed with an aqueous solution of KOH (Beijing Chemical Company, 82 wt%). The mixture was homogenized by stirring for 1 h, followed by transferring the material into a Teflon-lined autoclave for crystallization at 150 °C for 10 h. The zeolite with L nanocrystal clusters were obtained as precursor. Second, 2 g Pluronic P123 was dissolved in the mixture of H₂O and hydrochloric acid solution at 35 °C. After complete dissolution, 3.94 g *n*-butanol was added and the mixture was stirred for 1 h. Then a certain amount of the mixture with the precursor zeolite L species and TEOS was added to the above solution with vigorous string, resulting a gel of SiO₂:Al₂O₃:P123:*n*-butanol:HCl:H₂O with a molar ratio of 1:0.05:0.015:1.4:2.3:215. The mixture was stirred at 35 °C for 24 h and transferred into a Teflon-lined autoclave at 100 °C for 24 h under static conditions. The resulting solid product was collected by filtration, washed, dried and calcined at 550 °C for 6 h in air to remove the organic template.

Zeolite L was synthesized as mentioned above, but the crystallization time of zeolite L was extended to 24 h. KIT-6 and Al-KIT-6 were prepared according to the published literature [12,20].

2.2. Preparation of catalysts

H-type materials of zeolite L and composite material L-KIT-6(LK) were obtained by ion-exchanged with a 1.0 M NH₄Cl aqueous solution at 90 °C for 1 h. Then they were washed and calcined at 550 °C in air for 4 h.

The corresponding catalysts with different supports (γ -Al₂O₃, zeolite L, KIT-6 and L-KIT-6(LK)) were prepared by a two-step incipient-wetness impregnation of ammonium molybdate and cobalt nitrate as active metal components separately. After each impregnation, the samples were dried at 110 °C for 12 h and calcined at 550 °C for 4 h in air to yield oxidic catalysts. All the samples were impregnated with the same loadings of 8 wt% MoO₃ and 4 wt% CoO. Then the obtained samples were crushed into 0.3–0.5 mm particles. According to the supports, the resulting catalysts were denoted as CoMo/Al₂O₃, CoMo/L, CoMo/KIT-6 and CoMo/LK. Table S1 lists the nominal component ratio of catalysts and the contents of MoO₃ and CoO of different catalysts determined by ICP-OES method. Both MoO₃ and CoO contents are close to the nominal ones (8 and 4 wt%, respectively).

2.3. Characterization of the supports and catalysts

X-ray powder diffraction (XRD) patterns of the samples were recorded with a Shimadzu X-6000 diffraction Cu K α radiation. For small angle scans, the 2θ range was from 0.7° to 5° (the diffractometer was operated at 250 mA), and for wide angle scans, from 5° to 80° (the diffractometer was operated at 30 mA).

Fourier transform infrared spectroscopy (FTIR) absorbance spectra were performed in the wave numbers range from 4000 to 400 cm⁻¹ on a MAGNA-IR 560 spectrophotometer. The transparent discs were pressed using 2 mg of the samples mixed with 200 mg of KBr.

Nitrogen adsorption–desorption isotherms were measured in a Quantachrome Autosorb-iQ automated gas sorption analyzer at 77 K. The specific surface areas of the samples were calculated using the Brunauer–Emmett–Teller (BET) method. The total volumes of micro- and mesopores were calculated from the amounts of nitrogen adsorbed at $p/p_0 = 0.98$. The pore size distribution (PSD) was derived from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. Nonlocal density functional

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