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RESEARCH PAPER

Effect of Alumina Support on the Formation of the Active Phase of Selective Hydrodesulfurization Catalysts Co-Mo/Al_2O_3

Qiherima[1,3], LI Huifeng[2], YUAN Hui[2], ZHANG Yunhong[1], XU Guangtong[2,*]

[1]The Institute for Chemical Physics, Beijing Institute of Technology, Beijing 100081, China;
[2]Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China;
[3]Department of Pharmacy, Inner Mongolia Medical College, Hohhot 010059, Inner Mongolia, China

Abstract: Two different commercial alumina supports were used for the preparation of selective hydrodesulfurization (HDS) catalysts Co-Mo/Al_2O_3. The effect of support properties on the HDS activity and selectivity of the corresponding Co-Mo catalysts were studied by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, scanning transmission electron microscopy-energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The HDS activity and selectivity were measured using a continuous flow fixed-bed microreactor. The Al_2O_3 support with higher crystallinity and fewer hydroxyl groups had a moderate metal-support interaction, which resulted in an increase of the average slab length and stacking number of MoS_2. This gave more formation of the active CoMoS phase and an increase in HDS activity and selectivity.

Key words: alumina; property; cobalt; molybdenum; hydrodesulfurization; active phase

Al_2O_3 is one of the most promising support because of its abundance and good properties such as high surface area, good pore distribution, and good stability. Al_2O_3 is widely used as the support of hydrotreating catalysts in the petroleum refining industry [1]. The different physiochemical properties of alumina can greatly influence the catalytic activity of the catalysts [2–7]. Domínguez-Crespo et al. [5] found a correlation of particle size of the alumina support with the NiMo oxide catalysts, and the final NiMoS catalyst, and reported that this was important in determining the changes of the active sites during the annealing and sulfidation steps. Sakashita et al. [6,7] investigated the effects of surface orientation and crystallinity of the support on the microstructure of supported Mo catalysts, and showed that the microstructure of the MoS_2 clusters can be controlled by tailoring the surface orientation of the alumina support. However, there is little information available in the literature about the effect of alumina on the formation of the active phase and hydrodesulfurization (HDS) activity and selectivity of the corresponding CoMo catalysts due to the lack of suitable techniques that can directly provide information on the active sites.

The aim of this work is to study the effect of the surface characteristics of two different commercial alumina supports on metal-support interaction and its correlation with HDS activity and selectivity of CoMo catalysts by a variety of techniques, including X-ray diffraction analyses (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX), X-ray photoelectron spectrometer (XPS), and in situ FT-IR of adsorbed CO.

1 Experimental

1.1 Catalyst preparation

Two different commercial alumina, Al_2O_3-1 and Al_2O_3-2, obtained from Changling Division of SINOPEC Catalyst

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***Corresponding author.** Tel/Fax: +86-10-82368613; E-mail: gtxu@sina.com

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Company, were used without further treatment. Co-Mo/Al_2O_3-1 and Co-Mo/Al_2O_3-2 with the same loading of 2.5% CoO and 8.0% MoO_3, were prepared by the pore volume co-impregnation method with an ammonia solution of cobalt nitrate and ammonium heptamolybdate, followed by drying at 393 K for 2 h and calcination at 693 K for 4 h.

1.2 Catalyst characterization

The sample used for FT-IR was pressed into a self-supporting wafer and placed in an infrared cell. The sample was degassed at 673 K for 4 h. Surface hydroxyl groups on the alumina were determined at 373 K on a Nicolet 6700 Fourier transform infrared spectrometer. Support acidity was determined after the same surface pretreatment. Pyridine was introduced into the cell at 373 K. After adsorption for 15 min, the sample was evacuated at 473 K and 623 K, and the FT-IR spectra were recorded using 64 scans with a resolution of 4 cm^{-1}.

The surface area and pore volume of the samples were determined by N_2 physisorption using a Quantachrome Autosorb-6B automated system.

XRD patterns were recorded in the $2\theta = 5^{o}–80^{o}$ at steps of 0.02^{o}/s on a Philips X'Pert diffractometer using Cu K_α radiation at 0.15418 nm, 40 kV, and 50 mA.

TEM images of the sulfided catalysts were recorded on a Tecnai G^2 F20 S-TWIN microscope equipped with a STEM unit and a Thermo Noran EDX system. The particle size distribution was determined by counting about 500 particles. The average particle length ($\overline{L}$), stacking number ($\overline{N}$) and stacks per 1000 nm^2 ($\overline{D}$) were determined by manual measurement and calculated as follows [8]:

$$\overline{L} = \sum_{i=1}^{n} n_i l_i / \sum_{i=1}^{n} n_i$$

$$\overline{N} = \sum_{i=1}^{n} n_i N_i / \sum_{i=1}^{n} n_i$$

$$\overline{D} = (n/S) \times 1000$$

STEM-EDX was used to detect the distribution of the Co and Mo elements. The pretreatment of the sample was the same as used for TEM.

The catalyst was pressed into a self-supported wafer and placed in the IR cell. For the first procedure, the catalyst was dried at 423 K under N_2 flow for 1 h and was then sulfided with 10% H_2S in H_2 at 673 K. After 5 h, the catalyst was evacuated at 573 K for 3 h and finally cooled down to 100 K using liquid nitrogen. CO adsorption was performed by the introduction of a saturation amount of CO. The spectra of adsorbed CO reported in this study are subtracted spectra, i.e., the spectra of adsorbed CO minus the reference spectrum of the sample before CO adsorption.

The sulfided samples were transported into the preparation chamber of the spectrometer under the protection of argon. The spectra were recorded with a Thermo-Fishier ESCALAB 250 X-ray photoelectron spectrometer using monochromatic 150 W Al K_α radiations. The binding energies were referenced to the Al 2*p* line at 74.7 eV from the Al_2O_3 carrier. For the deconvolution of the S 2*p* and Mo 3*d* peaks, the following constraints were imposed: the spin-orbit splitting of the S 2*p* and Mo 3*d* peaks were fixed to be 1.15–1.18 and 3.15–3.20, respectively. The area ratios of S 2*p* and Mo 3*d* peaks were equal to the theoretical values of 2.0 and 1.5, respectively.

1.3 Catalytic activity evaluation

The catalysts were presulfided in situ with a sulfiding feed of 6 vol% CS_2 in cyclohexane at a pressure of 1.6 MPa and temperature of 593 K for 3 h. The catalytic activity tests were carried out in a continuous flow-fixed bed microreactor under the following conditions: 1.6 MPa, 533 K, 1.00 g catalyst used, 10% thiophene and 20% 1-hexene in heptane as feed at the feed flow rate of 0.16 ml/min, and a H_2 flow rate of 360 ml/min. After steady state conditions were reached, the liquid effluent was periodically auto-sampled and analyzed on-line by an Agilent 6890N gas chromatograph. The HDS activity (X_T), hydrogenation activity (X_H) and HDS selectivity factor (S) of the catalysts were calculated as follows [9]: $X_T = [(w_{T,1}-w_{T,2})/w_{T,1}]$, $X_H = [(w_{H,1}-w_{H,2})/w_{H,1}]$, $S = \ln(1-X_T)/\ln(1-X_H)$. Where $w_{T,1}$ and $w_{T,2}$ denote the thiophene content in the feed and products, respectively. $w_{H,1}$ and $w_{H,2}$ denote the hexene content in the feed and products, respectively.

2 Results and discussion

2.1 Distributions of hydroxyl group and acid site on the supports and their effect on the dispersion of the active metal component

The FT-IR spectra of the hydroxyl groups on the two alumina supports are presented in Fig. 1(a). The hydroxyl group amount of Al_2O_3-2 was notably less than that of Al_2O_3-1. The nature and concentration of the hydroxyl group can play an important role in the dispersion of the supported metal species. The deposition of the catalytically active components on the supports led to a strong decrease of the intensity of the band due to the hydroxyl groups, indicating that the hydroxyl groups were involved in the interaction with the metal precursors and the dispersion of the active metal species [10]. Therefore, as compared with Al_2O_3-1, there will be a weaker interaction between the metal species and Al_2O_3-2. This would benefit the sulfidation of the metal component supported on Al_2O_3-2 and formation of the sulfided active phase.

The FT-IR spectra of the chemisorbed pyridine were used to investigate the distribution of L and B acid sites on the support. Figure 1(b) shows the spectra after adsorption of pyridine on the support. The surface acid amounts of the two supports are presented in Table 1. There were only L acid sites on the two alumina supports at the two different temperatures. The results