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Influence of hydrothermally modified γ-Al_2O_3 on the properties of NiMo/γ-Al_2O_3 catalyst

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Abstract

The influence of hydrothermal modification of γ-Al_2O_3 on the properties of NiMo/γ-Al_2O_3 catalyst was investigated in this paper. The experimental results showed that the use of the modified γ-Al_2O_3 in the preparation of the NiMo/γ-Al_2O_3 catalyst led to the increase of the dispersion of the surface Mo and Ni oxides, favored the formation of the poly-molybdates and promoted the reduction of the active Mo oxides owing to the increase of the surface acidity of the modified γ-Al_2O_3. Therefore, the NiMo/γ-Al_2O_3 catalyst supported on the modified γ-Al_2O_3 exhibited a higher hydrodenitrogenation (HDN) activity than that supported on the untreated γ-Al_2O_3 in the temperature range of 300–340 °C.

Keywords: Hydrothermal modification; Dispersion; HDN; NiMo/γ-Al_2O_3 catalyst

1. Introduction

Mo and W sulfide catalysts supported on γ-Al_2O_3 and promoted by Co and Ni have been widely used for the industrial hydrotreatment of petroleum and liquefied coal [1,2]. However, the stringent environmental legislation and the increasing need for processing low-quality petroleum stocks containing more nitrogen compounds require the development of hydrodenitrogenation (HDN) catalysts with higher HDN activity.

The surface acidity of the Al_2O_3 support has a great influence on the activity of hydrotreating catalysts since the acid sites of the support is favorable for the dispersion of the active metals oxides via the acid–basic interaction between the acid sites and the basic metal oxides [3,4]. The acid sites of the Al_2O_3 support can also accelerate the hydrogenation reactions as hydrodesulfurization (HDS) and hydrodenitrogenation via the activation of the hydrogen [5,6]. Therefore, many methods have been developed to increase the surface acidity of γ-Al_2O_3 to improve the activity of the hydrotreating catalysts. The former works showed that the addition of materials such as zeolite [2], SiO_2 [7], Nb_2O_5 [6], B [8,9] and F [10] in the modification of γ-Al_2O_3 support can increase its surface acidity, leading to the increase of the hydrotreating activities.

In recent years, hydrothermal technology has been used as an alternative way to modify γ-Al_2O_3 support [11–13]. For example, Stanislaus et al. [11,12] synthesized NiMo/γ-Al_2O_3 catalyst with large pores by hydrothermal modification of γ-Al_2O_3 at 200–300 °C to avoid the rapid deactivation in the hydrotreating process of the residual oil. But the comparatively high temperature also caused the decrease of both the specific surface area from 167 to 28 m^2/g and the pore volume from 0.81 to 0.12 cm^3/g [13]. In our previous work, γ-Al_2O_3 was treated under moderate hydrothermal condition (140 °C) for 1.0–24.0 h and it was found that hydrothermal modification on the γ-Al_2O_3 led to the increase of its surface OH concentration and total surface acidity, especially the weak acidity [14]. In this paper, the γ-Al_2O_3 after hydrothermal modification was used to prepare NiMo/γ-Al_2O_3 catalyst to investigate the effect of the modified γ-Al_2O_3 on the dispersion and reduction of the active metal oxides and the HDN activity of the NiMo/γ-Al_2O_3 catalyst.

2. Experimental

2.1. Preparation of catalysts

Commercial γ-Al_2O_3 with an average agglomerate size of about 200 μm was treated in hydrothermal condition (140 °C) for 2.0 h, then dried at 120 °C for 4.0 h and calcined at 550 °C

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Table 1
Properties of the γ-Al_2O_3 supports

Support	Specific surface area (m^2/g)	Pore volume (mL/g)	Relative acidity
a	205	0.43	2.55
b	245	0.43	3.92

(a) Commercial γ-Al_2O_3 and (b) γ-Al_2O_3 after hydrothermal modification.

for 3.0 h. The basic properties of the γ-Al_2O_3 were shown in Table 1.

γ-Al_2O_3 with and without hydrothermal modification [14] were impregnated in a solution containing certain amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ to prepare NiMo/γ-Al_2O_3 catalyst. After impregnation, the samples were dried at 110 °C for 12.0 h and then calcined in air at 550 °C for 3.0 h. The amount of the active components was kept the same (3.8 wt% NiO and 17.8 wt% MoO_3, atomic ratio of Ni/Mo is 0.41) in both of the NiMo/γ-Al_2O_3 catalysts.

2.2. Characterization

X-ray photoelectron spectroscope (XPS, Model PHI-5300, PHI, USA) was used to study the surface composition in NiMo/γ-Al_2O_3 catalyst. Charge referencing was performed with adventitious hydrocarbon (C 1s, 285.0 eV) and the experimental error was ±0.2 eV. The atomic concentration percentages of the elements presented on the surfaces of the catalysts were estimated from the XPS analysis results.

The laser Raman spectra (LRS) were recorded on a Renishaw RM2000 spectrometer, using the Ar^+ laser excited at 514 nm as the laser source.

The hydrogen temperature-programmed reduction (TPR) behavior of the catalyst was performed with a self-established apparatus. A mixture of H_2 (5 vol.%) and N_2 was used as the reference gas and introduced (37 cm^3/min) into the loop containing 100.0 mg of the catalyst. The sample was then heated (10 °C/min) to 950 °C. The product gas was flown through a molecular sieve column to remove water. The consumption of H_2 was detected by an on-line chromatograph (Agilent 1790).

2.3. Catalytic activity

The catalytic activities of the NiMo/γ-Al_2O_3 catalysts were evaluated in a small stainless steel reactor (7.9 mm in diameter and 14.2 cm in height), using pyridine as the model compound. 0.5 g of the catalyst was held between two quartz layers. After sulfiding in a mixing gas containing H_2S (10%) and H_2 (90%) at 400 °C for 2.0 h, the catalyst was evaluated at 3.0 MPa with a concurrent flow of feedstock (0.3 cm^3/min) and H_2 (>99.99%, 90 cm^3/min). The feed comprising *n*-hexane (90.0 wt%), cyclohexane (8.3 wt%) and pyridine (1.7 wt%) was introduced by a liquid feedstock pump. The HDN activity of the catalysts was calculated in terms of the pseudo first order rate constant, k_{HDN} [10].

Table 2
XPS analysis of the NiMo/γ-Al_2O_3 catalysts (oxide state)

Catalyst	Binding energy (eV)		Atomic ratio	
	Mo $3d_{5/2}$	Ni $2p_{3/2}$	Mo/Al	Ni/Al
a	233.2	857.1	0.09	0.08
b	233.0	856.9	0.13	0.12

(a) Supported on the γ-Al_2O_3 without hydrothermal modification and (b) Supported on the γ-Al_2O_3 with hydrothermal modification.

3. Results and discussion

3.1. XPS characterization

The XPS spectra of Mo 3d and Ni 2p in the oxide NiMo/γ-Al_2O_3 catalysts are shown in Fig. 1, the corresponding binding energies (BE) and the atomic ratios are listed in Table 2. The binding energies of Mo $3d_{5/2}$ in both of the NiMo/γ-Al_2O_3 catalysts were in the range of 233.0–233.2 eV and identical with that of the Mo(VI) [15], but it is difficult to identify the detail Mo state from the binding energy. The binding energies of Ni $2p_{3/2}$ in both of the NiMo/γ-Al_2O_3 catalysts were quite similar with that of $NiAl_2O_4$ (857.2 eV) [15].

As shown in Table 2, further analysis of the atomic concentration percentages of the different elements in the NiMo/γ-Al_2O_3 catalysts indicated that the hydrothermal modification of the γ-Al_2O_3 led to the increase of the atomic ratios of Mo/Al ratio from 0.09 to 0.13 and the Ni/Al ratio from 0.08 to 0.12, respectively, indicating that the hydrothermal modification of the γ-Al_2O_3 led to a higher dispersion of the Mo and Ni oxides on the surface of the NiMo/γ-Al_2O_3 catalyst using the modified support. The improvement of the dispersion of the Mo and Ni oxides was attributed to the increase of the amount of acid sites of γ-Al_2O_3 after hydrothermal modifica-

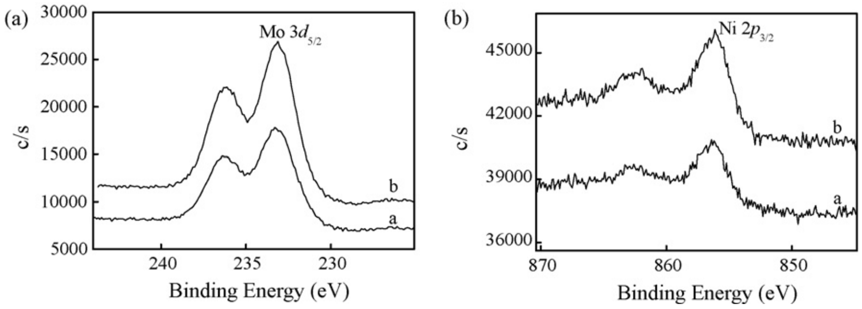

Fig. 1. XPS spectra of Mo 3d and Ni 2p of the NiMo/γ-Al_2O_3 catalysts (oxide state) using γ-Al_2O_3 support without (a) and with (b) hydrothermal modification.