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Hydroconversion of *n*-octane over nanoscale HZSM-5 zeolites promoted by 12-molybdophosphoric acid and Ni

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Abstract

12-Molybdophosphoric acid (PMo), Ni and Ni–PMo loaded on nanoscale HZSM-5 zeolites were prepared and characterized by BET, IR, XRD, Py-IR, NH_3-TPD, TG and SEM. The hydroconversion of *n*-octane over various catalysts was investigated in order to obtain light isomers alkanes and aromatics products with high-octane-number. The acid amounts of the catalysts were modified after the loading of PMo and Ni, and its relation to the activity of the reaction was discussed. It is concluded that the stability of aromatization is improved, and the yield of light iso-alkanes is enhanced due to the introduction of PMo and Ni. The improved activity of *n*-octane hydroconversion over PMo and Ni loaded nanoscale HZSM-5 zeolites could be attributed to the increase of the acid amounts and the synergetic effect between Brønsted and Lewis acid sites.

Keywords: 12-Molybdophosphoric acid; Nanoscale HZSM-5 zeolites; Hydroconversion; *n*-Octane; Aromatization

1. Introduction

The hydroconversion catalytic processes of long chain alkanes are of increasing importance for the petroleum industry due to the growing demand for light isomers of alkanes and aromatics, which are required in reformulated gasoline as high-octane-number enhancement. C_8 linear paraffin can be converted to a mixture of high-octane-number iso-alkanes and aromatics that can be added in the gasoline pool. Therefore, the investigation of *n*-octane hydroconversion has attracted increasing interest [1].

The catalysis of heteropoly acids (HPA) in solid state as well as in solution has received much attention owing to their unique acidic and redoxactivities [2–6]. Among them Keggin structured PMo is one of the most widely used catalysts with high catalytic efficiency [7,8]. HPA catalysts have been used in alkanes hydroconversion [1,9]. Yori et al. reported the hydroisomerization-cracking of *n*-octane over $H_3PW_{12}O_{40}$ (PW) supported on ZrO_2, SiO_2 and carbon. The results show that the supported HPA exhibits higher initial specific activity values expressed by mass unit of HPA than pure HPA [1]. Miyaji and co-workers reported the skeletal isomerization of *n*-pentane catalyzed by Pd–$_4SiW_{12}O_{40}/SiO_2$ [9]. Nevertheless, the use of HPA as catalyst modification in alkanes aromatization has not been reported.

HPA supported on different supports, such as SiO_2, active carbon, acidic ion-exchange resin, mesoporous molecular sieves [3] and USY [10] have been extensively investigated. Here, for the first time, we report the use of nanoscale HZSM-5 zeolites as a support of HPA. Nanoscale zeolites are promising catalytic and adsorbent materials that have higher surface areas and reduced diffusion path lengths relative to conventional microscale zeolites [11]. Nanoscale ZSM-5 zeolites exhibit higher activity, lower coke content and better stability in the conversion of methanol to hydrocarbons [12] and the oligomerization of ethylene [13]. They also exhibit increased selectivity and

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conversion of toluene into cresol and decreasing coke formation rate compared with commercial ZSM-5 zeolites [14]. Nanoscale ZSM-5 zeolites are thought to be an ideal material for the encapsulation of HPA molecules having a Keggin structure since they have the intergranular secondary pore.

In this paper, we investigated the hydroconversion of *n*-octane over the nanoscale HZSM-5 zeolites promoted by PMo and/or Ni. The results show that the introduction of PMo and Ni improves the catalytic activity and stability of nanoscale HZSM-5 zeolites. The effects of acidity and temperature on the activity of *n*-octane hydroconversion are demonstrated.

2. Experimental

2.1. Catalyst preparation

PMo was prepared according to a method previously described by Fournier [15]. The nanoscale HZSM-5 zeolites (the molar ratio of SiO_2/Al_2O_3 was 25.5) were prepared by the procedure reported in the literature [16]. The strip nanoscale NaZSM-5 catalyst was obtained (ϕ 1 mm× 2 mm) by extruding the mixture of 80 wt% nanoscale NaZSM-5 and 20 wt% alumina. Then it was calcined at 813 K for 3 h, followed by ion exchange with 0.4 mol/L NH_4NO_3 solution (three times), and re-calcined at 813 K for 3 h.

The PMo and Ni loaded on nanoscale HZSM-5 zeolites (NiPMo–ZSM-5) was prepared by the following steps: (1) The mixture of 1.70 g PMo and 0.99 g $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 20 ml deionized water. (2) Ten grams strip nanoscale HZSM-5 zeolites was added into the solution and soaked the mixture for 24 h. (3) The strip was dried at 373 K and then calcined at 593 K for 3 h.

The PMo or Ni loaded on nanoscale HZSM-5 zeolites was prepared in the same way as described above.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a DMAX2400 diffractor with a Cu Kα radiation. The IR spectra of the samples, either before or after the adsorption of pyridine, were collected on an EQUINOX55 spectrophotometer at 4 cm^{-1} resolution. The acidity was examined by temperature programmed desorption of pre-adsorbed NH_3 (NH_3-TPD). Pore volume and surface area were obtained on a Quantachrome AUTOSORB-1 by using the BET method. Adsorption capacities for *n*-hexane (*n*-C_6) and cyclohexane (*c*-C_6) were measured by the flow adsorption method. The adsorption capacity for 2,2,3-trimethylbutane (2,2,3-TMB) was used to characterize the secondary pores contained in the polycrystalline grains of HZSM-5 zeolites as given in the literature [17]. The TG was operated on a TGA/STDA851^e thermal analysis apparatus with the temperature rising rate of 10 K/min under the protection of N_2. The crystal size of HZSM-5 was determined on a JEOL JSM-6700F field emission scanning electron microscope (SEM).

2.3. Catalytic measurements

The reaction was carried out in a continuous flow fixed-bed reactor (diameter 10 mm). Reaction conditions are listed as follows: temperature 553–613 K, pressure 1.5 MPa, H_2/*n*-octane (mol ratio) 2.0, WHSV of *n*-octane 2.5 h^{-1}, and catalyst 1.68 g. The composition of the products was analyzed by a GC-8820 gas chromatograph equipped with FID and a OV-101 capillary column (50.0 m × 0.25 mm). Before each catalytic measurement, catalysts were reduced in flowing hydrogen (28 ml/min) at reaction temperature for 2.5 h.

3. Results and discussion

3.1. Characterization of the catalysts

The SEM image of the nanoscale HZSM-5 zeolites is shown in Fig. 1a. The crystal size of HZSM-5 zeolites is about 70–100 nm.

The adsorption features of the nanoscale and microscale ZSM-5 zeolites are shown in Table 1. There are significant differences in the physicochemical properties between these two kinds of crystals. Compared to the microscale ZSM-5, the nanoscale ZSM-5 zeolites have higher *c*-C_6 adsorption capacity and larger surface area. Moreover, its outstanding adsorption capacity for 2,2,3-TMB exhibits the existence of secondary pores whose openings are wide enough to allow free entry of relatively large molecules. The nanocrystal ZSM-5 with morphology of polycrystalline grains generates the secondary pores from inter crystal gap of nanoscale ZSM-5.

Table 2 presents the surface areas and pore volumes of the samples. The surface areas and pore volumes of the supported catalysts decrease remarkably compared with the nanoscale HZSM-5 support. However, they are still much higher than those of the pure PMo. After the addition of PMo and/or Ni, the BET surface area gradually decreases in the following order: NiZSM-5 > NiPMo–ZSM-5 > PMo–ZSM-5. The pore volumes of NiPMo–ZSM-5, NiZSM-5, PMo–ZSM-5 and HZSM-5 are 0.257, 0.377, 0.238 and 0.393 ml/g, respectively. A decrease in surface area and pore volume of the catalysts may be due to the blockage of inner and secondary pores by PMo and/or Ni particles during catalyst pretreatment.

X-ray diffraction of the samples is given in Fig. 1b. The pattern of HZSM-5 agrees well with that reported by Grassian (60 nm HZSM-5) [11]. The unpretreated PMo (Fig. 1b, line 5) shows the characteristic diffraction lines of HPA [19]. The diffraction pattern of the PMo sample pretreated at 593 K shows peaks corresponding to the anhydrous acid phase, which is resulted from the loss of crystallization water. The PMo–ZSM-5 catalyst shows no reflection line of crystal structure, nor does the NiZSM-5