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Influence of template on Si distribution of SAPO-11 and their performance for *n*-paraffin isomerization

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Abstract

SAPO-11 molecular sieves were synthesized using single agent (i.e. diethylamine (DEA), di-*iso*-propylamine (DIPA) and di-*n*-propylamine (DPA)) or a mixture of DEA and DIPA (named DEPA) as the template under hydrothermal conditions. XRD indicated that the directing effect of different templates for AEL structure decreased in the order of DEPA > DPA > DIPA > DEA. ^{29}Si MAS NMR showed that although all SAPO-11 samples synthesized at same Si content, that prepared with the mixed template contained more Si (4Al) sites, whereas Si (*n*Al, 4-*n*Si, $0 < n < 4$) environments were predominant in the samples synthesized with single template. The results indicated that the mixed template led to a better Si dispersion and then increased the number of total acid sites of SAPO-11. In the isomerization of *n*-tetradecane over different Pt/SAPO-11 catalysts, the sample prepared with DEPA showed high catalytic activity and selectivity for *i*-C_{14}, which were related to the most abundant weak acid sites of the sample.

Keywords: SAPO-11; Synthesis; Mixed template; ^{29}Si MAS NMR; Isomerization

1. Introduction

The removal of long-chain *n*-paraffins from lubricating oils is an important process in petroleum industry for obtaining high quality oils with lower pour points (lower melting point). This process is usually carried out by solvent extraction or by selective cracking these normal paraffins, resulting in significant yield loss. An attractive dewaxing procedure results through isomerization of *n*-paraffins to monobranched isoparaffins, eliminating the yield loss associated with *n*-paraffin removal by cracking or solvent extraction [1–4].

As is well known, isomerization employs a metal/acid zeolite catalyst that has been described as bifunctional. Noble metal supported on an acidic carrier, containing both hydrogenation and acidic components, are found to be potential catalysts for isomerization reaction. Preferably, SAPO materials loaded with Pd or Pt show a high performance in isomerization of long-chain alkane [5–8].

SAPO materials with different structures could be divided into three categories according to their pore size (i.e., small, medium and large pore molecular sieve, respectively). Organic amines played an important role in the synthesis of SAPOs for achieving a given structure or stabilizing certain phases via nonbonding interactions between the template and the host inorganic framework [9]. It was believed that a successful template had a good fit with the host framework. However, in some case a template could produce multiple structures, e.g. DPA was used in the synthesis of more than 10 different SAPO structures, such as SAPO-11, SAPO-31 and SAPO-41 [10]. Another phenomenon was that one structure could be prepared by different templates. For instance, SAPO-5 could be prepared by more than 25 different templates [10,11]. As a result, various SAPO materials were often found coexist in the same gel [12,13].

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Beside the unsteady structure, the number and strength of acid sites of SAPOs was also greatly influenced by the reagents used. It was reported that the acidic properties of SAPO materials depended strongly on the content, location and distribution of Si [14–16]. Hence, the reagents used would influence the incorporation of silicon into the framework and therefore influence the number and strength of acid sites of SAPOs. Although the role of organic templates had not been clearly understood yet in the synthesis of SAPOs, a widely used empirical view stated that the major role of the template was the packing effect (i.e., the template molecule occluded in the pore channel of SAPOs and formed a given structure) [17,18]. The non-bonding interaction of the template with the inorganic framework changed the model of Si substitution into framework, and then gave rise to the samples with different acidities. There were conflicting reports about the extent of catalytic conversion and selectivity, probably due to the different growth mechanism of SAPOs. For instance, SAPO-11 was found less active and selective in the isomerization of *m*-xylene than SAPO-5 which was synthesized with triethylamine [19], while the former was more active and selective than the later when both were synthesized with DPA [12].

The conventional synthesis of SAPO-11 often employed single agent as template, which included DPA and DIPA. However, the difference of acidic properties between the samples synthesized with different templates had not been compared in detail [20–23]. DEA was used as template in the synthesis of SAPO-5 [24], SAPO-34 [25] and SAPO-41 [26]. In some case, it also worked as an important secondary amine to synthesize a given structure [26,27], but had not been used in the synthesis of SAPO-11. Considering these facts, SAPO-11 in this work was synthesized by introducing a template system composing of two compounds (i.e., DEA and DIPA). The samples synthesized with single template were also prepared for comparison. The physicochemical properties of the SAPO-11 samples synthesized using different template were comparatively characterized by using XRD, N_2 adsorption–desorption, SEM, Py-FTIR, Py-TPD, and ^{29}Si MAS NMR, and their catalytic activities of these samples were also compared for *n*-tetradecane isomerization reaction.

2. Experimental

2.1. Synthesis of SAPO-11 with different templates

SAPO-11 samples were synthesized hydrothermally using a gel mixture with the following molar composition: $1.0Al_2O_3$:$1.0P_2O_5$:$0.5SiO_2$:1.0R:$49H_2O$, where R represents different directing templates. Pseudoboehmite (30 wt% Al_2O_3), orthophosphoric acid (85%) and silica sol (28% SiO_2) were used as source of Al, P and Si, respectively. DEA (Aldrich), DIPA (Aldrich), the mixture of DEA and DIPA (named DEPA and the molar ratio of DEA/DIPA was 1.0) and DPA (Aldrich) were employed as directing templates and the corresponding samples were named SAPO-11-DEA, SAPO-11-DIPA, SAPO-11-DEPA and SAPO-11-DPA. In a typical synthesis, pseudoboehmite was added to distilled water and the mixture was stirred for 30 min. Then, orthophosphoric acid was added dropwise and the mixture was stirred for another 30 min. Afterwards, the template was added dropwise with further stirring for 30 min. Finally, the Si source was added dropwise and the final mixture was stirred for 30 min to get a homogeneous gel.

The gel was transferred to a stainless steel autoclave and heated to 120 °C for 4 h, and then to 190 °C for 20 h. So-produced solids were washed with distilled water and dried at 100 °C overnight. To remove the templates in the pores of the sample, the products were calcined at 500 °C for 6 h in air with a heating rate 2 °C/min.

The Pt/SAPO-11 catalysts of 0.37 wt% Pt loading were prepared by incipient wetness impregnation method with H_2PtCl_6 solution, and then dried at 100 °C overnight and calcined at 400 °C for 4 h in air.

2.2. Characterization

The purity and crystallinity of hydrothermally synthesized SAPO-11 samples were analyzed using Rigaku X-ray diffractometer (XRD) with Cu Kα radiation at 30 kV and 20 mA in the scan range of 2° between 5° and 50°. The chemical compositions of the SAPO samples were determined by inductively couple plasma (ICP) spectroscopy. The micropore volumes and surface areas of the samples were measured by N_2 adsorption using a Micromertitics 2000 sorptometer at liquid nitrogen temperature. The morphology of SAPO-11 samples was examined by scanning electron microscopy (JSM-6360LV model, JEOL Ltd., Japan).

^{29}Si MAS NMR experiments were carried out on a Varian infinityplus 300 NMR experiments at the resonance frequency 79.5 MHz. ^{29}Si MAS spectra were acquired at a spinning speed of 4 kHz, spectral width of 25 kHz, pulse width of 4.5 ms, delay of 30 s and spectrometer frequency of 59.6 MHz; tetramethylsilane (TMS) was used as the external standard.

The acid strength of different SAPO-11 samples was determined by temperature-programmed desorption of pyridine, which was carried out by a flow system with a thermal conductivity detector. All catalysts (150 mg) were outgassed in argon flow at 600 °C for 30 min, which followed pyridine saturation by flowing pyridine/Ar stream at 100 °C for 5 min. The evacuation at 150 °C for 30 min was carried out to remove the physically adsorbed pyridine, then the catalyst was heated in a linear rate of 10 °C/min to 600 °C, and the detector signal of pyridine desorption was recorded.

FT-IR spectra of adsorbed pyridine recorded on a Nicolet Magna 550 Fourier transform infrared spectrometer at 4 cm^{-1} resolution. The samples were finely grounded and pressed into self-supporting wafer (10 mg/cm^2, diameter = 15 mm), and then placed into the measurement cell