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Hierarchical SAPO-34/18 zeolite with low acid site density for converting methanol to olefins

Yuxin Li, Yanghuan Huang, Juhua Guo, Mingye Zhang, Dezheng Wang, Fei Wei, Yao Wang*

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

The catalytic performance of a zeolite is largely determined by its framework topology, particle morphology and acidity. A hierarchical SAPO-34/18 zeolite with a low Si/Al ratio of 0.11–0.12 and well-ordered macropores was synthesized with the conventional hydrothermal method by just decreasing the Si content in the gel mixture, that is, the development of its hierarchical structure did not need the use of an extra template or post-processing demetallation. The hierarchical structure reduced the diffusion distance inside the zeolitic phase because the void space made it equivalent to being comprised of small zeolitic crystallites, which gave a catalytic performance akin to that of nanosized zeolite particles. Reactivity studies that used a thermogravimetry–GC combination that simultaneously measured coke in the zeolite in addition to the gaseous products from the methanol-to-olefins (MTO) process showed that the hierarchical structure and low acid site density resulted in a longer lifetime, lower selectivities to coke and propane and higher selectivities to propene and butene, that is, a better catalyst for the MTO process.

1. Introduction

SAPO-34 zeolite is of interest for the methanol-to-olefins (MTO) process because its large cages, small windows and milder acidity compared to ZSM-5 give it higher selectivities to alkenes [1]. However, while its small window size gives it shape selectivity to light alkenes, it also leads to diffusion limitation of the reaction because this causes large hydrocarbon molecules and coke to remain in the cages [2–4]. Thus, catalyst development of the SAPO-34 catalyst have focused on getting better stability and meeting the industrial needs for a higher selectivity to olefins, especially propene. There have been two main strategies for these: (1) use SAPO-34 that has only mild acidity [5,6], and (2) use tiny zeolite crystallites, either as nanosized particles or as large particles with a hierarchical structure [7–12]. Concerning the acidity, Mees et al. [5] reported that the coking of a SAPO-34 catalyst decreased linearly with acidity, and that with the decreased coking, the ethene/ethane and propene/propane ratios increased. A SAPO-34 catalyst with very low density acid sites, described as an AlPO-34 zeolite by the authors [13], was reported to give a high selectivity to alkenes in the MTO reaction. Concerning the second strategy, very fine zeolite crystals are difficult to use and would give high operational costs, and so hierarchically structured crystals are considered more practical [14].

Although there are many methods to prepare hierarchical zeolites, including the use of special template [11,15,16] and demetallation procedures [17–19], these suffered from one or more of the following problems: complicated synthesis procedure, high cost of template, difficult to scale up or the possibility of contamination because more templates or more procedures are involved. Here, we reported a simple method to prepare a hierarchical SAPO-34/18 zeolite with well-ordered macropores and low acidity which was obtained by simply changing the ratio of silica sol to pseudoboehmite, orthophosphoric acid and triethylamine (TEA) used in the starting gel. The method did not need to use extra template or demetallation procedures to produce the hierarchical structure. The advantage of having macropores in the particle is that they separate the solid zeolitic phase into patches so that the particle is virtually comprised of many much smaller crystallites, which results in much short diffusion distances inside these small internal zeolitic crystallites as compared to the diffusion distance in a solid particle of the same size without macropores. Fortuitously, the composition of the raw materials used for the zeolite synthesis also gave the zeolite a lower acidity, which was further advantageous

* Corresponding author. Tel.: +86 1062794130; fax: +86 1062772051.
E-mail address: wang_yao@tsinghua.edu.cn (Y. Wang).

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for giving lower coke selectivity and longer catalyst lifetime and higher alkene selectivity.

2. Experimental

2.1. Preparation of hierarchical SAPO-34/18 zeolite

The catalysts were synthesized by the hydrothermal method. The reagents used were silica sol (40 wt% SiO_2), pseudoboehmite (73 wt% Al_2O_3), orthophosphoric acid (85 wt% H_3PO_4) and triethylamine (TEA). Samples with two different morphological structures were synthesized hydrothermally by changing the gel composition of Al_2O_3:$xSiO_2$:1.15P_2O_5:2.7TEA:114H_2O (x = 0.05–0.5). Just by changing the value of x, two kinds of SAPO-34/18 particles were obtained: particles with a conventional solid structure with a high framework Si/Al ratio (named TS-C, x = 0.5) and particles with a hierarchical structure with a low framework Si/Al ratio (named TS-H, x = 0.05).

In the synthesis, the gel mixture was put into a stainless steel autoclave lined with Teflon where it was first aged for 24 h and then heated at 200 °C for 20 h. After cooling the product to room temperature, the zeolite was recovered by centrifuging and washed thoroughly with deionized water. Then the sample was dried at 110 °C for 8 h and calcined in air at 600 °C for 4 h to remove the TEA template.

2.2. Characterization

Scanning electron microscope (SEM) images were obtained with a high resolution scanning electron microscope (JEOL, JSM-7401) operated at 2–3 kV. Elemental analysis was performed by energy dispersive spectroscopy (EDS; JSM 7401F) and by inductively coupled plasma-mass spectrometry (ICP-MAS). X-ray diffraction (XRD) spectra were recorded on a Rigaku D/Max-RB diffractometer using Cu $K\alpha$ radiation at 40 kV and 20 mA. NH_3-TPD analysis was carried out on an automated chemisorption analyzer (Quantachrome ChemBETPlusar) from 100 to 600 °C with a temperature increase of 10 °C/min. Ar adsorption isotherms at 87 K were obtained with an automated physisorption analyzer (Quantachrome Autosorb iQ2). Mercury penetration measurements were conducted on a Micromeritics AutoPore IV 9500. Laser particle size analysis was used to get the sample size using a Master Sizer 3000, for which the sample was placed in a wet dispersion.

2.3. Diffusion rate measurements

Diffusion coefficient measurements were made with the sample placed as a fixed bed in an apparatus designed to perform the chromatographic method [20]. Before the measurement, the sample was dehydrated at 500 °C for 2 h in argon flow. After the catalyst had cooled to the measurement temperature (40 °C for propene and 100 °C for propane), which was chosen using preliminary experiments to determine the conditions where the adsorbates did not react, a carrier gas containing 10 mol% propene (or propane) was passed through the zeolite bed for 1 h to saturate the sample. A step change in the adsorbate concentration was then introduced by fast response mass flow controllers that were used to stop the adsorbate flow and increase the carrier gas flow rate to keep the total flow rate constant. The adsorbate concentration at the exit of the zeolite bed versus time (response curve) was recorded with a mass spectrometer (MS, Stanford Research Systems RGA-200). The diffusion coefficients were obtained by curve fitting the response curves to the parameters in an axial dispersion chromatographic model that included internal diffusion in the zeolite.

2.4. TG–GC catalyst activity testing

The coke accumulated in the catalysts were analyzed using a thermogravimetry (TG) and gas chromatography (GC) combination equipment. TG and GC were used, respectively, to detect the solid and gas phase products. The TG apparatus (Mettler Toledo, TGA/DSC-1/1500) functioned as a reactor that was used to measure the sample weight online, which gave the accumulated coke mass in the sample as a function of reaction time. The MTO reaction in the TG–GC equipment was carried out at 400 °C and atmospheric pressure with a feed concentration of 10.0 mol% methanol and 3.7 mg catalyst. The feed was Ar as a carrier gas at a flow rate of 40 cm^3/min (STP) which was saturated with methanol by flowing it through a bottle containing methanol placed in a thermostatic bath. The composition of the gaseous product at the outlet of the TG–GC equipment was determined as a function of reaction time by collecting gas samples at specified times in an automated GC sampling valve with 10 sample loops, which collected gaseous product data from the same experiment that was used to get the coking rate data. The gas samples were analyzed offline by a GC (Agilent 7890A) with a capillary PLOT Q column (60 m, 0.53 mm i.d., 70 °C to 220 °C at 4 °C/min and kept for 20 min) and a FID detector.

3. Results

3.1. Catalyst characterization

The SEM images in Fig. 1 showed that there were large morphological differences between TS-C and TS-H. TS-C comprised solid cubic particles with smooth surfaces (Fig. 1a), which is a morphology that is commonly reported for particles of SAPO-34. In contrast, the surfaces of TS-H (Fig. 1b and c) had plentiful 50 to 500 nm macropore openings. From a large number of observations using SEM, it was observed that the pore distribution on the TS-H surface had regularity, that is, they were observed to be well-ordered macropores with a unique structure which differed from those previously reported for mesoporous [21] and layered [8] SAPO-34. The 3D MAX software was used with the images of the cross-section (e.g., Fig. 1c) to deduce the morphological structure of the obviously hierarchical nature of TS-H (Fig. 1d). The result indicated that the hierarchical cubic catalyst particle was composed of four pyramids and two frustums, which were, respectively, about 2 μm high and 400 nm thick. The macropores at the crisscross intersection of the four pyramids were directed straight inwards to form a three dimensional well-ordered channel network, which was seen clearly in the cutaway view of the TS-H zeolites. The macropore channels also passed through the two opposing frustums.

The EDS analysis of the elemental compositions of the molecular sieves gave the framework Si/Al atomic ratio of TS-H as 0.11 and that of TS-C as 0.21. The Si/Al ratios of TS-H and TS-C measured by ICP-MS were 0.12 and 0.23, in agreement with the measurement by EDS. The peaks in the XRD patterns of the samples were assigned by comparing them with those of standard CHA and AEI structures. In the XRD pattern of TS-H (Fig. 2), the peaks at 16.9, 19.6, 21.3, 24.1 and 26.3° indicated the existence of the AEI structure, in addition to the standard CHA structure of SAPO-34. In addition, the absence of a peak at 10.6° indicated that the CHA and AEI structures were not just physically mixed particles. The XRD pattern of the catalyst was simulated using DIFFaX [10], a specialized computer program for studying crystals with stacking faults, which indicated the sample was an intergrowth structure with the CHA/AEI structures, namely, a SAPO-34 and SAPO-18 intergrowth crystal with a CHA and AEI structure ratio of 8:2. The XRD pattern of TS-C was almost the same as that of TS-H. Therefore, the two