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Research paper

Synthesis of hierarchical SAPO-34 nanocrystals with improved catalytic performance for methanol to olefins

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ABSTRACT

SAPO-34 molecular sieve was hydrothermally synthesized by using organosilane phenylaminopropyl-tri methoxysilane (PHAPTMS) as a part of silicon source and tetraethylammonium hydroxide as microporous template at 160 °C. The XRD, SEM and N2 adsorption/desorption characterizations revealed the hierarchical SAPO-34 is a nanocrystal assembly of 50 nm particles prepared in the system. The catalyst showed improved stability and unusual selectivity of propylene and butylene in methanol to olefins reaction by introducing the mesoporous structure and changing the surface acid sites distribution. The yield of light olefins in hydrocarbons was up to 86%, the selectivity of C3= and C4= reached more than 40% and 10%.

1. Introduction

SAPO-34 molecular sieve, first reported by the scientists of Union Carbide Company in the 1980s [1], is one of the most important members in the silicoaluminophosphate molecular sieve family. It has the framework topology of the natural zeolite chabazite and contains narrow 8-ring pore opening (0.38 nm) and large cavity (0.94 nm). This narrow pore opening induces a high selectivity in various catalytic reactions as well as in gas separation processes [2]. SAPO-34 are of high interest as acidic catalysts and have gained a lot of attention in methanol-to-olefin (MTO) reaction due to the contribution of the small pores, medium acidity, good thermal/hydrothermal stability and corresponding good catalytic performance [3]. However, the small micropores limited the diffusion and therefore influenced the mass transport of reaction species in the catalyst, resulting in rapidly deactivation by coke deposition during the MTO process. Preparation of SAPO-34 molecular sieves with nanoscale size [4] or hierarchical mesoporous network [5] are considered to be an effective solution approach, which could improve the catalytic activity and the resistance to coke deposition because of the increased external surface area, shortened diffusion paths and enhanced the accessibility of methanol into its cages.

The most common and simple method for preparing zeolites/molecular sieves is hydrothermal crystallization. Conventional SAPO-34 molecular sieve with large particles in micron size is hydrothermally synthesized at temperatures higher than 180 °C using tetraethylammonium hydroxide (TEAOH) as template [6a]. It has been indicated by Nishiyama et al. [7a] that small SAPO-34 crystals (800 nm in size) were formed when TEAOH was used as the structure-directing agents (SDA). However, so far the synthesis of smaller SAPO-34 crystals (below 800 nm) was difficult under normally hydrothermal conditions [6b]. In this work, we successfully synthesized SAPO-34 nanocrystals (ca. 50 nm) assemblies with hierarchical mesoporous structure under hydrothermal conditions by using organosilane phenylaminopropyl-trimethoxysilane (PHAPTMS) and fumed silica as silicon source and TEAOH as the microporous structure directing agents. The obtained material has both characteristics of nanocrystals and hierarchical mesoporous SAPO-34 mesopores accessible from the outside of the particle, and showed prolonged catalytic lifetime and high selectivity to light olefins ($C_2^=$-$C_4^=$) in MTO reaction.

2. Experimental

SAPO-34 molecular sieve samples were synthesized from the starting gels with the optimized molar compositions of 2.0TEAOH:Al_2O_3:2.0H_3PO_4:0.5SiO_2:xPHAPTMS:65H_2O:4.35CH_3OH (x = 0 or 0.16). Firstly, a certain amount of PHAPTMS (Aldrich, CAS Number: 3068-76-6) and fumed SiO_2 (Degussa, Aerosil200, a hydrophilic fumed silica with a specific surface area of 200 m^2/g) was added into CH_3OH/H_2O and stirred 5 h at 60 °C, and the desired amounts of TEAOH (Sigma-Aldrich, technical, ~20% in H_2O, CAS Number: 77-98-5), Al_2O_3 and H_3PO_4 (Analytical Reagent) were added in sequence and stirred continuously for another 5 h. Then, the obtained gels were transferred into stainless steel autoclaves, and heated at 160 °C for 10 days statically under

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autogenously pressure. The obtained products were filtered, washed thoroughly, dried and calcined at 600 °C for 8 h to remove the template. Finally, two samples, denoted as SAPO-34-S (x = 0) and SAPO-34-D (x = 0.16), were prepared. For comparison, conventional micrometer-sized SAPO-34 was prepared.

Powder X-ray diffraction (XRD) patterns were taken in a Shimadzu XRD-6000 diffractometer using Cu Kα radiation. The average crystal size of the sample was calculated by using the Scherrer Formula $D = K\lambda/\beta\cos\theta$; D is the mean size of the crystalline domains, which may be smaller or equal to the grain size, K is a dimensionless shape factor, with a value close to unity, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity, θ is the Bragg angle. Scanning electron microscopy (SEM) images were recorded with Hitachi S-4800II FE-SEM instrument. Nitrogen adsorption/desorption isotherms was conducted at −196 °C in a Quantachrome Quadrasorb SI instrument. Pore size distribution curves were calculated from the adsorption branch of the isotherm according to the DFT kernel in cylindrical silica pores. The total surface area was determined using the BET equation, and the external surface area and micropore volume were calculated using the t-plot method. The total pore volume was calculated from the adsorption point at $p/p_0 = 0.98$. The temperature-programmed desorption of ammonia (NH_3-TPD) was conducted on a Micromeritics Chemisorb 2750 to measure the acid sites on the SAPO-34 materials. The methanol to olefins (MTO) is performed in a fixed-bed reactor at atmospheric pressure. 0.15 g calcined catalyst was added into the reactor and activated at 550 °C in a N_2 flow of 50 mL/min for 2 h before starting reaction run, and then the temperature was adjusted to a reaction temperature of 400 °C. Methanol was fed by passing the carrier gas through a saturator containing methanol at 20 °C, which gave a weight hourly space velocity (WHSV) of 4.0 h^{-1}. The reaction products were analyzed using an online gas chromatograph, equipped with a flame ionization detector. Conversion was defined as the percentage of MeOH consumed during the MTO reaction. The selectivity of each olefin was calculated as the percentage to the amount (in mass) of MeOH converted to hydrocarbons.

3. Results and discussion

The XRD patterns of three samples are shown in Fig. 1. XRD patterns of the SAPO-34-S and SAPO-34-D were identical with that of conventional SAPO-34 with CHA topology structure. Compared with conventional SAPO-34, both exhibit the typical XRD peaks of SAPO-34 with well crystallinity, and no additional crystalline phase or amorphous silica were observed. The difference is only that the XRD peaks of these two samples are weaker and wider, demonstrating the formation of SAPO-34 with smaller crystal size, especially for SAPO-34-D because of the addition of PHAPTMS. The average crystal size of SAPO-34-D sample calculated by using the Scherrer Formula is 36.0 nm.

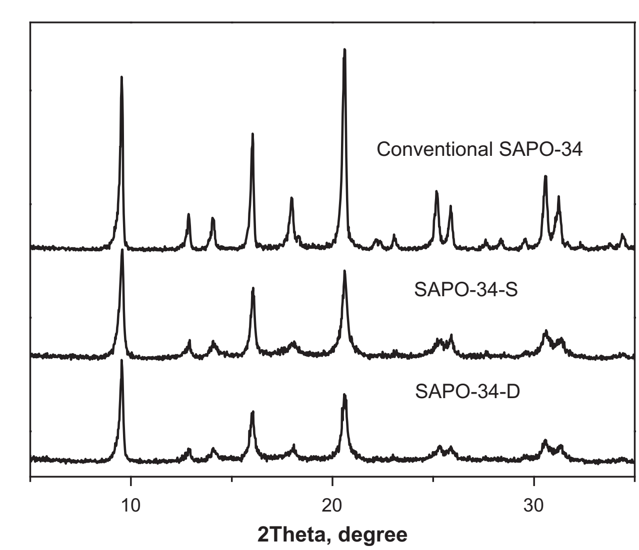

Fig. 1. XRD patterns of SAPO-34 samples.

Fig. 2 shows SEM images of the SAPO-34-S and SAPO-34-D in high magnifications. The SAPO-34-S shows cubic-like and surface smooth morphology with crystal size of about 150–350 nm (amplified images in Fig. S1), which is smaller than that of SAPO-34 sample synthesized under hydrothermal conditions by using TEAOH as SDA at 180 °C reported by Nishiyama et al. [6]. The result can be attributed to this synthesis system/method at lower crystallization temperature. Significantly different from the SAPO-34-S, SAPO-34-D presents as self-assembly morphology with particle size of about 1.0 μm, which is composed of the nanocrystals below 50 nm. The aggregation of nanocrystals results in the formation of intercrystal mesopores, which can be observed between the neighboring nanocrystals. The morphology of molecular sieves is impacted generally by the synthesis technology including template, resulting in different surface composite and properties, such as distribution of acid sites and defects [6]. The EDS results of the samples indicated the surface are Si-rich, Si/Al/P ratios are 14.4/46.5/39.1 and 11.6/42.7/45.7 for the SAPO-34-S and SAPO-34-D, respectively. The results are very similar to the report of Liu's group [7b], in which SAPO-34 was templated by diethylamine.

Fig. 3 provides the N_2 adsorption/desorption isotherms and corresponding pore size distributions for SAPO-34-S and SAPO-34-D samples. Both have high N_2 adsorption uptakes below p/p_0 of

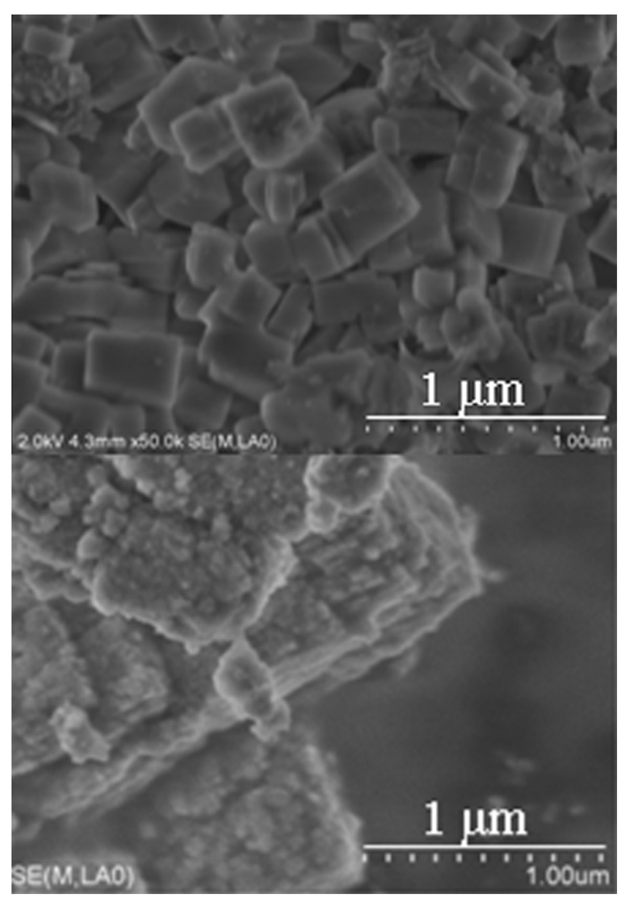

Fig. 2. SEM images of SAPO-34-S (top) and SAPO-34-D samples (bottom).