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Solid-state transformation of hollow silica microspheres into hierarchical ZSM-5 having tunable mesopores

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ABSTRACT

Mesoporous hierarchical ZSM-5 zeolites have been prepared via direct solid-state transformation of hollow silica gel microspheres without changing their spherical geometry. A two-stage hydrothermal method was used where tetrapropylammonium (TPA^+) directed the formation of the MFI subunits in the first stage. In the second stage these subunits aggregated around the self-assembled cetyltrimethylammonium micelles and then crystallized by TPA^+ templation. The mesoporous structure proved to be tunable in the pore size range of 3.2–4.8 nm by the addition of swelling agent 1,3,5-trimethylbenzene. Catalytic propene oligomerization showed less coke formed over mesoporous than microporous ZSM-5 catalysts.

1. Introduction

ZSM-5 has been widely used as catalyst in oil refining [1] and in chemicals production via aromatization [2], alkylation [3], and catalytic cracking [4]. However, the intrinsic microporous channels in ZSM-5 impose diffusion limitations [5]. Large hydrocarbon molecules retained within micropores deactivate ZSM-5 catalysts due to pore blockage or coking [6,7]. Hierarchical ZSM-5 catalysts containing mesoporosity have improved activity [8–10], thanks to shorter access to active sites [11,12], and faster diffusion of bulky products through the mesopores [13].

Recently, the synthesis of hierarchical ZSM-5 catalysts [14,15] has attracted much attention toward improving the catalytic activity [8–11] and increasing the lifetime [10,12,13]. Leaching with steam or acidic or basic chemicals is effective [10,12], but suffers from the loss of acid sites due to dealumination and it is difficult to control the uniformity of mesopores [14,16]. The synthesis of meso–microporous composites like ZSM-5/MCM-41 [17] is a good approach. But the composites are lacking the interconnection between ZSM-5 microporous channels and the MCM-41 mesopores. ‘‘Subunit-seed” [18] and replication [19] methods make use of protozeolitic nanoclusters to form mesostructural aluminosilicates with zeolite secondary building units in the framework. However, their hydrothermal stability is poor compared to conventional zeolites. A so-called “hard” [20,21] or “soft” [22] template pore-making method can generate hierarchical ZSM-5 with robust walls. These templates have average sizes >10 nm and thus result in pore size distributions with more than 10 nm width at half maximum. These materials are still not efficient for highly shape-selective catalytic reactions compared to conventional ZSM-5, unless the hierarchical ZSM-5 has supermicropores [23]. Nevertheless, these above-mentioned established synthesis methods use the hydrolysis of tetraethyl orthosilicate (TEOS) that facilitates the formation of the zeolite framework [24].

We report here a direct synthesis of hierarchical ZSM-5 using solid hollow silica gel microspheres as silica source and cetyltrimethylammonium (CTA^+) as the mesopore template because CTA^+ is able to direct the synthesis of ZSM-5/MCM-41 composites [17] and to transform MCM-41 into supermicroporous ZSM-5 [25]. Compared to conventional powder ZSM-5, the ZSM-5 having microspherical geometry does not require any binder to make practical catalysts. Our previous study has showed the improved fluid catalytic cracking (FCC) activity compared to the conventional ZSM-5, thanks to better contact with the feedstock [26]. Hierarchical ZSM-5 zeolites with microspherical geometry, therefore, may further provide improved activity and durability.

2. Experimental

2.1. Synthesis procedure

A two-stage method has been developed. In the first stage, 8 g silica gel microspheres (125–150 μm, Qingdao Haiyang Chemical

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Company) were impregnated with an aqueous solution of sodium aluminate ($NaAlO_2$, Al_2O_3 50–60%, Aldrich). The impregnated silica gel microspheres were dried at 120 °C for 12 h, followed by further impregnation with an aqueous solution of 5.5 ml tetrapropylammonium (TPA^+) hydroxide (TPAOH, 20% in water, Aldrich). The formed paste was moved into a Teflon-lined stainless steel autoclave and hydrothermally treated at 120 °C for 24 h. This hydrothermally treated mixture of TPA^+–silica gel microspheres was denoted as TPA^+–silica precursor.

In the second stage, an aqueous solution was prepared by mixing 1.28 g of *n*-hexadecyltrimethylammonium (CTA^+) bromide (CTAB, 98%, Aldrich), 2.13 g of tetrapropylammonium bromide (TPABr, 98%, Aldrich), and 6 g of deionized water. After stirring for 15 min, the TPA^+–silica precursor was added resulting in a final silica–gel mixture with the molar composition: SiO_2:0.011Al_2O_3:0.027CTAB:0.061TPABr:0.043TPAOH:4.30H_2O. This final mixture was loaded into the autoclave and hydrothermally treated at 138 °C for 60 h. The solid was recovered using filtration, washed thoroughly with deionized water, and then dried at 80 °C. Finally the product was calcined at 550 °C for 2 h in flowing nitrogen followed by another 4 h in flowing air, and was denoted as sample Z-1. The product synthesized by the identical procedure, but without CTAB addition in the second stage, was denoted sample Z-0.

2.2. Characterization

X-ray powder diffraction (XRD) was carried out on a rotating-anode Rigaku RU-200B series X-ray diffractometer with Cu Kα at 40 kV and 100 mA. The integration of the XRD peaks at 2θ of 7.9°, 8.7°, 23.0° and 23.9° was used to compare the relative crystallinity with the commercial ZSM-5 product (Zeoylst International). The IR framework vibrational spectra were determined on a Tensor 27 spectrophotometer (Bruker) using a KBr pellet of the sample. Scanning electron microscopy (SEM) was carried out on a Philips XL30 FEG instrument to characterize the morphologies. Elemental analysis of aluminum was performed on an inductively coupled plasma optical emission spectrometry (ICP-OES) instrument (Varian 710-ES). The ratio of silicon to aluminum in the samples was estimated using the ZSM-5 formula according to the aluminum amount determined by ICP.

N_2 adsorption/desorption isotherms were recorded at −196 °C using a Micromeritics ASAP 2020. Before measurements, samples were degassed at 350 °C for 24 h. Ammonia temperature-programmed desorption (NH_3-TPD) was carried out on a thermogravimetry (TG) analyzer combined with on-line gas phase analysis using an infrared (IR) spectrometer (Nicolet 380). Samples (0.05 g) were pretreated at 550 °C for 0.5 h in pure nitrogen (N_2) flow before cooling them down to the adsorption temperature (100 °C). After NH_3 (0.6 vol.%) flow was introduced into the system for one hour, the system was purged by a pure N_2 flow for another hour to remove physically adsorbed ammonia. NH_3-TPD was then conducted with a temperature ramp of 10 °C min^{-1} from 100 to 650 °C.

3. Results and discussion

The first synthesis stage is important for the formation of ZSM-5 subunit structures. TPAOH serves as a base to "dissolve" both silica gel and Al_2O_3, while TPA^+ serves as a structure-directing agent to form the subunits of the ZSM-5 structure. The TPA^+–silica precursor obtained in this stage was XRD amorphous, as shown in Fig. 1a. However, the IR spectra (Fig. 2b) showed a distinct shoulder at 543 cm^{-1}, indicating the presence of characteristic five-membered ring subunits of the MFI structure, because silica does not show any IR absorption near 550 cm^{-1} [27]. In addition, the IR band, corresponding to the T–O bending vibration, shifted from 469 cm^{-1} for silica to 463 cm^{-1} for the TPA^+–silica precursor.

The second stage plays a critical role for the formation of mesoporous ZSM-5 crystallites. During this stage, it is believed that TPA^+ serves as the template for the further crystallization of five-membered ring subunits into the ZSM-5 framework. The introduction of CTA^+ was used to assemble the subunits to crystallize and grow around the CTA^+ micelles to form a CTA^+ (micelles)–ZSM-5 composite. Synthesis conditions, such as crystallization temperature and time, affect the crystallinity and the morphology of the final product. In fact, after the final mixture of TPA^+–CTA^+–silica was hydrothermally treated at 138 °C for 24 h in the second stage, the product presented the typical ZSM-5 XRD patterns (Fig. 1b). With increasing crystallization time in the second stage, the relative crystallinity of the final product increased. The XRD patterns of sample Z-1 (Fig. 1d) were identical to those of sample Z-0 (Fig. 1c) synthesized without CTA^+ addition. Accordingly, the shoulder IR band at 543 cm^{-1} for the TPA^+–silica precursor became a strong peak while the T–O bending vibration in the IR spectra shifted to 449 cm^{-1} (Fig. 2c). Fig. 3 shows the SEM images of a single silica gel microsphere and the sample Z-1. It is obvious that the external surface of the microsphere was covered by ZSM-5 crystals while keeping the overall geometric shape of the sphere. Compared to the wall thickness of the microsphere (~50 μm), the size of the ZSM-5 crystals covering the surface was ~3.2 μm. Compared to commercial powder ZSM-5, the relative crystallinity was about 46%, indicating that not the entire shell of the silica microsphere has been transformed into ZSM-5 crystals.

Fig. 4a shows the N_2 adsorption–desorption isotherms of sample Z-0 and sample Z-1. It should be noted that there was a debate in the literature regarding the mesopore formation in MFI zeolite as evidenced by a N_2 adsorption–desorption hysteresis loop at $P/P_0 \sim 0.2$. The hysteresis loop can result from the filling of nitrogen molecules in the real pores [28] or from the phase transition of adsorbed nitrogen related to crystal size, aluminum content, and even the presence of defects in the some crystals [29]. However, if the distinct hysteresis loop occurs at $P/P_0 > 0.2$ or if the N_2 adsorption–desorption hysteresis loop starts at $P/P_0 \leqslant 0.2$ but the N_2 adsorption step jumps at least an order-of-magnitude higher

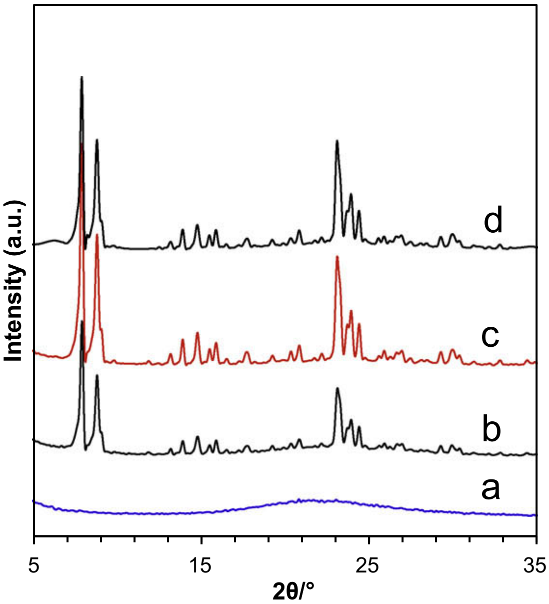

Fig. 1. XRD patterns of TPA^+–silica precursor (a), final mixture hydrothermally treated at 138 °C for 24 h (b), sample Z-0 (c), and sample Z-1 (d).