Hierarchically Structured Zeolite ZSM-5 Synthesized by Nanocasting Technique

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The hierarchical ZSM-5 was synthesized with interconnected macropores and skeletons by nanocasting technique. The skeletons can be templated to the morphology of pipes and rods in different conditions.

Zeolites have been widely used in industries as heterogeneous catalysts, particularly in the fields of oil refining and petrochemistry as solid acid catalysts, because of their specific features.[1] Although the micropores of zeolite have been well described as having excellent potential for chemical functions, their intricate pore and channel systems in the molecular size range (0.3–1.5 nm) are not efficient for processing large molecules of nanometer sizes. Recently, hierarchically structured zeolites have received considerable attention because these materials would combine the benefits of all pore-size regimes. In catalysis, the active sites are often located in the micropores and mesopores, while the macropores favor mass transfer and reduce transport limitations.[2] It generally synthesized relying on nanocasting pathway with "hard template," such as porous carbon (carbon black particles,[3] mesoporous carbon CMK-1 and CMK-3,[4,5] and colloid-imprinted carbon[6]), aerogel (carbon aerogel[7–9] and resorcinol–formaldehyde aerogel[9–11]), and other porous materials (polystyrene spheres,[12] mesoporous silica spheres,[13] polyurethane foams,[14] and wood cell[15]).

In this work, hierarchically structured ZSM-5 monolith (HZM) was synthesized using hierarchical carbon monolith as a hard template. The carbon monolith with co-continuous structure and trimodal pores was reported by Shi and Lu using silica monolith as the template.[16–20] Moreover, the morphology and pore size of the carbon monolith can be easily controlled, since the silica templates result from sol–gel conversion and can be molded in different shapes.[19]

The synthesis of hierarchically structured ZSM-5 monolith (HZM) was carried out by the following steps:[2] (1) synthesis of carbon monolith. It was prepared in the method used by Shi.[16,17,19] Firstly, the silica monolith was synthesized by combination of phase separation and sol–gel processes as reported by Nakanishi and Soga.[21] Secondly, the silica monolith was impregnated with an aqueous solution of sucrose and sulfuric acid (sucrose/sulfuric acid/water = 1.25:0.14:5 g). After being dried at 373 K, it was thermally treated at 433 K for 6 h. Then, the same procedures were repeated until no infiltration was observed. Subsequently, the composite material was carbonized at 1173 K for 6 h. Finally, the carbon monolith was liberated by dissolving the silica framework in a 1.0 mol·L^{-1} NaOH solution. (2) Clear solutions were prepared from tetrapropylammonium hydroxide (TPAOH), sodium hydroxide (NaOH), sodium aluminate ($NaAlO_2$), H_2O, and ethanol (C_2H_5OH) with composition (mole basis) $1Al_2O_3$:$7Na_2O$:10TPAOH:$5000H_2O$:2500EtOH designated as solution A, and $1Al_2O_3$:$7Na_2O$:15TPAOH:$5000H_2O$:2500EtOH as solution B, respectively. Part of the carbon monolith was impregnated to incipient wetness using solution A, and another part was impregnated to around 20% excess compared to incipient wetness using solution B. After evaporation of the ethanol, the carbon was impregnated with tetraethyl orthosilicate (TEOS) for $100SiO_2$:$1Al_2O_3$. After aging for 3 h at room temperature, the ZSM-5 was synthesized using steam-assisted conversion method at 433 K for 72 h. (3) The hierarchical ZSM-5 monolith replica of carbon monolith was obtained by calcining the as-synthesized carbon/zeolite composite in air at 873 K for 6 h. The hierarchical ZSM-5 monoliths synthesized using solution A and B were designated as HZM-A and HZM-B, respectively.

Figure 1 shows the X-ray diffraction (XRD) patterns of the hierarchical ZSM-5 monolith HZM-A and HZM-B. The HZM-A (Figure 1a) has peaks coinciding with conventional ZSM-5, which is weaker than that of HZM-B (Figure 1b). However, HZM-A shows a broad band in the 15–30° 2θ attributed to the amorphous silica. This result indicates that precursor gel has been successfully transformed into zeolite structure in the pores of carbon monolith, and the higher TPAOH amount obviously encourages the crystallization of ZSM-5.

Figure 2 shows the SEM images of the silica monolith and the hierarchical ZSM-5 monolith HZM-A and HZM-B. The morphology of the silica monolith shows the "interconnected structure" (Figure 2a), where both the silica skeletons and the macropores are continuous. The carbon replica of the silica monolith also shows the same structure with silica monolith (Figure 2b). The sizes of the textural pore for the silica and the carbon monolith are 1–2 and 0.5–1.5 µm, respectively. The SEM images of the hierarchical ZSM-5 monolith HZM-A are showed in Figures 2c and 2d. The fully interconnected, sponge-like macroporosity of the carbon monolith template is retained, and the size of the pores are 1–2 µm. Moreover, the skeleton of the HZM-A consists with pipes (Figure 2c), and these pipes are interconnected with each other (Figure 2d) with size of 0.5 µm, since the pores of the carbon template are interconnected

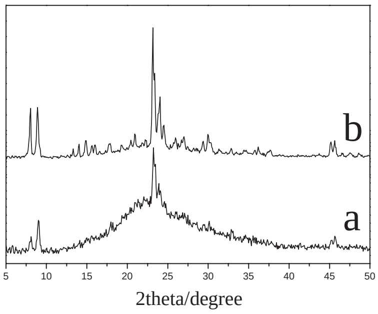

Figure 1. XRD patterns of the hierarchical ZSM-5 monolith HZM-A (a) and HZM-B (b).

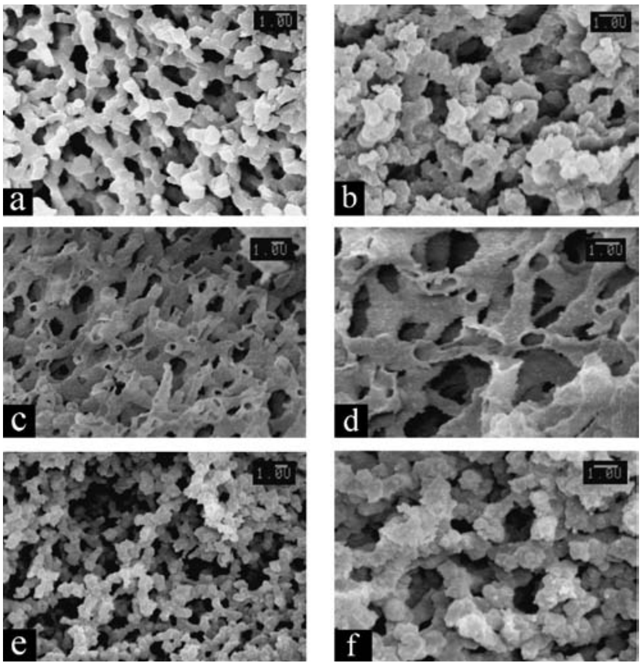

Figure 2. SEM images of the silica monolith (a), carbon monolith (b), hierarchical ZSM-5 monolith HZM-A (c and d), and HZM-B (e and f).

(Figure 2b). The HZM-B also preserves hierarchical pore structure of the carbon monolith template, and the size of the pores are 1–1.5 µm. The skeletons of the HZM-B are interconnected and consist of rods (Figures 2e and 2f).

The size of the skeleton and textural pores for the HZM are quite similar to those of the silica monolith contrast to Figures 2a and 2f, since the carbon monolith was the replica of the silica monolith, and the HZM was the replica of the carbon monolith. As shown in Figure 2, the most important difference is that HZM-B consists of zeolite rods as opposed to the pipes of HZM-A. For the synthesis of HZM-A, the pores of the carbon monolith were filled with solution A by an incipient wetness method. The size of the ZSM-5 crystals is small and a layer of well-interconnected membrane covers the surface of the carbon monolith, but the pore space was not entirely filled, since the quantity of the solid is insufficient to fill the entire pores of carbon monolith through incipient wetness. When the carbon was removed, the morphology like Figures 2c and 2d was observed. However, with the increase of the organic template TPAOH and 20% excess solution B compared to incipient wetness method, ZSM-5 crystals would grow up and was enough to fill the entire pores of the carbon monolith, and the interconnected rods were observed after the carbon removed (Figures 2e and 2f).

Various shaped carbon monoliths can be easily obtained by choosing silica templates, since the silica templates can be molded in different shapes from sol–gel conversion.[19] Similarly, the hierarchical ZSM-5 monolith can be nanocasted in different shapes.

In summary, the hierarchical ZSM-5 monolith was synthesized with interconnected macropores and skeletons by using carbon monolith as a hard template. The skeletons can be templated to the morphology of pipes and rods in different conditions. The successful incorporation of the macropores to the ZSM-5 should remarkably extends their applications because the macropores lead to easier access to the active sites.

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