Synthesis of Monolithic Zeolite Beta with Hierarchical Porosity Using Carbon as a Transitional Template

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With high thermal and hydrothermal stability and chemical resistance, crystalline microporous materials have been widely studied in catalysis as well as in separation and purification fields.[1−3] However, their intricate pore and channel systems in the molecular size range (0.3−1.5 nm) are not efficient at processing large molecules of nanometer sizes. Consequently, some recent research efforts have concentrated on overcoming this problem. One is decreasing the zeolite crystal's size.[4] However, filtration of the small zeolite crystals is difficult because of the colloidal properties of these materials. Another attempt is introducing mesopores or macropores linked to the zeolitic micropores. The resulting hierarchical pore-structured zeolites would further extend the applications of zeolites, because the material would combine the benefits of all pore-size regimes.[5] For instance, in catalysis, the active sites are often located in the micropores and mesopores, whereas the macropores favor mass transfer and reduce transport limitations. Several synthetic routes have been reported for the preparation of hierarchical zeolites. Conventionally, hierarchical zeolites with macropores and/or mesopores were obtained through a "hard template" route, such as porous carbon (carbon black particles,[6] mesoporous carbon CMK-1 and CMK-3,[7,8] colloid-imprinted carbon[9]), aerogel (carbon aerogel[5,10,11] and resorcinol−formaldehyde aerogel[11−13]) and other porous materials (polystyrene spheres,[14] polyurethane foams,[15] and wood cell[16]). Recently, zeolite nanosized assemblies with mesopores have been realized through transformation of the porous amorphous silica to zeolite nanocrystalline.[17]

Nakanishi and Soga[18] prepared the silica monolith with interconnected textural pores (macropores) and skeleton pores (mesopores) by combining the phase-separation and sol−gel processes. The shape and textural pore/skeleton pore size of the silica monolith are easily controlled by the adjustment of the preparation conditions. The silica monolith was applied in catalysis by Shikata and co-workers[19,20] recently. Silicalite-1 was formed on the inner wall surface of the silica monolith by the hydrothermal method. However, the silica walls were partly dissolved under highly alkaline hydrothermal synthesis conditions.

In this communication, we report a novel method of preparing zeolite beta monolith with a trimodal pore structure of interconnected macropores, mesopores, and micropores via the transformation of amorphous walls of silica monolith using carbon as a transitional template. First, the silica monolith was immersed in the mixture of sucrose and sulfuric acid solutions (sucrose:sulfuric acid:water = 2.5g:0.28g:10mL) until no infiltration was observed. After being dried at 100 °C for 6h, the monolith was thermally treated at 160 °C for 6 h. The composite materials were carbonized at 800 °C for 5 h under the protection of nitrogen to obtain the carbon/silica composite. Second, the clear aluminosilicate solutions were prepared from tetraethylammonium hydroxide (TEAOH), sodium hydroxide, sodium aluminate, and distilled water with composition (mole basis) 26:16.6:4.5:846 TEAOH:NaOH:Al_2O_3:H_2O. The carbon/silica composition was transferred to an autoclave for further reaction to crystallize zeolite beta at 150 or 165 °C for 48 h after being impregnated with the clear solution. The carbon was then removed from the as-synthesized material by calcination in air at 600 °C for 6 h. The as-synthesized beta monolith samples obtained at 150 and 165 °C were designated as B150 and B165, respectively. Actually, the carbon in the pores of the silica monolith acted as a transitional template to support the pore channels of the silica monolith beyond collapse during conversion of the amorphous walls of silica monolith to zeolite beta.

Figure 1 shows the photographs of the original silica monolith, carbon/silica composite, and as-synthesized beta monolith. All of them exhibit monolithic shapes. The size of these three monoliths is almost identical, 15 mm in length and 8 mm in diameter. The as-synthesized beta monolith was obtained by the conversion process of the original silica monolith. Various shapes of the as-synthesized beta monolith can be easily obtained, because the silica templates result from sol−gel conversion and can be molded in different shapes.

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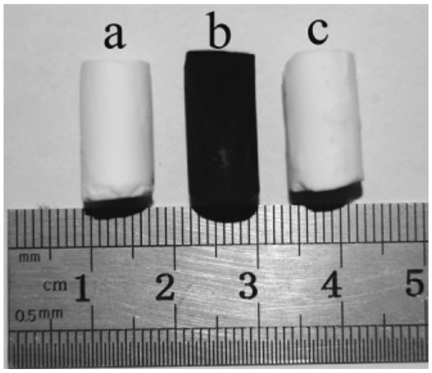

Figure 1. Photograph of (a) the original silica monolith, (b) carbon/silica composite, and (c) hierarchical zeolite.

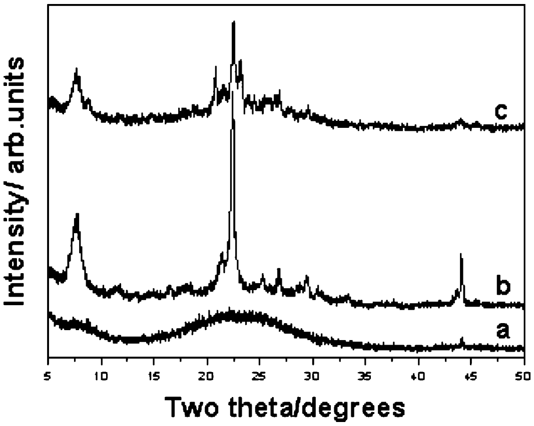

Figure 2. XRD pattern of (a) the original silica monolith, (b) B150, and (c) B165.

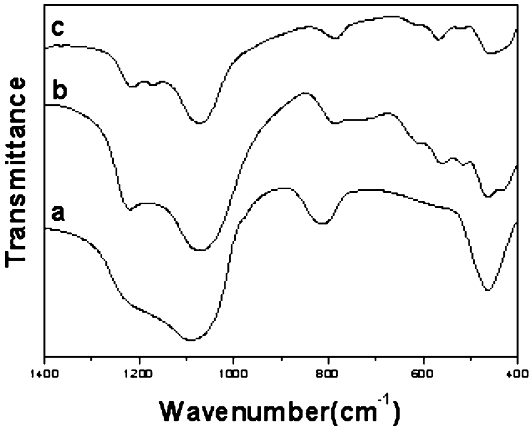

Figure 3. FT-IR of (a) the original silica monolith, (b) B150, and (c) B165.

Figure 2 provides the X-ray powder diffraction (XRD) patterns of the original silica monolith and as-synthesized beta monolith B150 and B165. The XRD results of B150 clearly show characteristic peaks that can be indexed as beta crystalline phase, whereas the B165 has composite peaks of both beta crystalline and MFI crystalline. With increasing temperature, part of the beta crystalline was constantly converted to MFI crystalline. From the intensity of peaks shown in the XRD patterns, almost all the amorphous silica was zeolitized in the synthesis conditions, and the carbon materials will not affect the crystalline process.

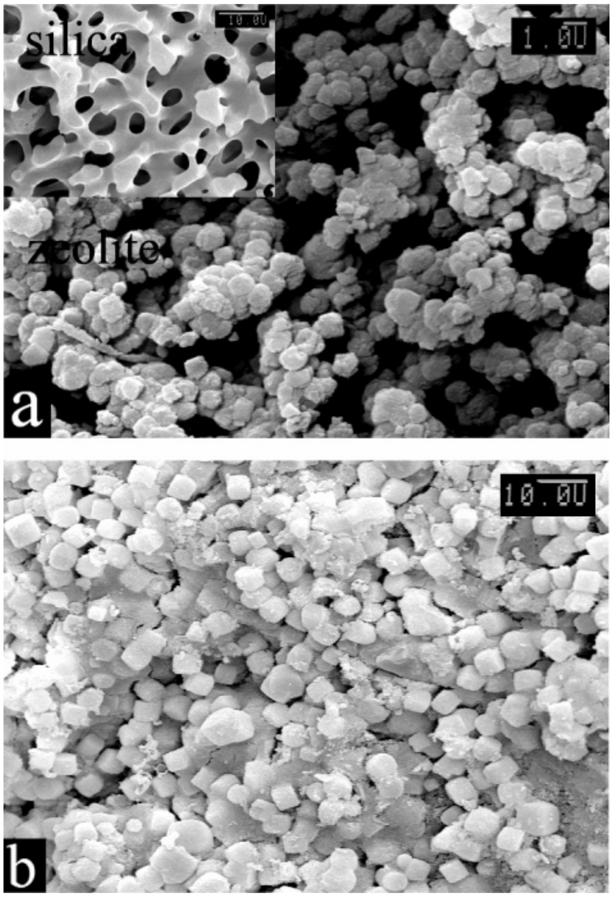

Figure 4. SEM images of (a) B150 and (b) B165. Also included in (a) are SEM images of the original silica monolith.

The hierarchical zeolite beta was further characterized by FT-IR spectroscopy, as shown in Figure 3. In the IR spectra, the band at 525 cm^{-1} of B150 and B165 is assigned to the presence of double four-membered rings in the zeolite beta structure, and the band at 565 cm^{-1} shows the vibration of five-membered rings in the zeolite beta structure. B165 has a band at 550 cm^{-1} that is the vibration of five-membered rings in the MFI structure. Higher temperatures can convert the beta crystalline to MFI crystalline.

In the zeolite synthesis process, the original amorphous materials contain Si−O and Al−O bonds, whereas the crystalline zeolite product contains Si−O−Al linkages. Because the product bond type is very similar to that present in the original materials, no great enthalpy change is anticipated; the outcome is most frequently kinetically controlled.[21] Because the kinetic control is a pervading influence throughout zeolite synthesis, the desired product is frequently metastable. When the temperature is increased, the products convert to more steady crystalline. The results of XRD and FT-IR data show this. Another viewpoint is that the decomposition of TEA$^+$ is not negligible and might assist in the formation of MFI nuclei when the temperature is increased.[22]

Figure 4 is a scanning electron micrograph (SEM) of the original silica monolith and the synthesized hierarchical zeolite beta monolith. The framework of B150 is similar to that of the original silica monolith, and interconnected

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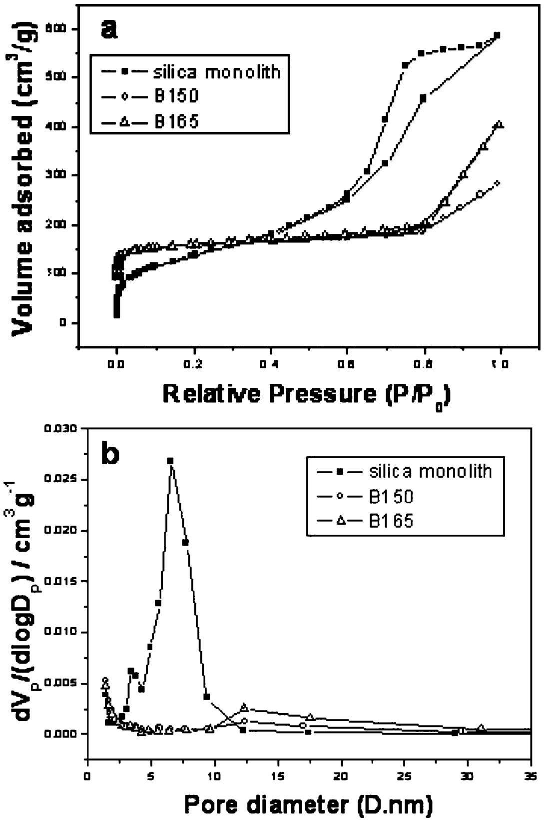

Figure 5. (a) Nitrogen adsorption−desorption isotherms and (b) the pore size distribution of the silica monolith (closed square), B150 (open circle), and B165 (open triangle).

textural pores with their uniform size of ca. 2 μm in width can be seen in the magnified image. The particles seen in the picture are small beta crystals, the size of which is about 0.5 μm. When the carbon/silica composite was treated at 165 °C, the crystals grow to about 3 μm on the surface of the carbon/silica composite. When the carbons are removed, the pores cannot be seen from the SEM picture of B165.

Compared with that of the silica monolith, the N_2 adsorption−desorption isotherms of B150 and B165 have a steep uptake below $P/P_0 = 0.02$ (Figure 5a), which is a typical signal of the existence of micropores. The original silica monolith exhibited type IV isotherm classification with an H1 hysteresis loop; a well-defined step occurred at $P/P_0 = 0.6-0.9$, indicating the existence of mesopores (Table 1); there is little increase in the adsorption until P_0, suggesting that macropores are also present. However, B150 and B165 show type I isotherms with an H4 hysteresis loop, which may merely arise from the presence of large mesopores (Table 1) embedded in a matrix with pores of much smaller size.[23]

Table 1. Texture Parameter of Original Silica Monolith and Beta Zeolite Monolith[a]

sample	S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_{mic} (cm^3/g)	V_{tot} (cm^3/g)	D_{mp} (nm)
silica monolith	492			0.908	6.55
B150	379	85.5	0.106	0.437	12.3
B165	443	26.7	0.0864	0.624	12.4

[a] S_{BET} = specific surface area; S_{mic} = micropore surface area, V_{mic} = micropore volume; V_{tot} = single point total pore volume; D_{mp} = mesopore diameter.

The pore size distribution for silica monolith, B150, and B165 calculated by the BJH method are shown in Figure 5b. The as-synthesized hierarchical zeolite beta monolith has a peak at 12.5 nm and the silica monolith has a relative shape peak at 6.5 nm (Table 1), according to the BJH calculation.

As shown in Table 1, the micropore surface area and micropore volume of B150 are larger than those of B165, whereas those of the original silica monolith are zero. With an increase in synthesis temperature, the zeolite crystal will grow, resulting in the reduction of the micropore surface area and micropore volume.

In summary, a synthetic method has been established for the fabrication of beta zeolite monolith with hierarchical pore systems through transformation of the amorphous walls of the silica monolith using carbon materials as a transitional hard template. The successful incorporation of the macropores and mesopores should remarkably extend their applications because the macropores lead to easier access to the active sites.

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Supporting Information Available: Synthetic process for carbon/silica monolith, hierarchical zeolite beta. This material is available free of charge via the Internet at http://pubs.acs.org.

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