Hydrothermal Conversion of Solid Silica Beads to Hollow Silicalite-1 Sphere

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Uniform hollow silicalite-1 spheres with a high intact ratio and good mechanical stability were fabricated through a novel and effective approach, which involved the seed-induced hydrothermal crystallization of mesoporous silica microbeads in an alkaline aqueous solution.

Hollow spheres of nano- and microscopic size have recently gained increasing attention because their unusual properties may find various potential applications in chemistry, biotechnology, and material science.[1] Up to now, the fabrication of hollow spheres comprising of a variety of species, such as polymers[2,3] and ceramics,[4–11] has been reported. Among them, the hollow spheres built of zeolites[6–11] represent a special group of hollow-structured materials for their large zeolitic microporosity and high thermal stability. This novel type of hollow spheres is expected to be applied as controlled storage and release containers, shape-selective adsorbents and catalysts. Hollow zeolite spheres are generally fabricated by the layer-by-layer (LbL) assembly of zeolite nanocrystals on polystyrene spheres, followed by the removal of template cores.[6–8] Additionally, Valtchev[10] obtained mechanically stable hollow zeolite spheres through a further secondary hydrothermal treatment after the LbL assembly process. These strategies can well produce hollow zeolite spheres, but the usage and removal of a large amount of polymer template usually lead to the concerned environmental contamination. In addition, according to some literatures[6,7] and our experience, the pathway to remove the polymer template by calcination usually brings on considerable shrinkage (larger than 20%) or even fracture to the products.

Very recently, our group[11] proposed an interesting pathway to prepare hollow zeolite spheres, which involved the vapour phase transport (VPT) treatment of zeolite-seeded mesoporous silica spheres. During this process, the hollow zeolitic shells could be spontaneously formed along with the consumption of silica spheres, therefore the template core removal procedure in conventional methods[6–8,10] can be avoided. As an important development of this strategy, here, we report a simple but more effective method for producing uniform hollow zeolite spheres with a much lower breakage ratio (<2%) and higher mechanical stability. This method involves the seed-induced hydrothermal crystallization of mesoporous silica microbeads in a tetrapropylammonium hydroxide (TPAOH) aqueous solution. In this process, not only the template core removal step can be avoided, but also the products possess a higher fraction of intact morphology and a stronger shell because of the much better inter-growth of zeolitic crystals formed under hydrothermal conditions compared to those prepared from VPT method.

Uniform mesoporous silica beads with size of 1.2 ± 0.1 µm (Figure 1a) were synthesized according to the literature.[12] For the preparation of hollow zeolite spheres, the as-synthesized silica microbeads were homogeneously seeded with silicalite-1 nanocrystals (50 ± 10 nm, prepared as described elsewhere[13]) through electrostatic adsorption (Figure 1b).[11] After washing with 0.01 M NH_4OH to remove the unbound seeds, the silicalite-1-coated silica beads (ca. 0.2 g) were immersed in a 5 mL solution of 0.1 mol L^{-1} TPAOH and then transferred to a Teflon-lined autoclave. Afterwards, the autoclave was enclosed and heated in an oven at 140 °C for 4 h. The final product was collected through centrifugation and washed with deionized water.

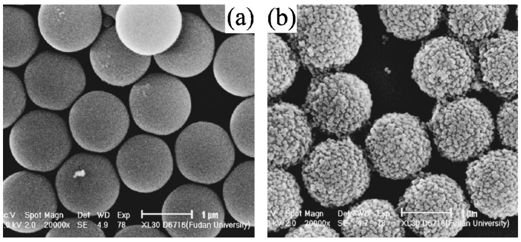

Figure 1. SEM images of the original (a) and the monolayer nanosilicalite-1 coated silica beads (b).

The scanning electron microscopy (SEM) images of the hydrothermally treated sample were shown in Figures 2a and 2b. The discrete and uniform spherical morphology of the original silica beads was well retained in the product, and a very little portion (<2%) of broken spheres demonstrated their hollow structure as indicated by both the arrow and the inset in Figure 2a. The original spherical zeolite seeds on silica beads grew to quadrate-like crystals with size of 80–150 nm (Figure 2b). These results were also proved by the transmission electron microscopy (TEM) analyses. The products clearly exhibit hollow structures with black circles outside presenting silicalite-1 shells (Figures 2c and 2d), indicating that the silica beads have been completely consumed. Since no additional silica was added to the synthesis solution, the silica beads should be the "nutrition" for the growth of silicalite-1 crystals on the shell. The shell thickness was about 150 nm, determined from the TEM image at high magnification (Figure 2d). The cavity diameter of the hollow zeolite spheres was about 1.2 µm, very close to that of the original silica beads, indicating that little shrinkage had occurred during the transformation of silica beads. The hollow zeolite spheres prepared by this method demonstrate good mechanical and thermal stability since no obvious morphological changes were observed when the product was subjected to sonication (HF frequency = 50 kHz, 120 W, 20 min) or calcination (in air, 600 °C, 10 h) treatment.

The transformation of silica beads was also proved by the X-ray diffraction (XRD) analyses. Both the original and the monolayer nanosilicalite-1-coated silica beads showed a wide dispersive diffraction signal at $2\theta = 15$–30° attributed to amorphous silica. In contrast, the XRD pattern of the hollow spheres displayed a flat baseline and sharp characteristic diffraction

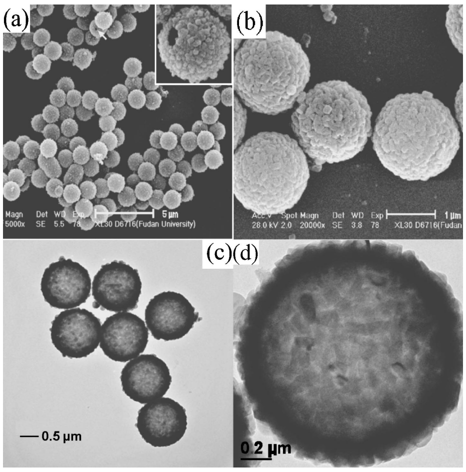

Figure 2. SEM (a, b) and TEM (c, d) images and of the hollow silicalite-1 spheres. The inset in (a) represents a broken sphere.

peaks of silicalite-1 with MFI crystal structure (Figure 3), indicating the complete transformation of amorphous silica beads and the high crystallinity of the product. These results were also reflected in their Fourier transform infrared (FT-IR) spectrum (Figure 3, inset). The band at 550 cm^{-1} confirmed that the sample possessed MFI type framework, and the intensity ratio of 550 to 450 cm^{-1} was indicative of the high crystallinity of the product.[14] The N_2 adsorption analysis further confirmed the transformation of silica beads. The original silica beads displayed a typical type IV isotherm of mesoporous materials, while the adsorption isotherm of hollow zeolite spheres after calcination in air at 600 °C for 6 h showed type I like behaviour. In addition, the micropore surface area increased from original 0 to 260 $\mathrm{m}^2\mathrm{g}^{-1}$ (*t*-plot) with the total Brunauer–Emmett–Teller (BET) surface area decreased from 660 to 360 $\mathrm{m}^2\mathrm{g}^{-1}$. All these facts clearly demonstrated that the nanosilicalite-1-coated silica beads were indeed converted to hollow silicalite-1 spheres after this hydrothermal process.

It was also found that pre-coating silica beads with a complete layer of silicalite-1 seeds was crucial for the successful preparation of hollow zeolite spheres. When the unseeded silica beads were used, only some large silicalite-1 crystals (ca. 1.5 µm) were observed after the same hydrothermal treatment. They should be formed from the leached species from the silica beads, because the size of the final silica beads was decreased to ca. 1.0 µm. It seemed that the pre-deposited silicalite-1 nanocrystals worked just like a "pump" which drew the silica species from the internal silica beads in the aid of the alkaline solution and simultaneously induced them to form the parts of the grown zeolite crystals in the hydrothermal system. As a result, the hollow spheres were formed with the dense shells composed of the intergrown zeolite crystals.

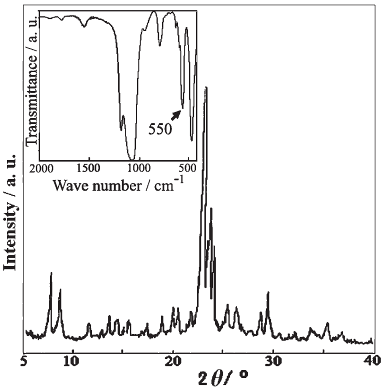

Figure 3. XRD pattern and FT-IR spectrum (inset) of the as-synthesized hollow silicalite-1 spheres.

In conclusion, we have demonstrated a simple and effective method based on the hydrothermal transformation of zeolite-seeded silica beads to fabricate uniform and mechanically stable hollow silicalite-1 spheres. The silica beads used here serve as a "nutrition" pool for the formation of hollow zeolite spheres besides as the scaffold, so that the template core removal process and the subsequent remarkable shrinkage and fracture to the product can be avoided.

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References

1 F. Caruso, *Chem.—Eur. J.*, **6**, 413 (2000).
2 E. Donath, G. B. Sukhorukov, F. Caruso, S. A. Davis, and H. Möhwald, *Angew. Chem., Int. Ed.*, **37**, 2202 (1998).
3 S. M. Marinakos, J. P. Nsovak, L. C. Brousseau, III, A. B. and House, E. M. Edeki, J. C. Feldhaus, and D. L. Feldheim, *J. Am. Chem. Soc.*, **121**, 8518 (1999).
4 F. Caruso, R. A. Caruso, and H. Möhwald, *Science*, **282**, 1111 (1998).
5 Z. Zhong, Y. Yin, B. Gates, and Y. Xia, *Adv. Mater.*, **12**, 206 (2000).
6 K. H. Rhodes, S. A. Davis, F. Caruso, B. Zhang, and S. Mann, *Chem. Mater.*, **12**, 2832 (2000).
7 X. D. Wang, W. L. Yang, Y. Tang, Y. J. Wang, S. K. Fu, and Z. Gao, *Chem. Commun.*, **2000**, 2161.
8 V. Valtchev and S. Mintova, *Microporous Mesoporous Mater.*, **43**, 41 (2001).
9 S. P. Naik, A. S. T. Chiang, R. W. Thompson, and F. C. Huang, *Chem. Mater.*, **15**, 787 (2003).
10 V. Valtchev, *Chem. Mater.*, **14**, 4371 (2002).
11 A. Dong, Y. Wang, Y. Tang, N. Ren, Y. Zhang, and Z. Gao, *Chem. Mater.*, **14**, 3217 (2002).
12 M. Grun, C. Buchel, D. Kumar, K. Schumacher, B. Bidlingmaier, and K. K. Unger, *Stud. Surf. Sci. Catal.*, **128**, 155 (2000).
13 A. E. Persson, B. J. Schoeman, J. Sterte, and J. E. Ottesstedt, *Zeolites*, **14**, 557 (1994).
14 G. Coudurier, C. Naccache, and J. C. Vedrine, *J. Chem. Soc., Chem. Commun.*, **1982**, 1413.

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