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Synthesis of Hollow Zeolite Composite Spheres by Using β-Zeolite Crystal as Template

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Core–shell microspheres with BEA and FAU zeolite structures (denoted as BEA–FAU) were prepared through a two-step hydrothermal crystallization process in which a β-zeolite was used as silicon source for the synthesis of Y zeolite as well as a template for the formation of hollow sphere. Scaning electron microscopy and intrusive mercury experiments displayed the as-synthesized sample had extra-large pores of 2–3 µm; a possible formation mechanism of BEA–FAU hollow spheres was proposed and discussed.

Inorganic hollow spheres with nanometer-to-micrometer dimensions have increasingly attracted interests because of their potential applications in catalysis, drug delivery, pigment, battery materials, or photonic crystals due to their unique structural, optical, and surface properties.[1–5] In recent years, employing template-directed methods to prepare hollow spheres has proven to be very effective. Sun and co-worker[6] succeeded in synthesizing hollow spheres of mesoporous silicon oxide by using triblock copolymer PEO–PPO–PEO as template. Li et al.[7] prepared hollow spheres of mesopous aluminosilicate with extraordinarily high hydrothermal stability by employing a copolymer as template. Caruso et al.[8] prepared SiO_2 and hybrid hollow spheres by using PS colloidal particles as template. Zhou et al.[9] reported a method for synthesis of ZnO hollow spheres using spherobacterium streptococcus thermophilus as a biological template. Ma et al.[10] synthesized CdS hollow spheres in aqueous solutions of a triblock copolymer.

In these reported results, it was a complicated process to modify the core surface for ensuring coating of shell materials, and the template hidden in the spheres was also difficult to remove. In the preparation of biphase MOR–MFI core–shell zeolite composite,[11] an obvious gap was left between the core and the shell; transportation of components from the core to the growing shell was also observed. The interspaces between the shell and core would be expanded if the core were further dissolved by the synthesis solution or consumed by the growing shell during the second-step synthesis. That would provide a new method to prepare the hollow spheres. In the present work, we reported the synthesis of a hollow sphere zeolite composite by using β-zeolite crystals as silicon sources for the synthesis of Y-zeolite as well as the filler template for the formation of hollow spheres.

The zeolite composite BEA–FAU was hydrothermally synthesized under static conditions via a two-step crystallization process. β-Zeolite was first prepared: 17.58 g of tetraethylammonium bromide (TEABr), 2.26 g of sodium aluminate (41 wt% Al_2O_3, 35 wt% Na_2O) and 0.58 g of sodium hydroxide (96 wt%) were dissolved in 35 mL of water and 5.8 mL of aqueous ammonia (27 wt%) to form a clear solution, then 37.51 g of silica sol (29 wt%, pH 9) was slowly added to the solution under stirring. The mixture was stirred for 1 h at room temperature, transferred into a 100 mL autoclave, and kept at 413 K for 236 h without stirring. The reacted mixture containing the synthesized β-zeolite was directly used in the second step; 3.22 g of sodium aluminate and 2.60 g of seeds of Y zeolite (prepared according to the molar composition of $13Na_2O:15SiO_2:Al_2O_3:320H_2O$, aged at 308 K for 18 h) were added to the reacted mixture; the $[OH^-]$ of the mixture was adjusted to $1.55\,mol\,L^{-1}$ by adding 1.41 g of sodium hydroxide, and the mixture was stirred at room temperature for 2 h. The final mixture was sealed into an autoclave and heated at 363 K for 22 h under autogenous pressure. The solid product was recovered by filtration and denoted as BEA–FAU.

An XRD pattern of the sample was recorded on a Rigaku Dmax/2500 X-ray diffractometer with Ni-filtered Cu Kα radiation at 40 kV and 80 mA. Pore size distribution was studied with an AUTOPORE II 9220 intrusive mercury apparatus. Crystal morphology and size were determined on a JSM-6301F scanning electron microscope (SEM).

Both the characteristic diffraction peaks of Y- and β-zeolites occur in the XRD pattern of the sample as shown in Figure 1a, indicating the coexistence of Y- and β-zeolites phase in the zeolite composite. Crystal morphology of the zeolite composite BEA–FAU differs from those of Y- and β-zeolites as shown in Figure 2. β-Zeolite and Y-zeolite show sphere-like crystal particles and octahedral morphology, respectively (not shown here). From Figure 2A, many hollow spheres with open sizes of 2–3 µm can be seen. It can be observed from Figure 2B, the hollow sphere has been opened, and a piece of debris of the core is still left in the shell. An intrusive mercury experiment was conducted on BEA–FAU so as to investigate the pore properties of the composite, as shown in Figure 1b. The pore size distribution of the zeolite composite illustrates the existence of

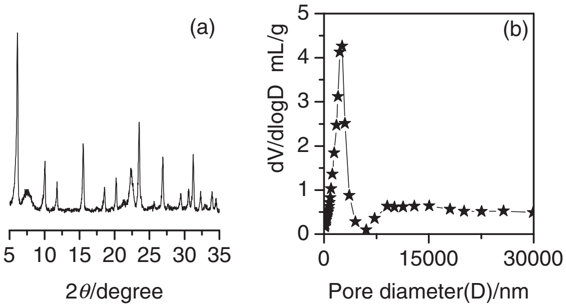


Figure 1. (a) X-ray powder diffraction pattern of zeolite composite BEA–FAU and (b) pore size distribution curve of BEA–FAU hollow spheres.

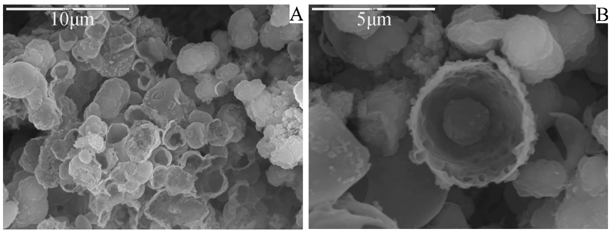


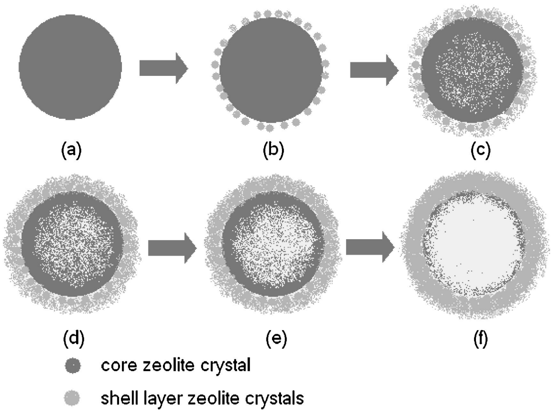
Figure 2. SEM images of hollow BEA–FAU spheres crushed by 3 MPa pressure.

a pore structure with pore size centering about 2.58 µm, which is in good agreement with the results observed by SEM.

Si extraction from β-zeolite during the second-step synthesis plays an important role for the formation of BEA–FAU zeolite composite. It is short of silicon species for the growth of Y-zeolite crystal during the second-step hydrothermal crystallization, the silicon sources can only be obtained from the degradation of β-zeolite etched by the synthesis solution. The interaction between the aluminum species from the synthesis solution and the silicon species extracted from β-zeolite crystal promotes the growth of Y-zeolite. During the second-step synthesis, there may be two nucleation centers for Y-zeolite crystal growing. One is in the synthesis gel. The other is on the external surface of β-crystal, the key fields responsible for the formation of BEA–FAU composite. It is no doubt that the two nucleation centers compete with each other; however, the external surface of β-zeolite crystal dominates in the competition due to its higher surface area.[12]

The mechanism of the formation of the hollow sphere zeolite composite is suggested in Scheme 1. Y-Zeolite nanoseeds are first adsorbed on the external surface of β-zeolite crystal due to its higher surface area,[12] which is a very important step for the formation of the hollow spheres (Scheme 1, (a) → (b)). Second, the nanoseeds begin growing because of the interaction between aluminum species from the synthesis solution and silicon species extracted from β-zeolite crystal, resulting in the formation of Y-zeolite polycrystalline shell around β-crystal, and β-zeolite crystal is, therefore, embedded into the shell (Scheme 1, (b) → (c)). Subsequently, the shell layer zeolites become thicker and thicker along with the extraction of silicon from the β-zeolite crystal (Scheme 1, (c) → (e)). Finally, β-zeolite crystal can even be exhausted and a cavity whose dimension is close to that of β-crystal is created in the shell where β-zeolite particles used to reside (Scheme 1, (e) → (f)). Thus, β-zeolite crystal not only serves as a source of nutrients for the growth of Y-zeolite crystals but also acts as the filler template for the formation of hollow spheres.

It was known that Al gradient would affect and control the Si extraction throughout the zeolite particles. A high framework Al concentration prevents Si extraction, while a low Al concentration leads to excessive extraction and formation of large pores.[13] The presence of an aluminum-poor interior and an aluminum-rich outer rim in β-zeolite crystals results in Si extraction favorably occurring in the aluminum-poor bulk rather than the aluminum-rich external surface. Subsequent alkaline treatment of β-zeolite crystal during the second-step synthesis will result in a preferential dissolution of the aluminum-poor center and the formation of hollow crystals with a relatively preserved outer surface.[13] The preserved external surface supports the shell layer of Y-zeolite growing, resulting in the formation of the core–shell zeolite–zeolite composite hollow spheres.



Scheme 1. Schematic representation of the process for the formation of BEA–FAU hollow spheres.

The size of the cavities from intrusive mercury experiments and SEM are very similar, but slightly larger than that of β-zeolite crystals synthesized in the first step. These strongly suggest that the cavities are produced by the dissolution of β-zeolite crystals.

In summary, hollow BEA–FAU zeolite composite spheres were synthesized by using β-zeolite crystal as fillers for the formation of the cavities as well as silicon sources for the synthesis of Y-zeolite shells. The thickness of the shell and the size of the cavity can be controlled by adjusting the reaction conditions.

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