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MATERIALS

Conversion of Fly Ash Cenosphere to Hollow Microspheres with Zeolite/Mullite Composite Shells**

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A seed-induced in-situ hydrothermal conversion technique is proposed to prepare novel hollow microspheres with zeolite/mullite composite shells from fly ash cenosphere (FAC), a solid waste with a hollow structure from coal power stations. Two groups of hollow microspheres were prepared, one with zeolite FAU/mullite composite shells and the other with zeolite LTA/mullite composite shells. The FAC in this study plays dual roles as both the template cores and the aluminosilicate nutrition contributor. The final products inherit the hollow spherical morphology of FAC and possessed bilayered shells, the outer dense shell of zeolite crystals and the inner porous shell of mullite. Such hollow zeolitic materials are expected to have many advantages in applications such as catalysis, adsorption, separation, and as releasing capsules.

1. Introduction

Zeolites are widely used in areas of catalysis, separation, ion exchange, and sensing because of their unique properties, such as high surface area, good thermal and hydrothermal stability, high shape selectivity of micropores, and superior ion-exchange ability.[1] Recently, several methods have been developed to prepare hierarchical zeolitic materials with various macroscopic morphologies including membranes,[2] spheres,[3] monoliths,[4] and zeolitic composites,[5] which might provide more benefits in the practical application of zeolites. Many artificial materials, such as cellulose acetate membranes,[2c] polystyrene spheres,[4a] carbon fibers,[6] and mesoporous silica spheres,[4d,7] have been used as templates to control the product structure and morphology. More interestingly, some natural materials, such as diatomite and wood[5a,8] have also been used for this purpose. In addition to their low cost, abundance, and environmentally benign character, their specific inherent multilevel structures are of great importance because they could be well replicated in the final products.

Recently, hollow zeolite spheres of dimensions ranging from sub-micrometer to micrometer have attracted considerable attention for their promising applications in catalysis, adsorption, or controlled release and storage, due to their hollow structures and zeolite shells.[7,9,10] These products are generally fabricated by the combination of the layer-by-layer (LBL) self-assembly technique and the sacrificial core–shell technique.[9] Additionally, Valtchev[10] obtained mechanically stable hollow zeolite spheres through a further secondary hydrothermal treatment before the removal of the template cores. Although these strategies can effectively produce the hollow zeolite spheres, the use and removal of a large amount of polymer template usually leads to high production costs and concerns regarding environmental contamination. Very recently, our group proposed a new scheme for the preparation of hollow zeolite capsules. In this method, the hollow structure could spontaneously be formed simultaneously with the consumption of the nanozeolite pre-seeded mesoporous silica cores during the chemical treatment.[7]

Fly ash (FA) is an aluminosilicate-rich waste produced in coal power plants and causes serious environmental problems. Great efforts have been made on the utilization of this waste. One of the efforts is to prepare zeolites by converting its active silica and alumina components.[11] Fly ash cenosphere (FAC) of different sizes can be obtained from FA by advanced size-grading techniques and has already been used as fillers in low-density materials. However, until very recently, little attention has been paid to directly transforming it into zeolite materials although its characteristic hollow spherical structure might endow the products with controlled morphology.

In this study, using FAC as the template cores and the nutrition provider, two groups of hollow zeolitic spheres with FAU/mullite and LTA/mullite (FAU: Faujasite LTA: Linde type A) composite shells were prepared by in-situ hydrothermal transformation of zeolite-seeded FAC. The resulting zeolitic materials not only preserve the hollow and spherical morphology of the FAC well, but also exhibit an improved mechanical strength due to the unique bilayered shells of a dense zeolite film on the inner mullite layer.

2. Results and Discussion

2.1. Fabrication Strategy

The fabrication procedure is illustrated in Scheme 1. The FAC was first seeded by nanosized zeolite FAU or LTA through electrostatic adsorption with the aid of polyelectrolytes.[9,12] Afterwards, the seeded FAC was hydrothermally treated in situ in a NaOH aqueous solution. During this pro-

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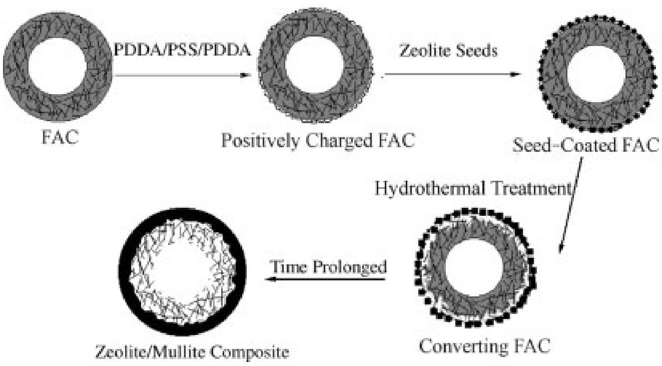
[**] This work is supported by the NSFC (20233030 and 20273016), Shanghai Science Committee (0249nm028), and the Doctoral Fund of Education Ministry. The assistance of Dr. H. Y. Zhu (The University of Sydney) with improving the English in the paper is gratefully acknowledged.

DOI: 10.1002/adfm.200304312



Scheme 1. Procedures for the conversion of FAC to hollow zeolite/mullite composite microspheres by seed-induced in-situ hydrothermal conversion.

cess, the active aluminosilicate species were gradually extracted out from the FAC shells and transformed into the outer dense zeolite layers under the induction of the zeolite seeds, whereas the inert mullite crystals were left forming the inner porous shells. The unique composite shells should endow the products the improved mechanical strength in addition to the general characteristics of hollow zeolite spheres. Using the size-selected FAC as raw materials, the hollow zeolitic spheres with sizes ranging from tens to hundreds of micrometers could be prepared. Moreover, this method is one of the most convenient and environmentally benign approaches for the preparation of hollow zeolitic spheres, since the template core removing process employed in most of the previous strategies was avoided.

2.2. Characterization of FAC and the Zeolite Seeds

Scanning electron microscopy (SEM) was used to characterize the structure and morphology of the original FAC. The sieved FAC has a spherical morphology with a diameter of 50–80 μm (Fig. 1A). Its hollow structure can be clearly observed from the SEM image of the broken FAC (Fig. 1B). The thickness of its dense shell is within a range from 2 to 4 μm. The X-ray powder diffraction (XRD) pattern (Fig. 2A) indicates that the FAC contains the crystalline phases of mullite and a small amount of α-quartz in addition to the main amorphous glassy phase.

The XRD patterns in Figure 3 clearly show that the prepared seeds are pure zeolite FAU and LTA crystals, respectively. SEM images indicate that the sizes of the zeolite FAU and LTA seeds are in the ranges of 50–100 nm (Fig. 4A) and 80–240 nm (Fig. 6A), respectively. The colloidal suspension of the above seeds are stable for several weeks at a ca. pH 10.

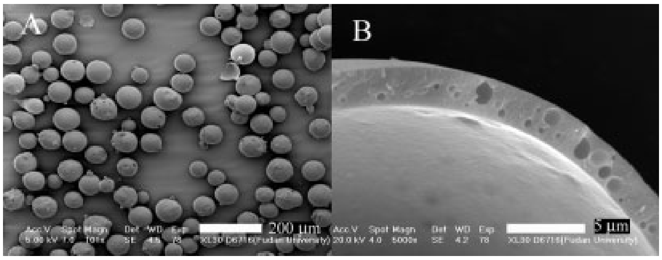


Fig. 1. SEM images of the sieved FAC (A) and a broken FAC particle (B).

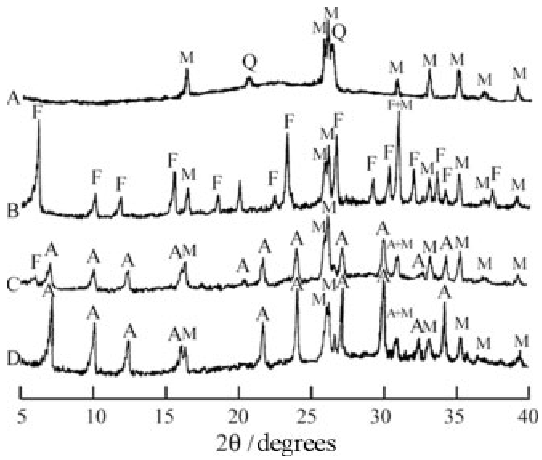


Fig. 2. XRD patterns of the original FAC (A) and the composite microspheres of FAU/mullite (B), LTA/mullite with hybrid FAU crystals (C) and LTA/mullite (D). (F, A, M, and Q in the figure represent the diffraction peaks of FAU, LTA, mullite and α-quartz, respectively.)

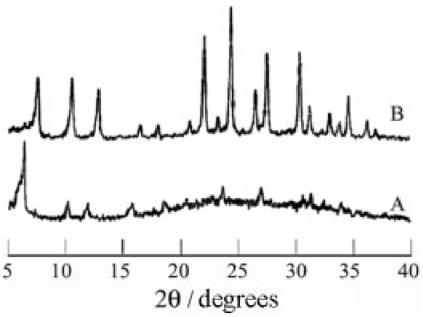


Fig. 3. XRD patterns of the zeolite seeds FAU (A) and LTA (B).

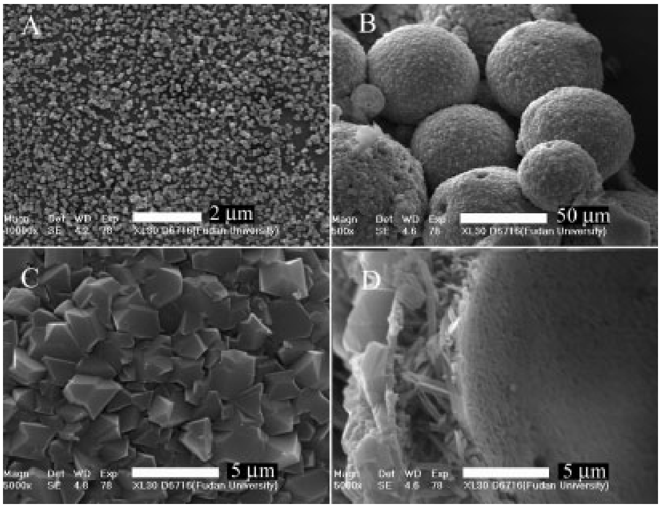


Fig. 4. SEM images of the surface of zeolite FAU-seeded FAC (A), the resulting FAU/mullite spheres at low (B) and high (C) magnifications, and the bilayered shells from the cross-section view (D).

2.3. The Hollow FAU/Mullite Composite Microspheres

Figure 4 shows the SEM images of the zeolite FAU-seeded FAC and the final products after a hydrothermal treatment at 100 °C for 2 days. A homogeneous coating of zeolite FAU seeds can be formed on the FAC after one cycle adsorption of FAU seeds with the aid of the polyelectrolytes (Fig. 4A). After the hydrothermal treatment, almost all of the products retained the initial spherical morphology of FAC (Fig. 4B), and the predeposited zeolite FAU seeds on the surface of FAC grew into octahedral crystals of 1–2 µm, which covered the shells completely (Fig. 4C). The XRD patterns of the products (Fig. 2B) confirm the formation of zeolite FAU crystals and the disappearance of the amorphous glassy phase and part of quartz; meanwhile no obvious changes in the mullite peaks are observed compared with the original FAC pattern (Fig. 2A). The SEM images indicate that the final hollow spheres possess bilayered shells, an outer layer of compact zeolite and an inner layer of rod-like mullite crystals (Fig. 4D). Because no additional silica and alumina constituents were added into the synthesis system, the zeolite growth must depend on the consumption of the "nutrients" in the FAC. It appears that the amorphous glassy phase and part of α-quartz in the FAC shells (Fig. 1B) were leached out in the hot alkaline solution and fed into the growth of the outer continuous FAU zeolite shells under the induction of the FAU seeds, leaving the rod-like mullite crystals as the inner porous shells (Fig. 4D). These facts also indicate that mullite is an inert component which can barely be converted under the experimental conditions, while α-quartz can be slowly dissolved and converted to zeolite.[11] The infrared (IR) spectra of the samples were measured as illustrated in Figure 5. The vibration band in the range of 900–1200 cm^{-1} is attributed to characteristic T–O (T = Si or Al) asymmetric stretching vibration of zeolite framework, and this confirms the existence of zeolite in the products (Fig. 5B). The Si/Al ratio of FAU was calculated to be ca. 1.2 from the shifting of the band at 757 cm^{-1}, according to the method in literature.[13a]

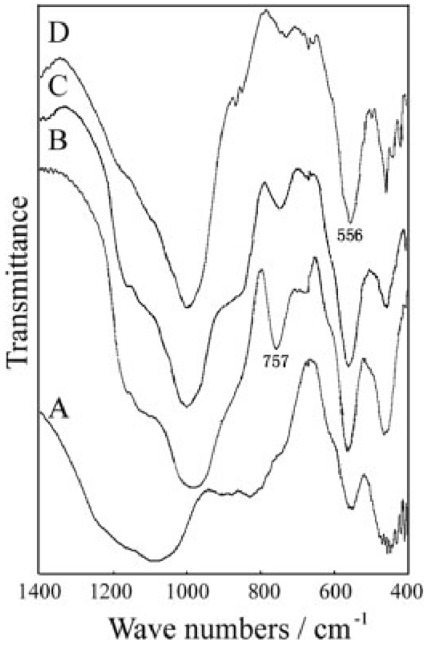


Fig. 5. IR spectra of the FAC (A), the resulting FAU/mullite spheres (B), and LTA/mullite spheres with (C) and without (D) hybrid FAU crystals.

2.4. The Hollow LTA/Mullite Composite Microspheres

We have also attempted to prepare hollow spheres with zeolite LTA/mullite shells using zeolite LTA seed under similar experimental conditions. A uniform LTA seeds layer could be deposited on the surface of FAC after electrostatic adsorption with the aid of polyelectrolytes (Fig. 6A). Although the obtained products still retain the hollow core–shell structure after hydrothermal treatment (Fig. 6B), the zeolite crystals on the sphere surface exist in two different morphologies, cubic and octahedral (Fig. 6C). The intergrown cubic crystals occupy a large proportion and form the dense zeolite shells, while the octahedral crystals disperse discretely on the outer surface. The XRD pattern (Fig. 2C) suggests that these two kinds of crystals can be attributed to zeolite LTA and FAU, respectively. According to their diffraction peak intensities (Fig. 2C), the former zeolite in a cubic phase is the main composition. The formation of a small amount of zeolite FAU could be due to the fact that the SiO_2/Al_2O_3 ratio in the FAC favors the formation of FAU under such synthesis conditions.

To prepare hollow zeolite/mullite spheres with pure zeolite LTA phase, additional alumina species were added to the synthesis solution to adjust the SiO_2/Al_2O_3 ratio of the synthesis system. As anticipated, the hollow microspheres with intergrown cubic zeolite LTA shells were obtained (Figs. 6D,E) after hydrothermally treating the zeolite LTA seeded FAC in the aqueous solution with a molar composition of 9:1:250 NaOH/$NaAlO_2$/H_2O at 100 °C for 2 days. From its XRD pattern (Fig. 2D), only the diffraction peaks of zeolite LTA phase

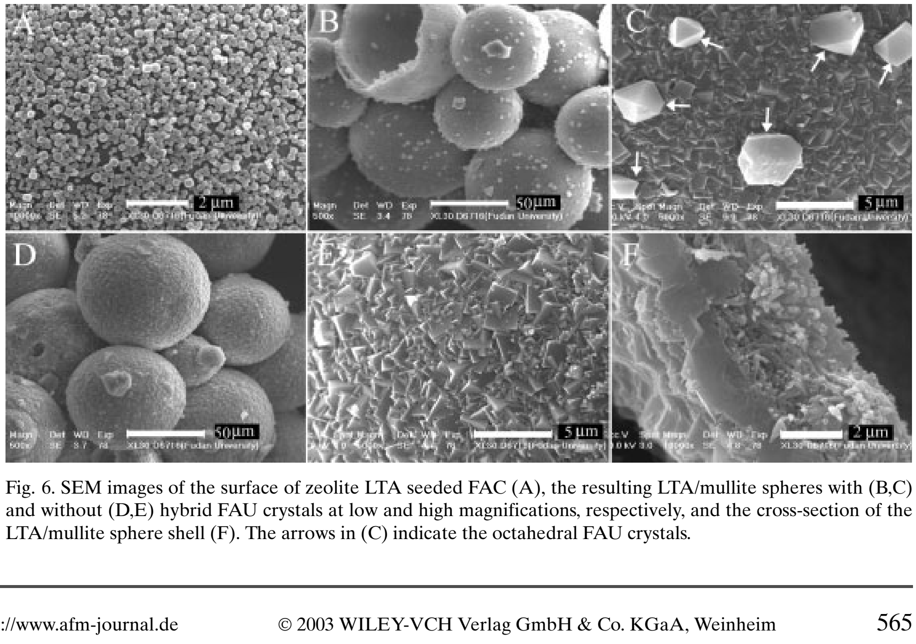


Fig. 6. SEM images of the surface of zeolite LTA seeded FAC (A), the resulting LTA/mullite spheres with (B,C) and without (D,E) hybrid FAU crystals at low and high magnifications, respectively, and the cross-section of the LTA/mullite sphere shell (F). The arrows in (C) indicate the octahedral FAU crystals.

are observed besides the inherited mullite phase. Similar to the FAU/mullite spheres, the products also possess bilayered shells except for the dense zeolite LTA films as the outer shells (Fig. 6F). The existence of zeolite LTA phase in the product is also confirmed by IR spectroscopy (Figs. 5C,D), and a Si/Al ratio of 1.0 is derived by comparing its vibration at 556 cm^{-1} with the data reported in the literature.[13b]

2.5. Effects of the Treatment Conditions

The zeolite seeds coated on the FAC play a crucial induction role in the formation of the hollow zeolite/mullite composite spheres. When the unseeded FAC was treated in the same conditions, zeolite GIS rather than FAU/mullite or LTA/mullite was produced. If the FAC was seeded with small amount of zeolite seeds, only a discontinuous zeolite layer formed on the outer surface. The continuity difference of the zeolite layers with the change of seeding amount can be clearly observed from the difference of the pictures of Figure 6E and Figure 7B. The latter clearly shows that a discontinuous LTA zeolite layer with many voids (Fig. 7B) was formed when the FAC with a small amount of LTA seeds (Fig. 7A) was used as the starting materials.

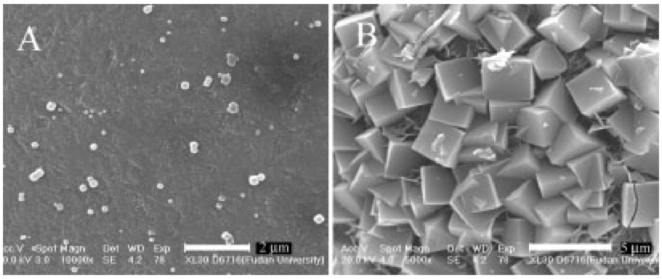


Fig. 7. SEM images of the FAC surface coated with a small amount of zeolite LTA seeds (A) and the resulting LTA/mullite spheres at high magnification (B).

Additionally, the aging before the crystallization and the shaking during the crystallization are other two important factors affecting the quality of the final products. It is found that some FAC particles were not completely converted into the hollow zeolite/mullite spheres without aging and shaking. This could be attributed to the fact that the zeolite-seeded FAC tends to float on the surface of the synthesis solution due to its hollow structure and low density, leading to the inhomogeneous soaking and reaction of the FAC.

2.6. Mechanical Stability and Adsorption Properties

It is predicted that the obtained hollow zeolite/mullite spheres should have improved mechanical strength because of their novel zeolite/mullite bilayered shell structure. Sonication treatment was applied to test the stability of the products. The products were sonicated for 10 min using a bath-type sonicator (frequency = 50 kHz, 120 W) and then assayed by SEM. It was found from multiple SEM images that over 90 % of the spheres remained intact after sonication (see Figs. 8A,C), and the dense intergrown zeolite membranes on the outer shells were also well-maintained, as shown in the SEM images at high magnification (Figs. 8B,D).

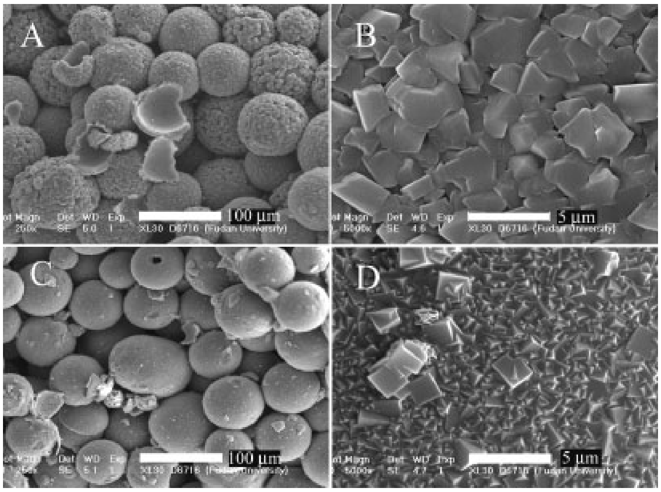


Fig. 8. SEM images of the FAU/mullite spheres (A,B) and LTA/mullite spheres (C,D) after sonication treatment for 10 min.

The texture properties of the FAU/mullite products were characterized by N_2 adsorption–desorption isotherms (Fig. 9). A strong adsorption as type-I isotherm at low relative pressure and a hysteresis loop at higher relative pressure of $P/P_0 > 0.45$ were observed for the final product. The strong adsorption at low relative pressure is due to micropores, and the hysteresis indicates the existence of mesopores in the products. The Brunauer–Emmet–Teller (BET) specific surface area and the micropore volume (by *t*-plot method of Lipens and de Boer[14]) of the FAU/mullite composite products are 330 m^2 g^{-1} and 0.14 cm^3 g^{-1}, respectively, while the surface area of the original FAC is below 1.0 m^2 g^{-1} and that of the FAU seeded FAC prior to the hydrothermal treatment is 3.5 m^2 g^{-1}, implying that zeolites in the FAU/mullite composite products mainly come from the conversion of the FAC. The corresponding Barrett–Joyner–

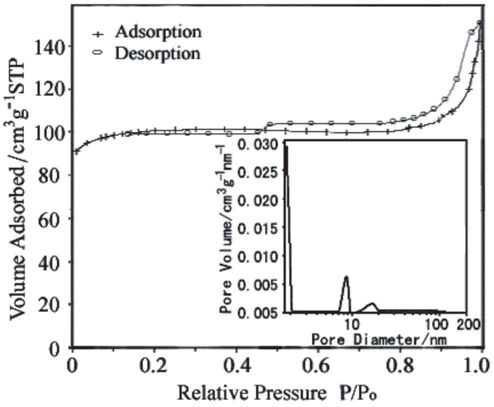


Fig. 9. Nitrogen adsorption–desorption isotherms of the hollow FAU/mullite composite spheres. The inset shows the pore size distribution calculated from the adsorption branch of the isotherm using the BJH method.

Halenda (BJH) pore-size distribution (Fig. 9, inset) shows that mesopores and macropores larger than 7 nm exist in the final FAU/mullite products. These can be attributed to the voids of the intergrown zeolites and the cavities formed by the leaching of silica and alumina constituents from the shell of FAC.

The adsorption of water and benzene on the samples were conducted using the dynamic adsorption method.[15] The samples were calcined at 500 °C for 1 h before measuring. The adsorption amounts of benzene and water of the resulting FAU/mullite products are 13.8 wt.-% and 16.7 wt.-% (which is 60 % of the water adsorption of commercial zeolite NaX[16]), respectively, whereas those of the FAU seeded FAC are below 0.5 wt.-%. These results provide further evidence for the generation of a great amount of zeolite components during the conversion of the FAC. The fact that the adsorption amount is lower than that of the commercial zeolites is reasonable because some inert mullite exists in the samples. Due to the small micropores of zeolite LTA, only the water adsorption amount was measured for the LTA/mullite products. The calcined LTA/mullite products have water adsorption of 15.6 wt.-%, which equals to 68 % of that of the commercial zeolite NaA (23 wt.-%).[16]

3. Conclusions

In summary, we have successfully prepared hollow spheres of FAU/mullite and LTA/mullite composites from an industrial waste of FAC by a simple technique of seed-induced hydrothermal conversion. The FAC acts as both the templates and the reactants for the formation of hollow spheres. The zeolite seeds play an important induction role for the conversion of FAC. This study may provide not only a promising approach for the disposal of the solid wastes from coal-fired power stations, but also a simple and practical route to prepare hollow zeolitic spheres for catalysis, adsorbents, controlled release capsules, and storage.

4. Experimental

Materials: The FAC used in this work was provided by the Research Centre for the Application of Fly Ash in Henan Province of China and has a listed chemical composition of SiO_2, 56.21; Al_2O_3, 29.45; Fe_2O_3, 3.60; CaO, 1.66; MgO, 0.85; K_2O, 0.78; Na_2O, 0.47; TiO_2, 0.52, and ignition loss of 3.51 wt.-%. The sample was isolated using a 200-mesh sieve, treated by floatation in boiling water to remove the fragments, and dried at 100 °C.

Tetraethylorthosilicate (TEOS, 98 %), and tetramethylammonium hydroxide (TMAOH, 25 %) were commercially purchased and used without further purification. Poly(diallyldimethylammonium chloride) (PDDA), $M_w < 200\,000$ and poly(styrene sulfonate), sodium salt (PSS), M_w 70 000 were from Aldrich. Aluminum foils (99.5 %, from Shanghai reagent company) was used as received.

Preparation of Zeolite Seeds: The seeds of zeolite FAU and LTA were synthesized following a procedure described in the literature [17]. The starting reactants were metal aluminum foils, TEOS, NaOH, TMAOH, and distilled water. The metal aluminum foils and TEOS were dissolved in the nearly equal amount solutions containing NaOH and TMAOH to form aluminate and silicate solution, respectively. The resulting aluminate solution was then added into the silicate solution with intensive shaking to form a clear homogeneous solution. The molar compositions of the overall solutions for zeolite seeds are both $2.46{:}x{:}1{:}3.4{:}370{:}13.6$ $(TMA)_2O/Na_2O/Al_2O_3/SiO_2/H_2O/EtOH$, except that the value of x is 0.032 for zeolite FAU and 0.43 for zeolite LTA. After aging overnight with stirring, the precursors were refluxed in polypropylene bottles at 100 °C without stirring for 2 days in the case of zeolite LTA seeds preparation, and 7 days for FAU. The crystals obtained were purified by centrifugation and redispersed in distilled water to a zeolite content of about 1.0 wt.-%. The pH of the colloidal zeolite seeds was adjusted to about 10 by addition of a dilute ammonia solution to make the seeds negatively charged.

Preparation of Hollow Zeolite/Mullite Spheres: The FAC was firstly positively charged through adsorption three layers of polyelectrolytes by alternatively soaked in 0.2 wt.-% of cationic PDDA and 0.1 wt.-% of anionic PSS solutions with a mass ratio of polyelectrolyte solution/FAC about 20 in the order of PDDA,PSS, then PDDA [7–12]. The negatively charged zeolite seeds were then deposited onto the FAC through soaking the positively charged FAC in the zeolite seeds suspension at a solution/FAC mass ratio of 5 [7]. The seeded FAC was finally rinsed in a dilute ammonia solution to remove excess zeolite crystals and dried at 100 °C.

For preparation of hollow FAU/mullite microspheres, 0.4 g of zeolite FAU seeded FAC and 5.0 mL of 2 M NaOH solution were mixed in a polytetrafluoroethylene-lined stainless steel autoclave. The autoclaves were enclosed and heated at 100 °C for 0.5–2 days. By simply substituting seeds LTA for FAU, the composite LTA/mullite spheres with a little hybrid zeolite FAU were obtained under the similar synthesis conditions. To obtain the zeolite/mullite spheres with only zeolite LTA, 0.4 g of zeolite LTA seeded FAC and 5.0 mL of solution with the molar composition of 9:1:250 $NaOH/NaAlO_2/H_2O$ were used as reactants while the crystallization temperature and time remained unchanged. All the products were washed with distilled water and dried at 100 °C.

Characterization: XRD data were obtained on a Rigaku D/max-IIA diffractometer with Cu Kα radiation at 40 kV and 20 mA. SEM images were taken with a Philips XL30 electron microscope. The N_2 adsorption–desorption experiment was performed on a Micromeritics ASAP 2000 instrument at liquid nitrogen temperature. The adsorption amounts of water or benzene of the samples were determined using the dynamic adsorption method according to reference [14]. The IR spectra were recorded on a NicoletMagna-550 FT-IR spectrometer. The standard KBr method was used to prepare samples for IR measurements.

Received: December 15, 2002
Final version: March 10, 2003

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