Core−Shell Polystyrene/Zeolite A Microbeads

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The ability to fabricate materials into spherical geometries, either hollow or solid, provides components with important performance capabilities for a wide variety of products.[1] Spherical microparticles that consist of either an organic or an inorganic core and a shell of different chemical composition have attracted much interest recently.[2] Usually in the core−shell structures the material of interest is exposed on the surface; that is, it forms the shell. The core has a templating function and controls the form and the size of the composite. The core−shell structures often exhibit properties that are substantially different from those of the materials building the composite, which makes them a welcome supplement to the single-phase spherical particles.

Applications for zeolite materials cover a broad range of areas such as catalysis, separation, ion exchange, sensing, and lately advanced optoelectronics. Most of the existing techniques for producing zeolites in the form of pellets, tablets, or other forms suitable for practical utilization use binders. Recently, considerable efforts have been targeted on the preparation of organized zeolite structures without using binding substances.[3] The dilution of the zeolite with the binding additive often decreases the efficiency of the product. Moreover, for some applications bulk zeolitic materials are not efficient and a thin zeolite layer on the surface of an appropriate support is sufficient. Homogeneous zeolite coatings have been reported for different types of inorganic supports.[4] These syntheses, generally performed via a classical hydrothermal treatment, have shown that the formation of the zeolite coating is very sensitive to the chemical nature, the morphology, and the position of the substrate in the reactor as well as the reaction conditions. Very often, however, even substrates compatible with the zeolite precursor system require a pretreatment of the support or application of seeds to grow a continuous film.[5,6] For the preparation of continuous zeolite coatings on small three-dimensional inorganic objects, a more sophisticated approach like seeding by pulsed laser deposition was applied.[7] The incompatibility between the organic substrates and the aluminosilicate precursor species is a serious obstacle for the preparation of zeolite layers on such supports and to the best of our knowledge zeolite films built of well-intergrown crystals have not been synthesized on organic polymer supports. The layer-by-layer (LbL) self-assembly technique,[8] which allows fabrication of multilayer assemblies onto charged substrates by spontaneous sequential adsorption of oppositely charged species, was used for the preparation of continuous zeolite layers on polystyrene supports.[9−11] However, the zeolite coatings prepared by this technique have a limited mechanical strength since the connection between the building particles is based on weak electrostatic interactions.

The present study reports the preparation of zeolite A shells built of well-intergrown crystals on an organic polymer surface. Core−shell polystyrene/zeolite A microbeads were prepared by application of a combination of LbL and hydrothermal synthesis techniques. Negatively charged polystyrene beads from gas permeation chromatography columns (Waters) with a diameter of 8−15 μm were used. Prior to the hydrothermal synthesis, the surface charge of the beads under investigation was reversed by treatment with a cationic polymer agent (Redifloc 4150, Akzo Nobel) to facilitate electrostatic adsorption of the negatively charged zeolite seeds. The modified support was seeded with zeolite A crystals with a size of about 40 nm, prepared according to ref 12. Polystyrene microbeads with a continuous layer of adsorbed zeolite A nanocrystals on the surface are shown in Figure 1a, b. Three or more adsorption steps were used for the adsorption of zeolite A crystals on the surface of the polystyrene beads. The SEM inspection after the first adsorption showed that some of the beads were not completely covered by zeolite A. This is probably due to the relatively high alumina content in the framework of zeolite A. The high concentration of aluminum on the surface of the crystals requires countercations that can deteriorate the electrostatic interactions between the cationic polymer and the zeolite crystals. In addition to the improved homogeneity of the zeolite shells, the increase of the number of adsorption steps has a positive effect on the ultimate thickness of the zeolite film.

The second step of the preparation consists of hydrothermal treatment of the polystyrene/zeolite microbeads in a zeolite A precursor mixture, resulting in the formation of a continuous zeolite film. The pretreated

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[1] Wilcox, D. L.; Berg, M.; Bernat, T.; Kellerman, D.; Cochran, J. K. Hollow and Solid Spheres and Microspheres: Science and Technology Associated with Their Fabrication and Application. *Mater. Res. Soc. Symp. Proc.* **1995**, *372*.

[2] Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019.

[3] Tosheva, L.; Mihailova, B.; Valtchev, V.; Sterte, S. *Microporous Mesoporous Mater.* **2000**, *39*, 91.

[4] Jansen, J. C.; Nugroho, W.; van Bekkum, H. In *Proceedings from the 9th IZC*; von Balmoos, R., Higgins, J., Treacy, M., Eds.; Butterworth-Heinemann: Stoneham, MA, 1993; p 247.

[5] Valtchev, V.; Mintova, S.; Vassilev, I. *J. Chem. Soc., Chem. Commun.* **1994**, 979.

[6] Tsapatsis, M.; Okubo, T.; Lovallo, M.; Davis, M. E. *Mater. Res. Soc. Symp. Proc.* **1995**, *371*, 21.

[7] Balkus, K. J., Jr.; Scott, A. S. *Microporous Mesoporous Mater.* **2000**, *34*, 31.

[8] Decher, G. *Science* **1997**, *277*, 1232.

[9] Rhodes, K. H.; Davis, S. A.; Caruso, F.; Zhang, B.; Mann, S. *Chem. Mater.* **2000**, *12*, 2832.

[10] Wang, X. D.; Yang, W. L.; Tang, Y.; Wang, Y. J.; Fu, S. K.; Gao, Z. *Chem. Commun.* **2000**, 2161.

[11] Valtchev, V.; Mintova, S. *Microporous Mesoporous Mater.* **2001**, *43*, 41.

[12] Mintova, S.; Olson, N. H.; Valtchev, V.; Bein, T. *Science* **1999**, *283*, 985.

10.1021/cm010927d CCC: $22.00

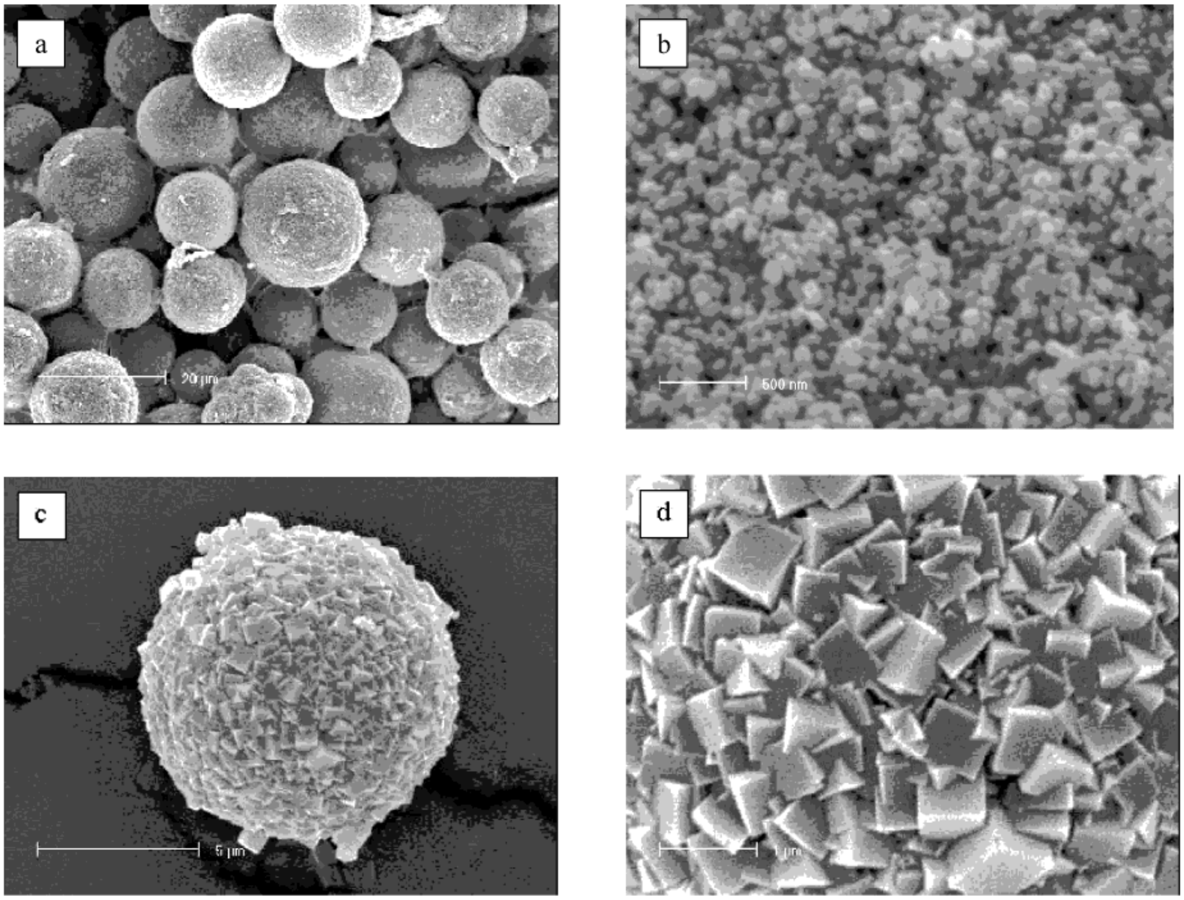

Figure 1. General (a) and close (b) views of pretreated microbeads comprising five layers of zeolite A nanocrystals deposited by LbL adsorption. A core–shell polystyrene/zeolite A microbead (c) and close view of the intergrown zeolite A shell formed after the hydrothermal treatment (d).

polystyrene beads were hydrothermaly treated with a synthesis gel of the following composition:

$$6.5Na_2O:1.0Al_2O_3:2.0SiO_2:110H_2O$$

The synthesis of zeolite A was performed at 60 °C for 2 h. After the synthesis, the polystyrene/zeolite composite was separated from the mother liquor, washed, and dried. Figure 1c represents a polystyrene/zeolite A microbead prepared according to the above-described procedure. A detail of the surface zeolite layer is shown in Figure 1d, where well-intergrown zeolite A crystals can be seen. The hydrothermal treatment was performed with a precursor gel free of an organic structure-directing agent. Thus, subsequent calcination to open the zeolite microporosity is not necessary.

X-ray diffraction (XRD) analysis detected the formation of zeolite after the hydrothermal treatment. Together with the zeolite peaks a halo emanating from the polystyrene can be seen in the XRD pattern (Figure 2a). The diffraction pattern of pure well-crystallized zeolite A was recorded after the calcination of the composite (Figure 2b).

The amount of zeolite A deposited on the polystyrene beads was found by thermogravimetric (TG) analysis in air (Figure 3). In the TG/DTG analysis of the as-synthesized polystyrene/zeolite A composite two distinct weight losses are observed. The first broad peak is in the temperature range 25–180 °C. This weight loss is obviously due to water desorption from the composite.

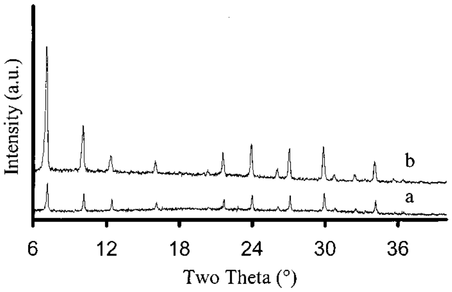

Figure 2. XRD patterns of polystyrene/zeolite A microspheres (a) and zeolite A shells obtained after combustion of the polystyrene support at 500 °C for 4 h (b).

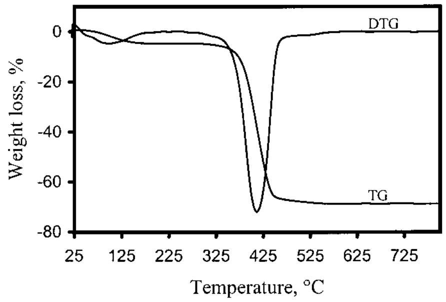

Figure 3. TG/DTG curves for a polystyrene/zeolite A composite.

The second weight loss, which can be attributed to the decomposition of the polystyrene macrotemplate and the charge-reversing agent adsorbed during the preliminary treatment of the beads, is in the range 300−550 °C with a sharp maximum at 410 °C. The weight losses in these temperature intervals are 4.7 and 64.1 wt %, respectively. Thus, the content of water-free zeolite A in the composite was found to be about 31 wt %.

Although no special tests were performed, the difference in the strength of the zeolite shells prepared by the LbL self-assembly technique[10] and according to the above-described procedure is easy distinguishable. No peeling or disintegration of the zeolite shells was observed after the hydrothermal treatment. Thus, different laboratory manipulations can be performed with the hydrothermally treated microbeads. There is no strong chemical bonding between the polystyrene support and the zeolite film formed on the surface; therefore, the stability of zeolite A shells is a result of the intimate intergrowth of zeolite crystals building the film.

In conclusion, zeolite A shells of intergrown crystals on organic polymer cores were prepared by a two-stage procedure. The incompatibility between the organic support and the inorganic shell was circumscribed by using negatively charged substrates, reversal of their surface charge, and adsorption of zeolite nanoseeds. The pretreated microbeads were subsequently subjected to a continuous growth in a zeolite precursor mixture. This opens up routes for the preparation of zeolite coatings on organic supports with arbitrary shape and size.

The core−shell polystyrene/zeolite A microbeads can be easily transformed into hollow zeolite microspheres by a simple calcination procedure. Both the core−shell and hollow zeolite microspheres constitute unique materials that could find numerous applications. For example, at low temperature the core−shell microbeads can be used in all traditional applications of the zeolite materials. The applications of hollow zeolite spheres can vary from drug delivery and storage materials to catalytic and separation processes to applications in cosmetics.

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