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Confined synthesis of silicalite-1 hollow spheres with a lamellar shell

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A novel synthesis strategy involving the integrated use of soft/hard templates was proposed for the confined synthesis of silicalite-1 hollow spheres with a lamellar shell. Replicated from macroporous carbon templates and directed by multi-quaternary ammonium surfactants, these silicalite-1 spheres exhibit a unique hollow nanoshell morphology, high crystallinity, and a novel hierarchical porosity consisting of hollow macropores, interlamellar mesopores and ordered micropores in zeolites.

Keywords: Hierarchical zeolite; Silicalite-1; Confined synthesis; Hollow sphere; Lamellar structure

Hierarchical zeolites have attracted rapidly growing attention due to their highly acidic property and superior shape selectivity inherited from micropores and shorter diffusion path length due to the presence of mesopores and macropores [1]. Many approaches have been developed for the fabrication of zeolites with hierarchical porous systems [2–5]; these approaches can be broadly categorized as either non-template or template. In comparison to the non-template approach, synthesis of hierarchical zeolites with removable templates provides a versatile means for the introduction of hierarchical porous structure into zeolites with controllable morphologies and topologies [6,7]. Moreover, an enormous variety of such templates exist, e.g. aerogel [8,9], silane [10], cationic surfactants [11], carbon nanotubes [12] and porous carbon [13].

Recently, Choi et al. [14] developed a bifunctional structure-directing agent of multi-quaternary ammonium surfactants for the generation of ultrathin MFI-type zeolites, and proposed the fabrication of hierarchical zeolites with soft templates [15,16]. In our recent work, three-dimensionally ordered mesoporous-imprinted (3DOm-i) zeolites with tunable morphology and Si/Al ratio were synthesized through confined growth by using three-dimensionally ordered mesoporous carbon as a hard template [17–19]. Such a facile and controllable approach has been expanded to the synthesis of 3DOm-i zeolites with a series of topologies, such as MFI, BEA, LTA, FAU and LTL [20]. Systematic characterization of cyclohexane transportation further confirmed the benefit of such three-dimensionally ordered mesopore systems for microporous diffusion [21].

In this paper, we report a facile synthesis and fabrication strategy of hierarchical zeolites through integrated use of soft/hard templates. Specifically, the hierarchical zeolites described here present a novel morphology of hollow spheres with a lamellar shell. The hollow spherical structures derived from the carbon templates provide macropores with a similar size, while the lamellar shells of highly crystallinic silicalite-1 are directed by multi-quaternary ammonium surfactants and exhibit not only interlamellar mesopores but also ordered micropores and also connect hollow macropores with the exterior. The synthesis approach reported here provides unique opportunities to design new types of hierarchical porous materials and quantitatively investigate the effects of a hierarchical pore system on the transitive and catalytic performance of zeolites.

The hard templates of macroporous carbon with a pore size of ~500 nm were replicated from colloidal crystal of close-packed monodisperse SiO_2 spheres prepared through a modified Stöber process [22,23]. The carbonization procedure used in this paper was similar to the work of Fan et al. [17].

The soft templates of bifunctional structure-directing agents (SDAs) $[(C_{22}H_{45}–N^{+}(CH_3)_2–C_6H_{12}–N^{+}(CH_3)_2–C_6H_{13})]Br_2$ for lamellar silicalite-1 were synthesized following

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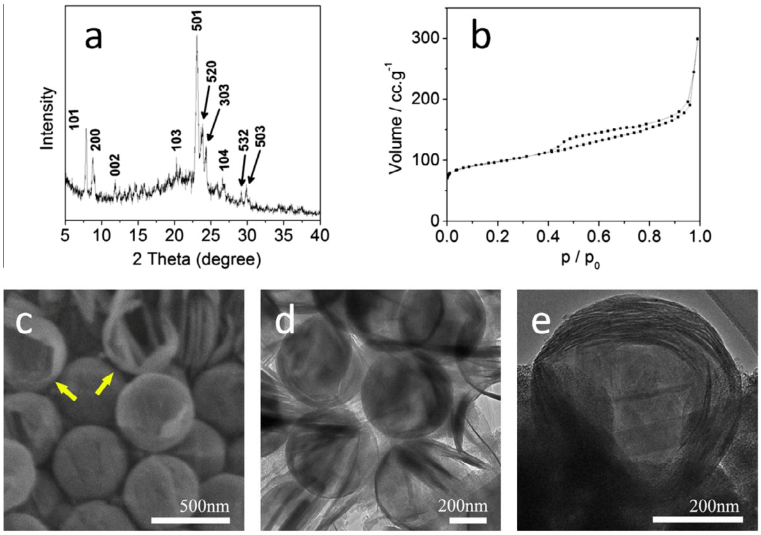

Fig. 1. Silicalite-1 hollow spheres with a lamellar shell: (a) XRD pattern; (b) nitrogen adsorption–desorption isotherm; (c) SEM image; (d) low-magnification TEM image; and (e) high-magnification TEM image.

the procedures reported by Ryoo et al. [14] Ion exchange was performed to transform the SDA from Br^- form to OH^- form by using IONAC NA-38 $[OH^-]$ form ion-exchange resin (J.T. Baker). The obtained SDA solution was successively concentrated using rotatory evaporation and vacuum drying, resulting in a gel state (45 wt.% in water, estimated by a pH detector).

The steam-assisted crystallization (SAC) method described by Jacobsen et al. [24] was used for the confined synthesis of silicalite-1 hollow spheres with a lamellar shell. The carbon templates were impregnated with an initial precursor solution with the composition of 50 SiO_2: 9 SDA: 390 H_2O: 200 ethanol under the assistance of ethanol volatilization. The impregnated carbon replicas were then placed in an open glass vial, and finally placed in a stainless steel autoclave where water was present outside the glass vial, and heated at 423 K for 3–9 days. The obtained products were filtered and washed with deionized water, and dried at 343 K, followed by calcination in air at 823 K for 6 h to remove the SDA and carbon replicas.

The obtained products were characterized by X-ray powder diffraction (XRD), N_2 adsorption–desorption, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD patterns were collected on a Bruker-AXS D5005 X-ray diffractometer with Cu K_α radiation. The specific surface area and pore size distribution were measured by N_2 adsorption–desorption on a Quantachrome Autosorb-1 system at 77 K. SEM imaging was performed on a JEOL JSM-6500F microscope with an acceleration voltage of 1–5 kV without coating the samples. TEM images were obtained using a FEI Tecnai G2 F30 microscope operating at 300 kV and a FEI Tecnai T12 microscope operating at 120 kV and collected using a CCD camera.

Figure 1 presents the 500 nm silicalite-1 hollow spheres with a lamellar shell synthesized within the confined space of macroporous carbon by 6 days of SAC treatment at 150 °C. XRD (Fig. 1a) of the sample showed a characteristic pattern with peaks at $2\theta = 7–9°$, 22–25° corresponding to the typical MFI-type framework. Nitrogen adsorption–desorption was used to characterize the porosity of the obtained silicalite-1 hollow spheres. The isotherm revealed that a major uptake occurred at low relative pressures of <0.01 and a broad hysteresis loop at a relative pressure of 0.45–0.95, indicating the coexistence of micropores and mesopores. The BJH pore size distribution calculated from the adsorption isotherm (as shown in Fig. S1) revealed a broad peak ranging from several to dozens of nanometer, underscoring the presence of irregular mesoporosity from the interlamellar structures that remained after the removal of SDA. A set of comparative textural parameters between the obtained hollow silicalite-1 spheres and conventional ZSM-5 (purchased from Zeolyst Int.), which has the same MFI framework, is shown in Table 1. It can be seen that the obtained silicalite-1 hollow spheres had slightly smaller surface area ($157\ m^2\ g^{-1}$) and volume ($0.07\ m^3\ g^{-1}$) of micropores than conventional ZSM-5 ($205\ m^2\ g^{-1}$ and $0.11\ m^3\ g^{-1}$, respectively), indicating the existence of low surface area materials (amorphous), as also observed in the XRD pattern (broad peak at 17–25°). Nevertheless, the obtained silicalite-1 hollow spheres showed much larger external surface area and total pore volume than conventional ZSM-5, and it is supposed that these were contributed by the mesoporosity of the lamellar shells.

An SEM image of the obtained silicalite-1 hollow spheres is shown in Fig. 1c. Isolated spherical particles with a similar size of ~500 nm were observed, which corresponds to the macropore size of the carbon template (as shown in Fig. S2). The surface of the spherical particle was smooth, indicating the crystallization and growth of zeolites had taken place in the confined space and along the macropore walls of the carbon.

Table 1. Nitrogen adsorption–desorption isotherm textural analysis.

Materials	S_{mic} [$m^2\ g^{-1}$]	S_{ext} [$m^2\ g^{-1}$]	S_{BET} [$m^2\ g^{-1}$]	V_{mic} [$m^3\ g^{-1}$]	V_T [$m^3\ g^{-1}$]
Silicalite-1 hollow spheres with a lamellar shell	157	239	396	0.07	0.42
Conventional ZSM-5	205	123	328	0.11	0.23