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Hierarchical zeolite structures with designed shape by gel-casting of colloidal nanocrystal suspensions†

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Hierarchical zeolite structures with designed shapes were fabricated by a ceramic processing method—gel-casting of colloidal nanocrytal suspensions.

There is considerable interest in porous zeolite and zeolite-type materials with designed shapes.[1–4] Hierarchical porous structures with different levels of porosity can significantly aid the diffusion of guest species through the inorganic network of pores and channels to improve their performance. Nanometer-sized zeolite particles have been used as building blocks to construct hierarchical porous structures such as films, spheres and fibers *via* templated self-assembly.[2–4] Very recently, a bulk-material dissolution technique has been developed for the preparation of various shaped MFI structures including tubes and fibers.[5] The shaped zeolite structures can faithfully reproduce the shapes of the starting bulk material. However, the conversion process is extremely slow (*e.g.* 1–2 months) and the final structure is usually a composite of the starting material and the zeolite with non-uniform microstructure.

Ceramic forming techniques such as pressing, extrusion, tape casting, dip (slip)-casting, and gel-casting are powerful for shaping inorganic materials due to their simplicity and versatility. In particular, gel-casting is a method for fabrication of complex-shaped ceramic bodies from ceramic particle suspensions by means of *in situ* polymerization, where a macromolecular network is created to hold the ceramic particles together before sintering.[6,7] Zeolite nanocrystals such as silicalite, ZSM-5, TS-1, Beta, A and FAU have been synthesized from precursor solutions,[9–13] and can be readily handled in colloidal systems. In this communication, we report the first demonstration of fabrication of shaped hierarchical zeolite structures with well-controlled microstructures using a ceramic forming technique—gel-casting. As an example, the gel-casting of colloidal silicalite nanocrystal suspensions was used to prepare hierarchical tubular silicalite structures (HTSSs).

Silicalite nanocrystals were hydrothermally synthesized using a clear synthesis solution.[4,14]‡ The silicalite nanocrystals with diameter *ca.* 50 nm and with narrow particle size distribution were re-dispersed in water with a solid loading of 30–40 wt%. Water soluble organic monomer acrylamide, crosslinker *N,N*′-methylenebisacrylamide, and initiator ammonium persulfate $(NH_4)_2S_2O_8$ were added to the colloidal silicalite suspension.‡ The gel-casting of the resulting colloidal suspension was carried out in a home-made mold. The fabrication process of HTSSs is illustrated in Fig. 1. Since the suspension with monomer, crosslinker, and initiator has low viscosity and good fluidity, it can be readily transferred into the mold. The suspension-filled mold was hand-shaken for a few minutes to release air bubbles inside the suspension. Once the temperature was increased to 50 °C, the monomers in the suspension were quickly polymerized and crosslinked free-radically into an elastic hydrogel.[6,7] A highly crosslinked polyacrylamide hydrogel obtained is expected to be compatible to silicalite nanocrystals whose surface silanol groups interact favorably with $-NH_2$ groups. The solidified suspension (a gelcast) was mechanically strong and was easily removed from the mold. The tubular gelcast was dried under ambient laboratory conditions for 2–3 days, and was then further dried at 100 °C overnight. A linear shrinkage of 4.0–4.5% of the gelcast was observed during the drying process. After drying, the tubular gelcast was sintered under air at a heating rate of 1 °C min^{-1} up to 500 °C, and kept at that temperature for 8 h to burn off the organic polymer and the structure-directing agent (tetrapropylammonium hydroxide),[14] and to sinter together the silicalite nanocrystals through condensation crosslinking of surface silanol groups of nanocrystals.[4,14] The sintering leads to a linear shrinkage of $< 0.5\%$. In order to examine the thermal stability of the HTSSs, another sample was sintered at 1000 °C for 2 h with the same heating rate.

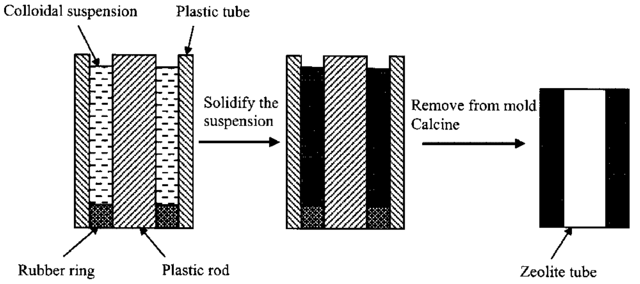

Fig. 1 Schematic representation of the gel-casting forming process for a hierarchical tubular silicalite structure (HTSS). The colloidal suspension consists of zeolite silicalite nanocrystals and organic monomer (AM), crosslinker (MBAM), and initiator $(NH_4)_2S_2O_8$.

Fig. 2 shows a photograph, SEM micrographs and XRD pattern of an HTSS. SEM images show uniformly distributed

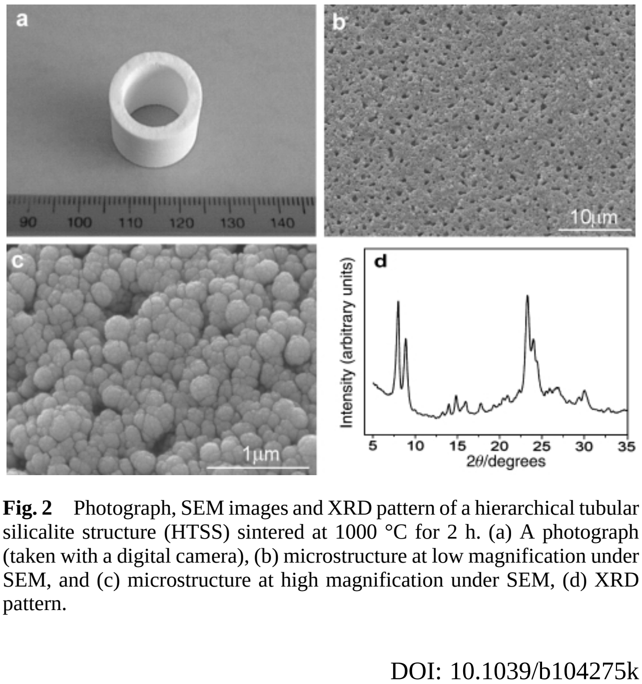

Fig. 2 Photograph, SEM images and XRD pattern of a hierarchical tubular silicalite structure (HTSS) sintered at 1000 °C for 2 h. (a) A photograph (taken with a digital camera), (b) microstructure at low magnification under SEM, and (c) microstructure at high magnification under SEM, (d) XRD pattern.

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† Electronic supplementary information (ESI) available: nickel doping procedure. S-Fig. 1: pore size distributions. S-Fig. 2: nickel and silicon mapping images. see http://www.rsc.org/suppdata/cc/b1/b104275k/

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submicrometer-sized pores in the HTSS at low magnification, and a hierarchical morphology of densely packed silicalite nanocrystals at high magnification. The submicrometer-sized pores were formed by packing of nanocrystal agglomerates during gel-casting. Small nanocrystals tend to agglomerate to minimize surface energy when the nanocrystal loading is high (30–40 wt%). This is confirmed by SEM observation that shows that there are already micrometer-sized pores in the dried gel-cast. The XRD pattern of the sample sintered at 1000 °C for 2 h matches the pure silicalite structure. This suggests that the HTSS sintered at 1000 °C retains the silicalite structure.

N_2 adsorption–desorption measurements were used to determine the mesopore and micropore structures of HTSSs. N_2 adsorption–desorption isotherms of samples sintered under different conditions are shown in Fig. 3. The adsorption steps at low relative pressures signify the filling of silicalite micropores, and the hysteresis loops at higher relative pressures are the consequence of N_2 filling the textural mesopores, and clearly the sample has a bimodal pore size distribution (see S-Fig. 1, ESI).† The pore size distribution is narrow in both the micropore and mesopore range. The sintering temperature has an influence on the pore structure of the HTSS. When the sintering temperature is increased from 500 to 1000 °C, the micropore volume and mesopore volume slightly decrease from 0.16 to 0.12 $cm^3\ g^{-1}$, and from 0.35 to 0.33 $cm^3\ g^{-1}$, respectively. The corresponding Brunaer–Emmett–Teller (BET) surface area drops from 516 to 423 $m^2\ g^{-1}$. The maximum pore size in the micropore range of HTSSs is 5.5 Å, which is characteristic of silicalite. The average mesopore size varies from 16.7 to 13.1 nm, which are similar to that of hierarchical materials self-assembled by pure silicalite nanocrystals.[4]

The HTSSs have three-level porosities including macropores (submicrometer), mesopores (16–13 nm) and micropores (0.55 nm). Based on a measured HTSS density of 0.85 g cm^{-3} and assuming a dense silica density of 2.3 g cm^{-3}, the total pore volume is estimated to be 0.74 $cm^3\ g^{-1}$. From the micropore and mesopore volumes obtained from nitrogen adorption–desorption isotherms, the macropore volume is calculated to be 0.29 and 0.23 $cm^3\ g^{-1}$ for HTSSs sintered at 500 and 1000 °C, respectively.

Gel-casting processing also offers an effective way to add functionalities to HTSSs by doping with other components.[7] Unlike commonly used impregnation methods, the dopant can be introduced easily into the colloidal suspension system so that the dopant concentration can be precisely controlled. The uniformity of dopant distribution also will be significantly improved. Here the doping of nickel is used as an example to illustrate that dopant can be easily incorporated. Ni-based catalysts are useful for various catalytic processes such as alkylation, methanation, hydrogenation of aromatic compounds and methane reforming. Elemental mapping images (S-Fig. 2)† clearly show Ni is uniformly distributed in the silicalite matrix.

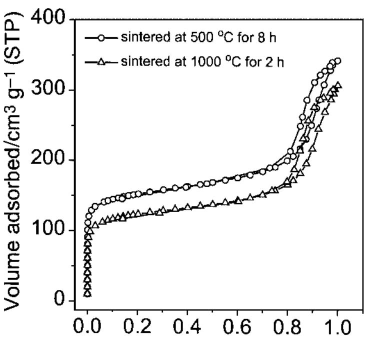

Fig. 3 Nitrogen adsorption–desorption isotherms of hierarchical tubular silicalite structures (HTSSs) sintered under different conditions.

We have demonstrated that hierarchical zeolite structures with designed shape can be readily obtained from colloidal zeolite nanocrystal suspensions simply by applying ceramic gel-casting processing. The hierarchical (macro-, meso- and micro-porous) zeolite structure can be readily functionalized by incorporation of a functional component, or by chemical grafting of organic functional groups. Zoned zeolite structures[15] with designed shapes can also be generated by adding a secondary growth step[8] to our gel-casting process. Our process should also allow the fabrication of shaped structures with mixed zeolites by using suspensions of two or more types of zeolite nanocrystals. It is believed that the strategy described here is promising for the preparation of various functional zeolite-based structures with designed shapes, in catalysis, separation membranes, and microelectronics, and work in these areas are in progress.

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Notes and references

‡ Aqueous colloidal suspensions of silicalite nanocrystals were synthesized as follows.[4,14] A clear synthesis solution was prepared by dropwise adding tetrapropylammonium hydroxide solution (TPAOH, SACHEM) into tetraethyl orthosilicate (TEOS, Aldrich) with strong agitation followed by 1–3 days of aging at 30 °C under stirring. The final solution has a molar composition 1 TPAOH : 2.8 SiO_2 : 11.2 EtOH : 40 H_2O. Crystallization was carried out at 80 °C for 3 days with a constant stirring at 250 rpm. A stable aqueous suspension of silicalite nanocrystals was obtained by repeated cycles of centrifugation at 15 000 rpm, decanting, and ultrasonic redispersion in pure water until the pH of the suspension was < 8. The solid loading of the suspension is 30–40 wt% for gel-casting. Water soluble organic monomer acrylamide, $CH_2{=}CHCONH_2$ (AM, Aldrich), crosslinker *N,N′*-methylenebisacrylamide, $CH_2{=}CHCONH_2)_2CH_2$ (MBAM, Aldrich), and initiator ammonium persulfate, $(NH_4)_2S_2O_8$ Aldrich) were added under stirring into the silicalite colloidal suspension. Final composition (weight ratio) : 5–10 AM : (0.05–0.1) MBAM : (0.01–0.025) $(NH_4)_2S_2O_8$: 90–95 silicalite solid. After the monomer, the crosslinker, and the initiator were dissolved, the whole suspension was ultrasonicated for 5–10 min to ensure good homogeneity.

Nitrogen adsorption–desorption measurements were carried out at −196 °C on a Micromeritics ASAP 2010 instrument. HTSS samples were crushed and ground for X-ray diffraction analysis (Siemens D-500 diffractometer using Cu-Kα radiation). SEM imaging and elemental mapping were conducted with a scanning electron microscope (SEM, Philips XL30-FEG at 20 kV) equipped with an EDAX detector.

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