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Hexagonal, hollow, aluminium-containing ZSM-5 tubes prepared from mesoporous silica templates†

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Hexagonal hollow ZSM-5 tubes were synthesized using mesoporous silica with a worm-like morphology as the template. A new method for aluminium incorporation during the hydrothermal synthesis step was developed.

Hollow zeolite spheres have been previously prepared using several different strategies based on the use of polymer templates.[1–3] Nanocrystalline zeolite seeds are typically deposited by electrostatic assembly onto a polymer template (latex or polystyrene spheres with diameters ranging from 1 to several hundred microns).[1–3] This step may be followed by additional similar steps for a layer by layer (LbL) preparation or a synthesis step that consists of seeded zeolite crystal growth. The final step is calcination in air to remove the polymer template leaving behind a hollow zeolite spherical shell.

Recently, hollow zeolite spheres were prepared using mesoporous silica (MS) as the template.[4–7] In this case, the template, MS, is consumed as the silica source during the hydrothermal zeolite synthesis step. This method utilizing MS as a template has several advantages relative to the other methods that use polymer templates: (1) the MS template is consumed as a reagent during the hydrothermal synthesis step and therefore does not need to be removed during a calcination step, (2) the shape of the MS template can be varied from spherical to worm-like by adjusting the relative concentrations of reagents used during the synthesis[7] and (3) the MS can easily be loaded with guest species prior to the hydrothermal synthesis step, in effect creating a ship in the bottle synthesis.

Previous results in the literature have focused almost exclusively on silicalite-1 hollow zeolite spheres prepared from silicalite-1 nanocrystals and MS.[4–6] However, the range of materials accessible by this synthetic methodology would be widely expanded if aluminium could be incorporated into the hollow zeolite structure during the hydrothermal synthesis step. Zeolites are widely used in applications, such as catalysis, separations and ion-exchange. In many of these applications, it is essential to use aluminosilicate zeolite materials rather than purely siliceous materials. The use of ZSM-5 seeds to prepare hollow zeolite spheres has been reported in the literature, but additional aluminium was not available for the hydrothermal synthesis step. The Si/Al ratio of the resulting hollow zeolite spheres was not reported, but it should be higher than the starting ZSM-5 seeds (Si/Al = 55) since no additional aluminium was available.[5] Additional attempts to prepare hollow spheres from zeolites Beta (Si/Al = 12.5) or Y (Si/Al = 1.5) were reported to be unsuccessful due to the lack of an aluminium source.[5]

In the study reported here, hexagonal hollow ZSM-5 tubes were prepared using MS with a worm-like morphology as the template. In addition, a new method was used to incorporate aluminium into the zeolite during the hydrothermal synthesis step. A schematic diagram of the key steps in the preparation of the hollow ZSM-5 tubes is shown in Fig. 1. Briefly, the hexagonal MS is coated with nanocrystalline silicalite seeds. The coated MS is impregnated with a solution of $Al(NO_3)_3$ and NaCl followed by a hydrothermal synthesis step to form the hollow ZSM-5 tubes. The resulting material was characterized by X-ray diffraction (XRD, Siemens D5000), scanning electron microscopy (SEM, Hitachi S-4000), ^{27}Al magic angle spinning NMR (MAS NMR) and inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer,) for elemental analysis.

First, MS was synthesized using cetyltrimethylammonium bromide (CTAB), sodium silicate (Na_2SiO_3), H_2O, and ethyl acetate as described previously.[7] By adjusting the relative amounts of CTAB, Na_2SiO_3, H_2O and ethyl acetate, the pore size and morphology of the MS can be varied.[7] SEM images of the synthesized MS with the worm-like morphology are shown at two different magnifications in Fig. 2a and b. Fig. 2b illustrates that the MS with wormlike morphology has a hexagonal shape.

Silicalite-1 nanocrystals with a size of approximately 20 nm were synthesized from a clear solution with the following composition: 9TPAOH : 0.16NaOH : 25Si : 495H_2O : 100EtOH where TPAOH is tetrapropylammonium hydroxide.[8] The clear solution was refluxed at 60 °C for 240 h, washed and centrifuged. X-ray diffraction verified the formation of the silicalite-1 phase. The MS tubes were modified with cationic poly(diallyldimethyl)-ammonium chloride (PDDA) and were then coated with the negatively charged nanocrystalline silicalite-1. An SEM image of the coated MS is shown in Fig. 2c.

Next, incorporation of an aluminium source was accomplished by impregnating the seeded MS with $Al(NO_3)_3$ and NaCl aqueous solutions. The latter provides Na^+ to balance framework charges resulting from aluminium incorporation. The seeded impregnated MS was dried in an oven at 90 °C for 1 h. (When the $Al(NO_3)_3$ was impregnated directly into the MS prior to the seeding step, the $Al(NO_3)_3$ did not remain in the MS tubes during the seeding step.)

The seeded, impregnated MS was suspended above a mixture of 30 mL triethylamine (Et_3N), 1 mL ethylenediamine (EDA) and 5 mL water in a teflon-lined autoclave and was heated to 160 °C for 48 h. The resulting hollow zeolite tubes are shown in the SEM images in Fig. 2d–f. A typical hollow tube (Fig. 2d) is approximately 20 μm long and 2 μm in diameter; however, there is a wide distribution of sizes for the tubes. An end-on image for an open tube is shown in Fig. 2e. It is apparent from this image that the synthesized zeolite tubes retain the hexagonal shape of the MS template and that the zeolite shell is approximately 300 nm thick. A magnification of the surface of the tube is shown in Fig. 2f.

The progress of the synthesis of the hollow zeolite tubes from the MS tubes was monitored by SEM and XRD. Samples were extracted for SEM and XRD analysis at various times during the hydrothermal synthesis. SEM images were obtained at 0, 1, 4, 16 and 48 h. and are shown in Fig. 3a–d and Fig. 2e, respectively. The gradual disappearance of the MS core can be observed in the SEM images. Initially, the tube is solid and contains MS in the center and nanosilicalite seeds on the outside(Fig. 3a). During the hydro-

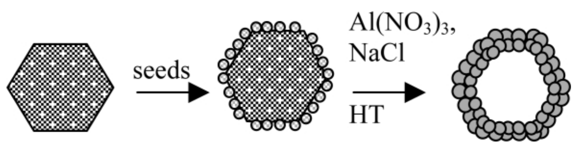

Fig. 1 Schematic diagram of the formation of hollow ZSM-5 hexagonal tubes. HT refers to hydrothermal treatment.

† Electronic supplementary information (ESI) available: XRD patterns for MS and MS coated with silicalite-1 during the hydrothermal synthesis procedure. See http://www.rsc.org/suppdata/cc/b4/b406753c/

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thermal synthesis, the MS is used as a reagent starting from the center of the tube and creating a hollow core that gradually grows larger until the MS is completely gone (Fig. 2e).

Incorporation of aluminium into the hollow ZSM-5 tubes was verified by ^{27}Al MAS NMR spectroscopy (300 MHz wide bore, Tecmag system) and by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer). The ^{27}Al MAS NMR of the seeded MS impregnated with $Al(NO_3)_3$ is shown in Fig. 4a. A peak is observed at ~ -2 ppm and is assigned to aluminium in octahedral coordination. After the hydrothermal synthesis step, the aluminium is incorporated into the ZSM-5 framework. The ^{27}Al NMR of the hollow zeolite tubes after the hydrothermal synthesis (Fig. 4b) shows an aluminium peak at ~ 50 ppm indicating that the aluminium is in tetrahedral coordination, consistent with what is found for aluminium incorporated into the zeolite framework.[9,10] The NMR spectrum after calcination of the hollow tubes in air at 500 °C is shown in Fig. 4c. The peak is still at 50 ppm, but has been broadened slightly. ICP analysis indicated that Si/Al = 28 which is close to the expected stoichiometry based on the composition of the synthesis gel.

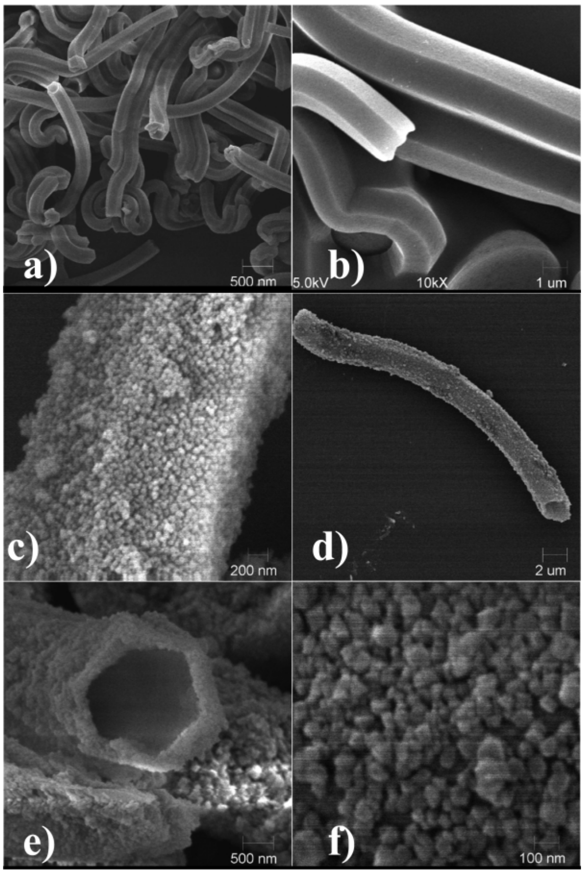

Fig. 2 SEM images of (a) and (b) MS silica with worm-like morphology at two different magnifications, (c) MS coated with nanocrystalline silicalite-1, (d), (e) and (f) hexagonal hollow zeolite tubes after hydrothermal synthesis shown at three different magnifications. The hexagonal shape of the tubes is indicated in (e).

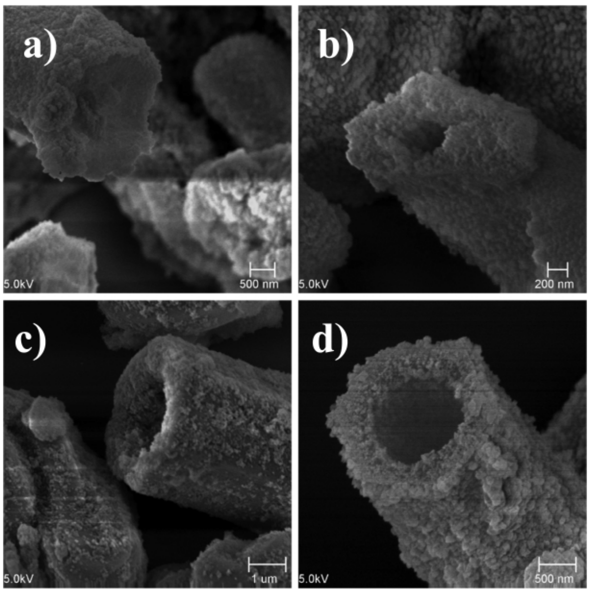

Fig. 3 SEM images of MS seeded with nanocrystalline silicalite after hydrothermal treatment for (a) 0 h, (b) 1 h, (c) 4 h and (d) 16 h.

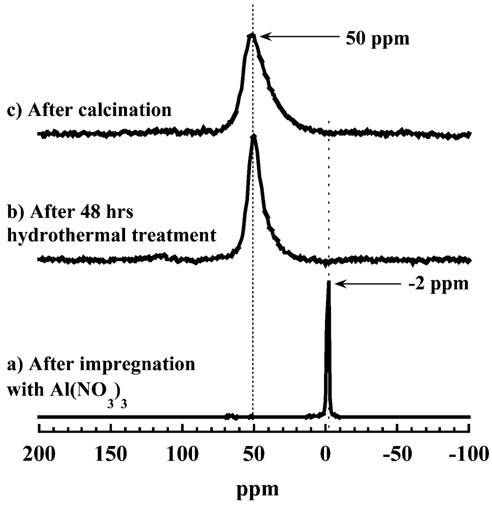

Fig. 4 ^{27}Al MAS NMR spectra of (a) MS coated with nanocrystalline silicalite-1 seeds and impregnated with $Al(NO_3)_3$ as the aluminium source, (b) the hexagonal, hollow ZSM-5 tubes after the hydrothermal synthesis and (c) after calcination of the hollow tubes.

Future research will be directed toward incorporating active species into the interior of the hollow ZSM-5 tubes. This can be accomplished by loading a metal species into the MS prior to the synthesis of the hollow zeolite shell. Previously, Fe_2O_3 and Ag nanoparticles have been incorporated into hollow silicalite spheres.[5] Metal ions could also be exchanged into the zeolite hollow tubes to produce catalytically active materials. The main advantage of the aluminium-containing hollow ZSM-5 tubes is the potential for applications in areas such as catalysis and ion exchange.

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Notes and references

1 V. Valtchev and S. Mintova, *Microporous Mesoporous Mater.*, 2001, **43**, 41.
2 V. Valtchev, *Chem. Mater.*, 2002, **14**, 4371.
3 X. D. Wang, W. L. Yang, Y. Tang, Y. J. Wang, S. K. Fu and Z. Gao, *Chem. Commun.*, 2000, 2161.
4 A. Dong, Y. Wang, Y. Tang, N. Ren, Y. Zhang and Z. Gao, *Chem. Mater.*, 2002, **14**, 3217.
5 A. Dong, Y. Wang, D. Wang, W. Yang, Y. Zhang, N. Ren, Z. Gao and Y. Tang, *Microporous Mesoporous Mater.*, 2003, **64**, 69.
6 A. Dong, N. Ren, W. Yang, Y. Wang, Y. Zhang, D. Wang, J. Hu, Z. Gao and Y. Tang, *Adv. Funct. Mater.*, 2003, **13**, 943.
7 G. Schulz-Ekloff, J. Rathousky and A. Zukal, *Int. J. Inorg. Mater.*, 1999, **1**, 97.
8 W. Song, R. E. Justice, C. A. Jones, V. H. Grassian and S. C. Larsen, *Langmuir*, 2004, **20**, 4696.
9 C. J. H. Jacobsen, C. Madsen, T. V. W. Janssens, H. J. Jakobsen and J. Skibsted, *Microporous Mesoporous Mater.*, 2000, **39**, 393.
10 W. Zhang, X. Bao and X. Wang, *Catal. Lett.*, 1999, **60**, 89.