Single-template synthesis of zeolite ZSM-5 composites with tunable mesoporosity†

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Hierarchically structured composites (TUD-C) with ZSM-5 crystals embedded in a well-connected mesoporous matrix were synthesized by using only one organic templating/scaffolding molecule (TPAOH).

Zeolites are microporous, crystalline aluminosilicates used extensively in heterogeneous catalysis, separation and adsorption.[1,2] The narrow micropores (typically sub-nanometre) are responsible for the excellent shape selectivity that results in preferential formation of desired products. However, these narrow pores also impose diffusion limitations that hinder transport of molecules to, and away from active sites. Retention of heavy products formed within the micropores can lead to deactivation by pore blockage.[3] A well-connected system of wide pores may reduce transport limitations.[4] In industrial applications of zeolites, meso- and macropores are often introduced in an empirical, poorly controlled manner.[1] Performance could be improved by rationally designing the broad pore channel network, but this requires the ability to easily control the broad channel sizes.[5]

Promising results in the synthesis of hierarchically structured zeolites were obtained by introducing ordered mesopores into zeolitic structures.[6–8] One of the challenges encountered in the synthesis of these materials is that the force exerted during zeolite crystal formation is much greater than that during meso-structure formation. Hard templates[9,10] and specially designed supramolecular templates[11] have therefore been introduced to preserve the meso-structure during crystallization. Jacobsen *et al.*[9] proposed an elegant route using carbon black to create intra-crystalline mesopores. Other templates, such as CMKs[10] and TPHAC,[11] accurately control the mesoporosity, but tend to be expensive, and the synthesis routes are rather involved.

Here we present a single-template route to synthesize a material with zeolite nano-crystals dispersed in a mesoporous matrix of tunable porosity. Because of the double templating/scaffolding function of tetrapropylammonium hydroxide (TPAOH) to direct both micro- and mesopore formation, no additional supramolecular template is needed. Hence, this method requires a minimum number of raw materials (four, including water), and it can be performed in one pot. The simplicity, flexibility, and tunability of this method are the most attractive features when compared to existing routes.

A series of samples (denoted as TUD-C) with Si/Al = 30 were prepared by a two-step procedure. In the first step, a homogeneous synthesis solution was prepared from TPAOH (1 M in water), tetraethyl orthosilicate (TEOS), and aluminium isopropoxide [$Al(^iPro)_3$]. The molar composition was 60 SiO_2 : Al_2O_3 : 14 TPAOH : 1800 H_2O. This solution was aged at room temperature under controlled evaporation for 10 days to obtain a transparent solid gel. In the second step, 0.3 g of the solid gel and 0.4 ml water were transferred into a specially designed autoclave, in which the solid phase was separated from the aqueous phase. During the crystallization, the solid was only in contact with steam, which is an essential difference compared to traditional zeolite synthesis. A series of samples was obtained upon heating at 130 °C for different durations. The products were dried at 80 °C, and subsequently calcined in air at 550 °C for 6 h to remove the organic materials. All resulting samples were monolithic.

TPAOH acts as a scaffold under the mild conditions of the first step, forming the meso-structure, which has been investigated previously.[12,13] This was confirmed by the N_2 adsorption isotherm and the corresponding pore size distribution (Fig. 1, 0 h sample). The near-linear uptake of the isotherm over the range $P/P_0 = 0.10$ to 0.50 indicates the presence of small mesopores in the solid gel. The high BET surface area (S_{BET}, 734 $m^2\ g^{-1}$, Table 1) of the solid

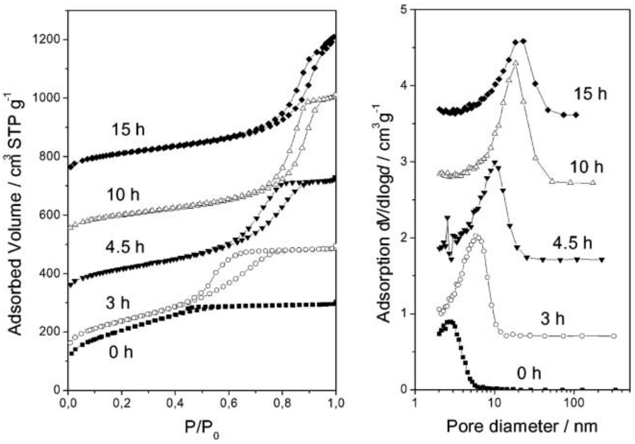

Fig. 1 Analysis of the pores by N_2 adsorption and desorption. (Left) The isotherms of TUD-C samples with different crystallization times. Samples 3 h, 4.5 h, 10 h, and 15 h were vertically offset by 50, 250, 450, 650 cm^3 STP g^{-1}, respectively. (Right) Pore size distributions corresponding to the adsorption isotherms. Samples 3 h, 4.5 h, 10 h, and 15 h were vertically offset by 0.7, 1.7, 2.7, 3.5 $cm^3\ g^{-1}$, respectively.

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† Electronic supplementary information (ESI) available: TEM images of sample 10 h, N_2 adsorption of sample 15 h upon hydrothermal treatment and experimental details. See DOI: 10.1039/b708822a

Table 1 Texture of the samples corresponding to Fig. 1

Sample time/h	S_{BET}/ $\mathrm{m^2\ g^{-1}}$	S_{external}/ $\mathrm{m^2\ g^{-1}}$	V_{micro}/ $\mathrm{cm^3\ g^{-1}}$	V_{meso}/ $\mathrm{cm^3\ g^{-1}}$	D_{meso}/ nm
0	734	—[a]	—[a]	0.42	3
3	658	571	0.040	0.64	6
4.5	602	392	0.085	0.64	10
10	535	266	0.114	0.75	18
15	580	269	0.130	0.71	20

[a] *t*-plot is not applicable because of the continuous distribution of pore sizes around 3 nm.

gel is comparable to that of SBA-15 mesoporous materials. ZSM-5 crystals are formed during the second step, where TPAOH acts as the well-known zeolite template at high temperatures.[7] This is a solid-phase crystallization process assisted by steam.[14] X-ray diffraction shows the characteristic peaks of ZSM-5 (Fig. 2). The intensity of the peaks increases from 0 h to 4.5 h, which shows the gradual conversion of the amorphous structure of the starting gel into a crystalline phase. The enhanced zeolite crystallinity is also indicated by an increase in micropore volume (V_{micro}) to 0.13 $\mathrm{cm^3\ g^{-1}}$ after 15 h (Table 1).

The isotherms from 3 h to 15 h (Fig. 1) show that the zeolite crystal growth does not lead to a deterioration of the mesoporous nature of the amorphous matrix. On the contrary, by controlling the crystallization time, the mesopore size (D_{meso}) can be systematically varied. As Fig. 1 shows, the average pore size increases from 3 nm in the starting dry gel to about 20 nm in the 15 h sample. A more detailed analysis (Table 1) reveals that the external surface area (S_{external}) decreases with crystallization time, but remains very high even after 15 h. The possibility of maintaining a high external surface area is attractive for catalytic applications involving large molecules, since in many cases the surface inside the micropores is not easily accessed.

High-resolution transmission electron microscopy (TEM) provides insight into the local structure of the amorphous and crystalline phases. Figs. 3a and 3b show that the 3 h sample is a composite with small zeolite crystals embedded in a mesoporous matrix. The crystals have a fairly uniform size of 120–150 nm in diameter. Not surprisingly, the 10 h sample contains larger crystals than the 3 h sample, *i.e.*, 150 to 250 nm in size (see Figs. S1 and S2, ESI†). These results are in quantitative agreement with calculations based on the application of Scherrer's equation to the XRD peaks. A high-resolution image (Fig. 3c) of the interface between the zeolite crystal and the amorphous mesoporous matrix clearly confirms the combined micro- and mesostructures. Some HRTEM images with 2D lattice fringes were also obtained, from which the ZSM-5 zeolite structure can be confirmed (see Fig. S3, ESI†). The pattern on the right hand side of the TEM micrograph in Fig. 3c resembles that of a foam-like structure, which is typical of disordered mesoporous materials as reported previously.[15] Preparation of the carbon replica of the starting solid gel (Fig. 3d) revealed a similar disordered morphology, further supporting the interconnected nature of the mesoporous system, as the carbon replica showed 3D mesoporous structures that are stable upon the removal of aluminosilicate. This would ensure efficient diffusion pathways to access the active sites of the zeolite crystals. Because of the disordered nature of the mesopores, it is not straightforward to derive pore sizes from the TEM images, and directly compare these to adsorption results. The structure of TUD-C shows similarities to that of zeolite/mesoporous matrix materials recently reported by Waller *et al.*[16] and Gagea *et al.*[17] However, TUD-C has a tunable mesopore size in a wider range, and requires fewer starting materials.

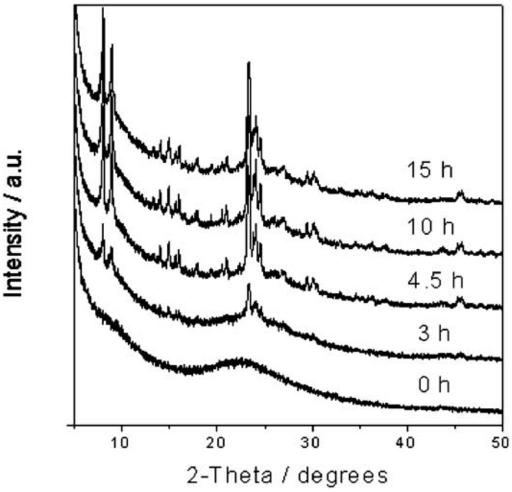

Fig. 2 XRD patterns of calcined TUD-C samples with different crystallization times.

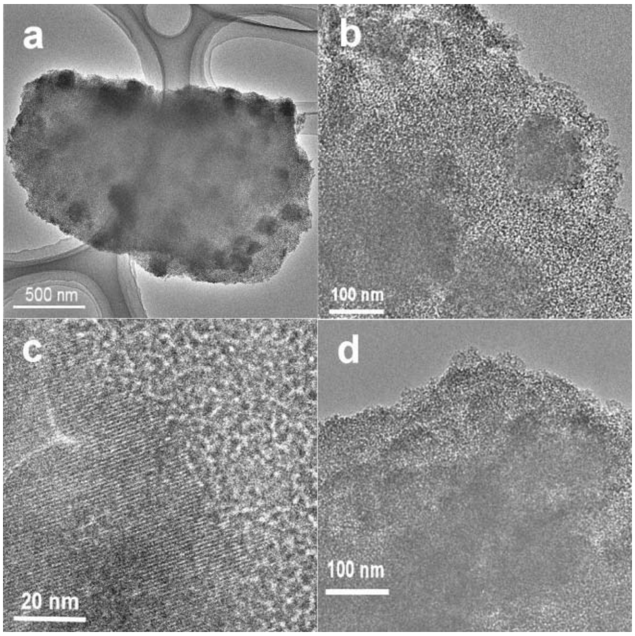

Fig. 3 TEM images of selected samples. a) Sample 3 h, an entire particle; b) sample 3 h, with an area near the surface showing a mesoporous coating embedding the zeolite crystals; c) sample 3 h, a bordering area between micro- and meso-phases; d) well-connected carbon replica of sample 0 h, showing a disordered mesoporous structure.

The structural configuration and the location of Al atoms were investigated by ^{27}Al MAS NMR spectroscopy (Fig. 4). The absence of a peak at 0 ppm and the single, pronounced peak at 56.7 ppm (corresponding to tetrahedral aluminium species) in the TUD-C 15 h sample demonstrate that Al is entirely incorporated in the framework. The presence of Brønsted acid sites[16] was confirmed by FTIR measurements (Fig. 5). The absorption band at 3610 $\mathrm{cm^{-1}}$ is characteristic of Brønsted acid sites,[18] where the

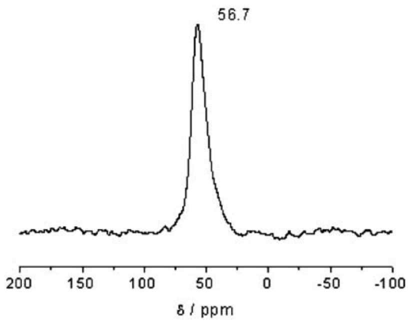

Fig. 4 ^{27}Al MAS NMR spectrum of sample TUD-C 15 h.

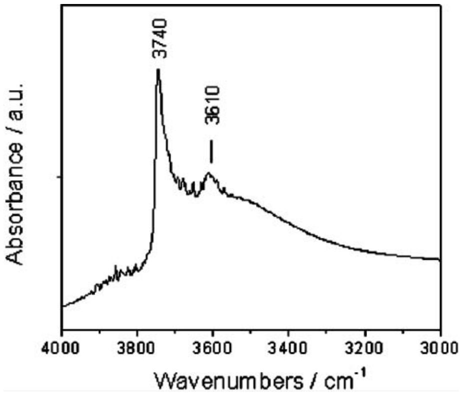

Fig. 5 FTIR spectrum of sample TUD-C 15 h. The adsorption band at 3610 cm^{-1} is characteristic of Brønsted acid sites.

Si–O(H)–Al bond is present. This is a promising feature for applications of TUD-C as a solid acid catalyst, *e.g.*, for catalytic cracking or alkylation.

Though TUD-C does not have a fully crystalline structure, severe thermal treatment in the presence of steam (800 °C with 20% steam for 2 h) only had a minor effect on the pore structure, which demonstrates a remarkable hydrothermal stability of our material (see Fig. S4, ESI†). It has been reported that solid-phase conversion leads to a better thermal stability compared to zeolites prepared by traditional methods.[14]

In summary, we have developed a new and facile synthesis route to obtain a ZSM-5 zeolite/meso-matrix composite with a minimum number of starting materials. Assemblies of TPAOH serve as a scaffold for the meso-structure. The zeolite crystals are embedded in a well-connected mesoporous framework. The size of the mesopores can be tuned over a wide range by varying the crystallization time. Using this solid-phase crystallization technique, our method could be extended to other types of zeolites. To improve the present synthesis route, we are investigating the influence of the Si/Al ratio and the temperatures applied in both steps. Our synthesis method distinguishes itself from existing ones in its remarkable simplicity, without need for separate mesopore templates. The demonstrated controllability of the mesopore size should allow optimization of zeolite performance.[5]

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