

Synthesis of mesoporous ZSM-5 zeolite crystals by conventional hydrothermal treatment†

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Well-defined ZSM-5 crystals with tablet habit, uniform size, controllable silica/alumina ratio, and high mesoporosity were prepared using conventional hydrothermal treatment under stirring. The key to obtaining high mesoporosity of the crystals was to stir a synthesis mixture containing a relatively high concentration of alumina.

Zeolites are industrially important microporous materials used for adsorption, ion exchange and catalysis.¹ ZSM-5 zeolite with MFI framework is used as catalyst for several reactions carried out in the petrochemical industry.² To decrease the micropore diffusion path and increase the catalytic activity, the crystal size can be decreased,³ or alternatively mesoporosity can be introduced in the crystals.⁴ Improved catalytic performance of the resulting mesoporous zeolites over conventional zeolites has been demonstrated in various hydrocarbon conversion processes⁵ and environmental processes.⁶ Therefore, much effort has been devoted to the development of zeolites with mesopores in addition to the micropores. Recently, several strategies by using different templates, such as caramel templating,⁷ dual template synthesis,⁸ colloid-imprinted carbons,⁹ well-ordered mesoporous carbon¹⁰ as well as desilication,^{11,12} detitanation,¹³ recrystallization¹⁴ and seed silanization¹⁵ have been pursued to introduce mesopores. However, the high cost of some of the various types of templates or troublesome preparation is still inevitable in most cases.

Relatively simple synthesis routes for preparation of mesoporous zeolites have also been reported. These routes include adding a nucleation promoter into the zeolite precursor solution,¹⁶ evaporating the precursor mixture¹⁷ or varying the crystallization temperature.¹⁸ However, the preparation of mesoporous zeolite crystals by conventional hydrothermal treatment has not been reported so far. Here, we report for the first time the preparation of well-defined mesoporous ZSM-5 crystals using conventional hydrothermal treatment under stirring.

The detailed synthesis process for mesoporous ZSM-5 and its characterization are given in ESI†. Here in Fig. 1a shows, SEM image of a silicalite-1 crystal prepared by present method but without adding the aluminum source to the synthesis mixture. The morphology appear to be twin free single crystals with tablet habit and a uniform length of about 2.8 μm in the *c*-direction, *i.e.* from one curved face of the tablet to another. The length of the crystals in the *a*-direction, *i.e.* in the direction perpendicular to the two straight faces, is about 2.0 μm . Consequently, the aspect ratio of the crystals (length in *c*-direction/length in *a*-direction) is 1.4. The surfaces of the crystals are quite smooth; however the image recorded at higher magnification clearly reveals growth steps on the surface, Fig. 1d, which appear similar to annual rings in wood. The growth steps clearly illustrates that these silicalite-1 crystals

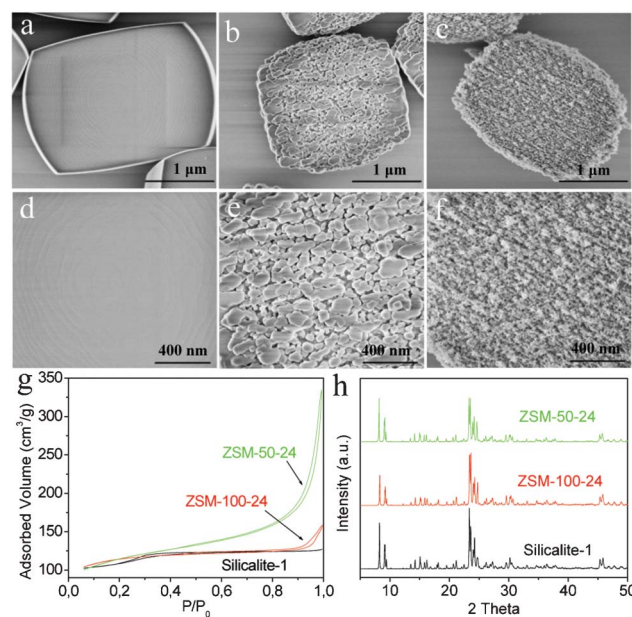


Fig. 1 SEM images of silicalite-1 (a), ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) (b), ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) (c) formed after 24 h of growth, (d)–(f) are enlarged views of (a)–(c), corresponding nitrogen adsorption-desorption isotherms (g) and XRD patterns (h).

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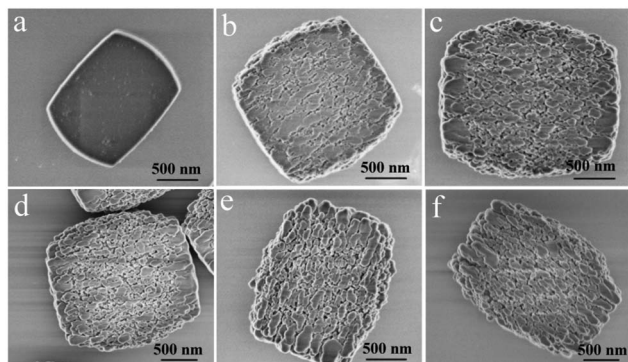


Fig. 2 SEM images of the ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) after growth 1.5 h (a), 3 h (b), 6 h (c), 24 h (d), 48 h (e), 72 h (f).

are built from very small building blocks. This phenomenon in agreement with the growth steps on ZSM-5 crystals observed by AFM.¹⁹ Fig. 2b shows a SEM image of a crystal grown for 24 h in a synthesis mixture with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 100 (sample ZSM-100-24). Again, the crystals are quite uniform with tablet habit. The length in c -direction is about 2.0 μm . The length in the a -direction is about 2.1 μm . So the aspect ratio has changed to 0.95, *i.e.* the length in the c -direction is less than in the a -direction, which is unusual for MFI zeolite. The surface is comprised of islands that are oriented with their longest direction parallel with the a -axis and relatively large mesopores are present between the islands, Fig. 1b and e. It appears that these islands are formed as a result of nucleation on an underlying crystal and that these nuclei predominantly grow in the a -direction, which results in a reduction of the aspect ratio. Fig. 1c shows a SEM image of the crystals grown for 24 h in a synthesis mixture with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 50 (sample ZSM-50-24). In this case, the aspect ratio is as low as 0.75 and the length of the crystals in the c -direction is about 1.8 μm . In this case, the islands are much smaller; resulting in much higher density of mesopores between the islands, as shown in Fig. 1f.

The nitrogen adsorption isotherm of the silicalite-1 sample is typical for a mostly microporous material with some mesopores, Fig. 1g. A small hysteresis loop is observed above $p/p_0 = 0.25$, indicates the presence of some mesopores in the microporous zeolite crystals. The mesopore volume for this sample is however as small as $0.06 \text{ cm}^3 \text{ g}^{-1}$, which is typical for large MFI crystals.²⁰ The N_2 adsorption isotherms of both ZSM-5 samples grown for 24 h with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ and 50 (ZSM-100-24 and ZSM-50-24, respectively) are typical for materials with both micropores and mesopores. Both ZSM-5 samples display hysteresis loops above $p/p_0 = 0.6$, however the mesoporosity of the ZSM-5 samples is much higher than for the silicalite-1 sample. The mesopore volume for the sample ZSM-100-24 is $0.12 \text{ cm}^3 \text{ g}^{-1}$, *i.e.* twice that of the silicalite-1 sample. The mesopore volume $0.38 \text{ cm}^3 \text{ g}^{-1}$ of the sample ZSM-50-24 is even higher and comparable to those of mesoporous ZSM-5 synthesized by other reported methods.^{7–18}

Fig. 1h illustrates X-ray diffraction patterns of samples silicalite-1, ZSM-100-24 and ZSM-50-24. The diffraction patterns are typical for MFI zeolite and no peak broadening or background due to

amorphous material was observed. The intensity of the XRD reflections is almost the same, indicating similar crystallinity of these samples.

The growth process of mesoporous ZSM-5 was revealed by interrupting the synthesis at various stages. Fig. 2 shows SEM images of the crystals grown for 1.5 h (a), 3 h (b), 6 h (c), 24 h (d), 48 h (e) and 72 h (f) in a synthesis mixture with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 100. The morphology of the crystal grown for 1.5 h is quite similar to that of the silicalite-1 crystals grown from the aluminum free synthesis mixture, *i.e.* smooth tablets with an aspect ratio of about 1.4. The main difference is that these crystals are a bit smaller with a length of about 1.5 μm in the c -direction. Although the synthesis mixture containing alumina, the crystals are almost free of aluminum, with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 628, Table S2, ESI.† These results show that almost aluminum free silicalite-1 crystals nucleate and grow in the beginning of the synthesis. As the synthesis time is extended to 3 h and longer, quite uniform crystals with tablet habit are obtained, but the morphology changes to that of mesoporous ZSM-5. The aspect ratio and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is decreasing, while the length of the crystals in the a -direction is increasing as the synthesis time is increased, Table S2, ESI.† These results shows that ZSM-5 zeolite, with a quite low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio nucleate and grow as a -direction aligned islands on the surface of the silicalite-1 crystals that had formed after 1.5 h of hydrothermal treatment. The resulting well-defined mesoporous ZSM-5 crystals after 72 h growth have tablet habits that are much longer in the a -direction than in the c -direction.

Crystals were also prepared under the same conditions but without stirring. Fig. 3a shows a SEM image of ZSM-5 crystals prepared in a synthesis mixture with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ for 72 h without stirring. In this case, the crystals have conventional MFI morphology with an aspect ratio of 1.67. The surfaces of the crystals are quite smooth and no mesopores or growth steps can be observed and the crystals have a wider range of particle size distribution. The morphology difference between static synthesized ZSM-5 and stirring prepared crystals is quite striking. As shown in Fig. 3b, the ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) crystals after stirring

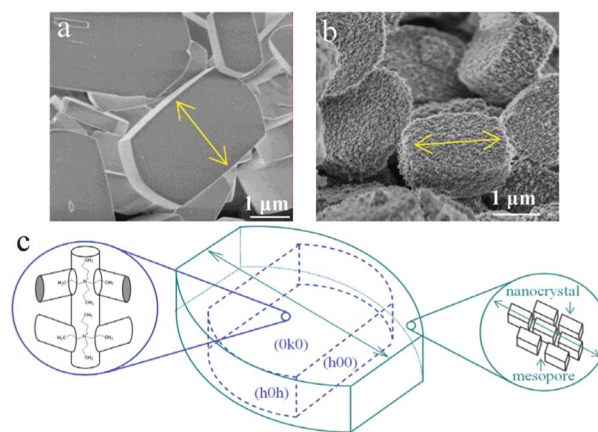


Fig. 3 SEM images of ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$) after growth 72 h under static condition (a), and ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) after growth 72 h under stirring condition (b), the structure of mesoporous ZSM-5 crystal (c).

grown for 72 h shows rough and moustache-like surfaces with an aspect ratio of 0.71.

The formation mechanism of single crystal mesoporous ZSM-5 can be described as below. Stirring make the single crystal with uniform size and shape, Fig. 3b. At starting point amorphous material in the synthesis solution was supersaturated, only microporous coffin-shaped single crystals were obtained. Zeolite nanocrystals began to form when the amount of remaining amorphous material in the solution was limited after being consumed. Because of their instability in the studied conditions these isolated primary zeolite nanocrystals tend to aggregate and self-assemble into polycrystalline particles around the surface of the coffin-shaped crystal. The uncompleted and hindered intergrowth of the neighbouring zeolite nanocrystals produced the mesoporosity. The proposed hierarchical structure of this mesoporous ZSM-5 crystal was given in Fig. 3c, it contains a microporous coffin-shaped core crystal and wrapped by a mesoporous shell composed of uniformly aligned zeolite nanocrystals. The arrows, parallel with the a -axis of the crystals, indicate the growth direction of the mesoporous crystal and the alignment of surface nanocrystals.

In alkaline synthesis solution, negatively charged inorganic species (Si, Al) directly interact with the cationic (TPA⁺) molecule to form microporous channels. While the mesoporous aligned structure is formed by a mediated route, the remaining TPA⁺ or Na⁺ cations electrostatically mediate between negatively charged zeolite nanoparticles and contribute to the formation of mesopores between them. An increasing Al-incorporation into the MFI structure gives crystals with high concentrations of intercrystalline defects. The surface nanoparticles intergrowth with each other through solution-mediated transport and precursor oriented attachment during crystallization. Since coordinative unsaturated aluminum (AlO⁴⁻) appears in ZSM-5 framework, the Al-containing zeolites possess stronger negative surface charge (zeta potential), which leads to the intergrowth of adjacent nanocrystals is poor. It is speculated that diffusive transport for precursors into mesopore between growing crystals is restrained for their similar charge. FTIR spectrum show silanol and acidic-OH groups on mesoporous ZSM-5 surface, Fig. S1, ESI†

In the synthesis of pure-silica MFI zeolite crystals, stirring is helpful for the produce of crystals with narrower range of particle size distribution. After the reaction is complete, the inner walls of Teflon tube are still clean, while the transparent precursor solution turns into opaque white colour, which means the zeolite particles evenly dispersed in the suspension, Fig. 4a and c. However, in the synthesis of mesoporous ZSM-5 crystals, stirring create a tornado shaped tertiary structure on Teflon wall, Fig. 4b. It is probably because the hydrophilic ZSM-5 crystals tend to aggregate to each other during the synthesis process and gradually accumulate its film thickness on Teflon walls, after the reaction is complete the suspension is semi-transparent for most crystals formed onto the Teflon walls, Fig. 4d. The symbolical rotation direction of this mesoporous ZSM-5 film, which formed on the surface of the Teflon cap, in agreement with the stirring bar's turning direction.

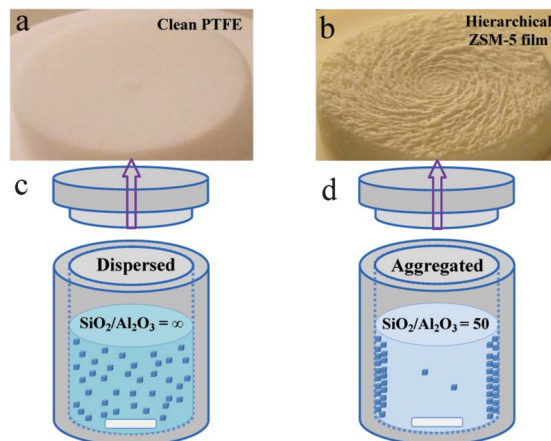


Fig. 4 Digital camera image of clean Teflon cap (a) and grown a hierarchical film of mesoporous ZSM-5 (b), schematic illustration of dispersed silicate-1 crystals in suspension (c) and aggregated ZSM-5 film on Teflon wall (d) after hydrothermal treatments.

Conclusions

In summary, the preparation of mesoporous ZSM-5 single crystals was reported. This is achieved by controlling SiO₂/Al₂O₃ ratios of a single template solution under stirring, without any extra additives or pre-/post-treatments. The mesoporous zeolite has significantly high mesoporosity; the method is low cost and facile for large scale production. With this new technique, hierarchical structures of ZSM-5 crystals and films will be more easily accessible for catalytic applications.

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