In Situ Assembly of Zeolite Nanocrystals into Mesoporous Aggregate with Single-Crystal-Like Morphology without Secondary Template

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Zeolites are widely used in heterogeneous catalysis, especially in petroleum and oil refining, because of their high acidity and shape-selectivity induced by molecular-sized microporosity.[1] The molecular-sized micropores, however, also limit the catalytic performance of the zeolite because of diffusion limitation.[2] To overcome this problem, several novel materials such as ultralarge micropore zeolite,[3] ordered mesoporous materials,[4] zeolite nanocrystals[5] and mesoporous zeolites were synthesized.[6] Among these materials, mesoporous zeolite was considered to be the most effective because it combines the advantage of zeolites and mesoporous materials,[7] as proved by catalytic and diffusional tests.[8]

The best known way to create mesopores in zeolites is dealumination. Although this technique improves the catalytic performance of zeolites,[9] recent 3D-TEM and PFG-NMR analyses indicated that the mesopores introduced by dealumination do not form an interconnected network and contribute little to molecular diffusion.[10,11] Desilication is now considered to be a more effective strategy than dealumination for introducing mesopores in zeolites.[12] For instance, Groen and co-worker have synthesized mesoporous ZSM-5 with excellent diffusion properties by desilication of uniform Al-distributed ZSM-5 crystals.[13] However, the properties and the accessibility of the mesopores were largely determined by the Al content and distribution in the parent zeolite. Highly expensive protocols is needed for the synthesis of the suitable parent zeolite crystal. Also, the selective removal of framework Si or Al by dealumination or desilication will lead to a decrease in crystallinity. With the hard and soft template concept, derived from the ordered mesoporous materials synthesis, mesoporous zeolites can now be synthesized in a more controlled manner. With carbon materials as the secondary template, various mesoporous zeolites with either intercrystalline or intracrystalline mesopores can be synthesized.[14] Several research groups have also reported that mesoporous zeolites can be synthesized through one-step hydrothermal reaction with specially designed amphiphilic organosilane or silyated polymers as the secondary template.[15] However, the use of high-priced secondary templates again makes these synthesis routes very expensive.

It is thus of interest to test if mesoporous zeolites can be synthesized without secondary template and post-treatment. A literature survey and our own research on carbon-templated mesoporous zeolites synthesis showed that in some cases mesopore in mesoporous aggregate of zeolite crystals resulted from the randomly oriented zeolite nanocrystals other than cast from carbon materials. For instance, in the synthesis of mesoporous zeolites with an ordered mesoporous carbon (CMK-3) being the secondary template,[14c,f] the size of the primary nanocrystals (20–30 nm) was much larger than the mesopore size of CMK-3 (approximately 4 nm). This indicates that the zeolite nanocrystals must be grown outside the mesopore system of CMK-3 and the mesopore structure of the mesoporous zeolites is resulted from the randomly oriented zeolite nanocrystals. It can thus be concluded that mesopore porogen is not strictly necessary to perform a mesoporous zeolite synthesis. The zeolite crystallization conditions should be carefully controlled for the synthesis of mesoporous aggregate of zeolite nanocrystals without secondary template because it has a large influence on the size and crystallinity of zeolite nanocrystals.[16] In the synthesis of mesoporous aggregates of zeolite nanocrystals, researchers generally use different methods to confine the zeolite growth, thus inducing the formation of zeolite nanocrystals. In this communication, we test the possibility

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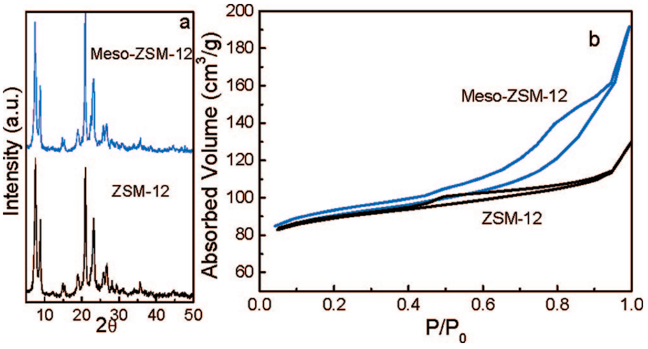

Figure 1. (a) XRD pattern and (b) nitrogen sorption isotherm of mesoporous ZSM-12 and conventional ZSM-12.

Table 1. Textural Parameters of ZSM-12 Samples

sample	S_{BET} (m^2/g)	V_{mic} (mL/g)	V_{total} (mL/g)	V_{mic}/V_{total} (%)
meso-ZSM-12	298	0.12	0.29	41
ZSM-12	292	0.13	0.18	72

to induce the formation of zeolite nanocrystals and subsequently assemble them into a mesoporous aggregate by enhancing the zeolite nucleation rate.

Our study started from ZSM-12 because of its importance and our unexpected results during the ZSM-12 synthesis. ZSM-12 has micropores that are slightly larger than those of ZSM-5. It is of interest for the shape-selective conversion of molecules that are slightly too large to react in the pores of ZSM-5,[12b,14e] such as the selective methylation of 2-methylnaphthalene.[17] Also the effect of a mesoporous secondary pore system on mass transport is expected to be much larger for ZSM-12, a zeolite with a one-dimensional micropore system, when compared with zeolites having a three-dimensional system such as ZSM-5 and β.[7] During the synthesis of conventional ZSM-12 crystals according to reference,[18] mesoporous aggregate of ZSM-12 nanocrystals with a morphology similar to common ZSM-12 were obtained. Nitrogen adsorption analyses of these samples showed a mesoporous character although mesopore volume is quite small (typical results are shown in Figure 1b. Hence we wondered if mesoporous aggregate of ZSM-12 crystals with higher mesoporosity can be synthesized by controlling the zeolite crystallization conditions. In zeolite synthesis, it is well-known that the degree of supersaturation has a larger influence on zeolite nucleation than on growth and has been verified by AFM study recently.[19] Hence a concentrated synthesis gel was used in the synthesis of our mesoporous ZSM-12. The detailed synthesis methods of mesoporous ZSM-12 as well as reference conventional ZSM-12 can be found in the Supporting Information.

The XRD patterns of mesoporous ZSM-12 and conventional ZSM-12 are shown in Figure 1a, which indicate that both samples consist of pure-phase MTW-type structured material. The intensity of the XRD reflections is almost the same, indicating a similar crystallinity of the two zeolite samples. No reflection was found in the small-angle XRD pattern in both samples, indicating there is no structural order in the mesopore scale. In the nitrogen sorption isotherm (Figure 1b) of the mesoporous ZSM-12 sample, besides the feature of high microporosity (large amount of nitrogen adsorbed at low partial pressure), an adsorption step with hysteresis loop at P/P_0 between 0.4 and 0.9, caused by the capillary condensation in the textural mesopores, can also be identified. This indicates the coexistence of micropores and mesopores in this sample. The parameters for the pore structure of both ZSM-12 samples are given in Table 1. The mesopore volume of mesoporous ZSM-12 is comparable to that of mesoporous ZSM-12 synthesized with carbon black being the hard template.[14e]

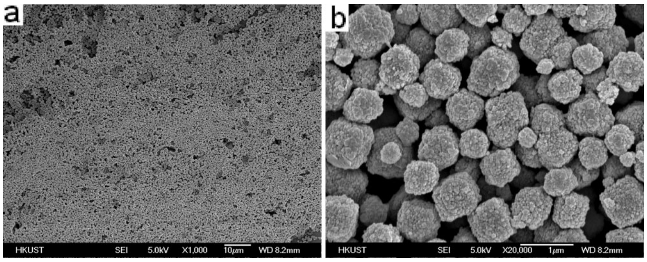

Figure 2. SEM images of mesoporous ZSM-12.

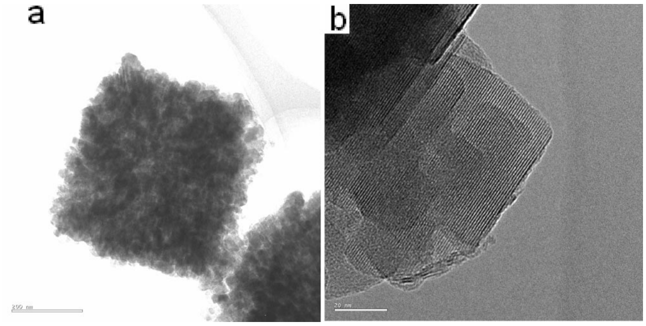

Figure 3. TEM images of mesoporous ZSM-12.

Figure 2 presents SEM images of mesoporous ZSM-12. In the image with low magnification (Figure 2a), uniform cubic crystals with a rough surface and a size smaller than 1 μm can be observed. The high resolution SEM image (Figure 2b) indicates that such single-crystal-like particles are constructed of primary nanosized zeolite crystals (with size between 20 and 30 nm). Figure 3a is a TEM image of mesoporous ZSM-12, which shows the assembly structure of the ZSM-12 nanocrystals and significant mesopores between the primary zeolite nanocrystals. Figure 3b is a HRTEM image of mesoporous ZSM-12, in which lattice fringes can be observed, again revealing the high crystallinity of this sample. Also, lattice fringes of different zeolite nanocrystals in the outer surface show similar direction. These results indicate that the mesoporous ZSM-12 is a polycrystalline zeolite with mesoporosity and that the surface tends to recrystallize into larger crystals through oriented attachment.

The hydrothermal stability of mesoporous ZSM-12 was tested by refluxing in boiling water for 120 h with a sample to water ratio of 1:10 (g/mL) and by increasing the crystallization time to 8 days. The meso- and microstructure of mesoporous ZSM-12 is stable during these treatments, as

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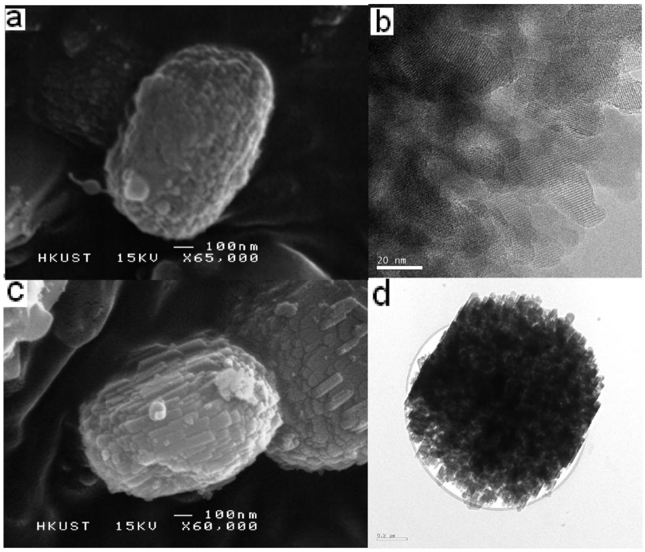

Figure 4. SEM and TEM images of mesoporous ZSM-5 after 6 h (a, b) and 24 h (c, d) crystallization.

confirmed by powder XRD and SEM (see the Supporting Information). These results indicate that the mesoporous ZSM-12, once formed, is highly hydrothermally stable, which is very important for industrial catalytic applications.

We further tested the possibility to synthesize mesoporous ZSM-5 under similar concept. A polyanion nucleation promoter ($H_2PO_4^-$) first reported by Kumar et.al.[20] was used to enhance the nucleation of ZSM-5. Detailed synthesis method can be found in the Supporting Information. As shown in Figure 4, uniform mesoporous aggregate of zeolite nanocrystals with size smaller than 1 μm is formed after 6 h crystallization. The size of the primary zeolite nanoparticles is about 20–30 nm. The XRD pattern shown in Supporting Information indicates that this zeolite sample has a highly crystalline MFI structure. As the crystallization time increases to 24 h, the size of the mesoporous aggregate does not change obviously, except that of the crystals on the surface becomes larger. Also, the less well defined morphology of the zeolite obtained after 6 h of reaction develops into a typical morphology of common ZSM-5. Large zeolite particles and significant mesopores can be seen in the TEM images. Nitrogen adsorption analysis reveals that there are a large number of mesopores in these samples. The BET surface area and mesopore volume is 375 m^2/g and 0.20 mL/g, respectivity. The parameters for the pore structure of both ZSM-5 samples are given in the Supporting Information. Similar synthesis concept can be extended to other zeolite syntheses, such as of mesoporous TS-1, ZSM-11, and ZSM-22.

Assembly of zeolite nanocrystals into hierarchically materials has gathered a lot of research interests; however, most of such work needs inorganic and organic templates.[21] Very recently, it has been reported that zeolite nanoparticles can be used for further zeolite crystallization by dissolvation or aggregation.[22] The report, though different from present research in both research purpose and product, is helpful for understanding our synthsis results. The formation of mesoporous zeolite and single-crystal-like morphology can be depicted as follows. In our synthesis method, the zeolite crystallization conditions were controlled to favor the formation of zeolite nanocrystals. In mesoporous ZSM-12 synthesis, the concentration step carried out by refluxing at 80 °C made the molar ratio of H_2O/SiO_2 decrease from 15 to 8, leading to a higher degree of supersaturation and higher ratio of nucleation to growth rates. Hence, primary zeolite nanocrystals are formed in the initial reaction period and they self-assemble into polycrystalline particles because isolated zeolite nanocrystals are not stable in the hydrothermal reaction condition. The imperfect intergrowth of the zeolite nanocrystals causes the observed mesoporosity. The aggregate then tends to grow into a single crystal and a single-crystal-like morphology gradually develops. The nanoparticles in the center intergrow with each other, whereas the nanocrystals on the surface of the aggregate grow with the remaining amorphous material as monomer through Ostwald ripening and oriented attachment with each other during crystallization. The recrystallization reaction will continue from the outer surface to the inner part of the aggregate. Mesoporous aggregates of zeolite nanocrystals will form if the amount of remaining amorphous material after the nucleation step in the synthesis solution is small. The recrystallization reaction will stop after the amorphous material is totally consumed. If amorphous material in the synthesis solution is too much, only microporous single crystals will finally be obtained. Hence, the mesoporous aggregate of zeolite nanocrystals is an intermediate phase in zeolite synthesis. The mesoporous aggregates with single-crystal-like morphology are a kinetically favored product under certain conditions.

In summary, mesoporous aggregate of zeolite nanocrystals can be synthesized without secondary template by self-assembly of in situ formed zeolite nanocrystals. As-synthesized mesoporous aggregates have single-crystal-like morphology, high hydrothermal stability and high mesoporosity. Thus it proved that mesoporous zeolites can be synthesized through carefully control of the crystallization conditions without using a secondary template. Such a synthesis route allows mesoporous zeolites to be synthesized with a cost similar to or even lower than that of conventional zeolites and thus opens a new, cost-effective, and industrially applicable way to the synthesis of mesoporous zeolites.

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Supporting Information Available: Synthesis methods of zeolite samples, results of hydrothermal test of mesoporous ZSM-12 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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