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Organotemplate-Free and Fast Route for Synthesizing Beta Zeolite

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Beta Zeolite with a three-dimensional network of 12-ring pores[1–3] as one of the most important catalytic materials has been widely used in the petroleum refining and fine chemical industries.[4] Normally, the synthesis of Beta zeolite takes for 2−5 days in the presence of organic templates (structure-directing agents, SDAs) such as tetraethylammonium (TEA^+) that direct the assembly pathway and ultimately fill the pore space.[3]

Although Beta zeolite exhibits excellent properties in a series of catalytic reactions,[4] its wide applications are still challenging by the use of organic templates such as TEAOH in the synthesis, because the use of organic templates not only increases the cost but also results in consumption of energy and pollution for environments by the removal of these organic templates at high-temperature calcination. Therefore, it is strongly desirable to synthesize Beta zeolite with the fast crystallization rate in the absence of any organic templates.

Historically, there are a lot of examples for organotemplate-free syntheses of zeolites such as A, X, Y, MOR,[5] ZSM-5,[6] ECR-1,[7] and ZSM-34,[8] but organic templates are necessary for the modern synthesis of zeolites such as Beta, MFI, and MWW.[1–4] In addition, the introduction of seeds crystals into the starting aluminosilicate gels could accelerate the crystallization rate of zeolites significantly, and typical examples are seeded syntheses of zeolites such as X,[9] MOR,[10] MFI,[11] Beta,[12] high silica A,[13] and ITQ-27.[14] Notably, it is still not successful to synthesize Beta zeolite in the absence of organic templates yet.[1–4,12] Fortunately,

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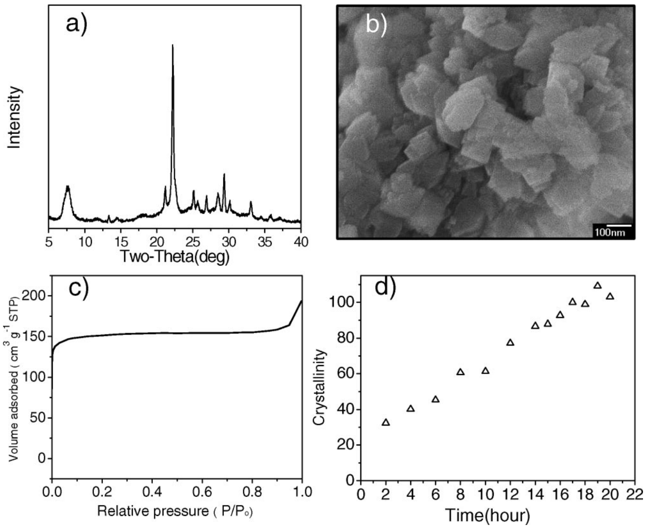

Figure 1. (a) XRD pattern, (b) SEM image, and (c) nitrogen isotherm of as-synthesized Beta-OTF and (d) the dependence of sample crystallinity on crystallization time for Beta-OTF zeolites. The sample of as-synthesized Beta-OTF crystallized at 17 h was denoted as 100% crystallinity.

Beta structure as one of natural zeolites has been found in the mineral in the past decade,[15] which offers a possibility to synthesize Beta zeolite in the absence of organic template.

We demonstrate here an organotemplate-free and fast route for synthesizing Beta zeolite by the addition of calcined Beta seeds in the starting aluminosilicate gel in the absence of any organic templates. Very importantly, the addition of Beta seeds not only directs the growth of Beta crystals in the aluminosilicate gel in the absence of organic templates but also reduces crystallization time significantly. In addition, it is not necessary to calcine the sample because as-synthesized Beta zeolite already has opened micropores. These features for the synthesis of Beta zeolite would be very important for avoiding environmental pollution and reducing production cost.

As a typical run, organotemplate-free synthesis of Beta zeolite (Beta-OTF) was carried out in aluminosilicate gel with molar ratio of 40 SiO_2/1 Al_2O_3/10 Na_2O/570 H_2O at a temperature of 140 °C for 17−19 h in the presence of calcined Beta zeolite seeds with particle sizes of 60−100 nm. Figure S1 (Supporting Information) shows the X-ray diffraction (XRD) pattern of the calcined Beta seeds, confirming the structure of Beta zeolite. Conventionally, Beta zeolite (Beta-TEA) was synthesized in the presence of TEAOH. Figure 1a shows the XRD pattern of Beta-OTF, giving a series of peaks at 7.6, 13.4, 14.4, 21.2, and 22.2° associated with BEA structure.[3] In contrast, we cannot obtain Beta zeolite in the absence of Beta seeds under the same hydrothermal conditions. Clearly, this example indicates the importance of primary crystalline solids (seeds) in starting aluminosilicate gels for the synthesis of Beta zeolite. Furthermore, scanning electron microscopy (SEM) image of Beta-OTF (Figure 1b) shows almost uniform crystals (about 100−160 nm) with similar morphology, suggesting a pure phase of the sample. Figure 1c shows a nitrogen isotherm of as-synthesized Beta-OTF, exhibiting a steep increasing in the curve at a relative pressure $10^{-6} < P/P_0 < 0.01$, which is characteristic of Langmuir adsorption due to the filling of micropores.[2] These results confirm that as-synthesized Beta-OTF has opened micropores, and therefore the combustion of the samples could be avoided. In contrast, it is necessary to take a calcination step for opening the pore space of Beta-TEA.

It is interesting to note that the crystallization time of Beta-OTF is very short, compared with that of Beta-TEA. For example, the synthesis of Beta zeolite at 140 °C normally takes for 3−4 days,[3] and the increase of synthesis temperature to 170 °C results in a significant decrease of Beta crystallization time, giving 24 h.[16] By the use of the sodium and potassium mixture, Beta zeolite could be synthesized at 15 h.[17,18] However, in these cases, organic template (TEA^+) is necessary. Figure 1d shows the dependence of sample crystallinity on crystallization time for Beta-OTF zeolites. Interestingly, when the crystallization time reaches at 17−19 h, the samples show a good quality of the Beta structure (Figure S2, Supporting Information). Obviously, the growth of Beta zeolite crystals is greatly accelerated after the addition of Beta seeds in the starting aluminosilicate gel. Generally, hydrothermal synthesis of zeolites includes induction and crystallization periods.[2,3] Clearly, the addition of Beta seeds in the synthesis remarkably reduces the period of inductive steps, which is confirmed by the crystallinity of Beta-OTF samples increasing with crystallization time of 2−20 h (Figure 1d).

To understand the synthesis of Beta-OTF in the absence of organic template, the crystallization of Beta-OTF samples was characterized by transmission electron microscopy (TEM) and SEM techniques. Figure 2 shows high-resolution TEM images of the samples crystallized at 1, 10, and 17 h for the synthesis of Beta-OTF samples, respectively (Figure S3, Supporting Information). Interestingly, a part of Beta seed in the sample crystallized at 1 h is observed, and this Beta seed is embedded in amorphous aluminosilicates (Figure 2a); when the crystallization time is increased to 10 h, a large amount of amorphous aluminosilicate is crystallized (Figure 2b); when the crystallization time is increased up to 17 h, almost all of the amorphous aluminosilicate is crystallized, forming crystals of Beta zeolite (Figure 2c). These results suggest that the synthesis of Beta-OTF results from the growth of Beta seeds in the starting aluminosilicate gel in the absence of organic templates, and the starting zeolite seeds in the gels are very important for the synthesis of zeolites, which are well consistent with previous reports by Bein et al. and Schüth et al.[19] They discovered that the mechanism for synthesis of A and MFI zeolites is nucleated at first where zeolite seeds are embedded in amorphous

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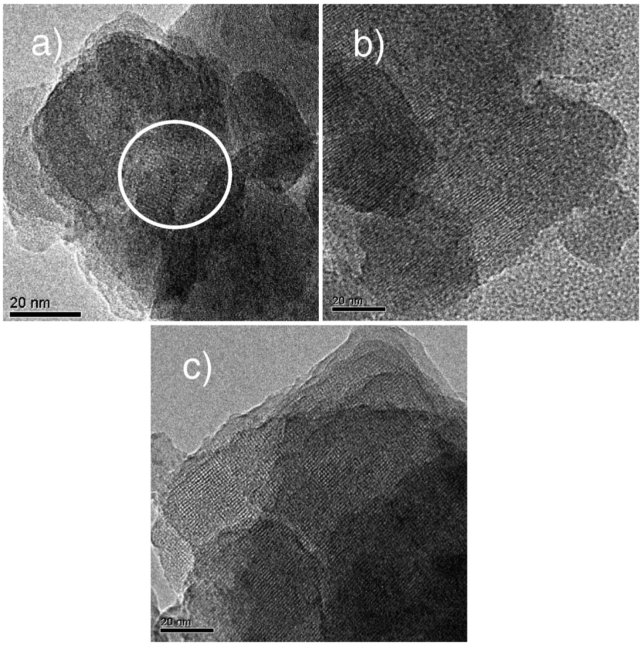

Figure 2. High-resolution TEM images of the samples crystallized at (a) 1, (b) 10, and (c) 17 h for the synthesis of Beta-OTF zeolites, respectively.

phase, and then the zeolite seeds grow up.[19] In our case, the zeolite seeds for synthesis of Beta-OTF is directly added into the starting gel rather than the nucleation from the starting gel. Moreover, Figure S4 (Supporting Information) shows SEM images of the samples crystallized at 2, 10, and 19 h for the synthesis of Beta-OTF samples, respectively. Notably, the morphology of the sample crystallized at 2 h is characteristic of the amorphous phase (Figure S4a, Supporting Information), suggesting that the zeolite seeds are completely embedded in the amorphous phase, in good agreement with TEM image of Figure 2a. When the crystallization time is increased to 10 h, a large amount of zeolite crystals are formed (Figure S4b, Supporting Information), confirming that the crystals are grown from the amorphous phase. When the crystallization time is increased up to 19 h, it is almost of a pure phase of zeolite crystals (Figure S4c, Supporting Information), which is in accordance with TEM image of Figure 2c.

In summary, an organotemplate-free and fast route for synthesizing Beta zeolite by addition of calcined Beta seeds in the starting aluminosilicate gel in the absence of any organic templates is provided. This route could avoid the calcination of organic templates in Beta zeolite for the consumption of energy and the pollution to the environment, which would be very helpful for the *green* synthesis of Beta zeolite.

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Supporting Information Available: Synthesis and characterization (XRD of Beta seeds and XRD, TEM, and SEM images of Beta-OTF crystallized at various times; PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

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