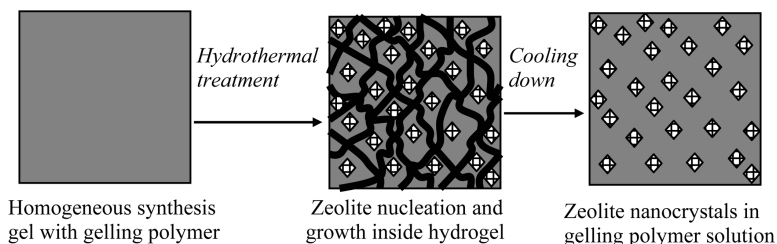


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Synthesis of Template-Free Zeolite Nanocrystals by Using in Situ Thermoreversible Polymer Hydrogels

Huanting Wang,[†] Brett A. Holmberg,[‡] and Yushan Yan^{*‡}

Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521, and Department of Chemistry, The University of Hong Kong, Hong Kong, P. R. China

Received May 12, 2003; E-mail: Yushan.Yan@ucr.edu

There has been considerable interest in the synthesis of zeolite nanocrystals because they can serve as a model system for fundamental studies of zeolite crystal growth,^{1–3} as seeds for secondary growth of zeolite films and membranes,⁴ as building blocks for construction of hierarchical porous crystalline structures, and for preparation of polymer–zeolite nanocomposite membranes.^{5–10} For most of these applications, *dispersible* zeolite nanocrystals with small size are preferred or required.^{5–10} Zeolite nanocrystals are usually synthesized via hydrothermal procedures using aqueous clear solutions. Organic templates are usually required to reduce the crystal size.^{1–11} The use of an organic template has several significant drawbacks. First, the colloidal nanocrystals so obtained contain organic template in their void spaces, and for many applications^{5–10} the template has to be removed, which often is achieved by calcination, leading to irreversible aggregation. Second, the use of template in the synthesis tends to change the Si/Al ratio of the final products that could drastically affect their application. For example, zeolite A, synthesized by using organic template, has a Si/Al ratio greater than 1, and as a result, after Na⁺ exchange it has a pore size larger than 4 Å.¹¹ In contrast, template-free synthesis leads to Si/Al = 1 and zeolite 4A after Na⁺ exchange. The slight change in pore size impacts the air separation capability of zeolite A dramatically.¹² Third, organic templates involved in the syntheses are very expensive, and their use could also be environmentally unfriendly.

Efforts have been made to minimize template-free zeolite A crystal size in the synthesis system of Na₂O–SiO₂–Al₂O₃–H₂O.^{13–15} However, only mean NaA crystal sizes of about 0.5 μm can be obtained by manipulating synthesis parameters.¹⁴ Zeolite NaX crystal size in the organic-additive-free synthesis has been controlled to some degree by using a temperature-controlled shaker.¹⁵

Space-confined synthesis has recently been developed to produce both template and template-free zeolite nanocrystals.^{16,17} Carbon black¹⁶ and starch¹⁷ have served as space confinement additives, and they have to be burned off at high temperatures (e.g., >400 °C) after synthesis, which may not be suitable for preparation of colloidal zeolite nanocrystals, because the high-temperature treatment can lead to nanocrystal aggregation and lower nanocrystal crystallinity.

Here we report a novel strategy of using thermoreversible polymer hydrogels to control zeolite growth rate and thus produce size-controllable zeolite nanocrystals from template-free precursors. The thermoreversible gelling polymers involved can be readily removed after zeolite synthesis by simple washing, and the zeolite nanocrystals obtained are readily redispersed in various solvents.

Hydrogels are three-dimensional networks of polymer chains that are cross-linked via either physical or chemical bonds, and they

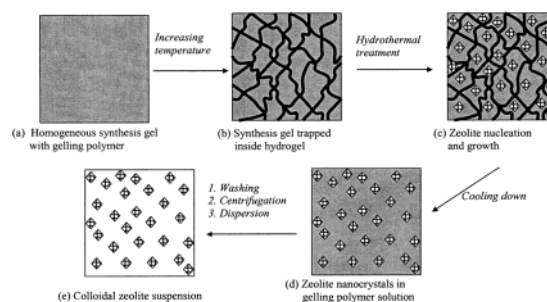


Figure 1. Schematic representation of synthesis of template-free zeolite nanocrystals by using in situ thermoreversible polymer hydrogels.

can entrap a large volume of water.¹⁸ Among polymer hydrogels, thermoreversible polymer hydrogels have an interesting gelation behavior, which is reversibly responsive to temperature. In particular, the polymers that gel at elevated temperatures and turn back to solution at room temperature are attractive because the temperature profile of their solution–gel transition can very nicely fit that of hydrothermal synthesis of zeolite. The three-dimensional adjustable pores of polymer hydrogels can potentially serve as microreactors or nanoreactors for controlling zeolite growth. The general synthesis procedure is illustrated in Figure 1.

In this Communication, as an example, we use methylcellulose (MC) to illustrate thermoreversible polymer hydrogel-controlled synthesis of zeolite NaA and NaX nanocrystals in the system of Na₂O–SiO₂–Al₂O₃–H₂O. Zeolite A (LTA) and Faujasite (FAU) are particularly attractive for this purpose because of their low synthesis temperature and their widespread applications in catalysis, separation, and ion-exchange.^{9–17} The synthesis of their micrometer-sized crystals has been well established in template-free Na₂O–SiO₂–Al₂O₃–H₂O systems.^{11,13–15} MC is one of the important hydrophobically modified celluloses, and its physical properties and thermogelation mechanism have been extensively studied.^{19–21} At room temperature, MC is water soluble, and it can be homogeneously incorporated into the zeolite synthesis system of Na₂O–SiO₂–SiO₂–H₂O. Upon heating, the MC aqueous solution becomes turbid and solid-like above ca. 50 °C due to MC gelation. Zeolite nanocrystals grow inside the MC hydrogel networks. When MC gel is cooled to room temperature, MC becomes water-soluble again. Therefore, as-synthesized zeolite nanocrystals can be very easily retrieved by repeated cycles of centrifugation, decanting, and ultrasonic redispersion in pure water until MC is completely washed away.

Zeolite NaA nanocrystals (denoted Z-MC-P) were synthesized from the synthesis system with a weight composition of 3.56 Na₂O: 1.59 SiO₂:1.00 Al₂O₃:32.12 H₂O:3.48 MC by adding MC powder into zeolite synthesis gel with a molar composition of 5.85 Na₂O: 2.7SiO₂:1.00 Al₂O₃:182 H₂O. Zeolite FAU nanocrystals (denoted Z-MC-S) were synthesized from the synthesis system with a weight

[†] The University of Hong Kong.

[‡] University of California, Riverside.

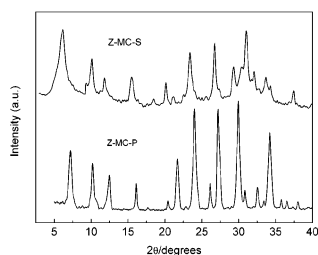


Figure 2. XRD patterns of zeolite crystals: (a) Z-MC-P (NaA nanocrystals) and (b) Z-MC-S (NaX nanocrystals).

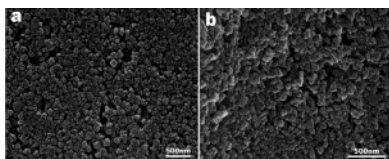


Figure 3. SEM images of zeolite crystals: (a) Z-MC-P (zeolite NaA nanocrystals) and (b) Z-MC-S (zeolite X nanocrystals).

composition of 3.67 Na₂O:1.65 SiO₂:1 Al₂O₃:83.93 H₂O:7.08 MC by adding 10 wt % MC aqueous solution into zeolite synthesis gel with a molar composition of 6.04 Na₂O:2.80 SiO₂:1.00 Al₂O₃:114.64 H₂O. All zeolite crystallization was carried out at 80 °C for 3 h. The powder X-ray diffraction patterns shown in Figure 2 indicate a pure zeolite A phase for Z-MC-P and a pure FAU phase for Z-MC-S. The diffraction peaks for both samples were significantly broadening, indicating small crystal size. The crystal size was determined to be 98 nm for Z-MC-P and 70 nm for Z-MC-S. The relative crystallinity was calculated to be 95% for Z-MC-P and 89% for Z-MC-S. From elemental analysis results, sample Z-MC-P had a Na:Si:Al molar ratio of 1.00:1.02:1.05, confirming a 4A structure. Sample Z-MC-S had a Na:Si:Al molar ratio of 0.98:1.12:1.00, and its Si/Al (1.12) falls in the range of 1–1.5 for zeolite NaX structure. Therefore, Z-MC-S is identified as zeolite NaX. Scanning electron microscopy was used to determine the morphology and size of as-synthesized zeolite crystals. SEM images of the two samples are shown in Figure 3. Zeolite NaA crystals (Z-MC-P) had a small particle size, ranging from 20 to 180 nm. The majority of crystals were below 100 nm in size. Zeolite NaX nanocrystals (Z-MC-S) had even smaller crystal size than zeolite NaA nanocrystals. Zeolite NaX nanocrystal size ranges from 10 to 100 nm. TEM studies show that both zeolite NaA and NaX nanocrystals are highly crystalline (see S-Figure 3, Supporting Information). These are consistent with the XRD results. Without using MC, the crystal size of zeolite NaA (denoted Z) increased significantly; most zeolite NaA crystals grew to 1–2 μm in size (see S-Figures 1 and 2, Supporting Information). Washed colloidal suspensions of nanocrystals were analyzed by dynamic light scattering (DLS). The mass median diameters are 165 and 120 nm for NaA and NaX nanocrystals, respectively. This suggests good dispersibility for both colloidal suspensions, although the NaX nanocrystals may have agglomerated slightly.

Both NaA and NaX (Z-MC-P and Z-MC-S) samples were measured with N₂ adsorption–desorption to determine zeolite surface area and pore volume (see S-Figure 4, Supporting Information). Zeolite NaA nanocrystals showed a BET surface area of 200 m²/g, and the micropore volume was calculated to be 0.06 cm³/g by using the *t*-plot method, which implies fairly low N₂ adsorption through well-defined micropores.²² The NaA nanocrystals obtained

had an external surface area of 70 m²/g, whereas micrometer-sized zeolite 4A crystals exhibited a very low external surface area (<2 m²/g).²² This further supports the fact that the zeolite NaA nanocrystals, as prepared, have small crystal sizes. The BET surface area of zeolite NaX nanocrystals was calculated to be 416 m²/g. The external surface area of NaX nanocrystals was 99 m²/g, which is 2 times greater than that of commercial zeolite X,¹⁵ confirming the nanometer sizes of the NaX nanocrystals obtained in this study.

We have successfully synthesized zeolite nanocrystals from template-free precursors, and thermoreversible polymer hydrogels are very effective for controlling zeolite nanocrystals. More research work is under way to explore the mechanisms of zeolite nucleation and growth under different composition of zeolite synthesis gel and structure of polymer hydrogel. It is believed that the strategy developed here provides a unique, effective, and potentially general approach for synthesis of zeolite nanocrystals and other nanocrystals with controllable size under hydrothermal conditions.

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Supporting Information Available: Experimental procedure and S-Figures 1–4 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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