Synthesis of Zeolite Nanocrystals at Room Temperature

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Zeolite A nanoparticles were synthesized under room-temperature conditions from a very reactive organic-template-free gel system. The optimization of the syntheses parameters, namely, the composition of the initial system and the careful choice of the reactants, allowed the crystallization to be accomplished within 3 days. At this stage the individual zeolite crystals were in the range of 100–300 nm without well-developed crystal faces. The prolongation of the synthesis time up to 10 days led to formation of larger well-faceted cubic crystals averaging about 400–500 nm in size. The high-resolution transmission electron microscopy (HRTEM) study revealed that a thin layer of amorphous material covers the zeolite particles acting as a binder between individual zeolite crystals. The postsynthesis treatment of the product in NH3 media under ultrasonic radiation disintegrated the loosely attached zeolite particles and decreased the fraction of zeolite A particles with low colloidal stability. The employed approach, however, did not result in complete disintegration of aggregated crystals. The zeolite crystals obtained under ambient conditions were characterized by XRD, SEM, dynamic light scattering, and N2 adsorption measurements.

Introduction

During the past decade terms such as “soft” or “green” chemistry are commonly used in the preparation of solid-state compounds, where mild conditions and environmentally friendly preparation procedures are highly desired. Very often, these procedures involve treatment at low or moderate temperatures. Recently, successful attempts to decrease the crystallization temperature in the synthesis of microporous zeolite-type materials have been made.1,2 In addition to economic and environmental benefits, the low-temperature syntheses open new avenues for fundamental studies of chemical reactions. Generally, the zeolite syntheses are performed in the temperature range of 90–200 °C for periods of time between several hours and several weeks.3,4 It is well-known, however, that aging under ambient conditions has a pronounced effect on the subsequent crystallization process. Several research groups suggested that the aging step results in the formation of viable nuclei, which induce crystallization upon raising the temperature.5–7 Provided zeolite nuclei are formed under ambient conditions, there are neither thermodynamic nor chemical constraints that should interfere with the subsequent growth of the crystallites. However, as should be expected, the kinetics of such a crystallization process is relatively slow. Despite the fact that natural zeolites are known to often grow at low temperatures in closed alkaline and saline lake systems,8 few examples, however, show the feasibility of ambient temperature synthesis of aluminosilicate zeolites on a laboratory time scale. After 47 days of aging at ambient conditions, a liquid-free gel was partially (ca. 20%) converted into zeolite X.9 Using a conventional Na2O–Al2O3–SiO2–H2O system, Sand et al.9 synthesized zeolite A with a crystallinity of about 70–80% after 28 days synthesis at room temperature. The long duration of these syntheses and only partial transformation of the initial gel into zeolite make them not very useful for practical applications. A substantial reduction of the synthesis time combined with full conversion of the initial system into zeolite-type material under room-temperature conditions would make such syntheses very useful from both academic and applied points of view, since they might be used for investigation of the mechanism of zeolite formation on one hand and for production of nanocrystals on the other. Very recently, such a study was performed on a system yielding zeolite X for about 3 weeks of treatment at room temperature (RT).10

The synthesis of zeolite nanocrystals in the form of stable colloidal suspensions was one of the important events in zeolite science during the past decade. Several microporous materials, among others MFI-, LTA-, FAU-, and BEA-type materials, have been prepared in the form of colloidal suspensions with narrow particle size distribution.11–15 The synthesis of zeolite crystals with narrow particle size variation requires homogeneous distribution of the viable nuclei in the system. Therefore, the homogeneity of the starting system and simultaneity of the events leading to

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the formation of precursor gel particles, and their transformation into a crystalline zeolitic material, are of primary importance. In general, very diluted systems containing abundant amounts of tetraalkylammonium hydroxides are used in the synthesis of zeolite nanocrystals. The alkaline cation concentration in such systems has to be very limited in order to avoid the flocculation of the gel particles. All these factors together with the careful choice of the silica source allow the stabilization of “clear” starting solutions, where only discrete gel particles are present. A serious drawback, that has important economic and environmental impact, is the large amount of organic structure-directing agents (SDA) used in such preparations. In addition, the organic SDA requires high temperature calcination of the zeolite in order to open zeolite porosity, which leads to aggregation of the individual particles. Recently Wang et al. have developed a calcination procedure, where an organic polymer network is used as a temporary barrier during the calcination in order to prevent zeolite nanocrystals aggregation. Nevertheless, the synthesis of discrete zeolite crystals from organic SDA-free systems is highly desired, since it would open an alternative route for preparation of nanooctaers. The present study reports on the synthesis of zeolite A (structure type LTA) nanocrystals at room temperature for a relatively short period of time from SDA-free system.

**Experimental Section**

The room-temperature synthesis of zeolite A was performed from a system with the following composition: xNa2O/0.64Al2O3/1.0SiO2/EtOH, where x = 3–8, y = 0.4–0.55, and z = 80–150. The reactants used were the following: Na2SiO3·H2O (Fluka, 27 wt % SiO2, 14 wt % NaOH), NaAlO2 (Riedel-de-Haën, 54.3 wt % Al2O3, 43.4 wt % Na2O), NaOH (Merck, 98 wt %), and distilled water. In a typical preparation, clear sodium silicate and aluminate solutions were first prepared. These two solutions were prepared by mixing 10 g of H2O, 5 g of NaOH, and 10 g of Na2SiO3·H2O, and 10 g of H2O, 6 g of NaOH, and 23 g of NaAlO2, respectively. The zeolite precursor mixture was produced by vigorous 90 min mixing of the clear alkaline silicate and aluminate solutions. The resultant gel was stored in an oil bath (T = 25 ± 1 °C) in sealed polypropylene bottles. Small aliquots of the mixtures were taken at different periods of time, i.e., 0, 6, 21, 29, 44, 52, 67, 93, 144, and 240 h. After taking aliquots, the samples were kept in order to disperse the settled particles. Prior to taking aliquots, the colloidal suspension was purified by speed centrifugation and redispersion steps in water. The product samples were shaken in order to disperse the settled particles.

Further increase of the Na2O content in the system did not reduce the crystallization time. 5 reduced more than 3 times the crystallization time. Further increase of the Na2O content in the system did not accelerate the formation of zeolite A. A relatively rapid crystallization of the zeolite was observed at H2O/SiO2 ratios between 120 and 150. The variations of the water content influenced also the purity of the crystalline solid. The vigorous mixing of the alkaline silicate and aluminate solutions produced a precursor gel where all components were expected to be homogeneously distributed.

All components of the initial system were varied in order to optimize the crystallization time (Table 1). The Na2O/SiO2 ratio had the most pronounced effect on the kinetics of zeolite formation. The increase of this ratio from 3 to 5 reduced more than 3 times the crystallization time. Further increase of the Na2O content in the system did not accelerate the formation of zeolite A. A relatively rapid crystallization of the zeolite was observed at H2O/SiO2 ratios between 120 and 150. The variations of the water content influenced also the purity of the crystalline solid.

The particle size analysis of the zeolite nanocrystals crystallized in the solution was performed with a HPPS ET (Malvern) particle size analyzer. The X-ray diffraction (XRD) powder data of the samples were collected on a STOE STADI-P diffractometer using Cu Kα1 radiation. Micrographs of the samples were taken with a Philips XL 30 LaB6 scanning electron microscope (SEM). Nitrogen adsorption measurements were carried out on a Micromeritics ASAP 2010 surface area analyzer after outgassing the samples at 350 °C. 29Si NMR spectrum of the initial silicate solution was collected with a DFS 400 Brucker spectrometer (contact time 10.5 µs, recycle time 30 s). The structural evolution of the gel species was tracked down with high-resolution transmission electron microscopy (HRTEM) using a FEI-Philips CM300 microscope in low-dose mode, operating at 300 kV accelerating voltage, equipped with a LaB6 electron gun, and EDAX energy-dispersive X-ray spectrometer (EDS). Samples were prepared by diluting the suspension of the reaction products in distilled water, ultrasonication them, and depositing a drop onto Cu grids coated with a thin (5 nm thickness) holey carbon support film.

**Results and Discussion**

The crystallization temperature has a pronounced effect on the ultimate zeolite crystal size. As a rule, lower temperatures lead to smaller particle sizes, however, at the expense of a substantial decrease of the crystallization rate. To obtain zeolite A in a reasonable period of time under ambient conditions, a highly alkaline, very reactive initial system was employed. Besides the temperature, the crystallization kinetics of any particular zeolite is affected by the alkalinity and composition of the reaction mixture. It was found that the zeolite formation is very sensitive to the nature of the reactants, in particular that of the silica source. Thus, a great variety of silica sources, which differ in their specific surface area, impurities, and ability to dissolve in alkaline mixtures have been employed so far in zeolite syntheses. The silica source can influence different aspects of the zeolite crystallization, including the kinetics of crystal growth and the properties of the final product. Since the crystallization temperature was as low as 25 °C, in order to reduce crystallization time special attention was paid to all other factors controlling the kinetics of zeolite growth. A silica source containing low-mass species was employed and further depolymerized by adding sodium hydroxide so as to obtain a completely transparent initial solution. The state of the silica in the solution was studied by 29Si liquid NMR spectroscopy. Under the conditions used, only a single peak at ~72 ppm characteristic of silicate monomer was detected. The latter was mixed with a clear sodium aluminate solution where Al(OH)4- is the dominant anionic species. The vigorous mixing of the alkaline silicate and aluminate solutions produced a precursor gel where all components were expected to be homogeneously distributed.

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showed that the prolongation of the synthesis time led to substantial changes in the crystal size and morphology. The product obtained for 3 days is uniform in size with individual particles ranging between 100 and 300 nm (Figure 2, parts a and b). After 5–6 days of synthesis, faceted crystals can be seen (Figure 2c), and after 10 days of room-temperature crystallization much bigger cubic and cuboctahedral crystals with well-developed (100) faces (Figure 2d) were the main fraction of the product. Although the 3 days product was fully crystalline according to the XRD investigation, the crystals continued to grow. At that stage, however, the nutrients are mainly provided by dissolution of the smaller and less stable zeolite nanoparticles, i.e., the system enters in the Ostwald-ripening stage.

The small crystal size of the 3 days material was confirmed by the N₂ adsorption measurements. As known, zeolite A in its sodium form does not adsorb the N₂ molecule. Indeed, the adsorption/desorption isotherm of the product was of type III, typical of nonporous materials (Figure 3, trace a). The increase in the volume adsorbed at very low relative pressures was due to the presence of a small amount of micropores, most probably related to the adsorption of N₂ molecules at the pore openings. The specific surface area of this sample was 85.6 m²·g⁻¹, which suggests nanometer size particles. For comparison, micrometer size (3–4 μm) zeolite A crystals synthesized at 95 °C for 6 h from the same initial system showed external surface areas of 3.1 m²·g⁻¹. Further, the Ca²⁺ form of materials synthesized under ambient conditions and at 95 °C was analyzed by nitrogen adsorption. The corresponding adsorption/desorption isotherms are shown in Figure 3. As can be seen, the material synthesized at room temperature (Figure 3, trace b) has a lower micropore volume in comparison with that of the reference sample (Figure 3, trace c). In contrast to pure microporous materials, the steep uptake at low relative pressures is not followed by a flat curve. Instead, an inclination of the curve with an increase of the relative pressure and a second uptake at a high relative pressure, indicative of some textural mesoporosity, can be observed. Due to this secondary porosity, the material synthesized at room temperature showed a higher total pore volume compared to that of the reference zeolite A sample.

The 3 days zeolite A sample was studied by dynamic light scattering (DLS) in order to evaluate the particle size distribution. According to this investigation, a suspension with a relatively broad (150–1050 nm) particle size distribution was obtained with a peak centered at about 350 nm (Figure 4).

The zeolite A product was further studied by HRTEM to understand the reason for the difference in the crystal size measured by DLS and SEM. According to the TEM study, the product contained mostly aggregates built of

<table>
<thead>
<tr>
<th>sample</th>
<th>molar composition</th>
<th>synthesis time days</th>
<th>structure type</th>
</tr>
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<tr>
<td>1</td>
<td>3Na₂O·0.50Al₂O₃·1.0SiO₂·200H₂O</td>
<td>12</td>
<td>Am², LTA</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
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<td>5</td>
<td>LTA, Am² trace</td>
</tr>
<tr>
<td>4</td>
<td>6Na₂O·0.50Al₂O₃·1.0SiO₂·200H₂O</td>
<td>4</td>
<td>LTA</td>
</tr>
<tr>
<td>5</td>
<td>8Na₂O·0.50Al₂O₃·1.0SiO₂·200H₂O</td>
<td>4</td>
<td>LTA, SOD</td>
</tr>
<tr>
<td>6</td>
<td>6Na₂O·0.40Al₂O₃·1.0SiO₂·200H₂O</td>
<td>6</td>
<td>LTA, U⁸</td>
</tr>
<tr>
<td>7</td>
<td>6Na₂O·0.50Al₂O₃·1.0SiO₂·200H₂O</td>
<td>5</td>
<td>LTA, U⁸ trace</td>
</tr>
<tr>
<td>8</td>
<td>6Na₂O·0.55Al₂O₃·1.0SiO₂·200H₂O</td>
<td>4</td>
<td>LTA</td>
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<tr>
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<tr>
<td>10</td>
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<td>3</td>
<td>LTA</td>
</tr>
</tbody>
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a Am = amorphous. b U = unidentified phase.

![Figure 1](image)
individual crystals. The careful inspection of these aggregates revealed that all crystals were covered with a shell of material with amorphous appearance (Figure 5a). Besides the absence of lattice fringes, a substantial difference in the contrast between this material and underlying zeolite was observed. The lower contrast of the material building the shell suggests a composition of lower average atomic number (Z contrast). Having in mind that both zeolite and amorphous material were obtained from the same Na₂O-Al₂O₃-SiO₂-H₂O system, the contrast difference was attributed to the formation of a shell of highly hydrated amorphous material. This material covers both the individual crystals and the aggregates with a 5–10 nm shell. The formation of such a thick layer of amorphous material onto the zeolite particles is not typical for zeolite syntheses at elevated temperatures. Obviously, at RT conditions it is difficult to achieve a complete conversion of the amorphous precursor, which resulted in materials with lower micropore volume and textural porosity (see Figure 3). XRD analysis indicated that the amount of the amorphous material is low. This residual amount of amorphous precursor serves as contact cement binding the well-shaped individual crystals into random aggregates, deteriorating the colloidal nature of the product. As a consequence, after 1 week of aging, about 80 wt % of the product precipitated at the bottom of the vessel. Figure 5b shows a close view of the amorphous material binding two individual crystals, while Figure 5c represents a typical zeolite A aggregate. The cracks between the individual crystals, visible in Figure 5c, are most probably formed during the drying of the amorphous material. It is worth mentioning that the number of aggregates built of intergrown zeolite A crystals was not very large. Therefore, a dissociation of the attached by the amorphous material zeolite A crystals could be achieved under appropriate conditions. An attempt to disintegrate the zeolite A aggregates was performed on a well-washed (pH = 7.9) sample with a 0.5 mol of NH₃ solution under ultrasonic radiation. The postsynthesis ultrasonic treatment of the product reduced substantially the particle size distribution without substantial changes in the average crystal size (Figure 4). The peak corresponding to the US-treated sample was centered at about 350 nm, and the particles ranged between 200 and 600 nm.
After keeping the suspension for 1 week at room temperature, sediment which corresponded to ca. 32% of the mass of zeolite was found at bottom of the vessel. Obviously, the ultrasonic treatment led to disintegration of the loosely attached aggregates, thus providing a material with a narrower particle size distribution. However, the obtained DLS still did not correspond to the SEM observation, where the main population of individual crystals was in the range of 100–300 nm. This result shows that more effective postsynthesis treatment will have to be developed in order to liberate the aggregated zeolite nanoparticles.

The TEM investigation revealed the presence of an amorphous shell around the zeolite A crystals synthesized under ambient conditions. A question that arises of is whether the zeolite pore system is accessible via this shell. The ion exchange experiments showed that the materials can be completely Ca\(^{2+}\) exchanged, which proves the accessibility of the intracrystalline pore volume. The latter was confirmed by the \(N_2\) adsorption measurements performed on the Ca-exchanged sample (Figure 3b).

Although larger nanocrystals with broader particle size distribution with respect to the synthesis from clear solutions\(^a\) were obtained, still the product is in the nanometer size range. Note that a great part of the zeolite A product behaves as colloidal particles and thus can be used for different applications. For example, for the preparation of thin films by spin-coating or seeding of supports that can be subjected later to secondary growth. The room-temperature syntheses of zeolites open up also routes for the preparation of zeolite films under mild temperature conditions, which is highly desirable for supports that cannot withstand the hydrothermal treatment at elevated temperatures. A further advantage of the organic-template-free room-temperature synthesis is the relatively high yield. On the basis of the silica conversion, the yield in the system under investigation was calculated to be 83%. The reference experiment, where LTA-type zeolite was synthesized from a clear homogeneous solution rich in tetramethylammonium cations, yielded 9.7% zeolite.

**Conclusion**

The present investigation has demonstrated that zeolite A can crystallize within 3 days under room-temperature conditions from an SDA-free system. This synthesis of the zeolite is longer than that at elevated temperatures, where the crystallization time can be reduced to tens of minutes. On the other hand, the crystallization time is comparable and even shorter than that of other types of zeolites at elevated temperatures. This relatively rapid transformation of the amorphous aluminosilicate species into a zeolite A material under room-temperature conditions was achieved by a fine-tuning of all parameters affecting the crystallization kinetics. The present synthesis approach leads to much faster crystallization of zeolite A under ambient conditions compared to already published studies,\(^3,9\) where synthesis experiments last from one to several months and did not yield fully crystalline products.

The postsynthesis US broke free the loosely attached particles and provided a product with a narrower particle size distribution. In the current study the fraction of the silica converted into zeolite A reaches 83%, whereas in the previously published experiment the yield of zeolite A nanoparticles in the presence of an organic SDA (TMA) was only about 10%. Thus, the room-temperature synthesis of zeolite nanoparticles from organic-template-free precursors offers an attractive alternative for the prepa-

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**Figure 5.** TEM images of (a) the amorphous material covering an individual zeolite A crystal, (b) close view of the interface between two zeolite A crystals bound by amorphous material, and (c) an aggregate of zeolite A crystals, where cracks due to the drying of highly hydrated amorphous material can be seen.
ration of colloidal zeolite crystals. Furthermore, the utilization of systems yielding zeolite nanocrystals under ambient conditions might provide important insights into fundamental aspects of the mechanism of zeolite crystallization.

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