Nucleation and crystal growth features of EMT type zeolite synthesized from an organic-template-free system

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Nucleation and Crystal Growth Features of EMT-Type Zeolite Synthesized from an Organic-Template-Free System

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Supporting Information

ABSTRACT: The process of formation of ultrasmall EMT-type zeolite from organic-template-free homogeneous suspensions is presented. The formation of transparent uniform suspension utilizing sodium aluminate, sodium silicate, and sodium hydroxide under controlled mixing is found to be of primary importance to control the nucleation and growth process of EMT-type crystals. The investigation of zeolite intermediates reveals the formation of uniformly sized gel particles (5−10 nm in size). The mean hydrodynamic diameter of the crystalline EMT-type zeolite corresponds to the size of the amorphous particles formed after preparation of the clear precursor suspension. Controlled formation of uniform precursor particles predetermines, to great extent, the following nucleation and growth steps and, thus, the characteristics of the ultimate product. The amorphous particles are transformed to single EMT-type crystals 6−15 nm in size at 303 K within 36 h. Small changes in the initial composition or the preparation procedure lead to the formation of other sodalite-cage-containing zeolites. Thus, it is of critical importance to control the nucleation kinetics in order to obtain the EMT-type material as pure phase. Besides the EMT zeolite, the crystallization fields of other zeolites upon low-temperature synthesis conditions are studied. The careful control of gel chemistry, combined with slow nucleation kinetics at low temperature, can provide access to important nanoscale zeolites while avoiding the use of expensive organic templates.

KEYWORDS: EMT-type zeolite, organic-template-free synthesis, nucleation kinetics, precursor suspension, nanocrystals

INTRODUCTION

Zeolites are metastable crystalline aluminosilicate molecular sieves with uniform pores of molecular dimensions. Conversion to more-stable porous or dense phases is often observed in zeolite-yielding systems. The analyses of zeolite-yielding systems did not reveal a thermodynamics-dependent relationship between the formation of a particular zeolite and the Gibbs free energy.1,2 Study on the formation of a high-silica zeolite-type material, involving the use of organic structure-directing agents, resulted in a similar conclusion.3 Thus, thermodynamic analyses of different systems yielding zeolites suggest that kinetic factors are of major importance for the formation of a particular zeolite.4 More precisely, the kinetics of nucleation is the critical step that determines the product of a zeolite synthesis. Hence, mastering zeolite formation, to a great extent, means fine control of zeolite nucleation and adjusting the complex of chemical and physical conditions of the desired zeolite to reach the viable nuclei size and win the race with competing phases. The nucleation kinetics is particularly important when the target is a zeolite structure with high free energy that easily could be transformed to an energetically more favorable phase. Usually, the increase of pore volume and decrease of framework density lead to the formation of less-stable zeolite structures.5 Low framework density structures—in particular, those with extra-large pores—are very important, from a practical point of view. Recently, the quest for such materials has become urgent, because of the heavy and extra heavy crude oils that remain to be processed. Organic structure-directing agents are usually employed to direct the formation and stabilize the framework of low-framework-density molecular sieves. For instance, very open Ge-silicate molecular sieves have been synthesized recently.6 However, few of these structures survive the template combustion and the hydrolysis of germanium. Thus, classical aluminosilicate zeolites remain...
the most important class of crystalline microporous materials, from a practical point of view.

For almost half a century, zeolite Y (FAU-type) has been the backbone of the oil-refining industry. Another material that might face severe conditions in the petroleum refining is the EMT-type zeolite, which is the hexagonal counterpart of the cubic zeolite Y.7,8 Because of the different arrangement of faujasite sheets in EMT (ABAB sequence), compared to cubic faujasite (ABCABC sequence), the EMT structure possesses two types of cages called hypercages (1.24 nm×0.73 nm×0.73 nm) and hypocages (0.61 nm×0.75 nm×0.65 nm) while the FAU-type material comprises only one supercage (1.15 nm×0.74 nm×0.74 nm).9,10 This difference in the arrangement of zeolite building units leads to different pore connectivity and, thus, different properties. Indeed, the EMT material has shown interesting catalytic properties, for instance, in fluid catalytic cracking and alkylation.11,12

Pure EMT-type material was obtained by employing a very expensive organic structure-directing agent (18-crown-6 ether).7 The latter was the main obstacle to making the material applicable for practical uses. However, the use of other structure-directing agents and various initial systems have resulted in intergrown EMT-FAU (CSZ-1, ECR-30, ZSM-20, ZSM-3) materials.13–19 Thus, until recently, the synthesis of pure EMT-type zeolite was possible solely by employing an exotic template (18-crown-6 ether).20 Many attempts have been carried out to reduce the consumption of crown ether, for instance, by recycling organic structure-directing agents (OSDAs) after the synthesis21 or using the “SINTEF” tumbling approach,72 surfactants,23 and less-expensive organic and inorganic auxiliary additives.24–26 Although the synthesis of the EMT-type zeolite was optimized, still the use of 18-crown-6 ether remained indispensable for the production of this promising material.

In order to slow the nucleation kinetics and shed more light onto the mechanism of zeolite formation in conventional organic-template-free hydrogel systems, we have synthesized a series of zeolites at room temperature.27 Room-temperature syntheses allow one to study zeolite formation under quasi in situ conditions and, thus, follow the physical and chemical evolution of the system during the induction and the following nucleation and growth stages. Employing this approach, we have studied the formation of zeolite A (LTA-type) and zeolite X (FAU-type) in detail. Under such conditions, the crystallization of hydroxysoalite (SOD type) has also been observed. All three materials comprise the same building units as an EMT-type structure. Hence, the formation of EMT-type zeolite could be expected if the gel chemistry is united with the right nucleation kinetics. The extensive experimental effort, where all components of an initial gel were varied in a very large range, resulted in the successful synthesis of EMT-type material from an organic-template-free system.28 By decreasing the crystallization temperature and tuning the gel composition, the conditions that favor the formation of less-stable phase (EMT) and avoid the formation of competing zeolite structures (FAU, SOD) were found. These conditions have also promoted the nucleation over the growth; thus, a larger number of nuclei yielding ultrasmall crystals were obtained.

In the present work, a detailed study of the crystallization of nanosized zeolites from organic-template-free Na2O–Al2O3–SiO2–H2O precursor systems is reported. The crystallization field diagram of synthesized zeolites including EMT, FAU, and SOD is constructed, upon tuning the Na2O and H2O contents in the precursor suspension, the temperature, and the heating time. Besides, the kinetics of crystallization of EMT-type ultrasmall crystals from a template-free precursor suspension is studied providing valuable information on the amorphous precursors, the zeolite intermediates, and the final crystalline material.

### EXPERIMENTAL SECTION

#### Crystallization Field Diagram of Zeolites Synthesized from Template-Free Precursor Suspensions

The triangular crystallization field diagram for the xNa2O:1Al2O3:S.15SiO2:yH2O system was constructed by varying the concentrations of Na2O (x = 17.5–19.5) and H2O (y = 240–640), as well as the crystallization time (12–44 h). The reactants used and procedures for the preparation of initial suspensions and sample treatment after different periods of crystallization are provided below.

**Synthesis of Ultrasmall EMT Zeolite.** Organic-template-free EMT-type nanocrystals were synthesized as follows: solution A was prepared by dissolving 9.074 g of sodium aluminate (Strem Chemicals, 56.2% Al2O3, 39.5% Na2O) and 1.61 g of sodium hydroxide (Prolabo, 97%) in 100 g of distilled water followed by mixing with 44.00 g of sodium hydroxide to give a clear suspension; solution B was prepared by adding 57.692 g of sodium silicate (Prolabo, 27% SiO2, 8% Na2O) and 20.00 g of sodium hydroxide in a 250-mL bottle containing 80 g of distilled water, followed by stirring until the solution became completely transparent. Both solutions were cooled in an ice bath (277 K). Then, solution A was poured slowly into solution B under vigorously stirring. A turbid suspension was formed with the following molar composition: 18.45Na2O:1Al2O3:5.15SiO2:240H2O. The suspension was continuously stirred for 5 min, and then kept at 303 K. The colloidal samples were periodically collected (8 h, 16 h, 20 h, 28 h, and 36 h) and purified to pH 8 prior drying at room temperature.

**Characterizations.** Powder X-ray Diffraction (XRD) Analysis. Powder samples were measured using a PANalytical X’Pert Pro diffractometer with Cu Kα monochromatized radiation (λ = 1.5418 Å). The samples were scanned in the range 4°–50° 2θ, with a step size of 0.02°.

**Transmission Electron Microscopy (TEM).** Diluted colloidal suspensions of nanomaterials were sonicated for 15 min and then 2–3 drops of fine particle suspensions were dried on carbon-film-covered 300-mesh copper electron microscope grids. The crystal size, morphology, and crystallinity of solids were determined via transmission electron microscopy (TEM), using a JEOL Model 2010 FEG system operating at 200 kV.

**Dynamic Light Scattering (DLS) Analysis.** The hydrodynamic diameters of the nanoparticles in the suspensions were determined with a Malvern Zetasizer Nano. The analyses were performed on samples with original concentrations without any pretreatment of the colloidal suspensions. The back-scattering geometry (scattering angle = 173°, HeNe laser with 3 mW output power at a wavelength of 632.8 nm) allows measurements at high sample concentration, since complete penetration of the incident light through the sample was not required.

**Chemical Analysis.** The chemical composition of the samples was determined by X-ray fluorescence (XRF) spectroscopy with a MagiX PHILIPS PW2540.

**Nuclear Magnetic Resonance (NMR) Spectroscopy.** 29Si MAS NMR spectra were recorded on a Bruker Avance 400 (9.4
T) spectrometer using 4-mm-outer diameter (OD) zirconia rotors and a spinning frequency of 12 kHz. A single pulse excitation (30° flip angle) was used with a recycling delay of 30 s. The $^{29}$Si resonance of tetramethylsilane (TMS) was used as a chemical shift reference. The chemical composition of the samples was determined using the Engelhardt and Michel equation.

$N_2$ Sorption Analysis. Nitrogen adsorption/desorption isotherms were measured using Micrometrics Model ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 523 K under vacuum overnight prior to the measurement. The external surface area and micropore volume were estimated by alpha-plot method using Silica-1000 ($22.1 \text{ m}^2 \text{ g}^{-1}$ assumed) as a reference. The micropore and mesopore size distributions of solids were estimated by nonlocal density functional theory (NLDFT) and Barrett–Joyner–Halenda (BJH) methods, respectively.

The skeletal density of the solids obtained after different crystallization time was determined with a Micromeritics Model ACCUPYC 1330 pycnometer, using helium gas (99.995% purity).

■ RESULTS AND DISCUSSION

The triangular crystallization field diagram for the $xNa_2O:1Al_2O_3:5.15SiO_2:yH_2O$ system was constructed by varying the concentrations of $Na_2O$ and $H_2O$ (see Figure 1).

![Figure 1](link)

Figure 1. Triangle diagram representing the crystallization fields of the phases formed from the system $xNa_2O:1Al_2O_3:5.15SiO_2:yH_2O$ at 303 K ($S$ = hydroxysodalite, $E$ = EMT-type zeolite, $X$ = FAU-type zeolite, $Am$ = amorphous phase).

In the systems under study, FAU-, EMT-, and SOD-type zeolites and amorphous material were identified in the final products. Crystalline EMT-type zeolite was obtained in a restricted crystallization field bordered between $x = 18.3–18.8$ and $y = 240–640$ (see Figure 1). The duration of the experiments varied between 12 h and 44 h. This time interval was selected because only the amorphous phase was observed at early stages of zeolite formation, and for periods longer than 44 h, phase transformation was observed. The stability of EMT crystallites was relatively low, since the extension of the crystallization time over 44 h resulted in a partial transformation of EMT into SOD-type material. The optimal conditions for EMT growth were at $x = 18.5$ and $y = 240$, when pure ultrasmall crystallites were synthesized. The water content in the system was important not only to obtain the desired zeolite, but also to control the crystallization rate and metastability of the synthesized material. When the water content was increased to $y = 340$, still pure and highly crystalline EMT zeolite was obtained after 36 h, but it was rapidly converted to hydroxysodalite at longer crystallization times. Further increases in the water content ($y = 600$) resulted in a slower crystallization rate and the formation of a mixture of amorphous material and FAU- and EMT-type zeolites. The amorphous material is the dominant product, while FAU- and EMT-type zeolites were present in approximately equal amounts.

Since the crystallization field of EMT was clearly identified, we have used the optimized precursor system (18.45Na$_2$O:1Al$_2$O$_3$:5.15SiO$_2$:240H$_2$O) to study the crystal growth kinetics. As previously mentioned, the interest in this material is due to very open structure and large pores. In addition, the well-defined crystal habit and ultrasmall size have an important impact on the performance of zeolite materials in different applications. Careful analysis of the system is also a part of our efforts to shed more light on the nucleation and growth of EMT zeolite, which is indispensable if the goal is the controlled formation of zeolite materials.

The initial precursor suspensions (5 and 60 min), the intermediates (8, 16, 20, and 28 h), and the final crystalline (36 h) product were characterized by a set of complementary methods. Alumina- and silica-containing initial solutions were water-clear, whereas after their mixing, a turbid colloidal suspension was obtained after 5 min of stirring at 277 K. The aluminosilicate solid extracted from that suspension prior to treatment was completely amorphous, according to XRD (see Figure S1 in the Supporting Information). This suspension
contains amorphous particles that developed over the time of stirring (see Figure 2). Several minutes after mixing the two initial solutions, the suspension consisting of isometric particles embedded in aggregates with random shape and a morphology that is not well-defined is obtained (see Figure 2a). Upon longer (60 min) mixing, the aggregate disappeared and only well-defined particles relatively uniform in size are obtained. Some of the particles display straight edges, suggesting some level of organization (Figure 2b). Interestingly, these nanoparticles exhibit size and even morphology similar to that of the final EMT crystallites.

Neither the initial suspension stirred for 60 min nor the solid subjected to hydrothermal treatment at 303 K for 8 h showed any level of long-range order (see Figure 3a). The samples were carefully inspected by TEM, but no evidence for short-range order was found (see Figure 4). Hence, the morphological features of EMT precursor particles cannot be associated with crystalline organization, at least at the level of available analytical methods.

The formation of initial gel particles should be considered in the light of initial alumina and silica sources employed. Both of them provide monomeric or low-weight species. Slow mixing of the two solutions at very low temperature (277 K) decreased the noncontrolled polymerization of aluminosilicate species, and thus the formation of relatively small in size gel particles is stimulated. As a consequence, small isolated gel particles are formed, which ensure the fast exchange between solid and liquid phase and uniformity of the reaction in the system.30 Another important issue is the low crystallization temperature (303 K), which limits the Ostwald ripening. First evidence for high range order in the solid was observed after 16 h of hydrothermal treatment, when the most intense peak of the EMT-type zeolite appears in the XRD pattern (Figure 3b). The peak was broad, revealing the small size of crystalline zeolite domains. The nanoparticles do not change their size and morphology; just crystalline fringes appear in some of the particles (Figure 4a), while others remain completely amorphous (see Figure 4b and Figure S2 in the Supporting Information). Upon heating to 20 h, the crystallinity slightly increases but the amorphous phase still dominates the solid. The broadening of the Bragg peaks is significant, indicating that the crystals are very small. The extension of crystallization time to 36 h provided fully crystalline EMT-type material (Figure 3e). The product was homogeneous, comprising hexagonal plate crystals 6−15 nm in size (see Figure 4c). The crystals are similar in size, but they differ slightly in morphology. Some of the particles, although fully crystalline, retained the morphology of the initial amorphous particles. At the same time, well-shaped hexagonal plates with characteristic EMT-type zeolite morphology can be seen (Figure 4d).

The size of the particles in the amorphous and crystalline suspensions was also measured by DLS. The particle size...
The external surface area of the sample is 85 m² g⁻¹ observed by TEM and DLS. The sample obtained after 8 h of hydrothermal treatment exhibits a slightly higher external surface area (105 m² g⁻¹) (see Table 1). Higher external surface area is measured for the sample after 16 h of hydrothermal treatment (121 m² g⁻¹). The increase of the external surface area is coupled with the first evidence for the presence of micropores (0.02 cm³ g⁻¹) in the sample. Low micropore volume matches well with the very low crystallinity according to the XRD analysis (see Figure 3b). A substantial increase in the micropore volume (0.11 cm³ g⁻¹) is observed after 28 h of synthesis (Table 1). It should be mentioned that the increase of the total pore volume is primarily related to an increase in the textural porosity. The isotherm of the sample that was treated for 28 h exhibits a clear uptake at low relative pressure, which is characteristic for microporous zeolite-type materials (see Figure 6). Further increases in the micropore volume were observed in the sample collected after 36 h (0.15 cm³ g⁻¹) (Table 1). In a typical Type I isotherm, the uptake at low relative pressure is followed by horizontal adsorption and desorption branches. However, in the case of nanosized EMT-type samples, the isotherms were inclined with the increase in partial pressure and terminated with a large hysteresis loop (Figure 6). These particularities of the isotherms are obviously related to textural porosity.

### Table 1. External Surface Area, Micropore, Mesopore, and Total Pore Volumes of the Solid Samples Obtained for Different Crystallization Times

<table>
<thead>
<tr>
<th>sample</th>
<th>external surface area (m² g⁻¹)</th>
<th>micropore volume (cm³ g⁻¹)</th>
<th>mesopore volume (cm³ g⁻¹)</th>
<th>total pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 h</td>
<td>105</td>
<td>0.00</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>16 h</td>
<td>121</td>
<td>0.02</td>
<td>0.81</td>
<td>0.83</td>
</tr>
<tr>
<td>20 h</td>
<td>130</td>
<td>0.04</td>
<td>0.89</td>
<td>0.85</td>
</tr>
<tr>
<td>28 h</td>
<td>180</td>
<td>0.11</td>
<td>0.60</td>
<td>0.71</td>
</tr>
<tr>
<td>36 h</td>
<td>220</td>
<td>0.15</td>
<td>0.67</td>
<td>0.82</td>
</tr>
</tbody>
</table>

However, the width of the particle distribution curves decreases with increasing crystallization time, which proves the formation of small, more-isolated particles in the crystalline suspension. Two peaks in the particle size distribution curves are measured only in the suspension treated for 8 h: one is centered at 8 nm and the other, with lower intensity, appears at 20 nm. As the crystallization time increased, the second peak disappeared, which is consistent with the observation that particles with similar sizes are present in the suspension. The DLS results suggest also that the crystal growth at low temperature involves the transformation of primary amorphous particles to crystalline EMT-type material without substantial changes of their crystal size. This observation can be explained with reorganization of the gel structure under interactions with the liquid media and without reduction or increase of the size of primary particles. Thus, the size of gel particles predominates, to a great extent, the size of the EMT zeolite crystals, which is also consistent with the TEM observations.

In summary, the ultimate size and the shape of the particles are almost constant during the entire process of hydrothermal treatment. The growth of the EMT-type zeolite at the expense of the amorphous solid is completed within 36 h at 303 K. Further treatment at this temperature results in the partial transformation into hydroxysodalite (see Figure S3 in the Supporting Information). The full crystalline sample (36 h) after drying is shown in the SEM images (see Figure S4 in the Supporting Information). As can be seen, the ultrasmall crystals tend to form agglomerates while drying; however, the individual particles are loosely attached and easily distinguished.

The development of the crystalline EMT phase is related to the chemical and physical changes of the gel particles. Although the TEM investigation did provide indication for substantial changes in the morphology of the precursor particles after 60 min stirring at room temperature, their characteristics have been studied by N₂ adsorption (see Figure S5 in the Supporting Information). The adsorption–desorption isotherm of the aluminosilicate precursor was Type III, which is characteristic of nonporous material. The hysteresis loop at high partial pressure (P/P₀) reveals the presence of textural mesopores. The external surface area of the sample is 85 m² g⁻¹, which is in good agreement with the small size of the amorphous particles observed by TEM and DLS. The sample obtained after 8 h of hydrothermal treatment at 303 K.

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**Figure 5.** Dynamic light scattering (DLS) curves of suspensions after (a) 8 h, (b) 16 h, (c) 20 h, (d) 28 h, and (e) 36 h of hydrothermal treatment at 303 K.

**Figure 6.** Nitrogen adsorption–desorption isotherms of the samples after (a) 8 h, (b) 16 h, (c) 20 h, (d) 28 h, and (e) 36 h of hydrothermal treatment at 303 K.
respectively. Besides the characteristic EMT-type zeolite micropores (0.73 nm), mesopores with a relatively narrow pore size distribution centered at 30 nm are measured (see Figure S6 in the Supporting Information). The results from nitrogen sorption for the series of samples are in a good agreement with the XRD and TEM data. As the crystallinity of the samples increased, an increase in micropore volume was recorded. The prolongation of crystallization time over 36 h resulted in a decrease in micropore volume and specific surface area, because of the transformation of EMT-type zeolite in hydroxysodalite. As known, the N$_2$ molecule is too big to pass through the small windows of the sodalite structure.

Besides morphological changes, the evolution of the solid phase from amorphous to crystalline EMT-type material is related to changes in the density. Generally, the framework density decreases when a solid is built of large open rings, which is the case for zeolitic materials. The skeletal density of the solids obtained after mixing of the initial reactants (60 min) and low-temperature hydrothermal treatment for different crystallization times was measured using helium (see Figure S7 in the Supporting Information). The density of the initial gel and that of sample treated for 8 h at 303 K are similar (≈2.70 g cm$^{-3}$). After 14 h of hydrothermal crystallization, a gradual decrease in the density is observed as the lowest value (2.09 g cm$^{-3}$) is reached after 36 h. Thus, the framework density measurements of the intermediates are in a good agreement with N$_2$ sorption and XRD analysis of the samples. However, according to density measurement, the samples obtained after 16 and 20 h of hydrothermal treatment possess close characteristics, which was not highlighted by the other analyses. Our interpretation of this result is that, at this stage (16 h), important changes occur in the solid phase, leading to a decrease in the framework density; however, long-range order in the zeolite structure is still not achieved and, thus, could not be detected by diffraction methods.

The morphological and structural changes described in the previous section are, without any doubt, related to the chemical reactions that occur in the system. According to the chemical analysis, the Si/Al ratio in the solid phase changed from 1.39 in the initial gel to 1.17 in the ultimate crystalline product. This information, however, is not sufficient to follow the mechanism of the crystallization process. In order to understand the intimate reactions between silica and alumina species in the system under investigation, $^{29}$Si MAS NMR experiments were performed. The local environment of the Si atoms in the solid obtained after different crystallization time was analyzed (see Figure 7). The Si/Al ratio in samples was estimated according to the equation of Engelhardt and Michel:

$$\frac{\text{Si}}{\text{Al}} = \frac{\sum_{n=0}^{4} I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^{4} I_{\text{Al}(n\text{Al})}}$$

where $I_{\text{Si}(n\text{Al})}$ is the intensity of different Si$(n\text{Al})$ species, identified by decomposition of the $^{29}$Si MAS NMR spectra. A broad asymmetric signal is detected at $-84.7$ ppm in the sample after 8 h of treatment (Figure 7a). This band is composed of four different components, centered at $-82.8, -84.5, -88.0,$ and $-91.7$ ppm, which can be attributed to an amorphous phase and the Si(4Al), Si(3Al), and Si(2Al) coordinated species, respectively. The changes in the intensity of the latest three species were used for further calculation of the Si/Al ratio in the samples obtained after different crystallization times. According to other methods at this stage of the crystallization process, the solid does not contain a crystalline phase, and the Si/Al ratio is 1.37 (see Figure 8).

![Figure 7. $^{29}$Si MAS NMR spectra of the sample after (a) 8 h, (b) 16 h, (c) 20 h, (d) 28 h, and (e) 36 h of hydrothermal treatment at 303 K.](image)

![Figure 8. Variation of the distribution of Si$(n\text{Al})$ species ($n = 2, 3, 4$) and degree of crystallinity of samples hydrothermally treated for 8 h, 16 h, 20 h, 28 h, and 36 h at 303 K. The degree of crystallinity is calculated using the intensity ratio of the peak corresponding to the amorphous phase ($-82.8$ ppm) and the sum of all four peaks ($-82.8$ ppm, $-84.5$ ppm, $-88.0$ ppm, and $-91.7$ ppm).](image)
the increase of the ratio between different silicon environments, the amount of the amorphous phase (−82.8 ppm) decreased in the sample (Figure 7d). The changes in the Si/Al ratio cannot be explained only by rearrangement of the solid part of the system. Obviously, the observed changes in the Si environment are results of two parallel processes: (i) an extensive exchange between the solid and liquid components of the system, and (ii) rearrangement of the T (T = Si, Al) atoms in the solid particles. This process continues up to 36 h and finally leads to the formation of a fully crystalline nanosized EMT zeolite with an Al/Si ratio of 1.15. The $^{29}$Si NMR signal of the ultimate structure-directing agent is not employed. Thus, by tuning the chemical composition of the precursor suspension, temperature, and heating time, the preparation of ultrasmall pure EMT zeolite was achieved. This approach, that is, exploring the very early stages of zeolite formation to favor kinetically the nucleation of the desired zeolite and, thus, avoid the use of organic structure-directing agents might be applied to other zeolite types that, until now, have been obtained by means of organic-template-promoted crystallization.

Zeolite growth under low temperature conditions showed a peculiarly, namely, the transformation of primary amorphous particles into crystalline EMT-type material without substantial changes of their crystal size. This crystallization model includes reorganization of gel structure and extensive exchange with liquid media of the system, which supplies the growth of crystalline phase, without reduction of the size of primary particles. Thus, the size of gel particles predetermines, to a great extent, the size of the ultimate zeolite crystals that could be used to tune zeolite morphology.

From an environmental perspective, the synthesis reported in this work is also extremely beneficial, since the nanocrystals can be easily synthesized at low temperature without using any harmful compounds, scaled up, engineered, and regenerated. Therefore, the present synthesis approach offers exciting opportunities for both fundamental studies and potential industrial applications.

**CONCLUSIONS**

EMT-type zeolite was synthesized from organic-template-free system under low-temperature (303 K) hydrothermal conditions. In order to isolate the pure EMT-type zeolite, the synthesis of the precursor composition was combined with crystallization under very mild hydrothermal conditions that allowed fine control of nucleation kinetics. Thus, highly metastable Na-EMT-type zeolite is synthesized, which, under conventional hydrothermal conditions (∼383 K), would be easily transformed to more-stable zeolites if a specific organic structure-directing agent is not employed. Thus, by tuning the chemical composition of the precursor suspension, temperature, and heating time, the preparation of ultrasmall pure EMT zeolite was achieved. This approach, that is, exploring the very early stages of zeolite formation to favor kinetically the nucleation of the desired zeolite and, thus, avoid the use of organic structure-directing agents might be applied to other zeolite types that, until now, have been obtained by means of organic-template-promoted crystallization.

**ASSOCIATED CONTENT**

Supporting Information
This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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