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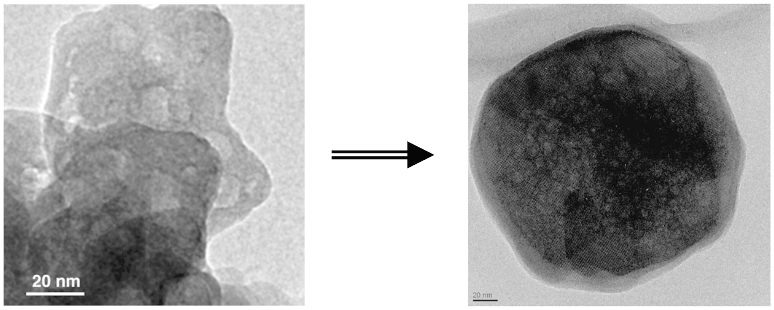

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Evidences for Zeolite Nucleation at the Solid−Liquid Interface of Gel Cavities

Valentin P. Valtchev*,† and Krassimir N. Bozhilov‡

Contribution from the Laboratoire de Matériaux à Porosité Contrôlée, UMR-7016 CNRS, ENSCMu, Université de Haute Alsace, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France, and Central Facility for Advanced Microscopy and Microanalysis, University of California, Riverside, California 92521

Received July 12, 2005; E-mail: Valentin.Valtchev@uha.fr

Abstract: The entire sequence of crystallization events, starting with formation of the initial organic-cation-free gel, proceeding through the zeolite nucleation stage, and finishing with complete transformation into LTA-type zeolite crystals, has been monitored by means of high-resolution transmission electron microscopy. Formation and development of voids, containing highly hydrated material transformed later into negative crystals, has been discovered in the solid part of the system. The evolution of these areas has been found to be an integral and noteworthy part of the chemical transformation of the gel that preceded the nucleation in the system. These void structures and, in particular, their solid−liquid interfaces have been identified as the specific locations where the formation of protozeolite nuclei took place. Further development of the system followed the classical for zeolite-yielding systems of crystallization that could be described by the autocatalytic model.

Introduction

Microporous zeolite-type materials are usually synthesized under hydrothermal conditions at relatively low temperatures and pressures. It is clear now that zeolite crystals are not formed via classical pathways, rather they follow much more complex routes that are far from well understood.[1−3] The difficulties in studying zeolite formation originate in its highly inhomogeneous nature and the interdependence of numerous parameters whose effects are difficult to evaluate in a straightforward manner.[4] Therefore, any new information concerning the events in the very early stages of zeolite formation, in particular, zeolite nucleation, is highly desired. It is accepted that the nucleation of microporous zeolite-type materials is heterogeneous; however, the spatial and temporal locations and topology of the nucleation events remain some of the most elusive problems to be resolved.

The complexity of the zeolite-yielding precursors often requires utilization of a very specific system in order to study a particular event. Lately, all new findings in the nucleation/crystal growth mechanism of zeolites have been based on investigations of a system yielding colloidal crystals. A characteristic feature of these systems is the presence of a limited number of well defined discrete amorphous precursor particles, which simplifies the interpretation of the results and decreases the probability for ambiguous conclusions. Such a clear solution containing only discrete gel particles has been employed to study the nucleation of tetramethylammonium(TMA)-containing LTA-type zeolite at room temperature.[5] The investigation allowed us to visualize by means of high-resolution electron microscopy the "birth" of zeolite nuclei, which emerged from the gel approximately in the center of each particle. A similar nucleation mechanism was observed at elevated temperature (90 °C) in the formation of a TMA-containing FAU-type zeolite, again from a clear solution containing discrete gel particles.[6] This particular case of zeolite nucleation could hardly, however, be generalized for all systems yielding zeolites. For instance, the nucleation of MFI-type materials from a clear solution is considered to result from an aggregation of preorganized units.[7,8] However, some later findings[9−12] are in serious disagreement with such a nucleation/crystallization scenario, and thus it is not generally accepted.

In contrast to the clear solutions, the conventional gel systems contain a large diversity of (alumino)silicate species, and the zeolite nucleation and crystal growth involve numerous simultaneous metastable equilibrium and condensation steps. The

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† Université de Haute Alsace.

‡ University of California, Riverside.

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crystallization in such systems has been described by the "autocatalytic nucleation" model, according to which the nuclei are formed in the gel and are liberated during its dissolution that promotes zeolite crystallization.[13,14] Further theoretical studies have revealed that this model can be applied successfully only to nuclei that are located near the outer surface of the gel particles.[15,16] The theoretical basis of zeolite nucleation would not be complete without the study of Nikolakis et al.,[17] which specifically addressed the nucleation in gel systems. In this contribution, the nucleation is treated as an interfacial phenomenon taking place at the boundary of the amorphous solid gel and the surrounding solution. This investigation has shown that the gel pore structure plays an important role in zeolite nucleation by controlling the interfacial area between the gel and the solution. In the present study, we provide HRTEM evidence for the effect of the gel structure on nucleation and localization of the initial zeolite A nuclei in a classical gel system free of an organic structure directing agent.

A number of studies addressing the mechanism of zeolite formation have been based on zeolite A yielding systems.[18−22] Such systems are particularly convenient for studying zeolite formation because of the relatively simple composition and rapid kinetics. In the present investigation, a very reactive gel system able to produce zeolite A at room temperature (RT) in less than 3 days was employed. This approach allowed us to study the zeolite formation with minimum invasive postsynthesis treatments and to track down the entire sequence of crystallization events. Although artifacts due to the sample preparation cannot be excluded, this approach provides reasonable protection of labile species during sample preparation.

Experimental Section

The composition of the gel-yielding zeolite A at room temperature was as follows: $12.0Na_2O:0.55Al_2O_3:1.0SiO_2:150H_2O$. The reactants used for the preparation of the gel were sodium hydroxide pellets (97%, Aldrich), sodium aluminate (54.3% Al_2O_3, 44.5% Na_2O, Riedel-de Haën), sodium silicate solution (14% NaOH, 27% SiO_2, Fluka), and distilled water. The initial mixture was stirred for 1.5 h and transferred in a polypropylene bottle. The sealed bottle was stored in an oil bath ($T = 25 \pm 1$ °C). Small aliquots of the mixture were taken at different periods of time. Prior to taking aliquots, the sample was shaken in order to disperse settled particles. The solid and liquid parts of the samples were separated by using a 0.1 μm filter (Bioblock). The solid was washed with distilled water and dried at room temperature.

A reference sample was synthesized from the same gel composition at 95 °C for 6 h. The solid was washed with distilled water and dried overnight at 80 °C.

The structural evolution of the gel species was tracked down with high-resolution transmission electron microscopy (HRTEM), in a FEI-Philips CM300 microscope in low-dose mode operating at 300 kV accelerating voltage, equipped with a LaB_6 electron gun, and EDAX energy-dispersive X-ray spectrometer (EDS). Samples were prepared by diluting the suspension of the reaction products in distilled water, ultrasonicating them, and depositing a drop onto Cu grids coated with a thin (5 nm thickness) holey carbon support film. To complement this study, scanning electron microscopy (SEM, Philips XL30 FEG), X-ray diffraction (XRD, STOE Stadi-P), infrared (EQUINOX IFS 55 BRUCKER), and ^{29}Si nuclear magnetic resonance (MSL 300 Bruker) spectroscopy were used. The specific surface area of the samples was analyzed by N_2 adsorption measurements (Micromeritics ASAP 2010) performed after outgassing the samples at 300 °C for 24 h.

The elemental analyses of the solids were performed on an X-ray fluorescence spectrometer MagiX (Philips). Prior to the analysis, the powdery sample was melted with $Li_2B_4O_7$ at 1300 °C. The resultant glass bead was analyzed under vacuum with a rhodium anticathode (2.4 kW). The mother liquor separated by filtration was further subjected to high-speed centrifugation ($g = 100000$) for 4 h (BECKMAN, Avanti J-301), decanted, and analyzed by atomic absorption spectroscopy (Varian Techtron AA6).

Results and Discussion

TEM Investigation. The aliquots taken from the initial system at different time intervals were analyzed by mutually complementing techniques, such as XRD, NMR, and IR spectroscopy, nitrogen adsorption, SEM, and TEM. Among them, HRTEM was used as the primary tool for direct observation of the events at nanometer scale. The TEM study showed that the mixing of the initial reactants resulted in the formation of an open network of large (500−3000 nm) nonuniform gel particles built up of globules with a diameter ranging between 20 and 50 nm (Figure 1A). The sample taken after the 6 h RT synthesis possessed a similar gel structure. However, the individual globules were larger in size and more densely packed, which probably is due to coalescence of several adjoining gel-like globules. Some of the globules developed inclusions of lower density which appear as bright spots in the interior of the gel-like globules (Figure 1B). Such inclusions have already been observed in a gel-yielding zeolite X (FAU-type) under ambient conditions.[23] On the basis of EDS analysis, electron diffraction, and contrast differences, these areas in the gel phase were interpreted as voids trapped in the amorphous gel mass and filled with highly hydrated or most likely liquid phase. The voids initiate the development of negative crystals, which is a term employed to describe faceted cavities inside solid materials or crystals filled with mother medium, which may be in the form of solution or gas.[24,25] In the case of zeolite X, such inclusions were observed immediately after mixing of the reactants, whereas in the present investigation, several hours aging at RT were needed to observe these structures. The difference in the kinetics of formation of the voids in both gels could most likely be attributed to the difference in the compositions of the two systems. The gel-yielding zeolite A was more concentrated and richer in alkali, which, without a doubt, plays an important role in the polymerization of aluminosilicate precursors. Despite the differences in the kinetics of formation, the fact that both gels contained analogous structures suggests similarities in the processes of the two systems. The possible role of these structures in the course of gel reorganiza-

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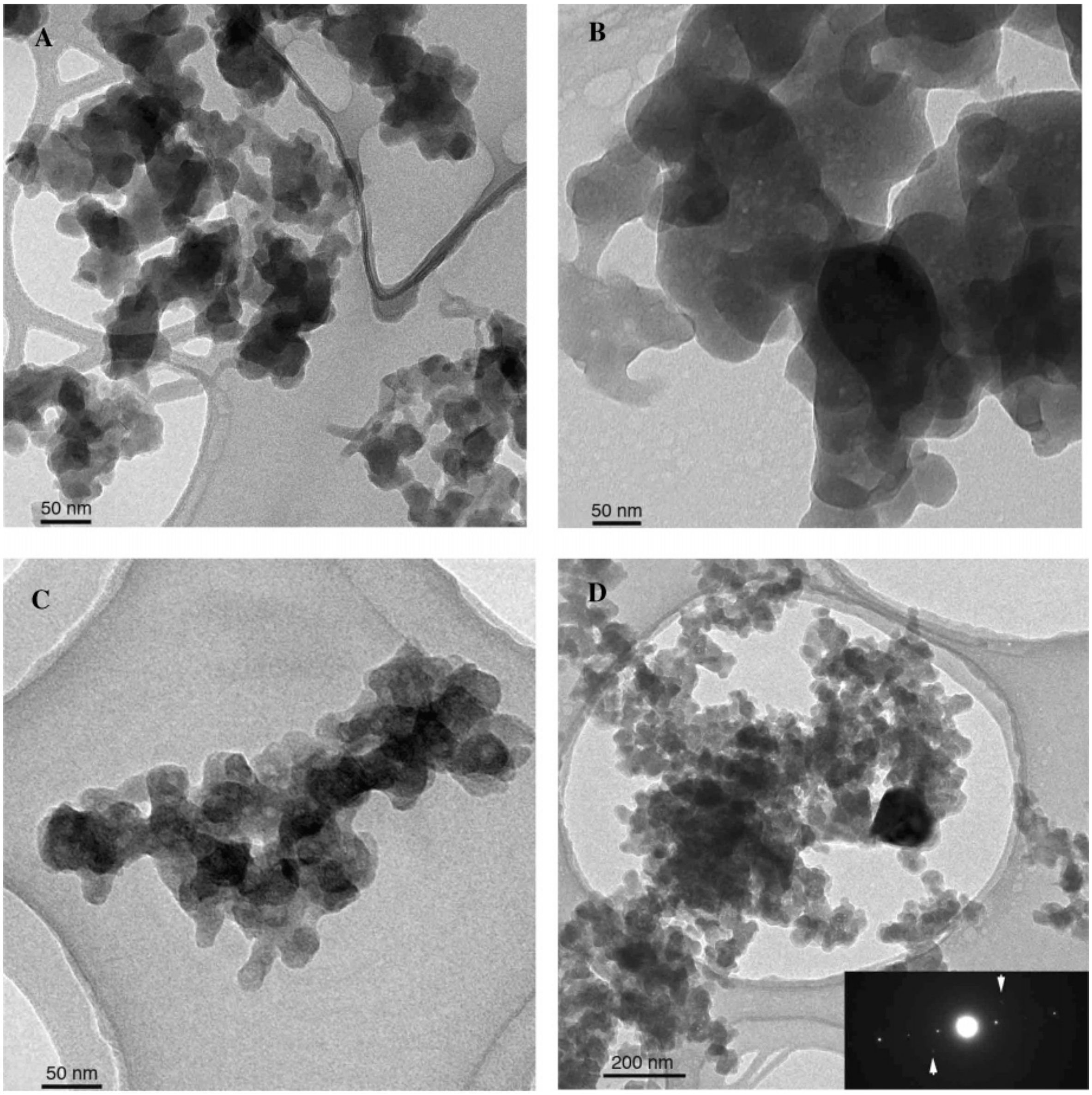

Figure 1. TEM micrographs showing the evolution of the structure of the solid precursor during the initial stages of gel transformation: after mixing of the reactants for 0 h (A), 6 h (B), and 21 h (C, D). As an inset in (D), a SAED pattern obtained from the same solid is shown. The reflections pointed by arrows correspond to the {800} planes of the LTA-type structure with *d* spacing of 3.0 Å. The row of reflections not marked are from the {002} family of planes of metastable α-Al(OH)$_3$ particles with *d* spacing of 4.4 Å, present in the first 21 h of synthesis.

tion was discussed in the study devoted to zeolite X formation without, however, convincing proofs to be provided. The aim of the present study was to elucidate the role of the negative crystals in the evolution of zeolite-yielding gels.

As can be seen in Figure 1, the number of voids has progressively increased with synthesis time. The 6 h aged gel contained mostly roundly shaped 3−5 nm voids (Figure 1B) and only a few bigger ones. After 21 h synthesis, the size of the bright-spot areas reached up to 10−20 nm (Figure 1C). Besides the number, a significant evolution in the size and morphology of negative crystals was observed. The curved outlines and the diffuse interface between the dense gel and the liquid inclusions were substituted by straight faceted boundaries. Closer views of negative crystals observed after the 6 and 21 h RT syntheses are shown in Figure 2. The change of the shape from curved to faceted is a direct proof that some reorganization has taken place at the dense gel−liquid inclusion interface. In other words, the straight outline of the interface suggests a periodicity and order typical of crystalline-type materials. This suggestion is supported by the detection of LTA-type material in the solid. Indeed, the selected area electron diffraction (SAED) pattern from the 21 h aged sample contained material with *d* spacings of 3.0 Å that corresponds to the {800} reflection from nuclei with the LTA-type structure (Figure 1D, inset). HRTEM imaging did not bring information about the exact location of the zeolite nuclei, which most probably was due to the fact that they are extremely unstable and collapse under the high intensity electron beam necessary for HRTEM imaging or they did not produce detectable contrast in TEM because they were fully embedded in the amorphous gel. Also present in all experiments from the first 21 h of synthesis are relatively large (100−400 nm) crystalline particles of metastable bayerite (α-Al(OH)$_3$) (Figure 1D and Figure 3 in the Supporting Information), which disappear completely during the later stages of growth. The fact that the aluminum hydroxides have been identified only by TEM and electron diffraction strongly

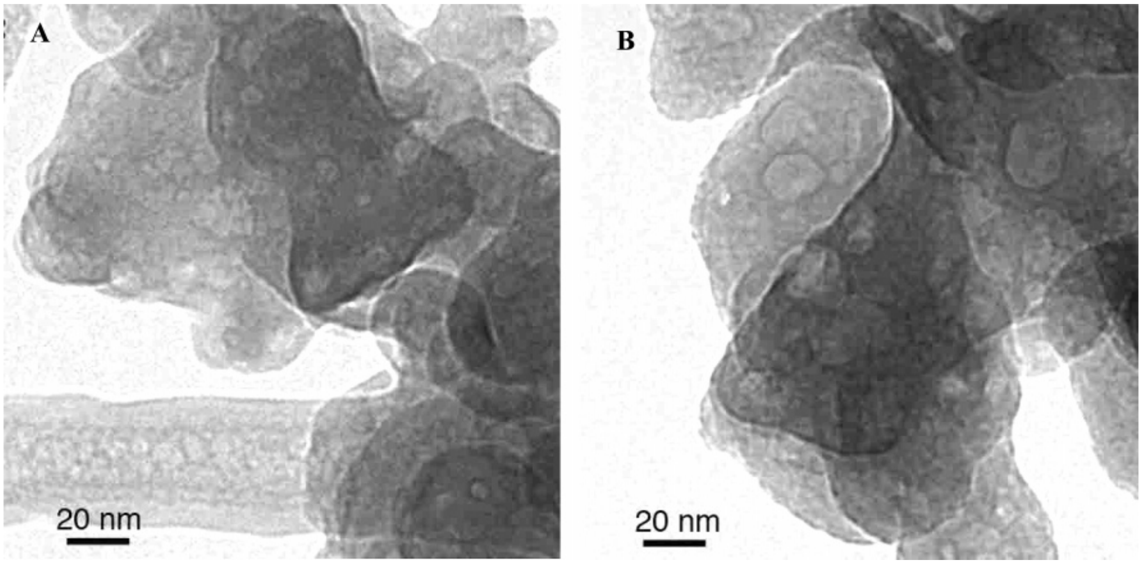

Figure 2. Close views of the gel structure after 6 (A) and 21 h (B) RT crystallization showing the evolution of the negative crystals.

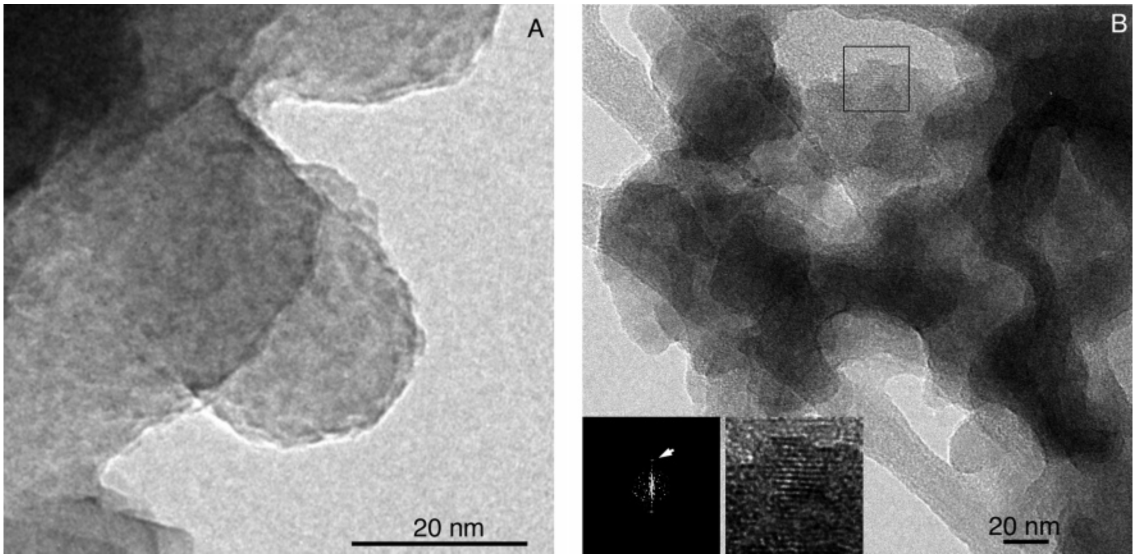

Figure 3. TEM micrographs of the product synthesized for 44 h showing a gel particle with faceted appearance (A). Zeolite A crystal formed at the interface of a cavity (B). As insets in (B), magnified view of the crystals and the lattice spacings resolved by HRTEM (left) and the corresponding FFT pattern revealing the 12 Å periodicity (right) are shown.

suggests that their total volume is relatively small, probably less than 3% since they have not been detected by XRD or NMR.

Further, the HRTEM showed that after 44 h RT crystallization the structure of the aggregates has changed in respect to the shorter durations. Large globular aggregates with open structure were replaced by smaller gel particles with more angular and faceted appearance (Figure 3A). It should be noted that during this stage the number of negative crystals decreased drastically. The disappearance of the larger aggregates and other changes in the gel structure are related, without doubt, to the dissolution and recrystallization of amorphous precursors. These processes have led to the formation of larger voids in the gel structure. In such a cavity, a 10−15 nm crystallite has been visualized (inset of Figure 3B). The lattice spacings resolved by HRTEM and the digital FFT of the lattice images correspond to a *d* spacing of 12 Å, characteristic of the zeolite A structure.

Complementary Studies. The first traces of crystalline LTA-type material in the powder X-ray diffraction pattern were observed in the 44 h experiment. Only the most intense peak corresponding to $d = 12.1$ Å was detected, which suggested that the amount of crystalline phase was close to the detection limit (3−4 wt %) of the XRD technique. However, this amount seems to be insufficient to record the structure-sensitive band (550 cm^{-1}) of LTA-type material in the IR spectrum of the sample. This band can be clearly seen in the spectrum of the 52 h sample, which can be considered the beginning of the crystallization period when the mass transformation of the amorphous precursor into crystalline LTA-type material took place. Similar results were obtained by ^{29}Si MAS NMR analysis, where little changes in the spectra of the samples aged less than 52 h were observed, namely, a slow decrease of the full width at half-maximum (FWHM) of the peak at about −89 ppm with the increase of the synthesis duration. Obviously, the NMR spectroscopy was not sensitive enough to describe the early stages of gel chemistry, which has already been reported by Shi et al.[26] The data obtained from all utilized methods of

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Table 1. BET Specific Surface Area (S_{BET}) of the Solids Obtained under Ambient Conditions

time, h	0	21	29	44	52	73	240	6[a]
S_{BET}, $\mathrm{m^2\,g^{-1}}$	6.5	9.1	12.7	26.0	50.3	85.6	29.8	3.1

[a] Reference sample was synthesized at 95 °C for 6 h.

analysis, however, are in agreement that the major part of the amorphous precursors was transformed into zeolite A between 52 and 73 h RT crystallization.

Surface and Chemical Analysis of Zeolite Intermediates. The events observed by HRTEM cannot be understood completely without a detailed analysis of the chemical evolution of the system and changes in the gel structure. Nitrogen adsorption measurements were used to study the latter since zeolite A in its sodium form does not adsorb the N_2 molecule, and thus the measured specific surface area (S_{BET}) corresponds to the external surface of the particles. The results are summarized in Table 1, where it can be seen that the S_{BET} increases progressively with synthesis time. During the first stage of the induction period (up to 29 h), substantial changes in the size and macromorphological features of the gel aggregates were not observed. Therefore, the increase of the specific surface area was mainly contributed to the short-range gel organization. This process was obviously a function of the chemical reaction taking place in the gel and the exchange between the solid and liquid parts of the system. Mesopore volume also showed an increase from 0.18 to 0.53 $\mathrm{cm^3\,g^{-1}}$ in the time interval 0−29 h, which was obviously due to the formation of gel cavities. After this period, the mesopore volume decreased, which was attributed to the gel dissolution and formation of cavities too large to be studied by N_2 adsorption. During the second stage of the induction period (29−52 h), the increase in the specific surface area is related to the decrease of the size of gel aggregates and formation of nanocrystallites. The mass transformation of the gel into crystalline nanosized material (52−73 h) decreased further the gel particle size and resulted in a $S_{\mathrm{BET}} = 85.6\ \mathrm{m^2\,g^{-1}}$. The prolongation of the synthesis time to 240 h had an opposite effect, that is, a substantial decrease of S_{BET} was recorded. During this period, the system entered the period of Ostwald ripening, when the crystals continued to grow at the expense of smaller and less stable crystals. After 3 days RT crystallization, the main population was 100−300 nm particles built of smaller crystals, whereas after 10 days, larger particles with size up to 700 nm were observed. It is worth mentioning also that the aggregated crystals dominated the 3 days product, while the solid obtained after 10 days contained, namely, individual crystals. The specific surface area of the 240 h sample was much smaller, suggesting a larger crystal size (Table 1), which was confirmed by the SEM observation (Figure 4A in the Supporting Information). The crystals, however, are still in the nanometer range (300−700 nm) and are much smaller than those of the reference sample (3−4 μm) synthesized from the same initial system at 95 °C for 6 h (Figure 4B in the Supporting Information).

Solid and liquid parts of the aliquots taken at different time intervals were subjected to chemical analysis. The trends were in good agreement, showing that the content of framework cations (Si and Al) increased in the solid and decreased in the solution with crystallization time. An opposite trend was observed in the behavior of sodium. The EDS analysis in the TEM at nanometer scale made obvious that the gel was highly inhomogeneous and local concentrations differed substantially from the global analysis (Figure 4). After some fluctuations during the induction period, the silicon and aluminum tended to reach a ratio typical of zeolite A (ca. Si/Al = 1). More surprising was the behavior of the structure-directing cation ($\mathrm{Na^+}$), whose content in the solid was extremely low at the beginning of the induction period and slowly increased with the evolution of the system (Figure 4). Although the sodium amount cannot be evaluated precisely by the EDS technique due to electron beam induced cation diffusion, the numerous analyses performed on each sample confirmed the trend. The examination of the results of the global and local analyses of the gel revealed the following: (i) during the polymerization of the aluminosilicate species, sodium was driven out of the gel; and (ii) at the beginning of the induction period, sodium was concentrated at the interface or in the close environment of the gel particles. The results of the EDS analysis coupled with the TEM observations suggest that sodium penetrates progressively in the solid matrix, breaking the gel structure and reorganizing the aluminosilicate species. Indication that formation of the negative crystals is directly related to sodium concentration is the fact that such structures were not observed in gel particles transformed into zeolite under the structure-direction effect of TMA cation.[5] It is difficult to imagine the reorganization induced by sodium without dissolution of the solid and transport via the solution. Hence, the increase of the sodium content in the solid part of the system is directly related to the structural transformation of the gel network observed by TEM. This complex process leads to local supersaturations, that is, to the conditions necessary for zeolite nucleation. It is worth recalling that the open highly hydrated structure of the gel allows sodium to penetrate in the volume of the amorphous particles, and its structure-directing effect is not limited only to the surface in contact with the liquid part of the system. Consequently, the chemical and structural evolution of the amorphous precursors spreads over the entire volume of the gel particles. Visual proofs for this evolution are the negative crystals observed in the gel, which increase in number and size with the increase of crystallization time. The formation of negative crystals is an important stage in the reaction process of the system, during which the reorganization of the gel structure leads to densification and, as a consequence, formation of liquid inclusions. As was pointed out above, the boundaries of a major part of

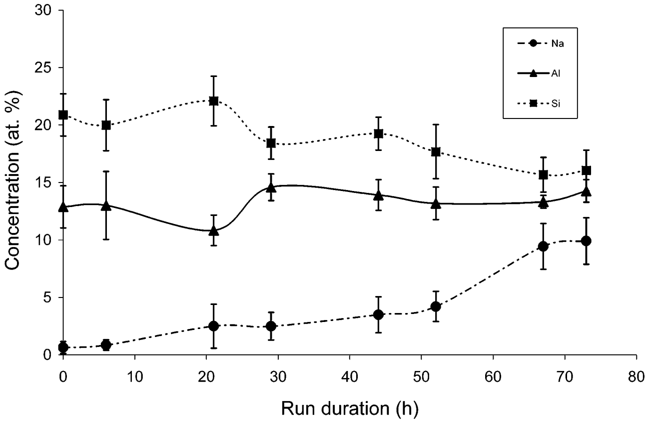

Figure 4. Average concentrations of sodium, aluminum, and silicon in the solid as a function of the synthesis time obtained by EDS analysis. Error bars represent one standard deviation of the analyses from the average. For each experiment between 14 and 16, analyses were performed.

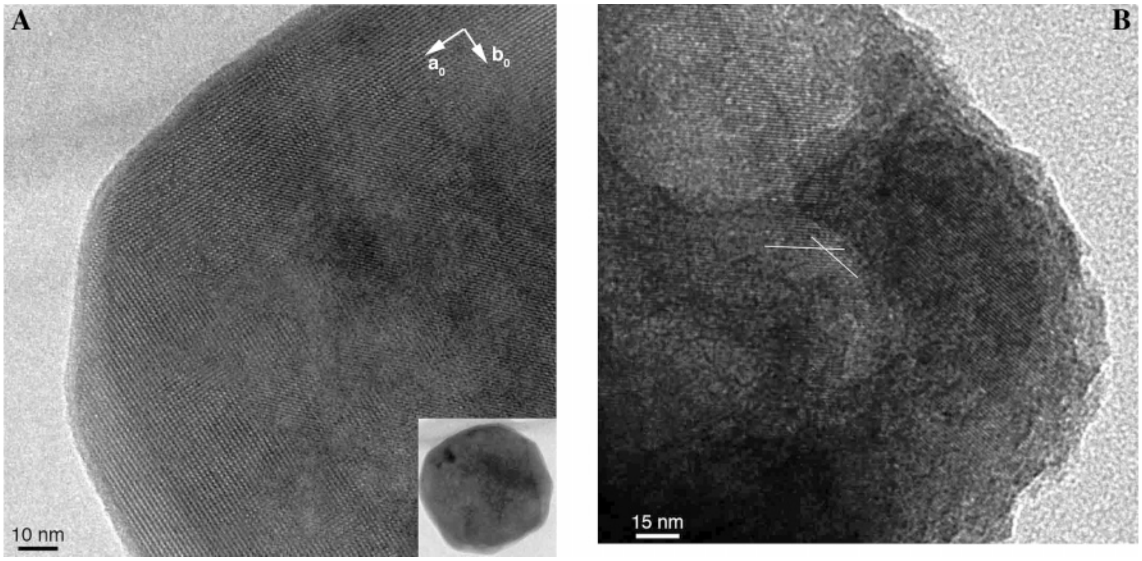

Figure 5. HRTEM images of an individual crystal (A) and an aggregate of intimately intergrown zeolite A crystals (B) observed in the 67 h product. The white lines show the orientation of equivalent lattice fringes for two different crystals in a region where the two crystals partially overlap. The lack of a pronounced contact plane and rational orientation between adjacent crystals exclude the possibility for the presence of contact or penetration twins.

the liquid inclusions became straight and faceted with the increase of synthesis duration. We consider these areas of a specific structural order as the protozeolite nuclei, which under favorable conditions develop into crystals. Two main factors, namely, chemistry and topology, determine whether any specific nucleus will become viable or disappear in the course of the crystallization. In other words, the supply of precursor material and the geometrical environment control this process.

The nucleation events observed during the formation of Na-A and TMA-A were somewhat different, which suggests differences in the structure-directing action of Na and TMA. As known, the size of hydrated Na cation and TMA is similar; however, the electronic characteristics differ substantially and thus their specific interactions with the aluminosilicate species. The amorphous precursor was progressively changed upon the effect of TMA and reached crystalline organization without visible long-range changes in the gel.[5] This process certainly includes changing of the Si−O−Al bond angles, local dissolution, and short-range transport. In contrast, the effect of Na on the gel network was much more pronounced, led to the above-described visible changes in the gel structure and eventually to the formation of zeolite protonuclei at the solid gel−liquid inclusion interface.

The studied crystallization process can be described by the autocatalytic nucleation model, according to which the nuclei are liberated from the gel and continue their growth in the liquid part of the system. Such a model suggests that each nucleus should produce one crystal. Indeed, the 67 h product, when some amorphous material was still present, contained well shaped zeolite A crystals (Figure 5A). On the other hand, a substantial part of zeolite forms aggregates of randomly intergrown crystallites (Figure 5B). Such type of intergrowth reveals a crystallization starting from different crystallization centers, which is typical of the transformation of a gel particle containing several viable nuclei. On the basis of this observation, a cohabitation of two crystallization mechanisms, growth from solution and progressive transformation of the gel phase, might be anticipated.

Conclusion

In summary, the room temperature synthesis approach allowed us to study the transformation of the amorphous zeolite A precursors with minimum invasive postsynthesis treatments. Although artifacts cannot be excluded completely, the gentle conditions and precautions taken during sample preparations make the TEM data as well as the complementary investigations reliable. Thus, the structure of the gel phase and its reorganization in the course of zeolite formation were followed with minimum alterations. Direct evidence obtained by high-resolution electron microscopy revealed the events preceding the zeolite A crystallization from an organic-template-free system. The process of nuclei formation includes the following main events: (i) formation of dense sodium-poor gel particles; (ii) slow penetration of sodium in the gel coupled with formation of liquid inclusions (negative crystals) with oval shape and diffuse and irregular borders; (iii) evolution of the liquid inclusions, that is, the boundaries became straight and faceted with the increase of synthesis duration; (iv) fusion of negative crystals and formation of larger cavities where the solid/liquid interface was situated the first zeolite A crystallite; (v) mass transformation of the precursor gel into zeolite crystals, providing individual crystals and complex aggregates. Thus, a direct relationship between the chemical evolution of the gel, its structure, and the appearance of the first zeolite A nuclei has been discerned. It should be underlined that the formation of negative crystals is an important stage of the gel reorganization, which led to formation of protozeolite nuclei at the solid−liquid interface of these structures. These findings, in particular, the nucleation events, are an experimental confirmation of the theoretical study by Nikolakis et al.,[13] which predicted that the gel microstructure plays an important role in zeolite nucleation.

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Supporting Information Available: XRD patterns of the samples synthesized for 44 h (A), 73 h (B), and 240 h (C); ^{29}Si

MAS NMR spectra of the samples synthesized for 21 h (A), 44 h (B), and 73 h (C); TEM micrograph (B) and indexed SAED pattern taken along the [101] axis (A) of bayerite crystals; SEM micrographs of the zeolite A crystals synthesized at RT for 10 days (A) and at 95 °C for 6 h (B). This material is available free of charge via the Internet at http://pubs.acs.org.

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