Imaging the Assembly Process of the Organic-Mediated Synthesis of a Zeolite

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Abstract: The mechanisms by which complicated structures assemble from atoms and/or molecules to macroscale entities are far from understood. Clear insights into the rules concerning complete assembly processes, whether they be organic, inorganic or hybrid organic–inorganic, are of general use. Here, we report on the assembly of the tetrapropylammonium-containing (TPA) pure-silica zeolite ZSM-5 (MFI), by monitoring in situ the processes that occur over scales spanning more than four orders of magnitude (0.17 nm – 6 μm). The combination of wide-angle, small-angle and ultra-small-angle X-ray scattering (WAXS, SAXS and USAXS, respectively) allows the direct imaging of the assembly process of the hybrid material TPA-MFI. It is shown that 2.8 nm entities, comprised of TPA and silicate, function as primary building units that aggregate to form structures up to 10 nm in size, which in turn form viable nuclei that initiate the growth of zeolite crystals. The nucleation mechanism of TPA-MFI thus involves ordering initially on the nanometer scale, followed by order at larger scales derived from the primary building units. The primary building units are specific for the crystal structure formed. The sequential formation of order from small (primary units), to medium (nuclei), to large scales (crystals) is consistent with other assembly processes, such as the construction of biological entities.

Keywords: crystal growth · nucleation · precursors · X-ray scattering · zeolites

Introduction

The elucidation of the mechanisms by which complicated macroscale objects self-assemble remains one of the most difficult challenges. Substantial efforts are currently underway to unravel the protein-folding problem, whose solution would provide a direct link between chemistry and biology. Likewise, pathways employed by living organisms to organise inorganic materials, such as bone formation and shaping, defy complete description at this time. Thus, there is a continuing need to understand the rules used for the formation of complicated structures. It is crucial to be aware that the assembly processes need not be the same over all scales.

The assembly of pure-silica zeolites by the use of organic molecules, which assist in the synthesis process and are accommodated in the final structures, is an example of an assembling hybrid system. Unlike inorganic materials that are formed in living systems (simple unit cells or building units in which the material is shaped over large scales), zeolites have extremely complicated unit cells. Additionally, there are no strong chemical bonds formed between the organic and inorganic fractions of the composite material; co-operative behaviour of weak interactions, such as Van der Waals forces, dictate the assembly process. Thus, isolation of intermediates is most likely to be destructive and only in situ observations are reliable. When an organic zeolite composite is synthesised, organisation on scales from sub-nanometer (organic molecule) to micron (final crystal) is important. Aside from the experimental difficulties that arise from the use of spectroscopic methods such as NMR, IR, Raman and UV/visible on zeolite reaction mixtures, these methods probe structures/interactions on a very small scale and can only provide information on one portion of the assembly process. Additionally, dynamic light scattering (DLS) can yield information over a larger scale region, but is subject to limitations when multiple-size populations exist or when large particles exist in high concentrations and when a heterogeneous gel phase is present. These difficulties are circumvented by the use of X-ray scattering. Small-angle scattering of X-rays and neutrons can provide information from scales between microns and Ångströms in a broad variety of systems, for example, in

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the structure of complex biological materials like wood and bone,[1] the microstructure of emulsions[2] and the evolution of the morphology and three-dimensional spatial arrangement of the precipitates during the decomposition of alloys.[3] However, many structures show variations on a broad range of scales and require a combination of techniques to be studied effectively. We used a combination of ultra-small-angle X-ray scattering (USAXS) and and simultaneous small-angle and wide-angle X-ray scattering (SAXS and WAXS, respectively) to continuously probe the extremely broad range of scales (0.17 nm – 6 µm) needed to monitor all precursors and products during zeolite crystallisation. The excellent X-ray sources at the Daresbury Laboratory and the European Synchrotron Radiation Facility were employed to allow in situ dynamic observations. We report on the assembly of Si-MFI from different synthesis mixtures with various structure-directing agents and silica sources as detected by these techniques. We present evidence that 2.8 nm primary units are the key intermediates for the zeolite synthesis.

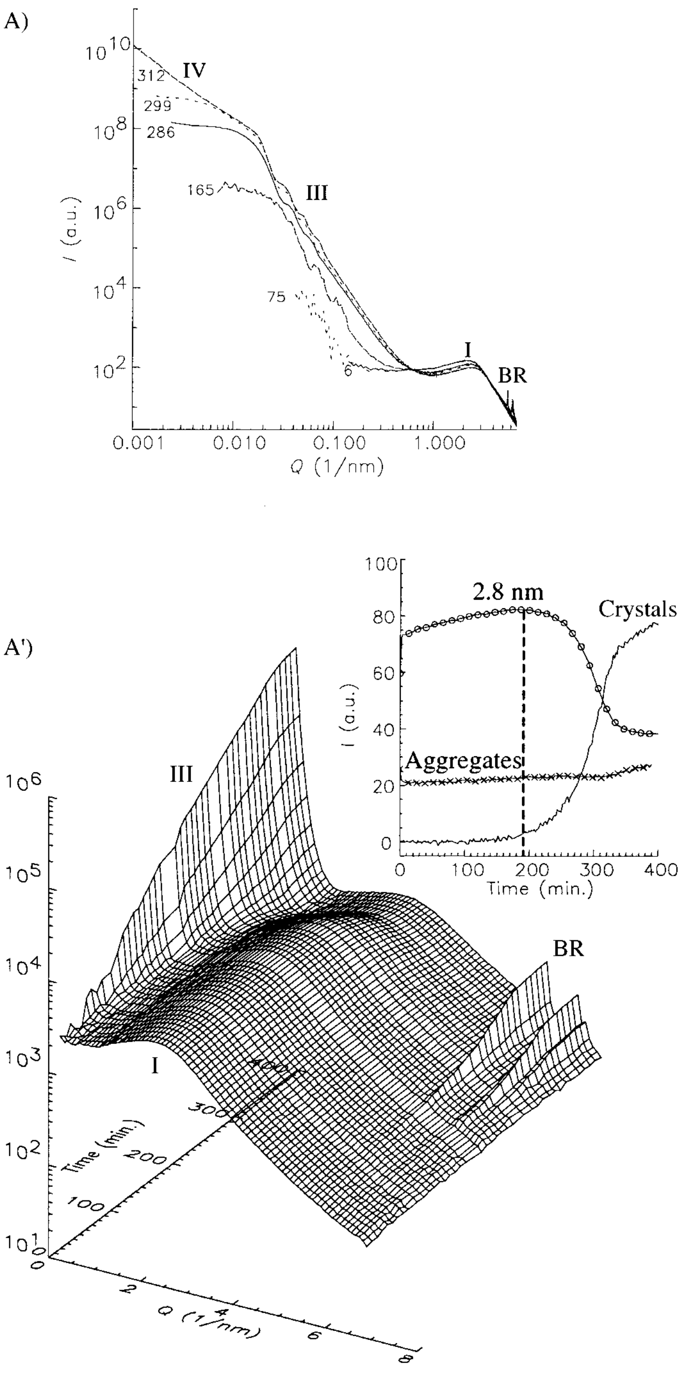
Experimental Section

Preparation of zeolite synthesis mixtures: Completely clear synthesis mixtures with chemical composition $x\,Na_2O$:1.22$(TPA)_2O$:10SiO_2:117H_2O were prepared with silicic acid as the silica source, as described elsewhere.[4] Here, x was varied to obtain Si/OH ratios between 2.12 and 3.02. For syntheses with bis-(tripropylammonium)hexamethylene dihydroxide (the dimer of TPA) and bis-(tripropylammonium-*N*,*N'*-hexamethylene)-*N''*,*N''*-dipropylammonium trihydroxide (the trimer of TPA), the ratio R/SiO_2 was maintained at 1.22:10 and 0.81:10 with $x = 0.848$ (Si/OH = 2.42). The synthesis temperature was 125 °C. Synthesis mixtures with TEOS as a silica source with chemical composition 4.5TPA_2O:25SiO_2:484.5H_2O:100EtOH were prepared as reported by Schoeman.[5] The ageing time between mixing the reagents and heating to the synthesis temperature of 125 °C was 24 h. The synthesis of Si-MFI from a heterogeneous gel phase with trimethylene-bis(*N*-hexyl-*N*-methyl-piperidinium) dihydroxide and tetraethylorthosilicate as the silica source with composition 10SiO_2:3.0 $R(OH)_2$:0.25Na_2O:350H_2O was performed at 160 °C, as described elsewhere.[6]

MFI/MEL intergrowth crystals were prepared at 125 °C from a synthesis mixture with the composition 0.55Na_2O:1.26$(TBA)_2O$:10SiO_2:150H_2O (TBA = tetrabutylammonium). Sodalite was crystallised at 110 °C from a solution with 0.55Na_2O:2.80$(TMA)_2O$:0.2Al_2O_3:10SiO_2:90H_2O (TMA = tetramethylammonium). Silicic acid was used as silica source and the preparation was that same as for Si-TPA-MFI.

Sample cell: To perform the in situ experiments, an electrically heated brass holder that contained a rotating round sample cell was designed. Rotation was necessary to keep the synthesis mixture homogeneous, since only a small spot near the centre of the cell was exposed to the X-ray beam. A rate of approximately two revolutions per minute appeared to be fast enough to prevent the premature precipitation of zeolite crystals. Two clear mica sheets (Attwater and Sons) were used as windows, with spacing provided by a Teflon ring (thickness 0.5 mm). The liquid sample could be heated under hydrothermal conditions up to 175 °C and contact between the sample and the brass cell was avoided during sample preparation and synthesis. The sample holder was heated from room temperature to a reaction temperature of 125 °C in only two minutes. This rotating cell was used for both the combined SAXS/WAXS and the USAXS investigation.

X-ray scattering measurements: The combined SAXS and WAXS experiments were performed at station 8.2 of the Synchrotron Radiation Source at Daresbury Laboratory (UK),[7] with a camera length of 0.8 ($0.4 < Q < 7\ nm^{-1}$) and 3.4 m ($0.1 < Q < 2.5\ nm^{-1}$) and position sensitive detectors.[8] The USAXS experiments were performed at the high-brilliance beamline ID2/BL4 of the European Synchrotron Radiation Facility in Grenoble (FR) with a Bonse-Hart camera type[9, 10] ($0.001 < Q < 0.3\ nm^{-1}$). A configuration with two analyser crystals was used, so no desmearing was necessary.[4] The scattering of water at the reaction temperature was used for the background subtraction.



Results and Discussion

The first event in the assembly of Si-TPA-MFI from a clear solution of TPAOH, SiO_2, NaOH and H_2O is the formation of particles with an average diameter of 2.8 nm (see Figure 1). These species, hereafter referred to as the primary particles, were monitored by in situ SAXS – WAXS and USAXS measurements. The existence of primary particles of this size has been previously reported by Schoeman,[5] but here, for the

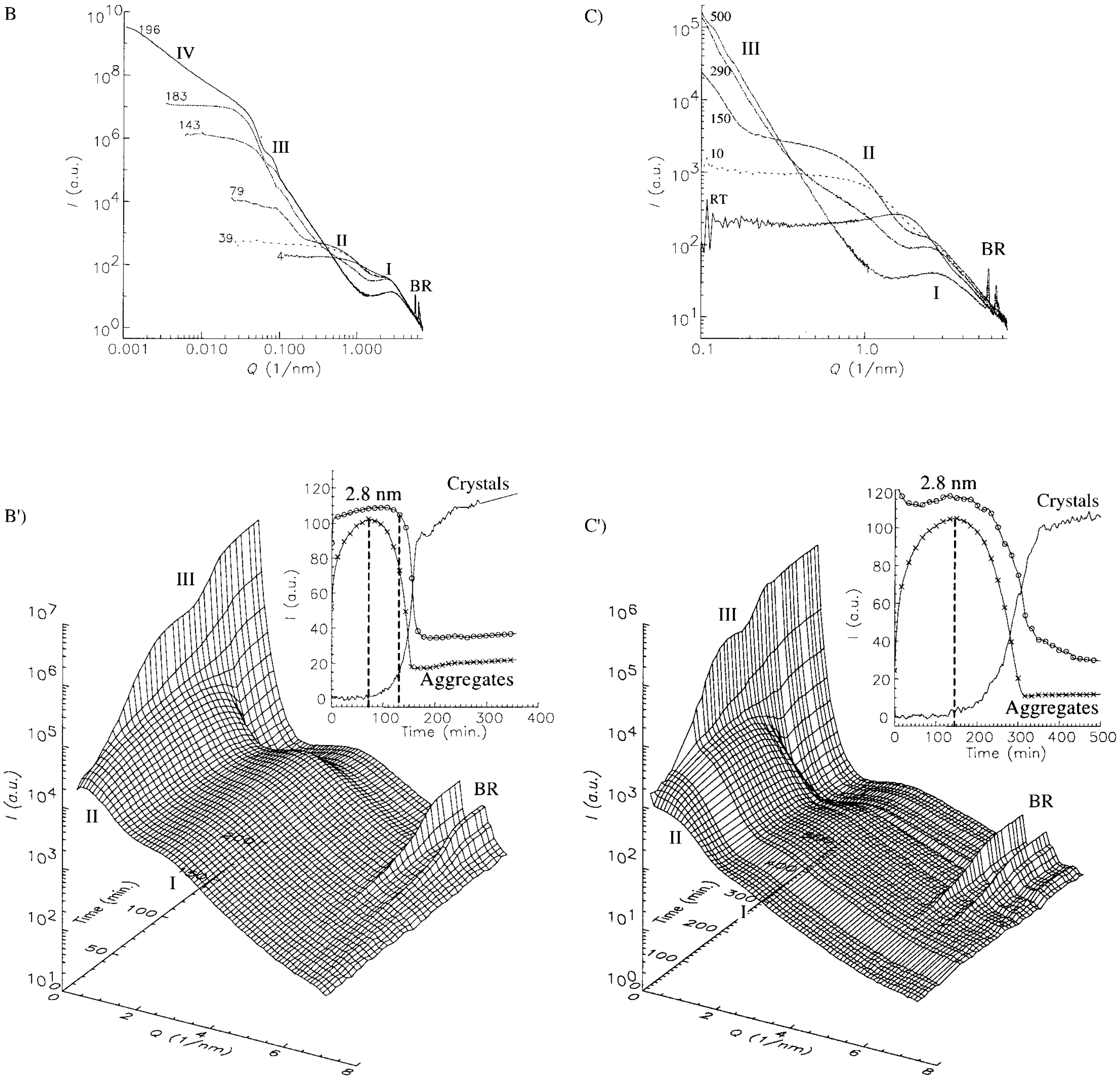


Figure 1. Time-dependent scattering curves for Si-TPA-MFI: A and A′: Si/OH = 2.42, B and B′: Si/OH = 3.02 and C and C′: Si/OH = 2.78 and TEOS as the silica source. The reaction times are denoted on the curves. Scattering particle types: **I** = primary units, **II** = aggregates, **III** = crystals, **IV** = crystal aggregates, **BR** = Bragg reflections. The inset figures on A′, B′ and C′ show the scattering intensity from the different particle populations and the crystallinity. The patterns at short reaction times in A, B and C do not extend to (very) small angles, since no (very) large structures are present in the sample, and so no excess scattering intensity was detected above the background.

first time, the specific time-resolved role of these particles in the assembly of long-range ordered materials is elucidated. IR spectra of these isolated composite species were obtained and showed a band at 560 cm^{-1}; this is interpreted to be indicative of five-membered silicate rings (also seen in the structure of Si-MFI zeolites). The samples were prepared by quenching the reaction mixture, which contained only the 2.8 nm particles, in liquid N_2 and freeze-drying or extracting the composite particles into an imiscible organic phase with subsequent evaporation of the solvent. This indicated that the TPA cations and silicate species interact in the primary particles and that the TPA cations affect the short-range ordering of the silicon atoms. Previously, Burkett and Davis showed by NMR that silicate species are in contact with TPA cations prior to the detection of long-range order by diffraction[11, 12] (the synthesis conditions were slightly different). ^{13}C NMR chemical shifts of composite species trapped by silylation were different from both free TPA cations in solution and TPA cations occluded in Si-MFI; this agrees with the data presented here in that the primary species are composites of TPA cations and silicate species that have not yet adopted the long-range order of Si-TPA-MFI. Finally, TPA cations have clearly been identified as being present in these primary particles.[5, 13]

The ability to simultaneously monitor a broad range of scales shows that primary units are converted into longer-scale entities in the nucleation process. The nucleation of Si-TPA-MFI is a two-step process: first nutrients must assemble into composite species, after which reorganisation and condensation reactions can form viable nuclei (we have observed crystals with the MFI structure type 8–10 nm in size by electron microscopy). The importance of the first step is shown by a series of experiments in which the formation of aggregates of primary units was changed by variation of the alkalinity of the synthesis mixture. In case of a relatively low alkalinity (Si/OH = 3.02) the formation of aggregates with a size of approximately 10 nm is facilitated (Figure 1B). At increasing alkalinity, the ability of the synthesis mixture to form such structures decreases, while there is no indication that particles larger than the 2.8 nm primary units are present at high alkalinities (Si/OH > 2.65).[14] Our time-resolved results show the correlation between the presence of precursors and the crystallisation behaviour. In the situation in which the primary units are the only precursors present, the onset of crystallisation coincides with the onset of the consumption of the primary units (Figure 1A′, vertical dotted line in inset). However, when aggregates are present (low alkalinity), the consumption of these aggregates coincides with the onset of the crystallisation process, while the effective consumption of the primary units starts significantly later (Figure 1B′, inset).

The growth curves of the crystals can be obtained from the scattering from the crystal surface at very small angles,[4] and show that the final size of the crystals is smaller in lower alkalinity conditions (Si/OH = 3.02), while the crystal-growth rate is independent of the alkalinity. Therefore, the faster crystallisation as observed from the area of the Bragg reflections (Figure 1B′, inset) is due to a higher rate of nucleation when the 10 nm aggregates are clearly present (Si/OH = 3.02). At high alkalinities (Si/OH = 2.42) the number of aggregates is sufficiently low that they cannot be identified from the scattering patterns; this is in agreement with the formation of a low number of viable nuclei and large crystals. At even higher alkalinities (Si/OH = 2.12) the rate of nucleation is extremely low and the primary units are the only precursors observable. The addition of a small number of Si-TPA-MFI crystals as seeds (mean diameter 68 nm) results in normal crystal growth and shows that entities for growth are present in the synthesis mixture even when nucleation is almost impossible. The correlation between the presence of aggregates of primary units and the rate of nucleation shows that the aggregation of primary units is an essential step in the nucleation process (see Figure 2), and that the formation of viable nuclei does not occur by the growth of the primary units by addition of ions from solution. When large numbers of aggregates are present (Si/OH = 3.02), a small fraction of these will transform into viable nuclei, while the remaining ones will dissolve owing to changing conditions brought on by the crystal-growth process.

Schoeman[5] monitored the early stages of Si-TPA-MFI formation by DLS. Three major differences in the reaction mixture compositions used by Schoeman and those reported here are that tetraorthosilicate was the silica source, ethanol was present in significant concentrations and no sodium cations were present. In order to make a direct comparison to Schoeman's previous results, the exact synthesis mixture was

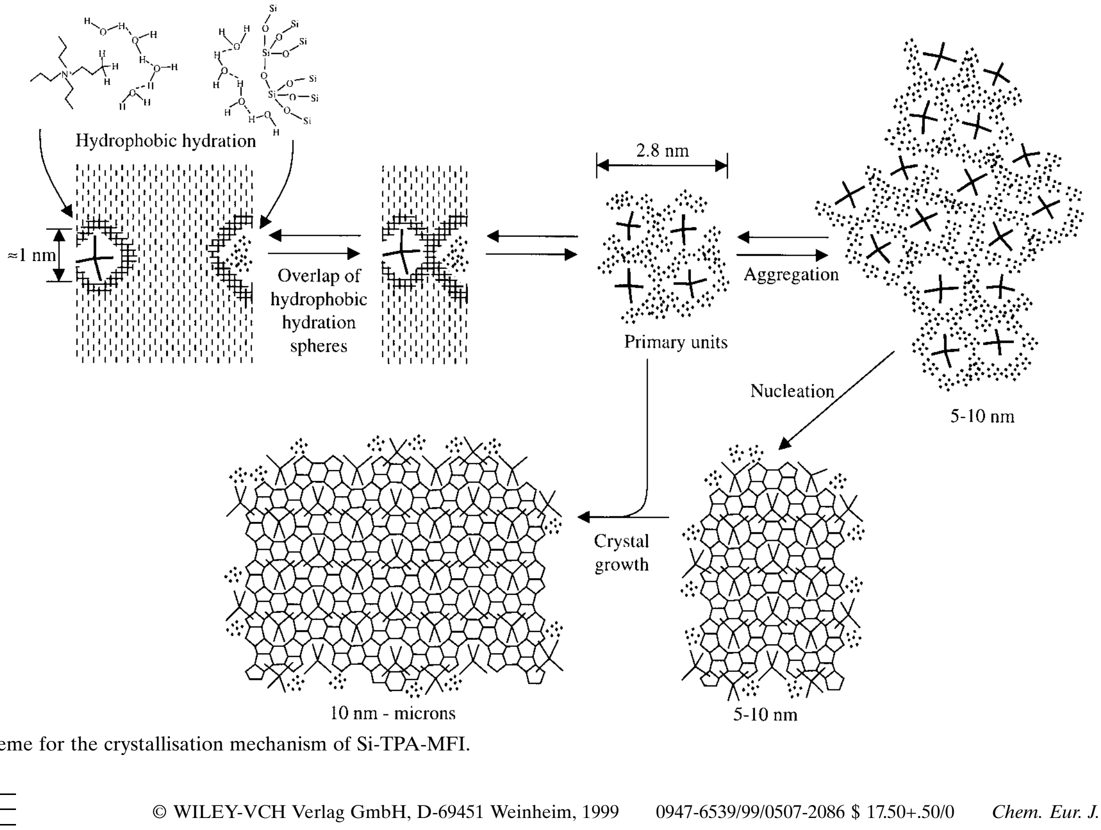


Figure 2. Scheme for the crystallisation mechanism of Si-TPA-MFI.

investigated here (Figure 1C). A higher reaction temperature of 125 °C was employed to increase the rate of formation owing to the limited, assigned synchrotron beamtime. The scattering pattern at room temperature shows 4 nm particles that, after heating, convert into two particle populations of 2.8 nm and ≈5 nm. For up to 150 minutes of heating, the 2.8 nm size remains and the ≈5 nm particles increase in size to ≈8 nm. These observations are in agreement with Schoeman's DLS results. From this point forward, our data reveal that the situation is more complicated and show a strong resemblance to our synthesis with silicic acid at Si/OH = 3.02 (Figures 1B and 1B′). These results clearly show the importance of following the full assembly process in situ and that our proposed mechanistic picture does in fact extend to the system investigated by Schoeman.

After the formation of the nanometer-sized viable nuclei, growth of crystals up to the micrometer range occurs. The scattering experiments show that the aggregates of the primary units do not participate directly in the growth process, since the linear crystal-growth rate is independent of their presence.[4] Figure 3 shows a HREM of MFI crystals prepared with the TPA dimer described below and the Fourier-filtered image[15] of this micrograph. Careful inspection of the microscopy data shows faulting with minimum domain sizes of approximately 2–4 nm. These data strongly suggest that the growth units are, in fact, the primary particles. Thus, when aggregates of primary units are present, they can dissolve back to smaller precursor particles and keep the concentration of the latter almost constant. This results in an almost constant scattering from the primary units in the case of low alkalinity until no scattering intensity from the 10 nm particles is observed.

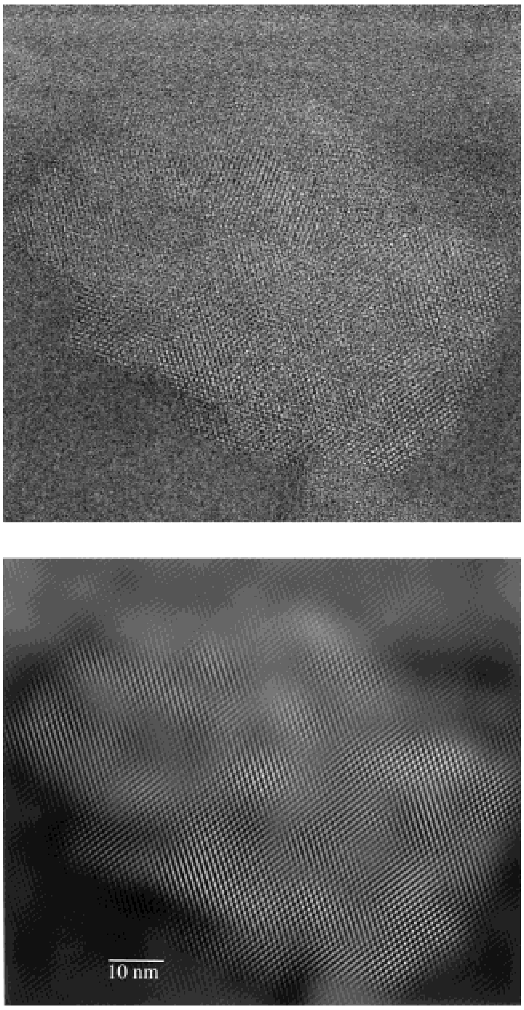


Figure 3. HREM (top) and Fourier-filtered image (bottom) of an Si-MFI crystal prepared from bis-(tripropylammonium)hexamethylene, the dimer of TPA, as the structure-directing agent.

When the linear growth of the Si-TPA-MFI crystals is complete, a sudden aggregation of the discrete crystals to structures larger than 6 μm occurs; this gives rise to the increase in scattering intensity at Q values lower than 0.02 nm^{-1} (see Figures 1A′ and 1B′). The mass-fractal dimension of 1.8 of these micrometer-scaled aggregates agrees with a diffusion-limited aggregation process. These structures have never been isolated and observed with techniques, such as electron microscopy, as a result of their vulnerability and the required sample treatment.

To demonstrate the specificity of the primary units for the crystalline structure formed, we used several organic molecules to direct the synthesis to the same crystal structure MFI (unit cell approx. 2.0 × 2.0 × 1.3 nm). Syntheses with the TPA$^+$ cation, a dimer of TPA and a trimer of TPA were performed from clear solutions with the same composition, with silicic acid as the silica source. Primary units with a size of 2.8 nm were found in all syntheses (Figure 4). The same precursor size was found when TBA cations were used to direct the synthesis to form MFI/MEL intergrowth crystals (unit cell approx. 2.0 × 2.0 × 1.3 nm). A completely different synthesis procedure in which a heterogeneous gel phase is present, with tetraethylorthosilicate as the silica source and a bis-piperidinium compound as the structure-directing agent known to

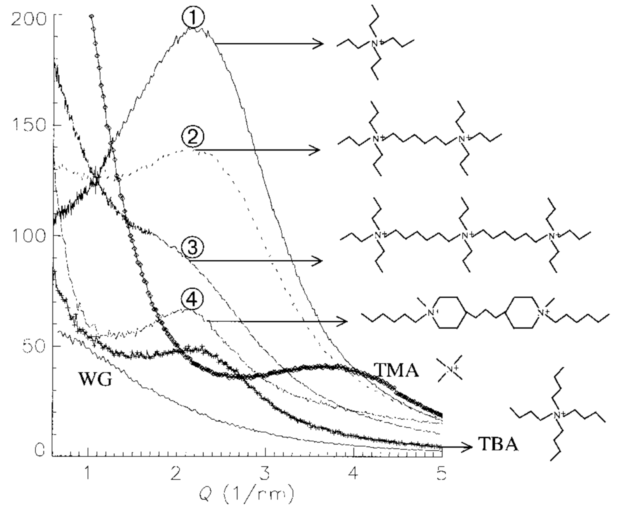


Figure 4. Scattering patterns for zeolite synthesis mixtures with different structure-directing agents (shifted vertically for comparison): **1** = TPA, **2** = bis-(tripropylammonium)hexamethylene, the dimer of TPA, **3** = bis-(tripropylammonium-*N*,*N*′-hexamethylene)*N*″,*N*″-dipropylammonium, the trimer of TPA, **4** = trimethylene-bis(*N*-hexyl-*N*-methyl-piperidinium), **WG** = water glass, no organics, **TBA** = tetrabutylammonium, **TMA** = tetramethylammonium. The diameter d of the particles can be determined from the peak maximum with the equation $d = 2\pi/Q$. The curves have been multiplied by arbitrary constants for ease of comparison.

produce MFI,[6] also showed the presence of 2.8 nm primary units. These data show that the formation of the primary units in these organic-mediated syntheses of MFI is independent of the structure-directing agent, alkalinity and preparation method. With the same reaction mixture that produces the heterogeneous gel phase for MFI, the organic additive trimethylene-bis(*N*-benzyl-*N*-methyl-piperidinium) gives either pure-silica zeolite beta or pure-silica zeolite ZSM-12.[6] The in situ scattering data for these syntheses show that the primary particle size for beta is 2.6 nm (unit cell approx. 1.3 × 1.3 × 2.4 nm) and 1.5 nm for ZSM-12 (unit cell approx. 2.5 × 0.5 × 2.5 nm). In another experiment, we synthesised zeolite sodalite (unit cell approx. 0.9 × 0.9 × 0.9 nm) with tetramethylammonium as the structure-directing agent in the presence of aluminium. Here the size of the precursors was 1.6 nm (apparent from the different position of the maximum in the scattering curves in Figure 4). Although the scaling between the unit cell size and the primary particle size is not perfect, there is clearly a correlation between the zeolite crystal structure and the dimensions of the primary particle. The scattering from a solution without organic molecules (no crystalline product) shows no formation of such precursors. These results lead to the conclusion that the primary units observed are indeed the entities that contain the order on a sub-nanometer scale needed for the construction of nanometer-scale order, that is viable nuclei.

Conclusions

Here, we have provided the first complete image of the nanometer-scale assembly process of an organic-mediated synthesis of a pure-silica zeolite. By monitoring a very large range of scales simultaneously, the pathways by which organisation is extended from the molecular scale to the crystalline scales is elucidated. First, the formation of nanometer-scale entities is observed, which are probably specific for the zeolite topology formed. These primary units have to form aggregates, which can transform into viable nuclei. Growth of the viable nuclei to macroscopic crystals can occur by addition of the primary units to the crystal surface. We believe that these mechanisms are not unique to the TPA-MFI system, but rather provide insight into the assembly of other complex systems.

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