Zeolites

DOI: 10.1002/anie.200604513

# Monitoring the Nucleation of Zeolites by Mass Spectrometry**

Stefan A. Pelster, Rainer Kalamajka, Wolfgang Schrader, and Ferdi Schüth*

The early stages of crystal formation are among the most elusive problems in zeolite science and possibly in all of solid-state chemistry.[1–4] This is largely because the nucleation step or nucleation phase causes major problems in experimental investigations, as the size of the aggregates most probably involved lies between small molecules and the extended solid.[5] Often-used techniques are NMR spectroscopy, diffraction, scattering with different types of radiation, transmission electron microscopy (TEM), and X-ray absorption spectroscopy. Each of these techniques reveals another "part of the puzzle" of the formation of a crystal from a precursor solution. In previous works we introduced electrospray ionization mass spectrometry (ESI-MS) as a suitable technique to investigate the oligomer distribution and its temporal development in prenucleating silicate solutions.[6–8] Herein, we extend this work to solution conditions, from which zeolite nucleation and crystallization occurs during the MS experiments. The results suggest that it is not single silicate oligomers that play a special role in zeolite formation, but that all silicate species present in solution act as a reservoir for the formation of a solid, finally crystalline phase.

We concentrated on the all-silica versions of ZSM-5 (MFI topology) and ZSM-11 (MEL topology), silicalite-1 and silicalite-2, respectively, which can both be crystallized from clear solutions. The formation of specific structures is directed by organic additives, tetrapropylammonium (TPA) in the case of the MFI structure and tetrabutylammonium (TBA) for MEL. It is unclear at which stage in the solid-state formation process the template ions exert their structure-directing effect and how this effect is actually brought about on a molecular level. There is strong evidence that crystalline structures are formed directly from colloidal particles that serve as a nutrient[9–11]—at least for some cases including silicalite-1 and silicalite-2. Other models involve the existence of small particles (below 10 nm) as crucial species in the formation of high-silica zeolites, although the further course of the reaction is again disputed. Aggregation of these particles to form crystals is the main aspect in some models,[12–14] but it has also been suggested that crystal nucleation and growth proceeds through the addition of monomers to smaller clusters.[15,16] Among the models that involve a particle-aggregation mechanism, there is disagreement whether the small entities that lead to zeolite formation have the same molecular structure and are essentially already small fragments of the zeolite framework, or whether they are only uniform in size and shape but disordered on the molecular level. The most specific model suggests one majority silicate species to be present in solution, which already exhibits the crystal structure of the final zeolite.[14] The other models would involve a rather broad variety of silicate species.[12,13] The results obtained with $^{29}$Si NMR spectroscopy on the silicalite-1 system are interpreted differently.[14,17]

We investigated nucleating silicate solutions leading to silicalite-1 or silicalite-2 under the structure-directing influence of tetra-*n*-propylammonium hydroxide (TPAOH) and tetra-*n*-butylammonium hydroxide (TBAOH), respectively, with ESI-MS. We applied dynamic light scattering (DLS) as an additional technique to monitor particle evolution in the range where ESI-MS fails (particle diameter $>1$ nm). The eventually formed solids were analyzed by X-ray diffraction (XRD) and TEM.

The condensation and oligomerization of the silicates were initiated by mixing tetraethoxysilane (TEOS) as the silica source and TPAOH or TBAOH as the template in water as the solvent. The clear solutions were aged for two days and afterwards heated to 92 °C. After certain time intervals samples were taken and examined by ESI-MS and DLS.

Figure 1 shows three different mass spectra of the TPAOH system that leads to silicalite-1. Prior to heating (24 h after mixing) a broad variety of silicate species are detected, the higher signals getting near to the upper limit of the instrument (*m*/*z* 2050). The highest signals could be attributed to a 32-mer, $Si_{32}O_{69}H_9^-$, whereas signals with lower intensity were observed for the well-known prismatic hexamer, $Si_6O_{15}H_5^-$, and the cubic octamer, $Si_8O_{20}H_7^-$. In between there are numerous species that emerge from each other by formally adding a $SiO_2$ unit (mass 60 Da). Many of those species have already been characterized in previous works.[7] Structural assignment of the higher-molecular-mass species, however, is not possible based on MS. A complete list of all detected species can be found in the "Supporting Information". Moreover, propoxylation of the major species is observed by the appearance of satellite signals at $(m/z)+42$. This finding can be attributed to gas-phase reactions in the mass spectrometer, which had previously been observed with solutions containing similar template molecules.[8] The degree of propoxylation increases with the mass of the silicates. The spectra thus seem to contain different interdigitated series of masses.

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[*] S. A. Pelster, Dr. W. Schrader, Prof. Dr. F. Schüth
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim (Germany)
Fax: (+49) 208-3062995
E-mail: schueth@mpi-muelheim.mpg.de

Dr. R. Kalamajka
Department of Life Sciences
Universitet Aalborg
Sohngaardsholmsvej 49, 9000 Aalborg (Denmark)

[**] Financial support by the Leibniz program of the DFG is gratefully acknowledged. We would like to thank H. Bongard for the TEM analysis.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

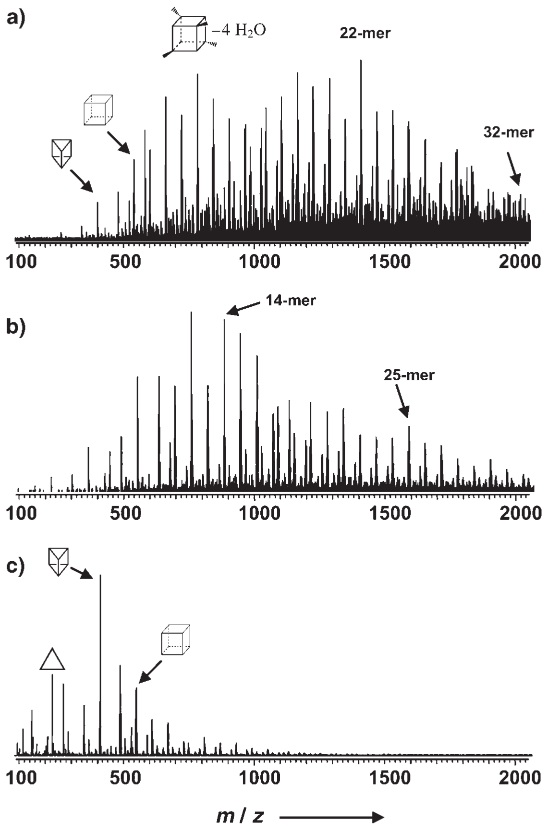

***Figure 1.*** Mass spectra of the TEOS–TPAOH–$H_2O$ system acquired immediately before (a), and after 6 h (b) and 61 h (c) of heating to 92 °C. Some of the silicate species are propoxylated. The polyhedra indicate the shape of the corresponding silicate oligomers.

Surprisingly, with proceeding reaction time a shift to smaller species can be detected, finally leading to the prismatic hexamer as the major silicate in solution. We noticed that the clear solution—obtained on passing the stage of opalescence after 12 h of heating—slowly turned milky after 15 h, thus indicating the formation of colloidal particles. However, these particles cannot be analyzed any more by ESI-MS. What is detected by this technique is in fact the distribution of the remaining silicate species in aqueous solution (about two-thirds of the total silicon content after synthesis, as estimated from $^{29}$Si NMR spectra). With reaction time this distribution is shifted toward smaller species. The formation of silicate colloids and zeolite crystals results in a decreasing silicate concentration in solution and depletion of the template species, which in turn causes the enhanced depolymerization of the remaining oligomers. This corresponds to earlier findings, according to which the tendency of the silicates to undergo condensation is decreased with decreasing concentration of soluble silicates.[7]

The mass spectra also show that at no time during the reaction—up to the upper *m*/*z* limit of the instrument—is there a highly prominent silicate species in solution, neither as a transient nor as a stationary species. Instead, we find a broad variety of different oligomers. The smaller species discussed by Kirschhock et al.[18] as crucial in the formation of the 33-mer (which itself is beyond the detection range of our instruments) do not seem to play a prominent role in solution. From these findings it appears that there is no distinct pathway leading to the silicalite-1 structure that involves highly specific silicate units, but rather the whole silicate pool acts as a reservoir for crystal formation and growth. Whether monomers or different oligomers are the nucleation and growth species cannot be decided on the basis of our results, as the interconversion processes between silicates in solution are fast in comparison with the timescale of zeolite formation.[19]

Simultaneously, particle growth was monitored by DLS (Figure 2). Prior to heating the detected particles have an average radius of 1 nm, which increases to 10–15 nm after 22 h. Finally, a broad size distribution of 10–40 nm is observed, which corresponds to the size of the crystals formed. These results are in good agreement with earlier findings.[11] When comparing ESI-MS and DLS data, it becomes clear that these two techniques analyze quite different species: ESI-MS detects species of up to about 1 nm size in aqueous solution, while light scattering yields information on colloidal and crystalline particles larger than 1 nm in diameter. Thus, the techniques perfectly complement one another.

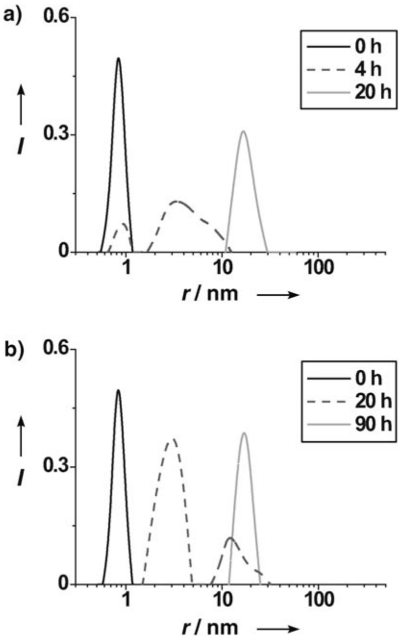

***Figure 2.*** DLS spectra of the TEOS–TPAOH–$H_2O$ (a) and TEOS–TBAOH–$H_2O$ (b) systems showing the evolution of the particle radius *r* after heating to 92 °C for certain times. *I* = light intensity.

To characterize the extracted solids at the end of heating (after 100 h) we applied XRD and TEM (Figures 3 and 4, respectively). The XRD patterns reveal a high degree of crystallinity and correspond perfectly to literature data for silicalite-1 synthesis.[20] We were able to determine the average diameter of the crystalline domains as 80–100 nm from the XRD line broadening using the Scherrer formula.

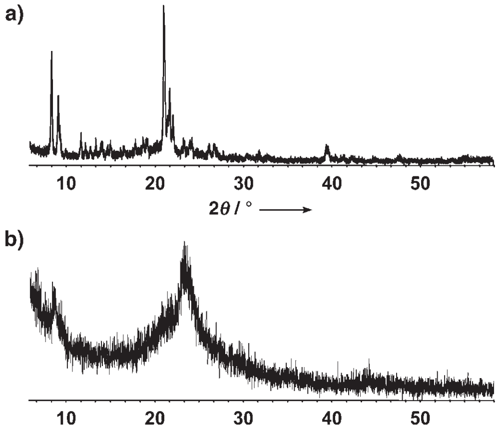

***Figure 3.*** XRD patterns of the extracted solids formed by heating of the TEOS–TPAOH–$H_2O$ (a) and TEOS–TBAOH–$H_2O$ (b) systems.

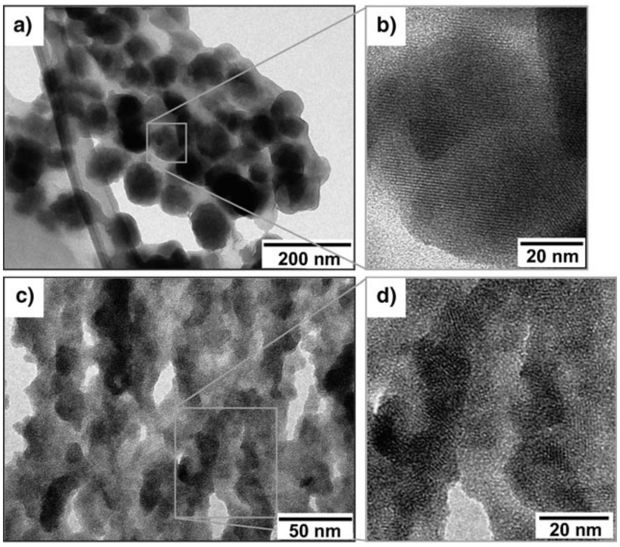

***Figure 4.*** TEM images of the extracted solids formed by heating of the TEOS–TPAOH–$H_2O$ (a, b) and TEOS–TBAOH–$H_2O$ (c, d) systems.

As is clear from the TEM images, the particles are uniform in size and shape and are well defined.

For comparison, we also studied the formation of solids from a synthesis mixture reported to result in the crystallization of silicalite-2, using TBA as a template. There is a remarkable similarity in the ESI mass spectra as well as in the data from DLS (see the Supporting Information). The detected species are essentially identical but the kinetics are different. Immediately after mixing, smaller silicate oligomers are observed than in the TPA system. Thus, the condensation reactions in the TBA system seem to be slower. It takes approximately 40 h before a distribution is reached as obtained in the TPA system after 3–6 h. The final oligomer distribution with species predominantly smaller than $m/z$ 500 is reached after about 50 h with TPA and after about 200 h with TBA. For TBA, the time until the onset of opalescence is 50 h, and precipitation was observed after 70 h of heating to 92 °C. Except for the different timescales, the DLS data also reveal a comparable particle growth when starting from a particle population of diameter 1 nm and resulting in a population of size 10–20 nm. The TEM investigation of the extracted solids at the end of the reaction shows the formation of crystalline structures with a size of 5–10 nm, as judged from the lattice fringes (Figure 4). From these images it could not be unambiguously determined whether the MEL structure had been formed. The very small domain size is also the reason why no clear reflections could be observed by XRD; the samples appear essentially X-ray amorphous (Figure 3 b). Only two very broad features corresponding to $2\theta$ values of about 7–8 and 23–24° (which correspond to a spacing range of 12.6–11.0 and 3.9–3.7 Å, respectively) are visible. In TEM, agglomerates of small crystalline domains (5–10 nm) could be detected, in agreement with other reports.[21]

In summary, we have investigated the nucleation stage of two different silicate systems that lead to silicalite-1 and silicalite-2, primarily by ESI-MS. During synthesis, the ESI mass spectra for both cases are remarkably similar and show a development toward smaller silicate species in solution, while simultaneously particle growth up to diameters of 40 nm (silicalite-1 system) and 20 nm (silicalite-2 system) can be detected by DLS. Only the timescales for the two systems were different, with the MEL system being slower. Significantly, no specific silicate oligomers dominating the solution population were detected at any stage of the solid-state formation process. This result suggests a pathway of particle formation via amorphous intermediates that would recrystallize, rather than a direct assembly process of defined silicate oligomers. The organic template molecules probably do not play a major role in the creation of defined oligomers, but they direct the crystallization of the primary solid, which is in line with observations of other workgroups.[22,23]

## *Experimental Section*

The two silicate model systems were synthesized by mixing the compounds in a ratio TEOS/template/$H_2O$ 1:0.36:18. After aging for 24 h at room temperature, the clear solutions were heated to 92 °C and samples were taken at certain time intervals. ESI mass spectra were recorded with a Waters ZMD quadrupole mass spectrometer with Z-spray alignment (capillary voltage 4 kV). A PD2000DLS instrument from PDI (scattering angle 90°) was used for DLS measurements. A mass normalization function was employed to obtain a concentration-normalized plot. TEM images of the extracted solids were recorded using a Hitachi 7500 microscope operated at 100 kV. XRD measurements were performed on a STOE Stadi P transmission diffractometer using $Cu_{K\alpha}$ radiation.

Received: November 3, 2006

**Keywords:** crystal growth · mass spectrometry · nucleation · silicates · zeolites

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