Zeolites

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Detection of Structural Elements of Different Zeolites in Nucleating Solutions by Electrospray Ionization Mass Spectrometry**

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Zeolitic materials are crystalline silicates, formed by corner-sharing TO_4 tetrahedra (T = Al, Si) with a regular array of microporous channels and/or cavities. This pore system, in combination with reactive intra- or extraframework species, is responsible for their unique properties and thus for their use in catalysis, chemical separation, and adsorption.[1] Their synthesis is directed towards a specific structure by the reaction conditions, the presence of structure-directing agents, often amines or organic ammonium salts,[2] or the introduction of specific heteroelements. For instance, zinc or germanium lead to the formation of new materials with a high fraction of three-ring (3R)[3] or double four-ring (D4R) units, respectively,[4] which are known to induce very open networks with large pore diameters.[5]

The formation of zeolites from solution occurs through a complex sequence of numerous reactions that are partly running in parallel. During these early steps, the final structure of the zeolite can be strongly influenced.[6] However, because of analytical limitations, little is known about the species occurring during these steps. Thus, various nucleation mechanisms have been proposed and are still controversially discussed in the literature.[7]

In previous investigations we have introduced electrospray ionization mass spectrometry (ESI-MS) as a powerful tool to investigate speciation and time-dependent oligomer distributions in silica solutions.[8,9] We have now for the first time succeeded in the identification of characteristic structural elements of three germanium-containing zeolites, that is, ZSM-5 (structure code MFI), polymorph C of zeolite Beta (BEC), and zeolite A (LTA), in the solutions immediately before nucleation.

Zeolite ZSM-5 and its pure silica form silicalite-1 (MFI) consist of two intersecting channel systems, limited by elliptical ten-ring (10R) openings.[10] Its germanium-containing, aluminum-free form was obtained by adding tetraethylorthosilicate (TEOS) to an aqueous solution, with germanium dioxide (GeO_2) as germanium source and tetrapropylammonium hydroxide (TPAOH) as organic template, and subsequent hydrothermal treatment. The speciation in solution was followed by ESI-MS. As TEOS hydrolyses immediately, the first mass spectrum was recorded one minute after combining the reactants. This spectrum is dominated by peaks corresponding to monomeric silicon (Figure 1 a) or germa-

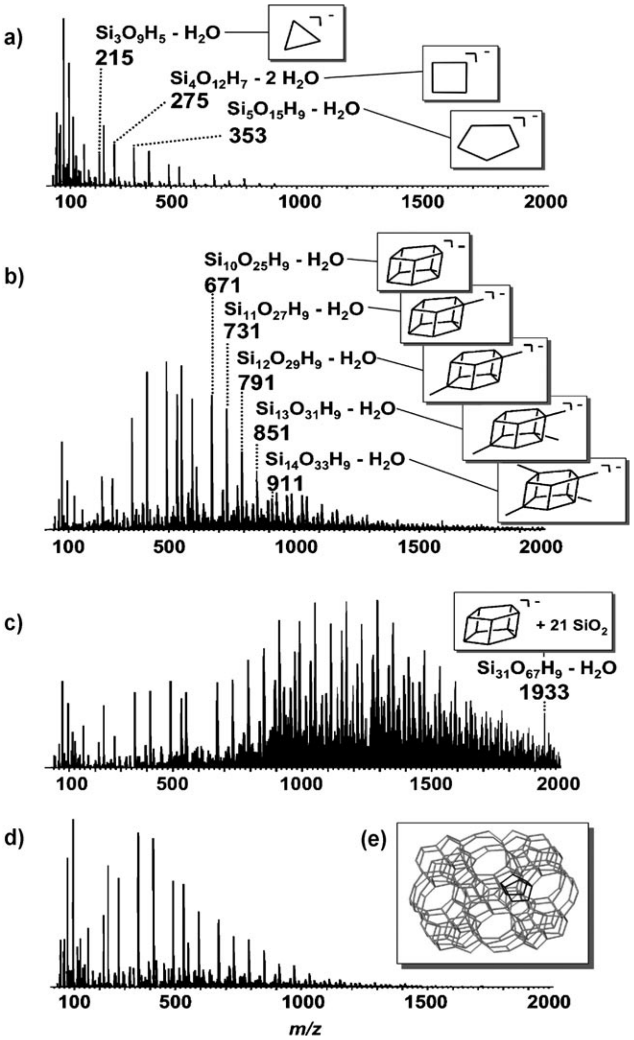

Figure 1. Time-dependent mass spectra recorded during the synthesis of ZSM-5 from an aqueous solution with the following molar composition: 0.962 SiO_2:0.038 GeO_2:0.36 TPAOH:20 H_2O. a) After combining the reactants, b) 2 h after mixing and heating to 95 °C, c) after 4 h, and d) after 4.5 h. Displayed species: the monodehydroxylated 3R, 4R, and 5R units (a); a series of species starting from the monodehydroxylated D5R unit (b,c), enlarged by formally attaching a SiO_2 molecule ($\Delta m/z$ 60 Da). e) Structure of zeolite ZSM-5 (MFI topology, taken from the International Zeolite Association (IZA) structure database).

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nium hydroxo species,their dimers, and monocyclic species. Satellite signals with a mass reduced by 18 Da, caused by the elimination of one water molecule, were observed as well (see Table S1 in the Supporting Information for a complete list of species observed). The occurrence of dehydroxylated species, which are only stable in the gas phase of the spectrometer, is characteristic for all the obtained mass spectra.[11]

With increasing reaction time and by heating the reaction mixture to 95 °C, species with higher masses start to occur. The resulting widespread peak distribution is characterized by signals with a mass difference of 60 Da, which indicates a series of species emerging from each other by formally adding SiO_2. No mixed species containing silicate oligomers and the organic template were detected under these conditions. Two possible structures can be attributed to the unit which represents the starting point of this series: either a double five-ring (D5R) or a dehydroxylated D4R unit enlarged by the attachment of two monomers to the corners of the cube. However, no signal corresponding to a D4R unit enlarged by one monomer was observed in solution, and thus it is highly probable that the basic unit is the D5R species. These do not occur in the structure of MFI as such. Nevertheless, the D5R species at least includes a major structural element of MFI-type zeolites, a five-membered ring (Figure 1 e), which could be incorporated into the growing zeolite by a similar mechanism to that observed for the exchange of larger units between D4R and D3R species.[9]

Furthermore, satellite peaks with an enhanced mass of 46 Da prove that in all the occurring species one silicon atom at most is exchanged against germanium (most probably because of the low germanium concentration in the synthesis solution). After 4 h the intensities are shifted again to species with smaller m/z values (Figure 1 d). Simultaneously performed dynamic light scattering (DLS) measurements have shown that exactly at this time colloidal particles, too large to be detected by ESI-MS, start to grow in solution (Figure S1 in the Supporting Information). The mass spectrum recorded after this time represents the remaining solution, with a decreased silicate concentration that leads to depolymerization and silicate species at lower masses. The final solid was proven to be ZSM-5 by X-ray diffraction (XRD; Figure S2 in the Supporting Information).

To determine whether the presence of characteristic structural elements immediately before nucleation is a more general phenomenon, two other systems were studied in detail. Zeolite Beta is known to be a highly intergrown hybrid of two distinct, but closely related structures, polymorphs A and B, which usually occur in a ratio of 60:40.[12] A third polymorph (C) with a three-dimensional pore topology, which has large linear channels defined by 12-membered rings, was for a long time predicted to exist as well (structure code: BEC). Its structure is formed by connecting D4R and four-ring (4R) units by O–Si–O bridges. As germanium is known to increase the stability of these units, the synthesis of polymorph C was carried out successfully by using framework substitution of silicon against germanium.[13]

Upon adding the silicon source (TEOS) to an aqueous solution containing GeO_2 and the organic template (tetraethylammonium hydroxide, TEAOH), it dissolves immediately. Thus, the first mass spectrum was recorded one minute after combining the reactants (Figure S4 in the Supporting Information). It shows a multitude of species, up to approximately 1400 Da. The main signals at m/z 95 and 141 can be attributed to monomeric silicon and germanium hydroxo species, $MO_4H_3^-$. As during the synthesis of ZSM-5, satellite signals with a mass reduced by 18 Da, caused by the elimination of one water molecule, were observed as well. The fact that species with higher masses were obtained in the first spectrum is in line with studies reporting an enhanced crystallization rate with increasing amount of germanium.[14]

With increasing reaction time and after heating the system to the reaction temperature (145 °C) the intensity of species with higher masses increases, while the intensity of species with smaller masses decreases. As in the synthesis of ZSM-5, after four hours the intensities are shifted to species with smaller m/z values, caused again by depolymerization as a result of the reduced silicate concentration in solution. Simultaneously performed DLS measurements showed that exactly at this time colloidal particles, too large to be detected by ESI-MS, start to grow in solution (Figure S3 in the Supporting Information). The analysis of the species distribution gives new insight into the nucleation of polymorph C.

Figure 2 a shows the ESI mass spectrum recorded immediately before particles start to grow in solution (see Figure S4 in the Supporting Information for the full series of time-dependent mass spectra). The low mass range is characterized by monomeric, dimeric, and monocyclic species (see Table S2 in the Supporting Information for a complete list of species). Units with the 4R species as basic structure, enlarged by condensing monomers to the corners of the square, were observed as well. Consecutive satellite peaks with a mass difference of 46 Da reveal that these units contain up to three germanium species in place of silicon atoms. The middle mass range is dominated by D4R units, enlarged by attaching monomers to the corners of the cube, which contain up to three germanium atoms.

The 4R and D4R species are structural elements of polymorph C of zeolite Beta, but rather unspecific ones, because they also occur in many other zeolites. However, connected D4R species bridged by one silicate unit are rather characteristic for zeolite Beta (Figure 2 b), and can be attributed to signals occurring in the higher mass range for units containing up to six germanium atoms (see enlarged part of Figure 2 a). Although this assignment is not absolutely certain, the isotopic patterns of the silicon and germanium give very precise information on the sum formula. There are no alternative consistent progressions of silicate species other than the one starting with two silicon-bridged D4R units. In particular, no indications of directly linked D4R units were observed in this system, in contrast to the synthesis of zeolite A (see below). The final solid was determined to be the polymorph C of zeolite Beta by XRD (Figure S5 in the Supporting Information) with a Si/Ge ratio of 2.4, slightly lower than that of the solution species. In a control experiment, the same synthesis composition was used, but TEAOH was replaced by TPAOH. This led to formation of the MFI structure, and the solution prior to formation of the solid

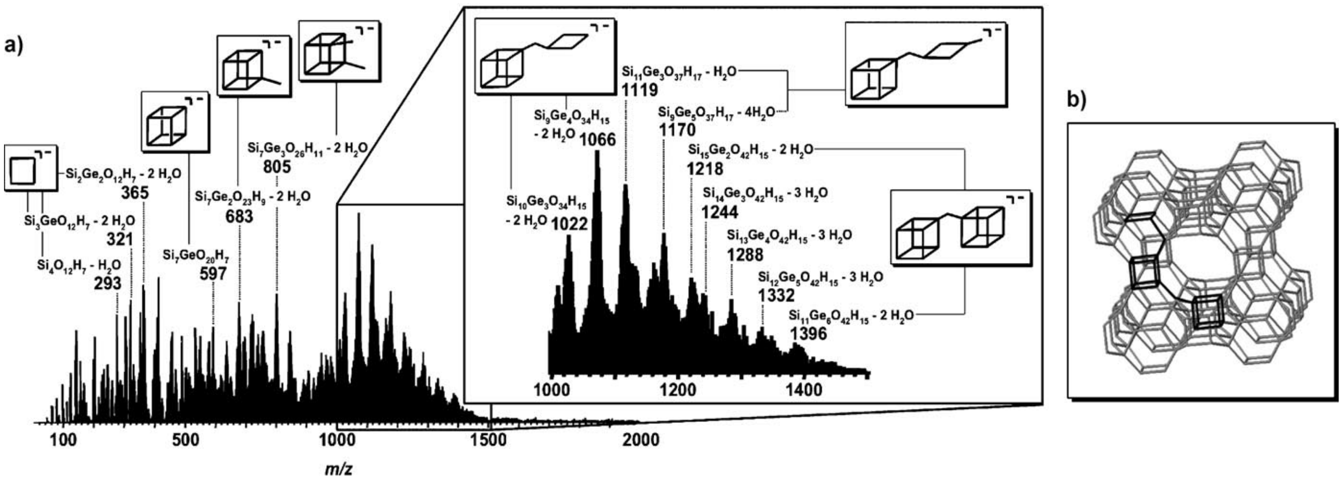

Figure 2. a) ESI mass spectrum recorded during the synthesis of polymorph C of zeolite Beta immediately before the first particles start to grow in solution. Molar composition of the synthesis mixture: 0.67 SiO_2:0.33 GeO_2:0.5 TEAOH:0.5 HF:37.5 H_2O. b) Structure of polymorph C of zeolite Beta (BEC topology, taken from the IZA structure database).

contained predominantly the 5R species, thus supporting the important role of the organic template.

Another zeolite containing D4R units is zeolite A (structure code: LTA). It can be built up by linking sodalite cages (β cages), related by translation along the cube axis, through D4R units. Hence, the zeolite A structure can be formed by linking D4R units over siloxane bonds directly. Its aluminum-free synthesis was developed by using the structure-directing effect of supramolecular self-assembled organic molecules in combination with an isomorphic exchange of framework silicon against germanium.[15] On adding the silicon source (TEOS) to an aqueous solution containing GeO_2 and the organic template, it dissolves immediately and results in a clear solution.

The first spectrum (Figure 3a) was recorded one minute after combining the reactants (see Figure S6 in the Supporting Information for time-dependent mass spectra). In line with the synthesis of zeolite Beta polymorph C, species with higher masses, up to 1400 Da, but with low intensities were observed as well. Their intensities increase with increasing reaction time and after hydrothermal treatment at 150 °C. After four hours the intensity of the species in the upper mass range starts to decrease again. As the reaction mixture contains less water than the synthesis gel of zeolite Beta (polymorph C), the system has a viscosity too high to perform DLS measurements simultaneously. Nevertheless, the shift of the species to lower masses can be taken as indication of colloidal particles in solution, as in the other two systems.

Data analysis of the species occurring during the synthesis of zeolite A revealed the presence of oligomers rather similar to those in the synthesis of polymorph C. The most significant difference was observed in the upper mass range (see enlarged part of Figure 3a): the signals can most straightforwardly be attributed to species representing D4R units that are directly linked over siloxane bonds (see Table S3 in the Supporting Information for a complete list of species). Their corresponding satellite signals ($\Delta m/z$ 46 Da), together with their isotopic pattern, prove that these species occur with up to six incorporated germanium atoms as well. These directly linked cubes are fingerprints of the zeolite A structure

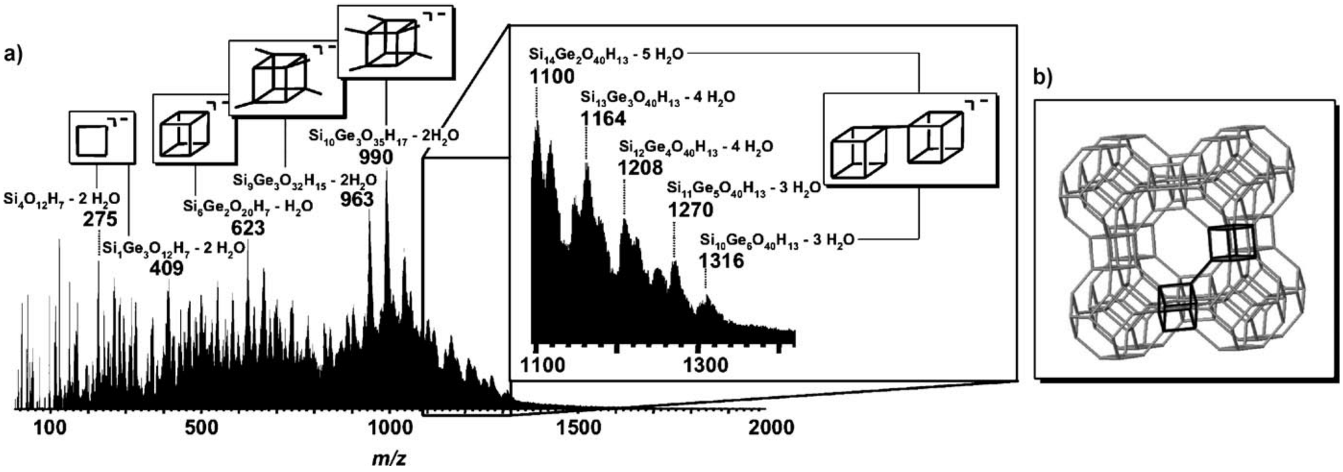

Figure 3. a) ESI mass spectrum recorded during the synthesis of zeolite A immediately before the first particles start to grow in solution. Molar composition of the synthesis mixture: 0.67 SiO_2:0.33 GeO_2:0.5 ROH:0.5 HF:20 H_2O. b) Structure of zeolite A (LTA topology, taken from the IZA structure database).

(Figure 3b). Furthermore, their compositions are in the range of the silicon-to-germanium ratio of the final solid (Si/Ge = 2.8). The final product of the synthesis was proven to be zeolite A by XRD (Figure S7 in the Supporting Information).

In summary, we have for the first time found clear evidence for the presence of different characteristic structural elements of zeolites in the prenucleating solution, obtained by using different templates and different synthetic conditions. This proves that the conditions of the reaction direct the polycondensation of silicate towards specific structures at the solution stage. While we would not claim, based on our results, that zeolite formation necessarily proceeds through the assembly of structural elements already present in solution, this certainly could be a viable scenario. It has become clear that the synthesis conditions for specific zeolites favor the formation of species characteristic of these structures already in solution. Whether they assemble directly, exchange structural fragments,[9] or depolymerize again to feed the silicate pool is still unclear. The necessary ingredients for zeolite nucleation by the assembly of structural subunits are, however, certainly in place, and the findings revealed herein can be used to guide future work on this important problem, as long as the systems are not too viscous to be injected into the mass spectrometer. In addition, the findings may present a new method for screening zeolite synthesis systems for novel structures. For this, one would need to vary the conditions and simultaneously monitor the species in the synthesis solution, for instance, by using a tubular reactor with continuously changing reactant composition. If new and interesting oligomeric species are detected, full-scale zeolite synthesis experiments could be initiated around the parameters discovered in the mass spectrometric study. Such programs have now been launched in our laboratory.

Experimental Section

The aluminum-free, germanium-containing zeolites were obtained from synthesis mixtures described in the literature cited, modified by increasing amount of water to avoid the formation of too dense gels and thus allow ESI-MS measurements.

Polymorph C of zeolite Beta was obtained by adding TEOS to a solution containing GeO_2, HF, and TEAOH with the following molar composition: $0.67\,SiO_2$:$0.33\,GeO_2$:0.5 TEAOH:0.5 HF:$37.5\,H_2O$.[13] After the complete hydrolysis of TEOS, the reaction mixture was transferred from the polypropylene vessel into a stainless-steel autoclave and heated to 145 °C. To enable continuous sampling even at elevated pressures without cooling the autoclave to room temperature, a stainless-steel capillary equipped with a valve was connected through the cap of the autoclave to the reaction mixture. The samples were then taken after defined time intervals and analyzed directly by using ESI-MS and DLS. Finally, the mixture was filtered and the obtained solid was washed with distilled water, dried at 100 °C, and characterized by XRD and energy-dispersive X-ray (EDX) analysis.

The synthesis of zeolite A was performed as for the polymorph C of zeolite Beta, but by heating the synthesis mixture to 150 °C and using a solution with the following molar composition: $0.67\,SiO_2$:$0.33\,GeO_2$:0.5 ROH:0.5 HF:$20\,H_2O$.[15] 4-Methyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3.2.1-*ij*]quinolinium hydroxide was used as organic template (see the Supporting Information for synthesis details). Samples were taken continuously and analyzed by ESI-MS. The obtained solid was washed with distilled water and characterized by XRD and EDX analysis.

ZSM-5 was obtained from an aqueous synthesis mixture with the following composition: $0.962\,SiO_2$:$0.038\,GeO_2$:0.36 TPAOH:$20\,H_2O$. The synthesis was carried out in a polypropylene vessel at 95 °C.[16] Samples were taken continuously and analyzed by ESI-MS and DLS. The obtained solid was washed with distilled water and characterized by XRD.

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