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Nucleation of ITQ-21 Studied by ESI-MS

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The nucleation pathway of zeolite ITQ-21 was studied by using electrospray ionization mass spectrometry (ESI-MS). The syntheses were performed with different silicon to germanium ratios and with different mineralizing agents. Silicate species with structural characteristics of the obtained material were found to occur already in solution, immediately before nucleation. In addition, by using fluoride (F^-) or hydroxide ions (OH^-) as mineralizing agents, it was possible to determine their influence on the nucleation pathway. In particular, a reaction-rate-accelerating rather than a structure-directing effect was determined for F^-.

Introduction

Zeolites are crystalline microporous silicates, which are extensively used in important application fields, such as heterogeneous catalysis, adsorption and separation.[1] This is due to their unique pore topologies and the possibility to introduce heteroelements, which can influence both the framework topology and reactivity of the obtained materials. Still, one of the challenges in zeolite science is the understanding of the formation pathway, which would allow the development of tailor-made of zeolitic materials with properties most suitable for a target application. One important structure-directing effect is exerted by organic structure directing agents (SDAs), leading to a defined zeolite phase especially during the synthesis of pure or high silica zeolites, respectively.[2−4] Furthermore, the structure-directing effect resulting from the introduction of various heteroelements in the synthesis mixtures is well-known, but still not well understood on a molecular level. Especially the substitution of silicon for germanium has to be mentioned, because it has led to the synthesis of several novel zeolitic materials with very open pore topologies.[5−9] Another approach to yield such materials is the use of fluoride in place of hydroxide ions. During the synthesis of zeolitic materials, fluoride is supposed to act not only as mineralizer but also as structure-directing agent.[10] However, because in general the liquid−solid phase transition is not accessible with most analytical techniques, little is known about zeolite formation from solution. The analytical limitations are mostly due to the size of the occurring species, which lies between those of the precursor molecules and the final solid, a range rather inaccessible both to molecular probes and to scattering techniques, at least if more than size information is desired.[11−15] However, electrospray ionization mass spectrometry (ESI-MS) has already been described as a powerful tool to give insight into prenucleating[16−18] and nucleating[19,20] solutions of zeolitic materials.

Zeolite ITQ-21 was recently discovered as an exciting catalyst suitable for various applications, such as the cracking of light vacuum gas oil.[21] This is due to its open three-dimensional pore topology, which allows the access to large cavities (diameter: 1.18 nm) via circular 12-membered ring-openings (diameter: 0.74 nm). Its structure can be built up interconnecting [$4^6 6^{12}$]-cages via double four ring (D4R) units. In addition, these cages

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can trap single four rings (4R), which are randomly oriented normal to the three crystallographic axes. Thus, the structure of zeolite ITQ-21 can be formed by bridging D4R and/or 4R motives via monomeric silicate units. Its properties can be tuned by varying the amount of incorporated aluminum and germanium atoms.[22] It has to be mentioned that the presence of germanium atoms in the synthesis mixture is required. Furthermore, it is possible to use both fluoride ions (F^-) and hydroxide ions (OH^-) as mineralizing agents.[23]

We here present detailed insight into the nucleation mechanism of zeolite ITQ-21 under various synthesis conditions. Especially the occurring silicate species as well as the influence of the mineralizing agent was studied.

Experimental Section

Synthesis. The N(16)-methylsparteinium cation was used as organic SDA to obtain zeolite ITQ-21. It was synthesized in its iodide form using a general synthesis route previously described in the literature.[24] Before use it was converted to its hydroxide form by using an anionic exchange resin (Amberlite IRN-78).

The fluoride-free synthesis was carried out in a polypropylene (PP) vessel; germanium dioxide (GeO_2) was dissolved in an aqueous solution of the organic SDA in its hydroxide form and afterward the appropriate amount of tetraethoxysilane (TEOS) was added as silicon source, leading to reaction mixtures having the following molar compositions:

(i) 0.5:0.5:0.5:4 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:H_2O

(ii) 0.67:0.33:0.5:4 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:H_2O

After defined time intervals, samples were taken with a syringe and directly injected into the mass spectrometer. At the same time, samples were also analyzed by dynamic light scattering (DLS). The obtained materials were characterized by means of X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX).

By using fluoride as mineralizing agent, synthesis mixtures having the following overall molar compositions were prepared:

(i) 0.5:0.5:0.5:0.5:20 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:HF:H_2O

(ii) 0.67:0.33:0.5:0.5:40 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:HF:H_2O

Because of the fast reaction rates, the syntheses were carried out using a tubular reactor connected to the mass spectrometer.[17] One syringe was filled with the silicon source (TEOS), whereas the other one contained all remaining reagents. ***Caution****: special attention is required in handling of HF.*

Characterization. All ESI mass spectra shown were recorded on a Micromass ZMD mass spectrometer equipped with an ESI source in Z-spray alignment and measured in the negative ion mode. No silicate species were detected in the positive ion mode, the obtained signal can rather be attributed to the used organic SDA. The flow rate for the fluoride free synthesis was set to 400 μL h^{-1}, whereas a capillary voltage of 3.5 kV and a desolvation temperature of 150 °C were applied. Using the tubular reactor, a flow rate of 120 μL h^{-1} was applied to the ESI source of the mass spectrometer, whereas the capillary voltage was set to 4 kV.

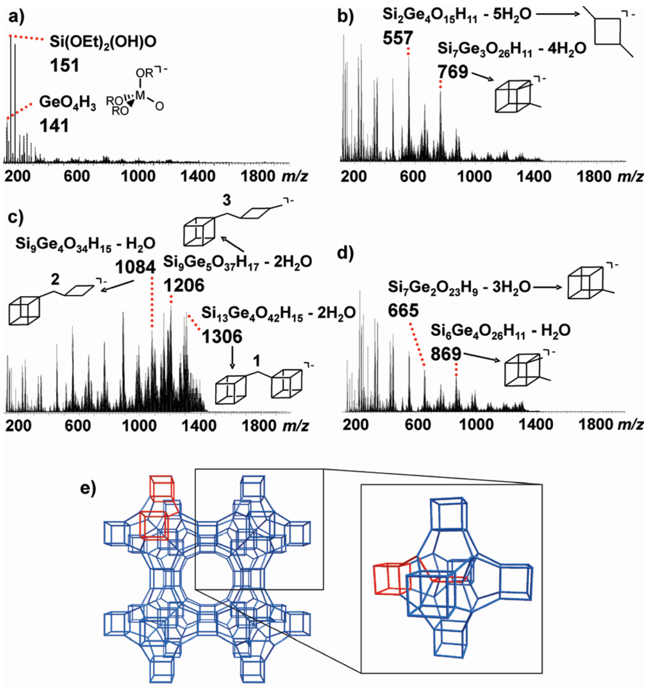

Figure 1. Time-dependent ESI mass spectra recorded during the synthesis of ITQ-21 from an aqueous solution with the following molar composition: 0.5:0.5:0.5:4 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:H_2O. (a) After combining the reactants, (b) 30 min, (c) 60 min, and (d) 70 min. (e) Structure of ITQ-21; inset: single 4R entrapped in a $[4^6 6^{12}]$-cage. Crystallographic information file reprinted with permission from ref 17. Copyright American Chemical Society, 2006.

The size of particles in solution was determined by dynamic light scattering (DLS) using a Malvern Instruments Zetasizer Nano-ZS (scattering angle 90°).

X-ray diffraction (XRD) measurements were performed on a STOE Stadi P transmission X-ray diffractometer using $Cu_{K\alpha}$ radiation.

The elemental compositions of the obtained materials were determined by energy dispersive X-ray spectroscopy (EDX, Oxford Instruments) attached to a Hitachi S-3500 scanning electron microscope.

Results and Discussion

Fluoride-Free Synthesis. In the presence of hydroxide ions as mineralizing agents, the nucleation pathway of zeolite ITQ-21 was studied using two different silicon to germanium starting ratios, Si:Ge =1 and Si:Ge =2, respectively. On adding the silicon source (tetraethylorthosilicate, TEOS) to the aqueous solution containing germanium dioxide (GeO_2) and the organic SDA, it dissolves immediately, leading to a synthesis mixture with no visible phase separation. For mixtures with the same molar amounts of silicon and germanium (Si:Ge =1), the first mass spectrum was recorded 1 min after combining the reagents; the spectrum shows a multitude of species, up to approximately 1420 Da (Figure 1). However, the dominant signals at m/z 141 and m/z 151 occur because of the dissolution and (partial) hydrolysis of the silicon and germanium source, respectively. They can be assigned to

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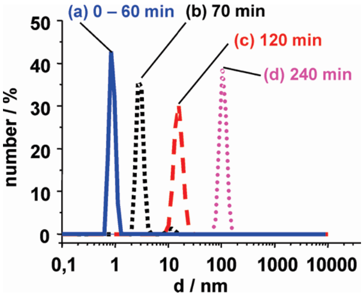

Figure 2. DLS spectra recorded during the synthesis of ITQ-21 from an aqueous solution with the following molar composition: 0.5:0.5:0.5:4 TEOS: GeO_2: N(16)-methylsparteinium hydroxide: H_2O.

monomeric germanium hydroxide $[GeO_4H_3^-]$ and partly hydrolyzed TEOS $[Si(OC_2H_5)_2(OH)O^-]$, respectively. Satellite signals having a mass reduced by 18 Da, caused by the elimination of one water molecule, were observed as well (see the Supporting Information for a complete list of occurring species). However, these species are stable only in the gas phase of the mass spectrometer and do not exist in solution as such.[25] The occurrence of such dehydroxylated species is characteristic for ESI mass spectra of silicates in general and were observed in all our studies of such systems. With proceeding reaction time, the intensity of silicate oligomers with higher masses increases, whereas the intensity of species with smaller masses decreases. However, after 70 min the intensities are shifted back to species with smaller m/z values. Simultaneously performed dynamic light scattering (DLS) experiments showed, that exactly at that time colloidal particles, too large to be detected by ESI-MS, start to grow in solution already at room temperature (Figure 2). This is in line with studies reporting a very fast nucleation for ITQ-21 especially at high germanium loadings.[22] Thus, the mass spectrum recorded 70 min after combining the reactants represents the remaining solution with a decreased silicate concentration. Because the silicate distribution as well as the intensities of the occurring species highly depends on the overall silicate concentration, the intensities of larger silicate species thus decrease because of the particle formation in solution. However, the analysis of the species distribution reveals detailed information on the nucleation pathway of zeolite ITQ-21: As can be seen in Figure 1, the low mass range is characterized by monomeric, dimeric, and monocyclic four-ring species. For the latter, satellite signals with a mass increased by 46 Da in combination with the isotopic pattern of the peaks reveal that up to three silicon atoms are exchanged for germanium in these silicates. Species having the 4R as basic structure, enlarged by attachment of monomers to the corners of the square, were observed as well. In these species, up to four silicon atoms were found to be substituted for germanium. A similar observation was made for the D4R unit, which is the dominant species in the middle mass range: on the one hand, the pure D4R was found with a maximum number of three incorporated germanium atoms; on the other hand its enlarged equivalent also occurs with up to four substituted silicon atoms. This is noteworthy, because the energetically favored number of germanium atoms in a D4R unit was calculated to be three[26] or four for very high germanium loadings,[27] respectively. However, by MS/MS experiments, detailed insight into the incorporation of germanium into these ring species in prenucleating solution had been obtained before.[28] It was shown that neither for the 4R nor for the D4R more than three germanium atoms were incorporated in the cyclic structures. When more than three germanium atoms were found in such silicate species, the fourth was always found attached at an exocyclic position to the corners.

As 4R and D4R species are found in the spectra in the middle mass range after intermediate reaction times, one may expect a condensation between those to lead to oligomers with characteristics of the structure of zeolite ITQ-21 (Figure 1): an oligomer which is built up by bridging two D4R units over a monomeric silicate unit (oligomer **1**), or an oligomer built up by bridging a D4R and single 4R over a monomeric silicate unit (oligomer **2**). The latter was found to be enlarged by adding a monomeric unit to the corner of one of the subunits as well (oligomer **3**). Exactly these structures can be assigned to signals occurring in the higher mass range, with two to six germanium atoms incorporated. The mass accuracy was high enough to allow, together with the isotopic pattern of the peaks, to attribute the shown structures to the recorded signals. These structural assignments are corroborated by a more detailed structural investigation of species with the same masses formed in stable, prenucleating solutions.[28] We were thus able to detect species in solution already carrying some structural characteristics of the resulting zeolite (Figure 1). It has to be mentioned that the mode in which 4R and D4R units are linked in these particular solutions highly depends on the used organic SDA, as was already shown in previous studies of reaction mixtures with similar compositions.[20] The final solid, obtained with proceeding reaction time, was determined to be ITQ-21 using X-ray diffraction (XRD, see the Supporting Information) with a silicon to germanium ratio of 1.27 (determined by energy-dispersive X-ray spectroscopy, EDX).

Zeolite ITQ-21 can be synthesized via a fluoride free route with an increased silicon to germanium ratio (Si/Ge =2) as well. The obtained DLS data show that the first particles form slower than in the synthesis route with higher germanium content (Figure 3). This is in line with studies reporting a crystallization kinetics that is dependent on germanium concentration.[23] For the lower germanium concentration, the time-dependent ESI mass spectra indicate a similar nucleation pathway as for the

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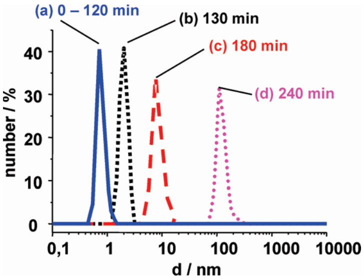

Figure 3. DLS spectra recorded during the synthesis of ITQ-21 from an aqueous solution with the following molar composition: 0.67:0.33:0.5:4 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:H_2O.

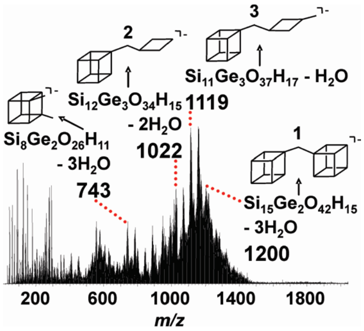

Figure 4. ESI mass spectrum recorded during the synthesis of ITQ-21 immediately before first particles start to grow in solution. Molar composition of the synthesis mixture: 0.67:0.33:0.5:4 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:H_2O.

synthesis with higher germanium loading (see the Supporting Information for time-dependent ESI mass spectra). The ESI mass spectrum, recorded immediately before first particles occur in solution (2 h after combining the reactants) can be seen in Figure 4. It is characterized by the same silicate species that occurred during the synthesis with a higher germanium loading. However, the dominant signals are now those that can be attributed to silicate species having a slightly lower germanium content; the ions contain roughly one germanium atom less compared to the synthesis route with higher germanium loading. This finding fits the increased silicon to germanium ratio of the final synthesis product (Si/Ge =1.95) determined by EDX (see the Supporting Information of the XRD pattern).

Fluoride-Containing Synthesis Route. To study the influence of the mineralizing agent on the nucleation pathway of zeolite ITQ-21, syntheses were carried out in the presence of fluoride ions as well. As for the fluoride-free synthesis route, two different silicon to germanium ratios, Si/Ge =1 and Si/Ge =2, were used. Initially, the fluoride-containing preparations of zeolite ITQ-21 were performed under the same conditions as in the fluoride-free synthesis route, differing only in the presence of fluoride ions and a higher water content. After dissolving GeO_2 in an aqueous solution of the organic SDA, HF, the required amount of water and TEOS were added. Consequently, TEOS dissolved immediately, leading to a reaction mixture with no visible phase separation. By studying the synthesis mixture with a silicon to germanium ratio of one, first particles—as detected by DLS—were found to occur in solution already 90 s after combining the reagents (Figure 5). Compared to the fluoride free synthesis (with the same Si/Ge ratio) this is a strong increase of the reaction rate. This fact is supported by the XRD pattern of the material isolated after one day; they show a significantly higher crystallinity compared to the material obtained from the fluoride free synthesis route (see the Supporting Information). These findings are perfectly in line with studies reporting a crystallization curve which is depending on the type of mineralizer.[23] To allow the time-resolved study of the nucleation mechanism in this system by ESI-MS as well, a tubular reactor was connected to the mass spectrometer. In such a system, each point along the reactor corresponds to a certain reaction time, thus allowing the acquisition of many mass spectra at nominally identical reaction time. The time-dependent spectra can be seen in Figure 6, indicating that the reaction pathway is similar to the fluoride free synthesis route. Starting from the monomeric tetrahydroxogermanate and partly hydrolyzed TEOS (*m*/*z* =123, 151) larger oligomeric (germano)silicate species start to grow in solution. However, because of first particle formation and thus lowered silicate concentration in solution, the intensities of species with higher masses decrease again after 90 s. By comparing the spectra for the fluoride-containing and fluoride-free synthesis route, recorded immediately before first particles start to grow in solution, it can be seen that the occurring signals are identical. They slightly differ in their intensities and the dehydroxylation degree of the occurring species. However, this can be due to the change of the flow rate into the mass spectrometer as well as the applied voltages, which was necessary for connecting the tubular reactor to the spectrometer. Disregarding these small differences, all occurring species are identical (see the Supporting Information for a complete list of occurring species). No difference in either their structure, or the number of incorporated germanium atoms was observed. This is in line with the Si/Ge ratio of the obtained material, which was determined to be 1.35, i.e., it is in the same range as the material isolated from the fluoride,-, free synthesis solution. The fact that no difference of the occurring silicate species was found for the two mineralizing agents, is particularly noteworthy. Refinement of X-ray powder diffraction data[22] and theoretical calculations[29,30]

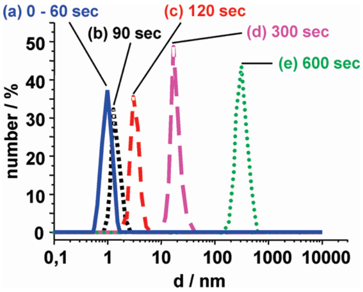

Figure 5. DLS spectra recorded during the synthesis of ITQ-21 from an aqueous solution with the following molar composition: 0.5:0.5:0.5:0.5:20 TEOS:GeO_2:N(16)-methylsparteinium hydroxide: HF:H_2O.

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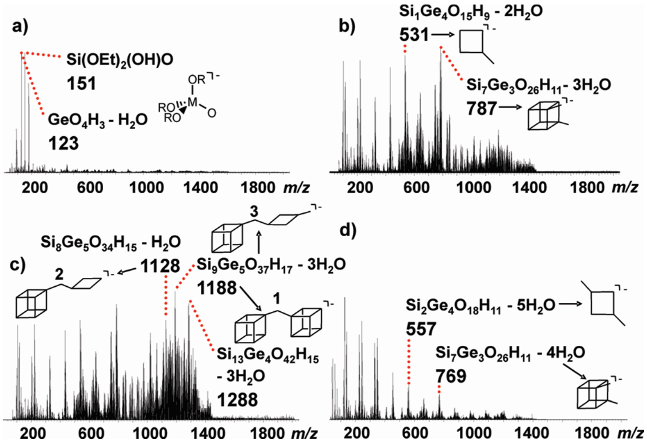

Figure 6. Time-dependent ESI mass spectra recorded during the synthesis of ITQ-21 from an aqueous solution with the following molar composition: 0.5:0.5:0.5:0.5:20 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:HF:H_2O. (a) After combining the reactants, (b) 30 s, (c) 60 s, and (d) 90 s.

suggest a preferred position of fluoride ions in the center of the D4R units. This is further supported by ^{19}F-MAS NMR spectra of the obtained crystalline material (see the Supporting Information), indicating an incorporation of F^- into D4R motives. However, as mentioned above, no signals that could be attributed to fluoride-containing species were observed in the ESI mass spectra, and in particular no signals of D4R units containing F^-. This fact is supported by liquid phase ^{19}F-NMR investigations on a solution, which is characterized by an increased water amount, thus providing long-term stability. Although this solution differs from the composition used to synthesize ITQ-21, the obtained silicate species are identical.[28] This solution shows no signals in the range characteristic for F^- entrapped in D4R units; rather one signal at −119.21 and one at −129.17 ppm (see the Supporting Information). The former one occurred in a control experiment with a solution containing only the organic SDA in its fluoride form as well. The latter has to be attributed to pentacoordinated $T(OH)F^-$, in particular $Ge(OH)F^-$ species,[31] which cannot be detected with ESI-MS because of the low binding energy between T-atom and fluoride. Nevertheless, the obtained data prove that F^- is not entrapped in D4R units already in solution, rather it has to be incorporated later during the synthesis.

In the fluoride-containing system, the synthesis starting from a silicon to germanium ratio of Si/Ge =2 was studied as well. As the DLS spectra show, first particles are formed as fast as for the higher Si/Ge ratio (Figure 7a). Furthermore, the XRD pattern of the materials isolated after one day shows again a much higher crystallinity compared to the material obtained from the fluoride free synthesis route (see the Supporting Information). This further supports the reaction rate accelerating of fluoride. As for the lower silicon concentration, Figure 7b reveals that the overall species distribution remains the same as for the fluoride free synthesis at Si/Ge =2, i.e., the occurring silicate species as well as their germanium amount are identical. Again, the main signals can be attributed to (germano)silicate species with lower germanium contents. The Si/Ge ratio of the obtained material was in the same range as for the fluoride free synthesis route (Si/Ge =2.13).

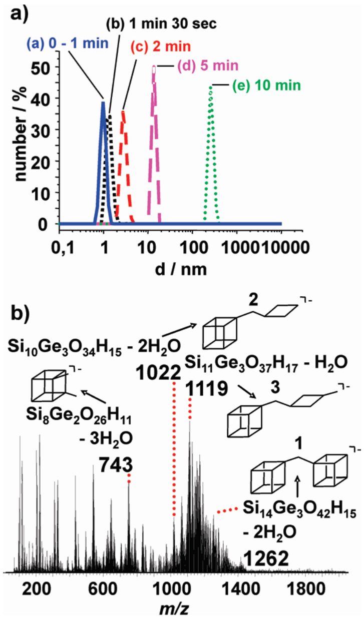

Figure 7. (a) DLS spectra recorded during the synthesis of ITQ-21 from an aqueous solution with the following molar composition: 0.67:0.33:0.5:0.5:40 TEOS:GeO_2:N(16)-methylsparteinium hydroxide:HF:H_2O. (b) ESI mass spectrum recorded immediately before first particles start to grow in solution.

Conclusion

By studying the (germano)silicate speciation of zeolite ITQ-21 under various synthesis conditions, we found clear evidence for the presence of silicate species with characteristic structural fragments of this zeolite already in solution. Furthermore, by using either OH^- or F^-, it was shown that the occurrence of these specific (germano)silicate structures in solution is independent of the mineralizing agent. The fluoride ions thus affect rather the kinetics of the zeolite formation, because first particle formation was found to occur approximately 1 order of magnitude faster than in synthesis mixtures with hydroxide ions as mineralizing agent. This could be due to faster condensation/hydrolysis reactions under the influence of fluoride, which allows the system to create suitable precursor species for zeolite formation more rapidly. A structure-directing effect of fluoride ions, on the other hand, appears to be rather improbable in the observed solution phases.

However, on the basis of our results, we can and would not claim that the formation of zeolite ITQ-21 necessarily proceeds via the assembly of the described structural elements already present in solution. Whether they assemble directly, exchange structural fragments,[18] or depolymerize again to feed the (germano)silicate pool is still unclear. If the detected species indeed are involved in the formation of first (F^- free) nuclei and if F^--containing

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D4R units are formed later during the synthesis, some F-D4R sites would stay empty. With respect to reports of as-made germanosilicates having F-D4R sites with occupancy factors slightly smaller than 1[5], this seems at least to be viable scenario. However, this question is highly challenging and has to be addressed in future work.

Still, the detection of silicate species with structural characteristic of the final zeolite already in solution is one step forward to understand zeolite formation on a molecular level. Whether this is a more general phenomenon or occurs only for specific zeolite types is still an open question. So far, this has been shown for four different materials,[20] including the present study of ITQ-21, all of them being germanosilicates. Work is under way to address the same question for the catalytically tremendously important alumosilicates.

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Supporting Information Available: Time-dependent ESI mass spectra recorded during the fluoride-free and fluoride-containing synthesis route; XRD pattern of the obtained materials; a list of all occurring silicate species; ^{19}F-NMR and MAS NMR data of a long-term stable solution and the obtained crystalline material (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.