

LETTERS

New Evidence for Precursor Species in the Formation of MFI Zeolite in the Tetrapropylammonium Hydroxide–Tetraethyl Orthosilicate–Water System

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Tetraethyl orthosilicate was hydrolyzed and polymerized in concentrated aqueous tetrapropylammonium (TPA) hydroxide solution at 0 and 10 °C and room temperature. The formation of silicate oligomers involved in the TPA-mediated self-assembly process of colloidal Silicalite-1 was investigated using ^{29}Si NMR. A pentacyclic dodecamer with four edge-sharing five-rings on a four-ring was detected as a new intermediate in the formation of Silicalite-1 zeolite. The formation of this pentacyclic dodecamer with a curved inner hydrophobic silicon dioxide surface is a new example of the structure-directing action of TPA. The temperature was found to be a key parameter with respect to the transformation of the intermediates with 11 and 12 Si atoms. At 0 and 10 °C, the tetracyclic undecamer having three five-rings on a four-ring was converted into the pentacyclic dodecamer by insertion of one additional silicate unit. At these low temperatures, it slowly underwent an intramolecular condensation and formation of capped double five-ring not leading to Silicalite-1 formation. At room temperature, three pentacyclic dodecamers rapidly condensed into the Silicalite-1 precursor. The involvement of the pentacyclic dodecamer in the self-assembly process offers an explanation for the absence of systematically missing T-sites in colloidal Silicalite-1.

On the basis of their experience with ^{29}Si NMR of tetraalkylammonium silicate solutions, Kinrade et al. discard the possibility of a direct interference of tetraalkylammonium template molecules in initial silicate hydrolysis and condensation steps.¹ Such intervention of tetrapropylammonium (TPA) is essential in the molecular mechanism of Silicalite-1 formation that we proposed.^{2–4} Before presenting a new evidence, let us recall the molecular picture of the formation of Silicalite-1 from tetraethyl orthosilicate (TEOS) and aqueous TPAOH solution as deduced from our earlier work.

Colloidal Silicalite-1 with a crystal size of ca. 100 nm can be synthesized by hydrolyzing TEOS in 40 wt % concentrated

TPAOH solution, subsequently diluting by adding about 30 wt % water, and heating to 100 °C.⁵ X-ray diffraction analysis of the colloidal Silicalite-1 product confirms its high quality and gives no indication for systematically missing silicon sites.⁶ Colloidal Silicalite-1 displays an IR doublet at 555–570 cm^{-1} , characteristic for pentasil zeolites and assigned to five-ring vibrations.⁶ Micrometer-sized MFI-type zeolite crystals show this IR feature at 550 cm^{-1} .⁷ The shift toward higher wavenumbers occurs in parallel with a decrease in particle size. In the standard synthesis mixture characterized by molar TPAOH/TEOS/ H_2O ratios of 1:2.7:43, dynamic light scattering (DLS) shows that the silicon is present in subcolloidal particles,⁸ having a very narrow size distribution. Small angle X-ray scattering (SAXS) also reveals the almost exclusive presence of a specific

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population of unique particles,^{4,9} further denoted as *nanoslabs*. The nanoslabs have in-plane dimensions of $4 \times 4 \text{ nm}^2$ according to transmission electron microscopy (TEM),¹⁰ and a thickness of 1.3 nm as derived from atomic force microscopy (AFM) height differences² and X-ray spectroscopy (XRS)² and SAXS¹⁰ analysis. These nanoslabs are a specific fragment of the MFI-type framework², measure 4 nm in the *b* and *c* crystallographic directions and 1.3 nm in the *a* direction, and occlude TPA cations in intersections according to ¹³C and ²⁹Si MAS NMR and thermogravimetric analysis (TG).^{2,11} The nanoslabs are composed of ca. 400 Si atoms,² fitting with the size, the Qⁿ distribution according to ²⁹Si MAS NMR, and the number of full and half cavities occupied by TPA.² These nanoslabs show the pentasil vibration at $570\text{--}590 \text{ cm}^{-1}$.¹¹ Titanium-containing nanoslabs exhibit catalytic selectivity similar to that of TS-1,¹¹ a titanium-doped Silicalite-1. The microporous nature of the MFI nanoslabs can be demonstrated with nitrogen and alkane adsorption.¹²

When dilution with water is omitted after the hydrolysis of TEOS in 40 wt % TPAOH, smaller particles are obtained depending on TPAOH/TEOS ratio. According to XRS and SAXS,^{4,10} the size of these particles is a discrete multiple of an elementary unit of specific size. This particular specimen, denoted as *precursor* in our original publication,⁴ can be obtained as single species when 4 mL of TEOS is hydrolyzed in 10 mL of a 40 wt % aqueous TPAOH solution (corresponding to a TPAOH/TEOS/H₂O molar ratio of 1:1.1:16).⁴ The pentasil vibration is further shifted to higher frequencies and appears at 590 cm^{-1} , further illustrating the shift to higher wavenumbers of the pentasil vibration with reduction of the particle size. The XRS signal of this specimen exhibits a maximum at a *d* value of 1.35 nm.⁴ The size of this precursor is much too large to be assigned to a cubic octamer having an apparent *d* value of only about 0.6 nm. Kinrade et al. expect the cubic octamer to be the dominant entity.¹

The next bigger unit obtained as stable species in mixtures with a TPAOH/TEOS/H₂O molar ratio of 1:1.9:16 was made up of 2 precursor units as observed with SAXS.¹⁰ Increasing the amount of TEOS relative to TPAOH (TPAOH/TEOS/H₂O of 1:2.7:16) leads to the formation of successively larger aggregates. Finally, after dilution with additional water to reach the standard composition, the dominant species reaches the size of $4 \times 4 \times 1.3 \text{ nm}^3$, containing 12 precursor units and showing the above-mentioned MFI properties.⁴ Thus, the precursor is made up of ca. 33 Si atoms ($1/12$ of 400).

The ²⁹Si NMR spectrum of a suspension prepared by hydrolyzing TEOS in 40 wt % TPAOH (TPAOH/TEOS/H₂O of 1:2.7:16) and aged for 2 weeks at room temperature is shown in Figure 1a.¹³ In the chemical shift range from 0 to -80 ppm , no signals were present except that of the internal tetramethylsilane (TMS) reference.

The spectrum shows two broad signals at around -90 and -100 ppm . The line broadening confirms the presence of particle-like species. In XRS, at this stage, particles composed of a discrete number of the precursor are dominant (Figure 2a). A similar ²⁹Si NMR spectrum is already observed after 120 min mixing time (Figure 1b). Besides the broad features, residual sharp lines are visible, which resemble the patterns obtained after shorter mixing times (60 and 45 min) and subsequent removal of unconverted TEOS through extraction in octane (Figure 1c and d). The X-ray scattering data corresponding to the ²⁹Si NMR spectrum in Figure 1b (Figure 2b) can be explained as a superposition of precursor units and its oligomers, the former being represented by the XRS peak with maximum

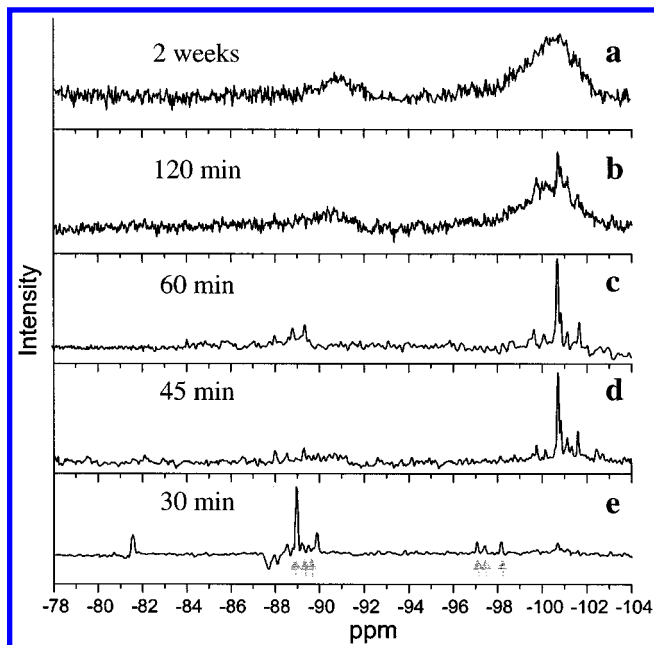


Figure 1. ²⁹Si NMR spectra at 0 °C after different stirring times of mixtures of TEOS (Sigma) and TPAOH (40 wt % aqueous solution, Acros) (TPAOH/TEOS/H₂O molar ratios of 1:2.7:16) at room temperature: (a) stirred for 2 weeks, no octane extraction; (b) stirred for 120 min, no octane extraction; (c) stirred for 60 min, octane extraction; (d) stirred for 45 min, octane extraction; (e) stirred for 30 min, octane extraction.

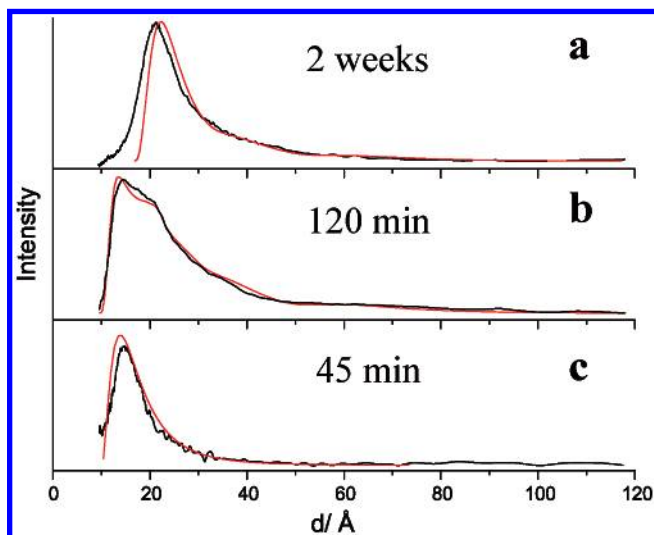


Figure 2. Experimental X-ray scattering curves as function of *d* value corresponding to samples from Figure 1 a, b, and d. Experimental lines (black) are compared to simulated scattering curves assuming aggregates of precursors (red lines): (a) simulation for 60% precursor dimers, 7% precursor triples, 7% half-nanoslabs, 13% nanoslabs, and 13% double nanoslabs; (b) simulation for 20% precursors, 30% precursor dimers, 28% precursor triples, 12% half-nanoslabs, 5% nanoslabs, and 5% double nanoslabs; (c) simulated for precursors only.

intensity at a *d* value of 1.35 nm. The NMR spectra in Figure 1c and d relate to the first signal that can be recorded with XRS (Figure 2c) and that appears after 45 min mixing of the TEOS with the TPAOH solution. The scattering data of Figure 2c can be assigned to a single population of particles with a size of $1.3 \times 1.3 \times 1 \text{ nm}^3$, identical in size to the precursor unit.

Gel permeation chromatograms⁴ showed that the precursor consists of three aggregated subunits having the same weight, each containing about 11 Si atoms. Considering that the precursor is made up from three subunits, the aqueous phase

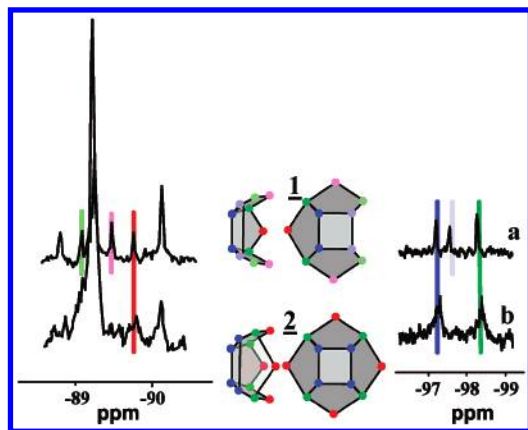


Figure 3. Illustration of the relation between tetracyclic undecamer **1** and pentacyclic dodecamer **2** and the experimental evidence of the transformation of **1** into **2** from ^{29}Si NMR. Spectrum a was obtained after stirring the mixture of TEOS and TPAOH aqueous solution (TPAOH/TEOS/ H_2O molar ratios of 1:2.7:16) for 30 min at 0 °C. After 120 min stirring at 0 °C, the NMR spectrum b mainly shows the presence of pentacyclic dodecamer **2**. In both experiments, unconverted TEOS was removed through extraction with precooled octane. The ^{29}Si NMR signals at ca. -89.3 and -90.1 ppm stem from the pentacyclic octamer³ from which the tetracyclic undecamer is formed by addition of three Si atoms.

should contain these units of about 11 Si atoms. NMR signatures of molecules related to these *monomers* should appear shortly before precursor formation. After stirring the concentrated mixture (TPAOH/TEOS/ H_2O of 1:2.7:16) for 30 min, an emulsion was obtained that slowly splits into two liquid phases when agitation was stopped. The removal of the organic from the aqueous phase was achieved by extraction with octane at 0 °C. In the octane solvent, TEOS was the only silicon-containing molecule observable with ^{29}Si NMR. In the Q^3 range (from -97 to -99 ppm) of the ^{29}Si NMR spectrum of a sample obtained after stirring at room temperature for 30 min (Figure 1e), three lines at -97.2, -97.5, and -98.2 ppm are prominent. These lines cannot be assigned to cubic octamer, showing a single peak at -98.6 ppm.¹⁴ In the spectrum of Figure 1e, the signals at 89.0 and 89.9 ppm were previously assigned to pentacyclic octamer, the signal at 81.6 ppm to the three-ring, and the signals at 87.7 and 88.1 ppm to bicyclic pentamer³. The phase shift of the signals of the bicyclic pentamer was ascribed to the presence of a residual octane layer³. In attempts to allow better observation of the early molecular steps, synthesis experiments were performed at 0 and 10 °C (20 experiments in total). The particular group of three lines in the Q^3 range was always linked in intensity to three additional lines in the Q^2 region (Figures 1e, 3a, and 4c and Figures 2, 3, and 6 of ref 3). After a reaction time of 30 min or shorter at 0 °C, 10 °C, or room temperature, the relative intensities of these six signals always correspond to ratios of 2:2:2:2:2:1 (Figure 1e and Figure 9 of ref 3). Only an entity with integer multiples of 11 Si atoms can account for this intensity ratio. The molecule should have either a 2-fold axis or a mirror plane on which a Q^2 atom is sitting. Considering that there are two more types of Q^2 and three types of Q^3 , only a few molecular structures are possible. Taking into account that FTIR hints at the presence of five-rings, the *tetracyclic undecamer 1* remains as the only possible arrangement (Figure 3a).

The same six signals with differences in relative intensity are also observed for mixing times longer than 30 min at 0 and 10 °C (Figures 3 and 4). This indicates that there is a conversion of tetracyclic undecamer into a structurally closely related molecule. One line in the Q^3 range at -97.6 ppm and two in

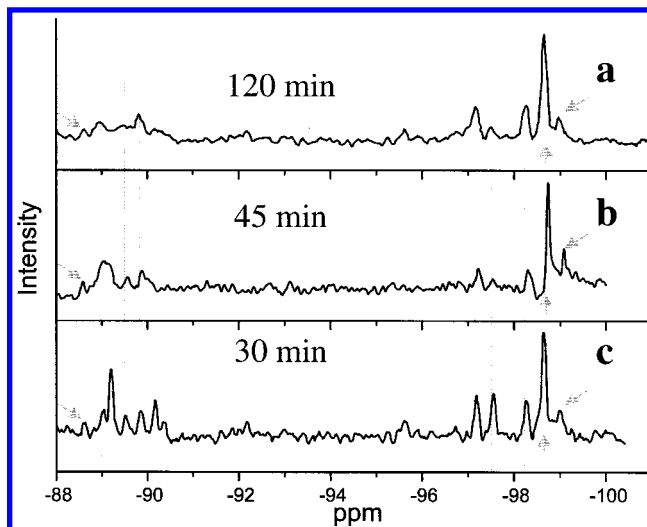


Figure 4. ^{29}Si NMR spectra obtained after different stirring times of a mixture of TEOS and TPAOH aqueous solution at 10 °C (TPAOH/TEOS/ H_2O molar ratios of 1:2.7:16): (a) stirred for 120 min; (b) stirred for 45 min; (c) stirred for 30 min. In the three experiments, unconverted TEOS was removed through extraction with precooled octane. Grey lines indicate the positions of the lines assigned to tetracyclic undecamer **1** and pentacyclic dodecamer **2**. Grey arrows mark signals assigned to capped double five-ring.

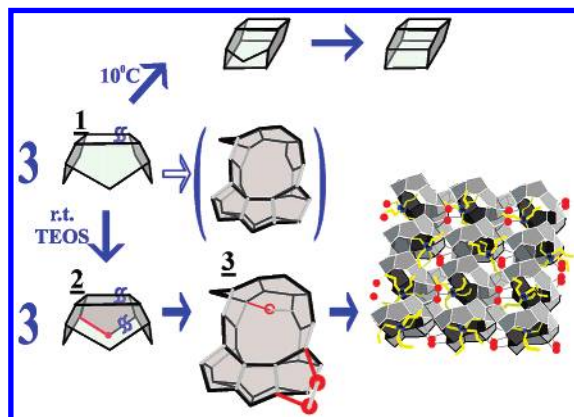


Figure 5. Model for the possible evolutions of tetracyclic undecamer **1**. At room temperature, pentacyclic dodecamer **2** is formed but quickly consumed in the formation of precursor **3**. Depending on incorporation of tetracyclic undecamers **1** versus pentacyclic dodecamer **2**, up to three Si atoms may be missing in the precursor **3** (red markings). The observation that there are no systematically missing T sites in the final Silicalite-1 product⁶ leads to the conclusion that most tetracyclic undecamers **1** convert first to pentacyclic dodecamers **2** before assembling into precursors **3**. At lower temperature (0 and 10 °C), precursor **3** is not formed. Instead, the tetracyclic undecamer **1** closes into the capped double five-ring, which at room-temperature condenses further. Some pentacyclic dodecamer **2** remains.

the Q^2 range at -89.1 and -89.6 ppm in parallel decrease in intensity (Figures 3 and 4). The new specimen with three ^{29}Si NMR lines (Figure 3b and 4a) related to the tetracyclic undecamer shows a peak ratio of roughly 1:1:1, with one type of Q^2 and two types of Q^3 . The *pentacyclic dodecamer 2* shows these characteristics (Figure 3b).

At room temperature, pentacyclic dodecamer **2** is not present in the ^{29}Si NMR spectra (Figure 1), pointing to a fast rearrangement upon formation. As observed with NMR, XRS, and gel permeation chromatography (GPC), precursor **3** (Figure 5) and its oligomers represent the stable state at room temperature. Consequently, the precursor can contain between 33 and 36 Si atoms, depending on the relative incorporation of

tetracyclic undecamers and pentacyclic dodecamers into the precursor (Figure 5).

At 10 °C, the ^{29}Si NMR spectra do not show the presence of the precursor (Figure 4 compared to Figure 1c and d). With time, the pentacyclic dodecamer remains present and the tetracyclic undecamer is consumed (Figure 4). A strong line at -98.7 in the Q^3 range develops along with weaker lines in the Q^2 and Q^3 range (-88.7 , -98.9 ppm). This points to an intramolecular condensation of tetracyclic undecamer, resulting in the formation of a capped double five-ring. An eventual further evolution into more condensed molecules, possibly a double five-ring, occurs after the sample is warmed to room temperature.³ The local environment of Q^3 silicon atoms in highly condensed, nonstrained, symmetric species such as double four-ring or double five-ring is very similar, resulting in similar chemical shifts.¹⁴

We experienced that the water content during the formation of the precursor is a critical parameter. Hydrolysis of TEOS in more diluted TPAOH solution results in less-specific particle populations and, consequently, after heating, in low-quality Silicalite-1 accompanied with an X-ray amorphous phase. Kinrade et al. prepared solutions from amorphous silica using diluted tetraalkylammonium (TAA) hydroxide solutions and added DMSO as organic solvent.¹ In their work (Figure 3 of ref 1), the $\text{H}_2\text{O}/\text{TAA}$ ratios were 311, 78, or 37, compared to the presently used ratio of 16. The critical $\text{H}_2\text{O}/\text{TPAOH}$ molar ratio for a change from a local direct templating effect to a long-range indirect influence of TPA should, therefore, occur somewhere between 16 and 37. With a large excess of water, the tetraalkylammonium cations can interact with water rather than with silicate species. The influence of template on the silicate species would then be of a more indirect nature and less-specific.

Kinrade et al. focused on work with TMA.^{1,15} They provide strong experimental evidence for the favored formation of cubic octamer using the small TMA molecule as template. It is well-known that synthesis mixtures containing TMA preferentially lead to the formation of even-membered-ring zeolites.¹⁶ On the other hand, TPA and tetrabutylammonium (TBA) build zeolites with five-membered rings.¹⁶ The ^{29}Si NMR spectrum of ref 1, Figure 3, clearly shows the formation of larger particles in the presence of TPA and TBA as evidenced by the broad NMR signals. The absence of this feature in solutions synthesized with TMA (Figure 2 of ref 1) hints at a different chemistry.

We do not, a priori, discard possible mechanisms for zeolite formation other than the templating and aggregation mechanism observed in our specific case. Instead, we believe that synthesis mixtures strive toward minimization of their energy. This energy state not only should be a function of temperature but could be

determined by the nature of the template molecule and the properties of the surrounding medium as well. Depending on such parameters, a colloidal-aggregation mechanism or a classical surface-growth mechanism might occur.

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- (13) ^{29}Si liquid NMR experiments were run at 0 °C on a Bruker AMX 300 MHz instrument. Optimization of the experimental conditions resulted in a selection of a pulse angle of 45° and a recycling time of 10 s to avoid saturation of the signals. Between 5000 and 10 000 spectra were accumulated. Samples were measured in cylindrical polytetrafluoroethylene (PTFE) sample containers surrounding PTFE tubes with tetramethylsilane (TMS) as standard. Test measurements before and after the main accumulation were performed to ensure sample stability during recording. All spectra were decoupled. After the indicated reaction times, any further sample handling including the extraction with octane and the storage was also done at 0 °C. Under such conditions, the ^{29}Si NMR spectra did not show any evolution upon storage (0 °C) for several weeks. In the experimental procedures of this work, silicate monomer was never observed.
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