Silicates

DOI: 10.1002/anie.200701927

Dynamics of Silicate Species in Solution Studied by Mass Spectrometry with Isotopically Labeled Compounds**

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Silica and silicates are abundant in the crust and the mantle of the earth. They are also indispensable in many fields of science and technology, such as cement, ceramics, glass, zeolites, and catalysts. The aqueous chemistry of silicates has thus been intensively studied in the past by different methods.[1] While the introduction of ^{29}Si NMR methods[2,3] allowed detailed insight into silicate speciation, dynamical information on various solution species[4] is still limited to small oligomers and short time domains.[2] Interconversion mechanisms of larger silicate oligomers remain largely unexplored. Larger oligomers have repeatedly been discussed as building blocks for zeolite formation,[5] but these suggestions have remained highly disputed.[6]

In order to study the interconversion process between oligomers, we have used electrospray ionization mass spectrometry (ESI-MS) in connection with isotopically labeled silicates. For aqueous silicate solutions as studied here, as well as for organic silsesquioxane solutions, ESI-MS has proved to be a very versatile technique.[7]

We have focused on two cagelike species: the octamer is known to be a very stable species in the presence of tetramethylammonium (TMA$^+$)[8] and the hexamer in the presence of tetraethylammonium (TEA$^+$).[9,10] To study the stability of these species and elucidate the interconversion mechanisms, kinetic experiments with isotopically labeled solutions were carried out. Naturally occurring silicon consists of three isotopes: ^{28}Si (92.2 %), ^{29}Si (4.7 %), and ^{30}Si (3.1 %). A solution containing the cubic octamer as the major species was prepared by dissolution of SiO_2 in an aqueous solution ($1\,SiO_2/1.1\,TMAOH/54\,H_2O$) for 24 h at 77 °C and aging at room temperature for 24 h, which leads to a stable system in which 55 % of all silicon atoms are present in the cubic octamer (^{29}Si NMR analysis). A solution containing the prismatic hexamer was obtained by using TEA hydroxide under the same conditions. For both species a second, identical solution, but made from ^{29}Si-enriched silica (96.7 % ^{29}Si, Euriso Top, France) was prepared in parallel. For mass spectrometric analysis, a previously described setup was used.[11] The individual solutions showed the same mass spectra, the only difference being that the main signals were shifted to higher mass due to the heavier silicon isotope. A superposition of the spectra of the octamer solutions containing the ^{28}Si and ^{29}Si silicate species in one plot is shown in Figure 1 a to provide a reference point. The intensities at masses other than m/z 551 or 559 are due to the small amounts of the other isotopes present in the respective starting solutions.

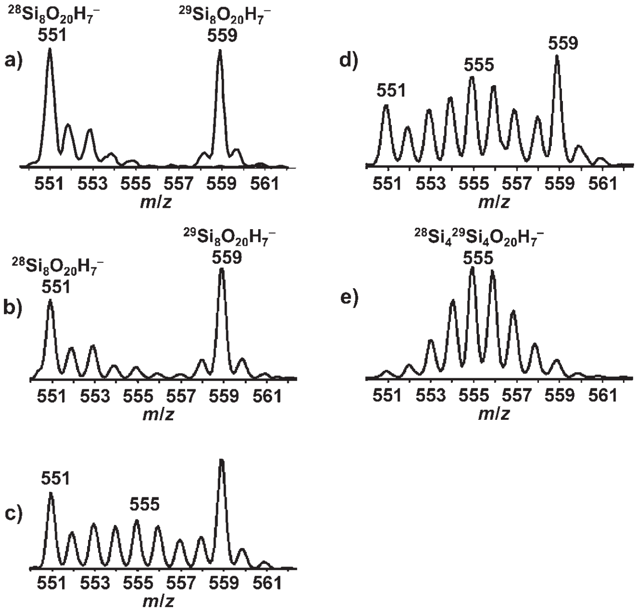

Figure 1. Temporal development of mass spectra with time in the m/z range of the cubic octamer. Reaction starts after combining solutions of the ^{28}Si cubic octamer (m/z 551) and the ^{29}Si cubic octamer (m/z 559) with stirring at 1000 rpm. $T = 35$ °C, molar composition $1\,SiO_2/1.1\,TMAOH/54\,H_2O$. Superposition of the spectra of the unmixed starting solutions (a) and spectra recorded 2 min (b), 55 min (c), 85 min (d), and 5 h (e) after mixing.

After the two solutions were combined, exchange of the ^{29}Si atoms between the silicate oligomers was observed, until the statistically expected distribution was reached. Figure 1 b–e shows the temporal evolution of a series of mass spectra in the m/z range of the cubic octamer after combination of the silicate solutions at 35 °C. Starting from a bimodal distribution of the peaks characteristic for the $^{28}Si_8$ octamer and the $^{29}Si_8$ species, a distribution centered around the $^{28}Si_4{}^{29}Si_4$ species develops with time. Significant for the interpretation of the

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[**] The authors acknowledge funding by the Leibniz program of the DFG, in addition to the basic funding by the Max-Planck-Society. We thank P. Phillips and Dr. B. Mynott for their support in the NMR analysis.

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

data is the fact that the distribution does not seem to move to the center from the edges, but that intensity for the $^{28}\mathrm{Si}_4{}^{29}\mathrm{Si}_4$ species starts to grow virtually from the beginning. This points towards a concerted exchange mechanism as opposed to monomer exchange. Figure 2 shows similar results for the atom exchange of the hexamer. A peak which corresponds to a $^{28}\mathrm{Si}_3{}^{29}\mathrm{Si}_3$ species starts to grow from the beginning. Due to the fast atom-exchange process the reaction mixture and the syringe were cooled to 5 °C, and four equivalents of ethanol were added to further slow down the reaction.

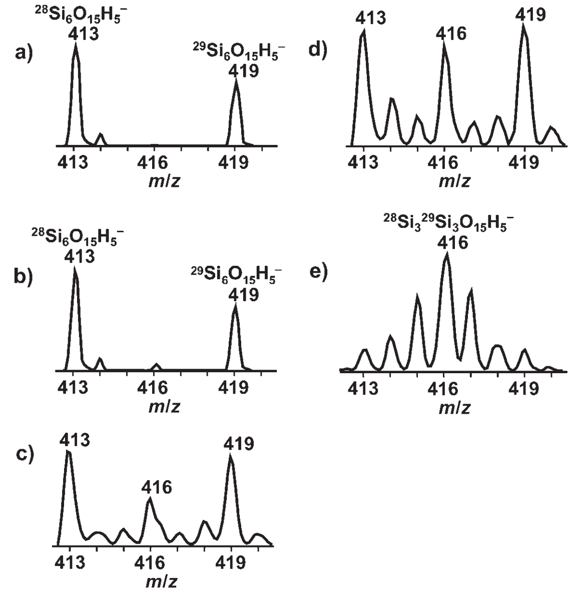

Figure 2. Temporal development of mass spectra after mixing of equally concentrated solutions containing the prismatic hexamer with natural-abundance silicon and ^{29}Si-enriched silicon. Composition 1 $\mathrm{SiO_2}$/1.1 TEAOH/54 $\mathrm{H_2O}$:4 ethanol. a) Superposition of the spectra of the unmixed starting solutions, b) immediately after mixing, c) after 15 s, d) after 60 s, e) after 1 h.

To understand the evolution of the spectra in a more quantitative manner, a kinetic model was developed involving all isotopomers of the silicate species and incorporating all possible exchange steps between them. This results in a set of coupled differential equations, which was numerically integrated while using the exchange rate constant as a fit parameter (see Supporting Information). Figure 3 shows that the best fit for the octamer was achieved in a model involving simultaneous exchange of four atoms. For the hexamer, a model involving exchange of three atoms at the same time provided the best fit. Note that after long reaction times any formally correct exchange model will yield the statistically expected distribution. Long reaction times are thus not useful for discriminating between models. Such a concerted, complete-face exchange could occur if two cubic octamers combined by linking one face of each cube to form a new cube and simultaneously releasing two cyclic tetramers. Furthermore, if two prismatic hexamers combined, they would be expected to link via the three-ring faces, which are less shielded by template molecules than the four-ring faces, and form a new hexamer and two single three rings. Although surprising at first sight, these concerted exchange reactions seem quite plausible from the point of view of silicate chemistry: exchange of only one corner would need either fission of three siloxane bonds to generate a vacant corner with subsequent reintroduction of a silicate monomer, or insertion of a silicon atom into the Si-O-Si bond on one edge of the cube. This could then exchange into a corner position by a concerted process involving a strained three-ring intermediate or a sequence of hydrolysis/recondensation reactions, and finally expulsion of the exchanged silicon atom (see Figure S1). Exchange of a full face appears to be a viable alternative to such sequences. The first step of this exchange reaction could be the formation of a single siloxane linkage between two cubic species, which has been observed previously by NMR spectroscopy.[12] This first connection would lock the two four rings in place, possibly helped by one template molecule coordinated to one face of each cube, so that probability of simultaneous or successive reaction at the remaining corners of the face would now be higher. Single four or three rings would be simultaneously released by this reaction, which may directly recombine or enter the silicate pool of the reaction mixture. These single rings equilibrate so rapidly in the reaction mixture that their mass spectrometric signatures can not be used to support the model. Note that no formation of highly improbable double- or triple-cube or -hexamer structures is necessary if the whole exchange process proceeds in a concerted manner.

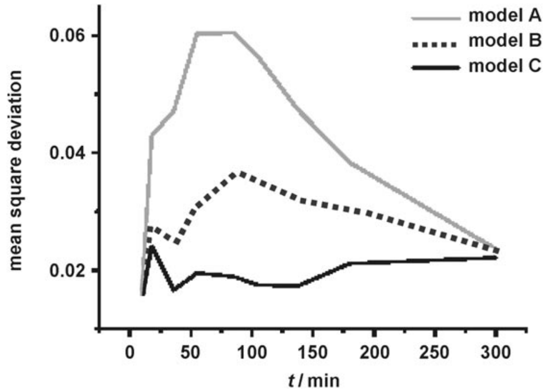

Figure 3. Comparison of the quality of the fit (expressed as mean-square deviation between model and experimental distribution for the cubic octamer) at different times for single-atom (model A), two-atom (model B), and four-atom exchange (model C). The fits converge towards the end of the experiment, because then a stationary state with the statistically expected distribution is reached. Model C fits the experimental pattern best over the whole time of the experiment.

If the exchange reaction is a concerted process, in a first approximation the reaction order with respect to octamer concentration is expected to be two, instead of one for monomer exchange. The concentration of cubic octamers was therefore reduced by lowering the silicon concentration, while keeping the TMAOH concentration constant. (Reduction of all concentrations leads to the formation of a variety of different species, see Figure S2). This led to strongly reduced initial exchange rates, as determined from the reduction of the *m*/*z* 551 signal at the onset of the reaction. For a concentration of cubic octamers (determined by ^{29}Si NMR spectroscopy) of 0.066 mol$\,$L^{-1} the rate is 9.6×10^{-4} mol$\,$L^{-1}min^{-1}, for 0.046 mol$\,$L^{-1} 9.3×10^{-5} mol$\,$L^{-1}min^{-1}, and for 0.026 mol$\,$L^{-1} 2.5×10^{-5} mol$\,$L^{-1}min^{-1}. This suggests a reaction order substantially exceeding even two, which can be rationalized by the higher relative concentration of TMA$^+$ in the solutions containing less silicon. Since the TMA$^+$ ions occupy the faces of the cubes,[10,13] their higher relative concentrations with respect to the cubes would lead to additional screening and thus stabilization of the system. This explanation based on the crucial role of tetraalkylammonium ions in stabilization of the cage-type species[4,9,10,13] is in line with the above results of isotope exchange for the TEA$^+$-stabilized prismatic hexamer. For the hexamer/TMA$^+$ system (calculations with TEA$^+$ are not available) it was calculated, that the TMA$^+$ on average only occupy the three square faces, but to a much lower degree the triangular faces.[10] Experimentally, exchange for the hexamer proceeds by about two orders of magnitude faster than for the octamer (Figure 2b–e), and the exchanged face is the less shielded triangular face.

Additional support for this concerted mechanism comes from experiments in which a silicate monomer solution was added to a solution of the ^{29}Si-labeled octamer. If monomer exchange were the decisive reaction, formation of partially ^{28}Si substituted species should be observed instantaneously. However, significant exchange was only observed after an appreciable time delay, probably necessary for the formation of a sufficient concentration of the ^{28}Si octamer, with intensity again appearing predominantly at $m/z=555$ initially (see Figure S3). Reduction of the rate in this case may also be due to the methanol released from TMOS hydrolysis, but the early appearance of the m/z 555 signal is significant.

The experimental setup also allows determination of the temperature dependence of the exchange reaction for the cubic octamer. Due to the two orders of magnitude faster exchange reaction, this is not possible for the prismatic hexamer. The reactions for the octamer were carried out at 23, 35, 45, and 55 °C. The rate constants for exchange were determined by fitting the development of the profiles. An Arrhenius plot of the logarithm of the rate constants against reciprocal temperature gives a straight line (Figure 4) and a calculated apparent activation energy of (136 ± 5) kJ$\,$mol^{-1}.

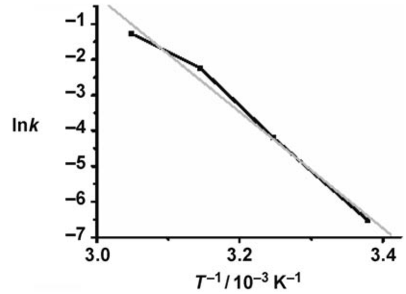

Figure 4. Arrhenius plot of ln*k* versus 1/*T*. The *k* values for the exchange reaction between the cubes were obtained from measurements of the temporal development of the species distribution at 23, 35, 45, and 55 °C and fitting of this development with the model of simultaneous exchange of four silicon atoms. From the slope an activation energy of (136 ± 5) kJ$\,$mol^{-1} can be determined.

The findings reported here have important implications for nucleation and growth processes of zeolites and other silicates, even though the experiments were carried out under conditions in which no zeolites form. First, if one extrapolates the rate to typical zeolite synthesis temperatures of 90 °C and higher, it is clear that the interconversion of even very stable oligomers in solution is sufficiently rapid to allow any growth species to be regenerated after it has been incorporated into a growing zeolite, since even very stable species are highly dynamic.

Secondly, one could consider a growing zeolite to be one very large oligomeric species. Based on the finding that concerted exchange of silicate species seems to be more probable than monomer exchange, one may speculate that such processes involving oligomer addition, be it whole oligomers present in solution or fragments of such species, could also be a major process contributing to the growth and possibly also nucleation of zeolites. This will certainly be dependent on the synthesis conditions. Under highly alkaline conditions, where monomeric species are more abundant, monomer addition could be the dominant process. Also at high growth rates, where redissolution equilibrium at the surface is not very important, addition of species will be the major factor, possibly involving oligomers with release of small fragments which do not fit the structure. However, the synthesis of some high-silica zeolites proceeds slowly over days or months at lower temperatures and relatively low alkalinity.[14] Under the conditions of synthesis of such zeolites, large oligomers are present[15] with a distribution which is largely independent of the added template. These units could easily be incorporated in orientations corresponding to the crystal structure by concerted processes such as those shown for the exchange between octameric and hexameric cage-type oligomers.

This study shows that detailed insight into the dynamics of silicate solutions can be obtained by ESI-MS in combination with labeled compounds. It seems straightforward to extend similar approaches to other systems. We are now studying the incorporation of aluminum and germanium atoms into silicate species, highly relevant to zeolite synthesis, since germanium stabilizes the double four ring important in the synthesis of materials with very large pores.[16]

Received: May 2, 2007
Published online: July 27, 2007

Keywords: hydrothermal synthesis · isotopic labeling · kinetics · mass spectrometry · silicates

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