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Mass spectrometric investigation of small silicate polyhedra in solution

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Abstract

The hydrolysis of tetra-methyl-ortho-silicate (TMOS) or tetra-ethyl-ortho-silicate (TEOS) in aqueous solutions at pH values of 1–2 was investigated by electrospray mass spectroscopy. In this study, small oligomer intermediates of silicates were formed and detected. Some of the structures are secondary building units as found in zeosils and zeolites. Here, we present the first H/D-exchange mass spectrometric experiments to determine the structure of silicates formed in acidic solution. Most of the observed oligomers take on polyhedral geometries. The results are compared with experiments of other groups, which have performed complementary experiments in alkaline solutions in presence of template molecules.

Keywords: Electrospray; H/D exchange; Silicates; Structure; Polyhedra

1. Introduction

The formation of zeolites and zeosils with unique properties is one of the most interesting challenges in material science. Since the variety of silicates is fascinating, the development of specialized materials with tailored properties, e.g., zeolites for highly selective catalysis or membranes for gas separation, is extraordinarily promising, and thus, gained major interest over the recent years. Even though much progress has been achieved, the formation of the bulk material is still not well understood microscopically. Particularly, the initial nucleation phase from the monomer to small oligomers in solution has not been investigated in sufficient detail. However, for a controlled synthesis of zeosils, zeolites and mesoporous structures from solution targeting specific properties, it is necessary to understand the stepwise transient formation of intermediates from monomer to oligomer to bulk material. Already in 1968, it was proposed that all zeosils and zeolites might be built-up from small oligomers of so-called secondary building units (SBU) [1,2]. These building units are rings and polyhedra. 20 different SBUs have already been detected by ^{29}Si NMR spectrometry [3], a method well established in silica chemistry. To obtain good signal-to-noise ratios in ^{29}Si NMR studies, one commonly requires concentrated solutions or substantial enrichment in the ^{29}Si isotope. In 2000, two polyhedra were detected using tandem MS-^{29}Si NMR spectroscopic methods [4]. Specifically, the ^{29}Si NMR data distinguishes between the different types of chemical environments of the silicon atom: Q_i denotes a tetrahedral coordinated Si atom, which is bonded through oxygen bridges to i- other Si-atoms. Still, it is difficult to obtain ^{29}Si NMR spectra sufficient enough to determine structures in diluted solutions without enrichment of ^{29}Si, because the formation of zeosils typically takes place in diluted solutions. As a result, ^{29}Si NMR only in combination with other experimental techniques provides enough sensitivity to determine the structures of intermediate silicates in solution. A very powerful method, which we propose here, is the utilization of the H/D exchange in mass spectrometry. Owing to this technique, we were able to find small polyhedral silicates even in diluted solutions.

In the experiments suggested here, we present a simple experimental setup that allows for the observation of a

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variety of silicate oligomers from an acidified aqueous solution of hydrolized tetra-methyl-ortho-silicate (TMOS) at pH values from about 1 to 4. The hydrolization itself has been investigated in 2002 with CI and EI [5].

2. Experimental

The solutions were prepared by mixing TMOS or TEOS with acidified water. In general, the hydrolysis of TMOS is faster than the one of TEOS. However, in an extensive series of hydrolization experiments using either alkoxy silicate (TMOS or TEOS), it was found that the silicate source did not influence the formation of the different oligomers. Even the intensity of the corresponding mass signals in both spectra remained identical. The hydrolysis of TMOS or TEOS including the effects of varying the pH value, the water–alcohol ratio, and the temperature, is described in the literature [6]. Typically, the solution was prepared by adding 1–10% v/v of TMOS or TEOS to water acidified with hydrochloric acid. The samples were mixed vigorously. In contrast to the formed silicates, the two alkoxy silicates are not soluble in water and two phases are present. As the tetra-alkoxy-silicate hydrolysis progresses, the second phase vanishes. Furthermore, the reaction rate of tetra-alkoxy-silicate hydrolysis can be controlled by adjusting the temperature, where a reduction in temperature slows the reaction.

The electrospray mass spectra were obtained using an API 3+ electrospray mass spectrometer from Applied Biosystems. The spectra were recorded in negative ion mode, i.e., the negatively charged ions were registered. In positive ion mode, no useful spectra could be obtained, suggesting that the silicates more easily form negative ions. The electrical potentials as well as the gas flow were adjusted initially towards an optimized ion signal and remained unaltered during the experiment. The optimized potentials with respect to ground were -5 KV at the electrospray needle, -650 V at the entrance skimmer, -60 V at the entrance cone and -30 V at the entrance lens of the quadrupole rods. The flow of compressed air (hydrocarbon free) through the assisted electrospray needle was kept at 0.6 l/min, the curtain gas flow was held at 1.2 l/min. The flow of the analyte through a deactivated silica capillary was adjusted to 12 μl/min. The H/D exchange was accomplished by the use of deuterium oxide (D_2O) (Aldrich) instead of water and DCl dissolved in D_2O (Aldrich). The TMOS and TEOS were used undeuterated. The deuterated solutions were prepared at the same concentration as the ^1H solutions.

3. Results and discussion

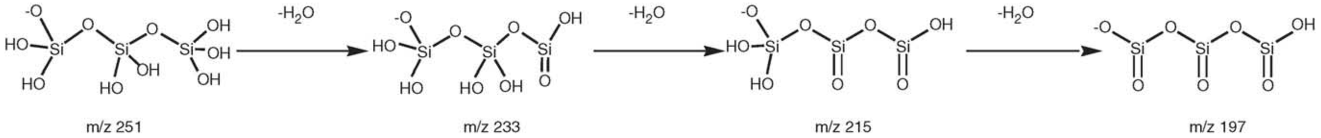
The principal reactions occurring during the hydrolyzation of TMOS and TEOS are given in the literature [5]. In our investigation, however, the primary products of the hydrolyzation reaction,

$$\mathrm{Si(OCH_3)_4} + n\mathrm{H_2O} \rightarrow \mathrm{Si(OCH_3)_{4-n}(OH)_n} + n\mathrm{CH_3OH}\ (n = 0\text{–}4)$$

were not observed owing to the relatively long time it takes to setup the mixed samples for electrospray and to the relative high dilution of the samples. Using partially hydrolyzed samples, one can obtain partially hydrolyzed silicates such as $Si(OCH_3)(OH)$. Contrary to our electrospray measurements, ^{29}Si NMR experiments are often performed in highly concentrated solutions with a volume ratio of 1:1:1 (TMOS:methanol:H_2O). For such solutions branched and unbranched chains rather than polyhedra were found in ^{29}Si NMR investigations [7,8].

During the electrospray process, chain forming silicates can experience a loss of water, i.e., the so-called dehydroxylation, schematically: Scheme 1.

As described above, all molecules are found as singly negatively charged species, which are obtained by the removal of a proton (H^+) from the molecule, thus leaving an anion that is subsequently detected. Mass spectra, which were recorded immediately after preparing the solution show – in contrast to spectra recorded at later times – the formation of chains. These chains can be found in a spectrum that was recorded only about 5 min after mixing the solution: The mass spectrum given in Fig. 1 shows a series of silicate chains. These signals originate from silicate chains that are at different hydration levels. Mass signals in the spectra of Fig. 1 can be assigned as follows: silicate dimer chain 137, 155, 173; silicate trimer chain (251), 233, 215, 197; silicate tetramer chain (329), 311, 293, 275, 257 and silicate pentamer chain (407), 389, 371, 353, 335, (317). The signal at 449 and 431 is assigned to a partially dehydroxylated silicate hexamer chain (485), (467), 449, 431, 413, (395), (377). The values in brackets are weak signals. Further, the first polyhedra can already be observed. The observed species are in full agreement with a schematic published in 2000 [4].



Scheme 1.

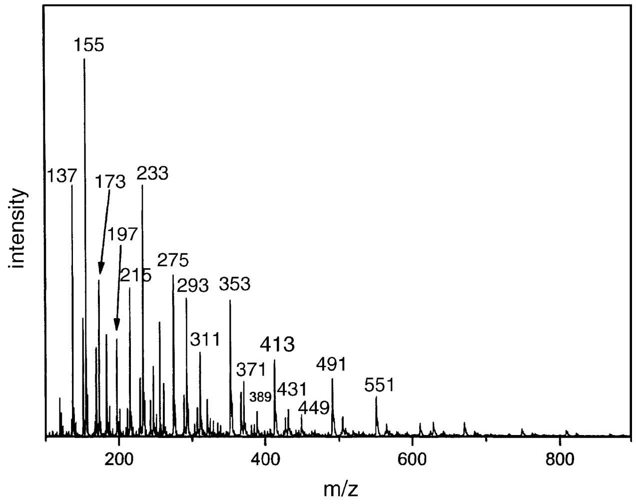


Fig. 1. Electrospray mass spectrum taken 5 min after mixing from a solution of 10 %vol of TMOS in H_2O at a pH value of 1. The signals labeled correspond to silicates forming small chains up to an *m*/*z* ratio of 449.

By simultaneous condensation and dissolution processes a pH and temperature dependent medium oligomer size is observed [9,10].

Progressing in time, the observable species develop from chains to polyhedra which are present in Fig. 2. This development from chain to polyhedra at pH smaller than 7 is in agreement with Iler [11]. The figure captures an H/D exchange experiment that was performed 1 h after preparing the solution at room temperature. The typical signal pattern providing the evidence for the presence of chains is missing here. The mass signals labelled as A denote the molecule with a *m*/*z* of 215, while B corresponds to an *m*/*z* of 233. The absence of the peaks 311 and 257 in the spectra recorded 1 h after mixing the solution are a strong support for a polyhedral structure as mentioned in Table 1.

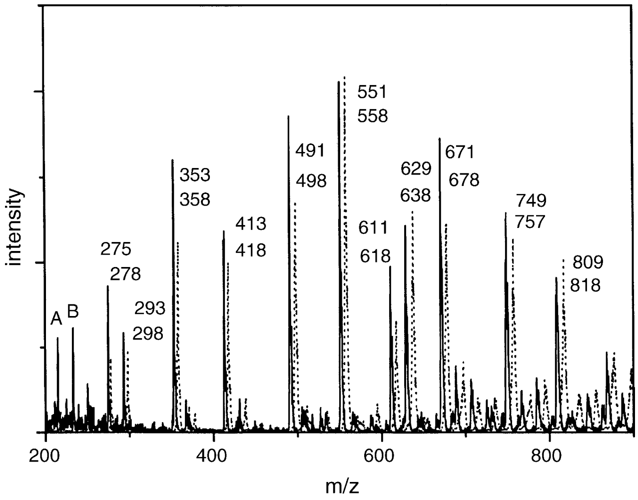
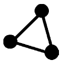
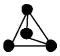
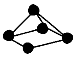
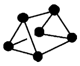
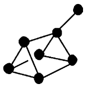
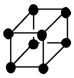
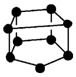
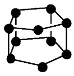
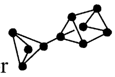
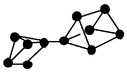
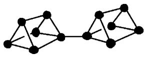


Fig. 2. Electrospray mass spectrum of a mixture of 10 %vol TMOS in H_2O at a pH value of 1 (full line) and an electrospray mass spectrum of a mixture of 10 %vol TMOS in D_2O at a pH value of 1 (dotted line). Both spectra were taken from solutions that were aged for 1 h at room temperature. In each pair of labels, the upper number designates a signal from solution with hydrogen while the lower number assigns a signal from deuterated solution. The labels A and B are the mass peaks A *m*/*z* = 215 (218), B *m*/*z* = 233 (238).

Our mass spectrometry experiments allowed for the observation of a large variety of small polyhedra with the use of H/D exchange. Among those, the smallest polyhedra is a cyclic trimer that corresponds to a signal for a singly negatively charged molecule at *m*/*z* = 233. Unfortunately, a chain of three silicates from the singly dehydroxylated molecule exhibits exactly the same *m*/*z* ratio. Consequently, for these units the determination of the morphology is ambiguous. The next significant pair of signals in the mass spectra occurs at *m*/*z* = 293 and 275. This pattern is attributed to a trimeric ring with an additionally –O–Si–O– sub-unit bridging over one side of the ring. This species contains two OH-groups on one of the bridging Si-atoms. From the H/D exchange experiment, it is derived that this molecule has five H-atoms that can easily be exchanged with D. At the bridging, Si carrying two OH-groups dehydroxylation can occur leaving a molecule with the *m*/*z* ratio of 275. As verified in the H/D-experiments, this molecule has three OH-groups. Accordingly, a chain with four silicon atoms would give rise for a series of signals exhibiting the *m*/*z* ratios 329, 311, 293, 275 and finally 257 for the completely dehydroxylated form. In support of this signal pattern, one would expect for the H/D-experiments that 9, 7, 5, 3 or 1 OH-groups are determined. However, this series was not found in our experiments. Only two signals at *m*/*z* ratios of 275 and 293 could be identified, leading to the conclusion that such chains are not present. The next molecule observed has a *m*/*z* of 353, the H/D exchange shows five OH-groups. A series of peaks with *m*/*z* = 407, 389, 371, 335, 355 and 317 with corresponding amount of 11, 9, 7, 5, 3, 1 OH-groups, respectively, is not present. Again, this strongly indicates the presence of a polyhedral molecule. The absence of signals at an *m*/*z* of 371 and 389 support the observation of polyhedra. The subsequent signal at an *m*/*z* of 413 is assigned to a prisma with five hydrogen atoms. For the reasons mentioned above an open structure with more than one OH-group at each silicon atom can be excluded. Furthermore, this conclusion is supported by the absence of mass signals at *m*/*z* of 431 and 449. A prismatic structure with a tail is found at 491. For the reasons mentioned above an open structure with more than one OH-group at each silicon atom can be excluded. A prismatic structure with a tail is found at 491. The signal found at an *m*/*z* of 551 is very interesting since it can be identified as a cubic silicate. These polyhedral structures at 413, 491 and 551 were also found previously in alkaline solutions in the presence of amines acting as a structure directing agent [4]. In that study, besides the electrospray mass spectrometry also ^{29}Si NMR experiments were performed to secure the morphologies.

The more intense signals assigned in our spectra arising from complex polyhedral anions are shown in Table 1. These polyhedral anions could be observed in solutions that were aged between several minutes to a few hours. In general, working at room temperature, after 5–10 h, we observed an increase of the signals at higher masses which is explained

Table 1
Plausible polyhedra structures determined 1 h after mixing by electrospray mass spectrometry from a solution containing initially 10 %vol TMOS in H_2O acidified with $HCl_{(aq)}$ at a pH value of 1 or 10 %vol TMOS in D_2O acidified with $DCl_{(D_2O)}$

Polyhedral	m/z observed in ^{1}H-experiment	m/z observed in ^{1}D-experiment	Hydrogen atoms
	215, 233	218, 238	3, 5
	275, 293	278, 298	3, 5
	353	358	5
	413	418	5
	491	498	7
	551	558	7
	611, 629	618, 638	7, 9
 or 	671	678	7
	749	757	8
	809	818	9

The shown structures are all singly negatively charged (not shown in the table). In the table, a silicon atom is represented by a ball and a Si–O–Si bond by a line. The found amount of hydrogen atoms is reduced by one due to the charge.

by the ongoing growth of the polyhedral structures from reactions between each other and remaining monomers. This growth can already be seen in the mass spectrum presented here. Finally, we obtained the well known highly viscous gel. Owing to this viscosity, further investigations by electrospray mass spectrometry were impossible.

4. Conclusion

In this mass spectrometry study, we have presented the successful determination of structures of small silicate oligomers by H/D exchange experiments. The formation of these oligomers in diluted aqueous solutions is shown to be independent of the tetra-alkoxy-silicate source. The small oligomers can be assigned to distinct polyhedral structures.

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