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**PAPER**

# Kinetic Monte Carlo modeling of silicate oligomerization and early gelation†

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We present a lattice-gas kinetic Monte Carlo model to investigate the formation of silicate oligomers, their aggregation and the subsequent gelation process. In the early oligomerization stage, the 3-rings are metastable, 5-rings and 6-rings are formed in very small quantities, 4-rings are abundant species, linear and branched species are transformed into more compact structures. Results reveal that the gelation proceeds from 4-ring containing species. A significant amount of 5-rings and 6-rings, sharing Si with 4-ring, form in the aging stage. These reveal the formation mechanism of silicate rings and clusters during zeolite synthesis.

## 1 Introduction

Understanding silicate oligomerization and gelation is of fundamental scientific and technological importance.[1–3] Condensation of silicate monomers leads to oligomeric units that condense further in different reaction steps to larger species and clusters. The mechanisms governing these processes are still not well understood.[2,4] The essential difficulty of studying the pre-nucleation process arises from the fact that the silicate oligomers are typically of the size of several $Si(OH)_4$ molecules, which is hard to access by most of the current experimental methods. Even if they are detected by microscopic techniques, the structural and reactive properties may not be distinguished due to their small size. Furthermore, some of the species exist for extremely short times and freely move throughout the available volume of solution, reducing the change of their appearance in the volume being examined.[5] The very early stages of solid-state formation from solution can be crucial in determining the properties of the resulting solids. Thus, higher levels of control over nucleation cannot be achieved without understanding the fundamentals of the elementary steps of silicate oligomerization.

A variety of spectroscopies and scattering techniques have been used to study the silica-based condensation reactions,[6–11] however the observation of these processes is still problematic due to the lack of adequate techniques to directly monitor the formation of silicate oligomers. Knight used [29]Si nuclear magnetic resonance (NMR) spectroscopy to study condensed silicate species present in aqueous solutions.[8] Using mass spectrometry, Pelster *et al.* investigated the temporal evolution of silicate species during hydrolysis and condensation of silicates.[10,12]

However, because of the multitude of simultaneous reactions in solution, it is difficult to extract information about individual events using only experimental data.[13]

Many theoretical methods have been used to model the early stages of solid formation.[13–22] Typically it is difficult for MD methods to model chemical reactions. Information about energetics of chemical reactions can be obtained by using DFT calculations, but kinetics cannot be predicted. Stable structures of silicate oligomers can be obtained from DFT calculations, but the most stable oligomers might not be the most preferable products. Moreover, DFT and MD methods are computationally very expensive and restricted to very small system and short simulation time (on the order of pico- or nanoseconds), thus relevant statistical information cannot be extracted. The time scale for the initial stage of zeolite formation is on the order of hours or even longer, which is not accessible to MD or DFT simulations. Monte Carlo models have emerged and have been proved to be good methods for modeling such systems.[15,17,20,23–26] Wu and Deem introduced a Monte Carlo model for silicate solutions for investigation of the nucleation process during zeolite synthesis in the absence of a structure directing agent.[17] Malani *et al.* presented a reactive Monte Carlo model, which is useful for modeling silicate oligomerization.[20] They have obtained agreement for the evolution of the $Q_n$ distribution upon comparing the simulation results to experimental observations. Lattice-gas Monte Carlo models were also used to model the formation of silica nanoparticles.[15,25] More recently, White *et al.* studied the initial stages of gel/cluster formation by using a coarse-grained Monte Carlo simulation, which represents all oligomers as point particles. They used quantum chemical-based interaction (dimerization) energies, which were determined through density functional theory computations.[27]

The effective modeling of the silicate oligomerization in solution requires a method that can simulate events at the microscopic

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length and macroscopic time scale. Kinetic Monte Carlo has the potential to shed light on the mechanism of silicate oligomerization and gelation processes. At the early stage of silicate oligomerization, various silicate oligomers can be formed, including linear, branched and ringed species. We have studied the silicate oligomerization from solution up to 4 silicate species.[16,19,23] Insight into the formation mechanism of larger silicate clusters is valuable. However, in the previous studies, DFT could not access larger clusters, continuum kMC could model larger systems, but larger clusters could not be predicted due to the coarse-graining effect. Here we use a lattice-gas kinetic Monte Carlo model to give insight into the mechanism of aggregation of silicate oligomers and the subsequent gelation. We use more accurate energy parameters than a previous Monte Carlo study.[27] We demonstrate the successful application of the multiscale simulation method to the silicate oligomerization and gelation processes, and reveal mechanistic information regarding the formation of silicate clusters.

## 2 Model and methods

We use a lattice-gas kinetic Monte Carlo model[28] to investigate the formation and aggregation of silicate oligomers and the gelation process. In the lattice-gas kinetic Monte Carlo simulations the system is treated as a grid. A grid is a collection of sites. Each site has a label that characterizes its properties; i.e., vacant, or occupied by some chemical species. A configuration of a silicate oligomer is then given by a particular distribution of labels. The change of the labels, meaning the evolution of a system, is given by diffusion and reactions of the silicate oligomers. This change can mathematically be formulated by the chemical Master eqn (1) and can be derived from first principles.[26] The chemical Master Equation describes the configurational change of a system as a function of time.

$$\frac{dP_\alpha}{dt} = \sum_\beta [W_{\alpha\beta}P_\beta - W_{\beta\alpha}P_\alpha] \qquad (1)$$

where $P_{\alpha(\beta)}$ is the probability of the system being in a configuration $\alpha(\beta)$ and $W_{\alpha\beta(\beta\alpha)}$ is the rate constant of the change of configuration $\beta$ into $\alpha$ ($\alpha$ into $\beta$). The rate constants determine the probability of a particular configuration and the speed of its creation and destruction. Values for the rate constants can come from electronic structure calculations or from experiments.

We have used the body-centered cubic (BCC) lattice with a distance between the cubic lattice points of 3.0 Å (to represent the Si–O–Si bond length, the O atoms are omitted for simplicity of the model) in the kMC simulations. This lattice allows the formation of 3-, 4-, 5-, and 6-rings. Earlier studies have used this lattice as well,[25] but have also used a simple cubic lattice.[15,27] The simulation box is 50 × 50 × 50 lattice points, which is 150 × 150 × 150 Å³ in size, and the initial monomer concentration is about 1 mol L⁻¹ (there are 2000 lattice sites occupied by monomers). In an earlier study, we used the same concentration of monomers to study the mechanism of silicate oligomerization under different conditions.[23] A much lower initial concentration of monomers (0.01 mol L⁻¹) was also studied,[24] which was suggested by White and Provis et al. in their comment.[29] The same mechanism of silicate oligomerization was found with the lower concentration.[24] The aim of this

paper is to study the gelation process. A high concentration of silicate where occur gelation is thus necessary. Each lattice site is occupied by a silicate monomer or vacant. The OH groups are course-grained into the silicon atoms.

The silicate oligomerization consists of a series of reactions, including linear growth reactions and ring closure reactions, each of which has its own activation energy. The activation energies are crucial parameters of the input of kMC. In the study of White et al.[27] the quantum chemical-based dimerization energy for all reactions was used. In our early studies, the activation barriers for linear growth, 3-ring formation and 4-ring formation were found to be quite different.[19,30] It is therefore important to use different activation barriers for linear growth, 3-ring formation and larger ring formation.

The initial monomers simply diffuse before they are able to react (become next nearest neighbors). When two silicon atoms become nearest neighbors, they are chemically bonded. The linear growth occurs via monomer addition or aggregation of dimers and trimers. Formation of the silicate rings (3-rings, 4-rings, 5-rings and 6-rings) occur via an intramolecular condensation reaction as has been suggested before.[19,30] The formed linear, ringed, and branched species can also diffuse, and aggregate to form larger ones. The newly formed silicate species can further change their shape to be more condensed. This is modeled by, for example, rotating newly aggregated 4-ring to form more bonds (keeping the formed bonds). The activation energies (and also for the reverse process) for linear growth, 3-ring formation, and larger ring formation are 61 (77, reverse), 72 (72, reverse), and 95 (111, reverse) in kJ mol⁻¹, respectively.[19,23] These parameters were initially obtained by CPMD simulations.[19] We considered a system consisting of one silicic acid Si(OH)₄ and its deprotonated form Si(OH)₃O⁻ with 64 water molecules. The simulation cell was a periodically replicated cubic box with a size corresponding to a density of solution around 1 g cm⁻³ under ambient conditions. The temperature was set at $T = 350$ K. There are two transition states in each bond formation of Si–O–Si. For instance, the activation energies of the linear growth are 44 (25, reverse) for the first transition state, and 42 (36, reverse) for the second transition state in kJ mol⁻¹. The condensation reactions are endothermic in the CPMD simulations. This is due to the contribution of entropy reduction from the water shell around the silicate molecules (more detailed information can be found in ref. 23). The reactions would not proceed with these parameters. Some of the activation energies were corrected in the study of the formation mechanism of silicate rings.[23] For instance, the activation energies of the linear growth are 44 (25, reverse) for the first transition state, and 42 (77, reverse) for the second transition state in kJ mol⁻¹ (the total activation energy is 61 kJ mol⁻¹). Here we use the total activation energy of 61 (77, reverse) kJ mol⁻¹ instead of two transition states to simplify the model. The diffusion of clusters with more than ten Si atoms was not modeled, because that would add too much complexity to the model. The role of pH has been studied in an earlier paper,[23] which is not the point of interest of this paper. We assume that two monomers can always react via the anionic mechanism,[30] in which there is one neutral and one anionic reactant. This means that the value of the pH is not assigned, and is assumed to be constant in the present study.

# 3 Results and discussion

The system starts with monomers only. They are distributed randomly in a cubic box under periodic boundary conditions. Monomeric species are initially abundant, thus dimerization that leads to the first stable product, the dimer, is fast. The formed dimers can initiate another reaction, the formation of trimers. The linear growth can lead to dimer, trimer, tetramer, pentamer and hexamer. Formation of the silicate rings (3-rings, 4-rings, 5-rings and 6-rings) occurs *via* an intramolecular condensation reaction. A multitude of silicate structures is formed, these can be linear, branched, cyclic, branched cyclic, and double rings. These silicate species can aggregate to form larger ones. The reverse processes are also possible. There are also monomers produced by hydrolysis reactions. Fig. 1 shows the change in fraction of silicate oligomers as a function of time. Monomers are abundant at this stage, the monomer addition is therefore the dominant process. Monomers are consumed rapidly, resulting in many small silicate oligomers. The linear species are not stable as can be seen from Fig. 1. The linear species are transformed into rings to be more condensed. At early times the formation of 3-rings is as fast as the 4-rings. With the increase in time, the number of 4-rings increases rapidly, the 3-rings are consumed at the same time. The 3-rings are not stable, they reopen to form a linear trimer, and serve as a source for the growth of larger species. This is in good agreement with our earlier work. In another study, we demonstrated by using an off-lattice kinetic Monte Carlo model the silicate oligomerization in water solution.[23] The 3-ring was found to be metastable, and 4-rings were the dominating species. However the larger species were not included in that work. In the present work, we focus on the aggregation and formation of larger silicate species. Fig. 1 demonstrates that the formation of 4-rings is very fast in the first 0.5 s, when supporting species are abundant. The formation of 5- and 6-rings is latter than the 3- and 4-ring formation. A slow increase in the concentration of 5-rings is found. The fraction of 6-rings follows that of the 4-rings. This is due to the fact that formation of 6-rings mainly occurs through aging of silicate clusters, *i.e.* 6-rings form *via* sharing Si with 4-rings. The total percentage is higher than 1, which is due to the
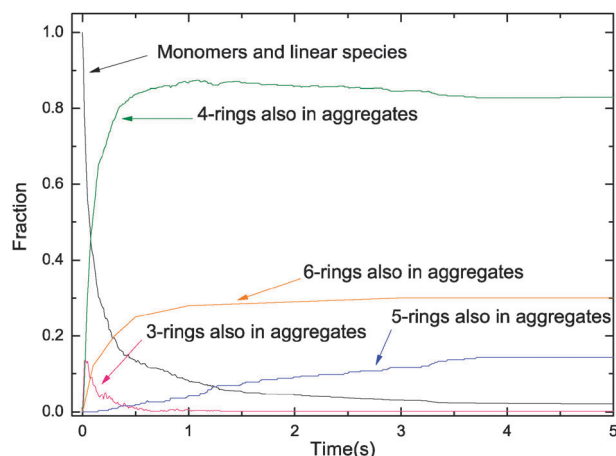


**Fig. 1** Change in the fraction of silicate oligomers as a function of time. Note: 4-rings, 5-rings and 6-rings share Si.
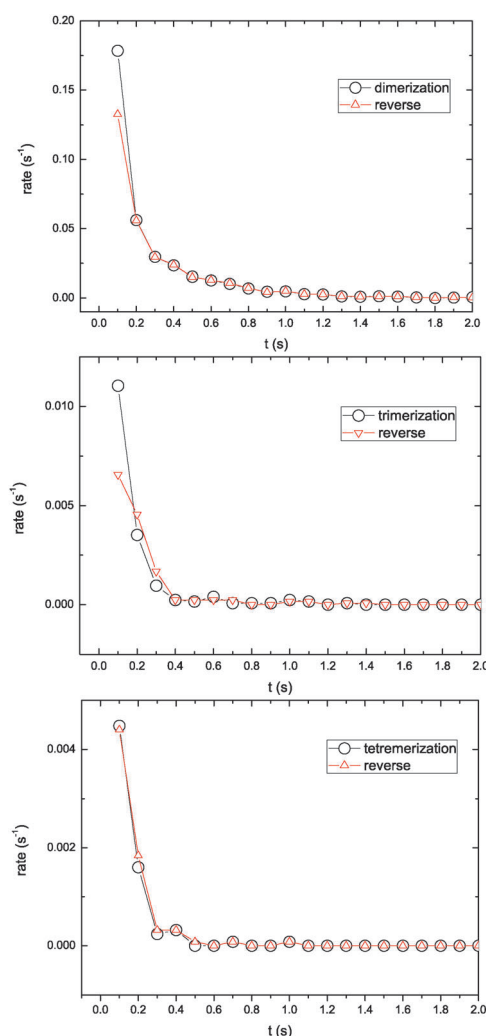


**Fig. 2** Change in the rate with time of silicate dimer, linear trimer and linear tetramer.

sharing of Si. It is very common to find the sharing silicon atoms in the zeolite structures.

Fig. 2 presents the change in rates of linear growth (and the reverse processes) with time. The forward process is initially faster. The rate of the reverse follows that of the forward process, and finally both have the same rates. This indicates fast monomer exchanges between silicate oligomers. The rate of monomer exchanges for dimers is much faster than for trimers and tetramers ($rate_{dimer}$ > $rate_{trimer}$ > $rate_{tetramer}$). Pelster *et al.* have used electrospray ionization mass spectrometry (ESI-MS) in connection with isotopically labeled silicates to study the interconversion process between oligomers.[31] They have focused on two cagelike species: the cubic octamer in the presence of tetramethylammonium (TMA$^+$) and the prismatic hexamer in the presence of tetraethylammonium (TEA$^+$). For both species a second, identical solution, but made from $^{29}$Si-enriched silica was prepared in parallel. After the two solutions were combined, exchange of the $^{29}$Si atoms between the silicate oligomers was observed. They have found that the interconversion of even very stable oligomers in solution is rapid, and the interconversion processes between silicates in solution are fast in comparison with the timescale of zeolite formation.[31]
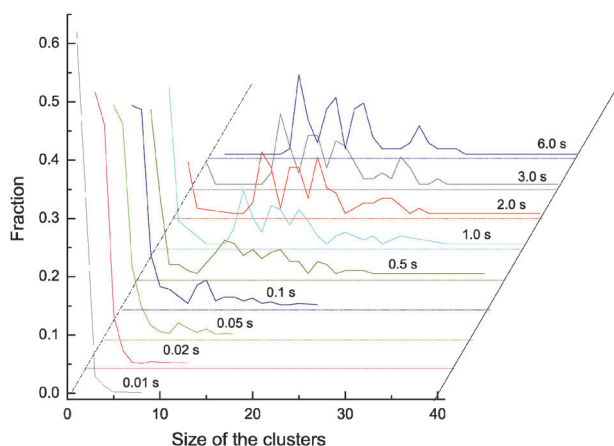
**Fig. 3** Cluster size distribution at different simulation times. There is a shift to higher values, by 0.05 in step, for clarity.



**Fig. 4** The change in average cluster size with time.

They also found that the exchange for the hexamer proceeds by about two orders of magnitude faster than for the octamer. Here, the fast interconversions (monomer exchanges) between silicate oligomers (dimer, linear-trimer and tetramer) are found through kMC simulations. The rates of monomer exchanges are found to be faster for smaller silicate oligomers. Thus, our calculated results are consistent with those obtained from mass spectrometric analysis.

The use of different ammonium salts as the organic template leads to different products, as already reported. Using mass spectrometry, Pelster *et al.* reported that the presence of $TMA^+$ favored the formation of double 4-rings, whereas in $TEA^+$ containing samples, the equilibrium is pushed to the side of double 3-rings.[10] Formation of double rings is therefore very sensitive to the template molecules.[12] Mass spectrometry studies showed lots of double 3-rings and double 4-rings in the presence of template molecules.[10] In this study, although a significant amount of 3-rings is formed at an early stage, the formation of double 3-rings is unfavorable. This may tentatively lead to the conclusion that the formation of double 3-rings is rather unfavorable in the absence of template molecules.

Fig. 3 gives the cluster size distribution at different simulation times. At $t = 0.01$ s, the major species are monomers and dimers, and the largest cluster is 9 Si in size. The fraction of monomers and dimers decreases rapidly with time, which results in a fast growth of the clusters. After 2 s, the species population is dominated by the clusters ranging from 9 to 23 Si in size. The largest clusters are 8, 11, 14, 21 37, at time 0.001, 0.002, 0.005, 0.1, 0.5 s, respectively. The largest cluster size increases rapidly during the first 0.5 s, and remains 39 for the rest of the simulation time. This reveals that, in the first 0.05 s, the dominant processes are dimerization and trimerization. After that, larger species form, and the aggregation proceeds, which results in the fast increase in the cluster size, as shown in Fig. 3. The fraction of small silicate clusters (smaller than 8 Si in size) is very small after 2 s. This is in agreement with the analysis of the change in average cluster size with time, as presented in Fig. 4. The average cluster size increases to 13.5 Si at $t = 2$ s, and is followed by a slow increase. Although the largest cluster stops growing after 1 s, there are still some amount of small species which can aggregate to increase the average cluster size.
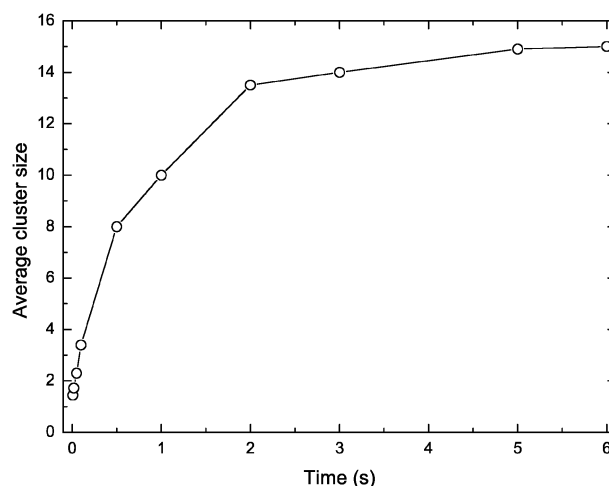
Finally, we give a schematic representation of the growth pathway (Fig. 5). In solutions, monomeric silicate molecules undergo condensation reactions that lead to the formation of silicate oligomers. These oligomers can be linear and ringed species. The linear species do not become longer than 6 silicon atoms, the largest ring can be a 6-ring. The initial species population is dominated by 4-ring containing species, as shown in Fig. 5. These varieties of oligomers then aggregate to form larger ones. The firstly aggregated structure is quite open. Many silicate clusters have branches. The aging occurs after the aggregates formed. As the aging proceeds, the clusters tend to be more condensed, the aging also results in the formation of 5- and 6-rings.

Depla *et al.* presented UV-Raman investigation of the initial silicate oligomerization reactions. In their work, chain growth, cyclodimerization, and branching were identified. Chains did not grow longer than pentamer, and ring sizes were limited to 6-rings. 4-rings were abundant species. Gelation proceeded from branched 4-rings and branched chains. In the present work, the calculated results are in good agreement with what are found experimentally. We also found that the 4-rings
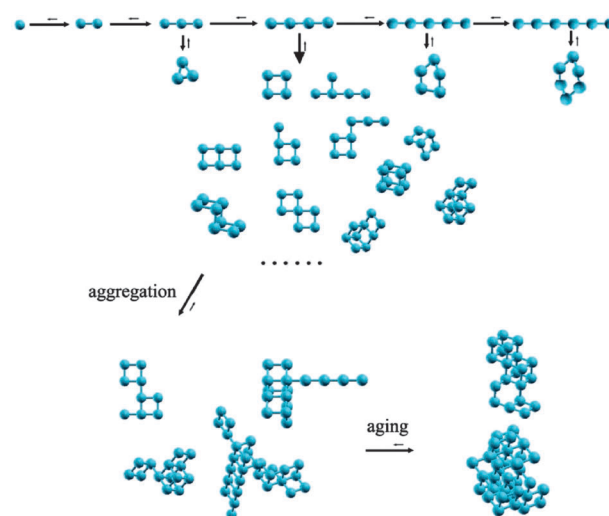


**Fig. 5** The reaction pathway leading to silicate clusters.

dominant the ring population. The formation of clusters proceeds from 4-ring containing species.

## 4 Conclusions

The silicate oligomerization and gelation have been studied using a lattice-gas kinetic Monte Carlo method. Good agreement with experimental studies has been obtained. The following key points were found. (1) Results reveal that linear species tend to close to form rings. (2) 3-rings are metastable, the formed 3-rings reopen to support formation of larger species. (3) 4-rings dominant the ring population. (4) 5- and 6-rings are rare in the early oligomerization stage. (5) The aggregation of silicate oligomers is followed by aging that leads to more condensed silicate clusters. (6) The gelation proceeds from 4-ring containing structures. (7) 5- and 6-rings are mainly formed during aging of the silicate clusters. (8) Fast monomer exchanges between silicate oligomers are found, which is consistent with experimental findings.

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