Zeolite Assembly

Oligomerization and Cyclization Processes in the Nucleation of Microporous Silicas**

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The nucleation and growth of zeolites and other microporous solids continues to pose many questions.[1,2] Whilst the general features of self-assembly through condensation polymerization are understood for siliceous systems, the conditions under which both natural and synthetic zeolites form render such a complex process extremely difficult to characterize experimentally. Thus, whilst the species initially present in silicate gels can be characterized by NMR spectroscopy with some certainty,[3,4] their charge state is more difficult to probe.[5] Similarly, although scattering methods can be used to tentatively identify larger (possibly nucleation) species,[6,7] the relative stability and lifetime of the smallest clusters, significant in zeolitic structures, such as four-membered rings, remain unclear. Furthermore, in the postnucleation regime, there is much debate as to which species are responsible for crystal growth: small oligomers or larger subunits. Indeed, it has been suggested that the growth of silicalite-1 (MFI zeolite) is controlled by a unique nanocluster,[8] although there is some debate about this proposal.[9] Moreover, characterization of zeolite surfaces suggests that much smaller units are responsible for surface growth.[10]

Here, we describe quantum chemical calculations that model some of the species present prior to nucleation and attempt to examine the pathways by which such key species may form and hence rationalize the assembly of zeolitic structures. In particular, we discuss the factors that drive the condensation polymerization of silicate oligomers and that favor the cyclization of such species: pH and solvent.

In the past decade there have been a number of computational studies of model structures involved in the nucleation process of silicates. Structures and energies for small clusters containing up to five silicon atoms were obtained by Pereira et al.[11,12] One conclusion that can be drawn from these results is that linear silicate species are favored over cyclic structures—a situation not conducive to the formation of zeolitic structures but instead one that favors the formation of amorphous silicates.[11] These early calculations were performed using a local DFT method and considered only neutral species, although solvation effects were included using the COSMO method.[13] The roles of water and organic templates in prenucleation gels were studied by Lewis et al.[14] and Catlow et al.[15] by more approximate molecular mechan-

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ics methods. They identified key roles for template molecules—preventing the collapse of large hydrophobic silicate clusters to more dense structures—and for charge interactions between anionic silicates and templating cations—maintaining intimate cluster–template interactions.

The formation of small cyclic species can be considered as central to the nucleation and growth of siliceous zeolites, since four-, five, and six-membered rings dominate such structures. However, as we have seen, ab initio calculations suggested that linear silicate oligomers are favored.[11] Herein we attempt to answer the following key questions: how does the cyclization process occur and what is the role of pH and solvation in forming such prenucleation species?

Details of the methods used are described in the Experimental Section and result from a systematic survey of available methods and tools. Further details of our evaluations will be published elsewhere, where the methods chosen will be shown to provide a good and self-consistent description of the geometry and energetics of these silicate systems. For example, trends in the successive deprotonation energies of monomeric and dimeric species are quantitatively reproduced.[16]

Experimentally, high pH is required for condensation reactions to occur: under such conditions the dominant silicate species will be anionic.[5] The basic reaction is given in Equation (1); further deprotonation gives $H_2SiO_4^{2-}$ and so

$$Si(OH)_4 + OH^- \rightarrow (OH)_3SiO^- + H_2O \qquad (1)$$

on, and is also possible with larger oligomers. For some of the small clusters present in the first stages of nucleation, we have calculated the relative stability of the various possible anionic species in both the gas phase and in solution (modeled by the COSMO solvation model; Table 1). The results show that it is thermodynamically favorable for an OH^- ion to deprotonate the monomeric species to form the monocharged anion $(OH)_3SiO^-$, both in the gas phase and in solution. Further deprotonation is, however, significantly less favorable, suggesting that such species will be present in lower concentrations and will likely be highly reactive.

Table 1: Calculated Gibbs free energies [kJ mol^{-1}] for the deprotonation of silica species in the gas phase and in solution. The ΔG value is given for the formation of the deprotonated species from the reaction of its parent species with OH^-; water is the other product.[a]

Species	$\Delta G_{deprot.}$ Gas	$\Delta G_{deprot.}$ Soln	Species	$\Delta G_{deprot.}$ Gas	$\Delta G_{deprot.}$ Soln
M^-	−229	−64	$3r^{3-}$	391	−46
M^{2-}	284	2	T^-	−375	−127
M^{3-}	814	66	T^{2-}	−8	−76
D^-	−294	−92	T^{3-}	315	−33
D^{2-}	116	−23	$4r^-$	−341	−123
D^{3-}	527	−21	$4r^{2-}$	7	−69
Tr^-	−342	−100	$4r^{3-}$	344	−33
Tr^{2-}	53	−63	P^-	−408	−141
Tr^{3-}	404	−4	$5r^-$	−384	−130
$3r^-$	−299	−60	H^-	−412	−135
$3r^{2-}$	57	−64	$6r^-$	−382	−115

[a] Codes used: M = monomer, D = dimer, Tr = timer, 3r = 3-ring, T = tetramer, 4r = 4-ring, P = pentamer, 5r = 5-ring, 6r = 6-ring, H = hexamer. The charge of the deprotonated species is given by the usual superscript. Thus, for example, the first entry is the deprotonation of a neutral monomer, $Si(OH)_4$ (M in our notation) by reaction with OH^- to give $(OH_3)SiO^-$ (M^- in our notation) and H_2O.

The change in free energy for the removal of a single proton by OH^- in the gas phase is quite large for all the linear oligomers considered; however, this value is reduced by a factor of three or four when a description of the solvent is included in the reaction. The role of the solvent is even more important for the second deprotonation. This emphasizes the important role of the water in stabilizing multiply charged anions, which is key in the condensation reactions and considered next. Whilst some of the free energies of deprotonation in our solvation model remain positive, they are clearly significantly lower than the corresponding gas-phase results. We estimate that our model may overestimate these energies by at most ≈25 kJ mol^{-1} based on a comparison with experimental equilibrium constants for the deprotonation of $Si(OH)_4$.[17] Such an offset can be attributed to many factors such as solvation and dilution, which we are currently investigating further.[16].

We therefore limit ourselves to a semiquantitative discussion of the reaction energetics and compare only relative energies, which we expect to be reasonably accurate for all the species considered. We also note that, as yet, these calculations do not consider interactions with charge-balancing cations, for example, H_3O^+ and Na^+, nor with organic templating agents. However, the presence of such species is likely to increase the stability of the more deprotonated species.

We now consider the condensation reactions of some of these clusters, both neutral and charged, again in the gas phase and in the presence of the solvation model (Figure 1, Table 2). The simplest condensation reaction, that of the dimerization of silicic acid [Eq. (2)] is found to be favorable in

$$2\,Si(OH)_4 \rightarrow (OH)_3SiOSi(OH)_3 + H_2O \qquad (2)$$

the gas phase for both neutral and charged species. However, when solvation is included, the free energy of the reaction is significantly less favorable for the neutral species than when charged species are considered. Similar trends are also observed for the condensation of larger oligomers. Our results, therefore, highlight the role of pH, which is also observed experimentally, in driving the initial polymerization processes to give these small oligomers. However, the reaction of two $Si(OH)_3O^-$ species ($M^- + M^-$) is very unfavorable, suggesting that stabilization of such species by cationic species or mechanisms for rearrangement by means of proton transfer will be significant. But it should also be noted that very high pH is not conducive to zeolite nucleation.[18]

Thus, our calculated condensation energies show how dimers, trimers, and larger oligomers can be readily formed, as in experiment, but only when the model includes a description of an aqueous medium at high pH. In particular, we note that condensation of neutral species is strongly disfavored beyond the formation of the dimer. Thus, at low

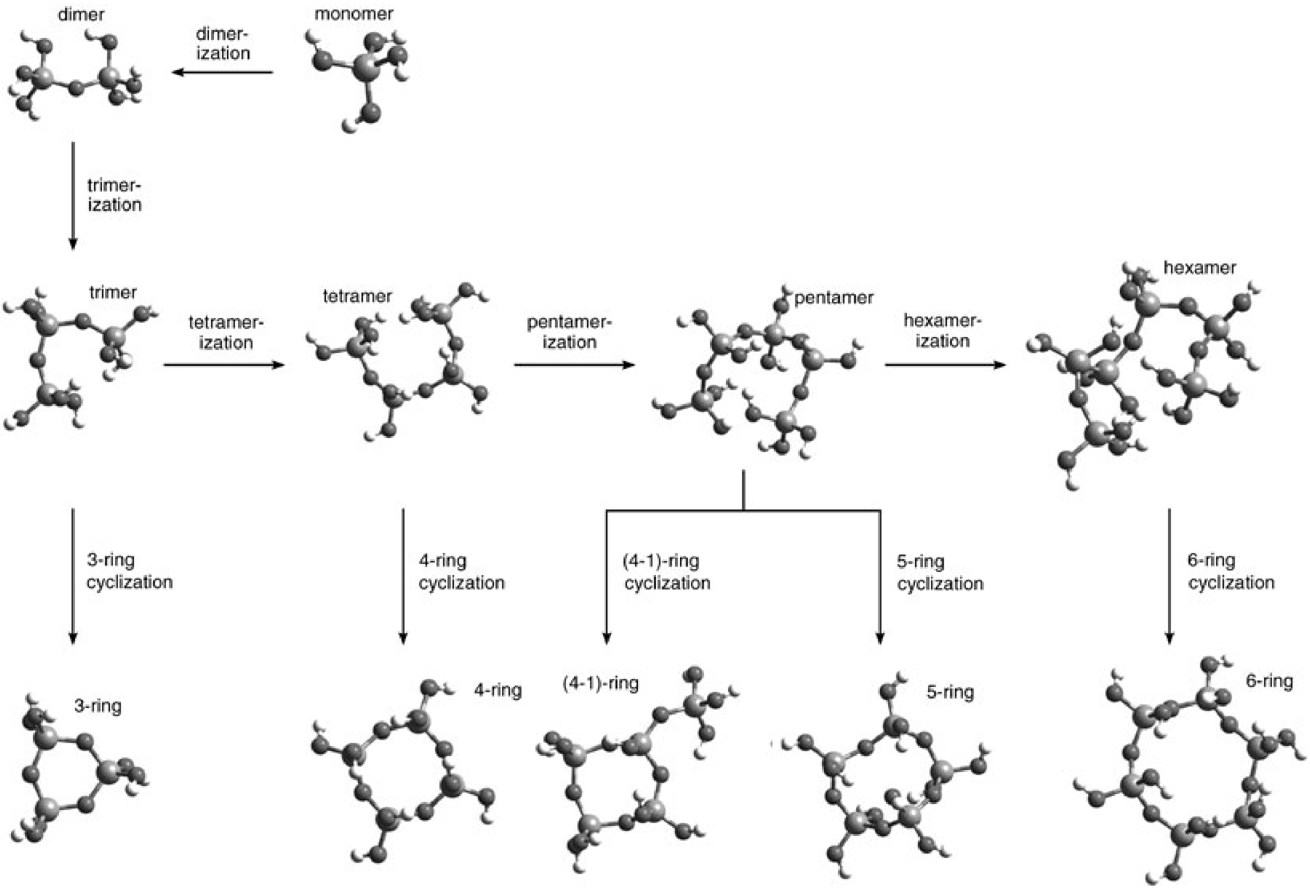

Figure 1. Condensation reactions for silicate clusters from monomer to hexameric species. For linear growth (e.g. tetramerization) the values are for the reaction of a silicate species with a monomeric species to give water as a product. For internal condensations leading to rings the other product is also water. The species codes are given in Table 1.

Table 2: Calculated energies [kJ mol^{-1}] for the condensation reactions depicted in Figure 1 forming silicate clusters from monomeric to hexameric species. For linear growth (e.g. tetramerization) the values are for the reaction of a silicate species with a monomeric species to give water as a product. For internal condensations leading to rings the other product is also water. The species codes are given in Table 1.

Dimerization

	Reactants	$T\Delta S$	ΔG
Gas	M,M	3	-14
	M^-,M	-14	-78
	M^-,M^-	-22	267
Soln	M,M	-8	0
	M^-,M	-14	-28
	M^{2-},M	-21	-53
	M^-,M^-	-28	13

Trimerization

	Reactants	$T\Delta S$	ΔG
Gas	D,M	-22	5
	D,M^-	-41	-107
	D^-,M	-25	-43
Soln	D,M	-20	6
	D,M^-	-39	-30
	D^{2-},M	-19	-42

Tetramerization

	Reactants	$T\Delta S$	ΔG
Gas	Tr,M	-20	-3
	Tr,M^-	-34	-149
	Tr^-,M	-15	-36
Soln	Tr,M	-21	12
	Tr,M^-	-24	-50
	Tr^{2-},M	-17	-27

Pentamerization

	Reactants	$T\Delta S$	ΔG
Gas	T,M	-17	-4
	T,M^-	-43	-183
	T^-,M	-29	-37
Soln	T,M	-20	3
	T,M^-	-19	-74
	T^{2-},M	-15	-13

Hexamerization

	Reactants	$T\Delta S$	ΔG
Gas	P,M	-14	-19
	P,M^-	-25	-201
	P^-,M	1	-22
Soln	P,M	-2	-5
	P,M^-	-26	-76
	P^{2-},M	-15	-40

3-Ring Cyclization

	Reactants	$T\Delta S$	ΔG
Gas	Tr	68	-37
	Tr^-	63	6
Soln	Tr	77	-61
	Tr^-	70	-21
	Tr^{2-}	67	-22

4-Ring Cyclization

	Reactants	$T\Delta S$	ΔG
Gas	T	83	-59
	T^-	62	-25
Soln	T	55	-48
	T^-	62	-44
	T^{2-}	69	-37

(4-1)-Ring Cyclization

	Reactants	$T\Delta S$	ΔG
Gas	P	80	-45
	P^-	76	-7
Soln	P	82	-55
	P^-	61	-21
	P^{2-}	69	-22

5-Ring Cyclization

	Reactants	$T\Delta S$	ΔG
Gas	P	80	-51
	P^-	74	-27
Soln	P	77	-65
	P^-	62	-53
	P^{2-}	30	-55

6-Ring Cyclization

	Reactants	$T\Delta S$	ΔG
Gas	H	72	-38
	H^-	64	-8
Soln	H	47	-40
	H^-	66	-20
	H^{2-}	50	-4

pH, where anionic species are less prevalent, polymerization is inhibited. We also note that for the trimerization reaction (and for the formation of higher oligomers) the dominant contribution to the free energy is a favorable change in enthalpy, which overcomes the adverse negative change in entropy.

Once trimers are formed, however, there is also the possibility of internal condensation to form rings, key zeolitic structural units. The lowest energy conformation for the trimer is almost cyclic, suggestive of an easy route for internal condensation to form a three-membered ring. Indeed, all our results suggest that the formation of a three-membered ring is likely, in accordance with NMR experiments where this cluster is observed.[8] However, the seeming ease of 3-ring formation raises the question of the role of this species in nucleation and subsequent growth processes, since these rings are extremely rare in siliceous zeolites. However, we should note that the formation of a linear tetramer from the trimer is more favorable than the closure of the 3-ring when doubly charged trimers are considered, in other words, those likely to be present at higher pH. Furthermore, the overall formation energy of a four-membered ring by means of the reaction of the more likely 3-ring species (i.e. charged) with a monomer is favorable. For example, the free energies of formation of a 4-ring (in solvation) from an anionic 3-ring with monomer and anionic monomer are -37 and $-42\,\mathrm{kJ\,mol^{-1}}$ respectively, whilst the reaction of a dianionic 3-ring and an anionic monomer (giving a trianionic 4-ring) is also exergonic by $11\,\mathrm{kJ\,mol^{-1}}$. In contrast, the reopening of 4-rings by reaction with further monomers is strongly unfavorable. We are currently investigating the activation barrier to trimer cyclization and also routes for subsequent ring opening. It is also of note that cyclization processes are favored by the entropic contribution.

As with the trimer, the tetramer can either polymerize further or form a ring. The free energy released, in each of the charge states considered, clearly indicates that cyclization is strongly preferred over further linear growth. Given the prevalence of the 4-ring in so many zeolite structures, we might expect its formation and stability to be very significant in zeolite nucleation and growth. We might also expect the process of (any) cyclization reaction to be kinetically favored, as it is unimolecular. Clearly we also need to consider reaction barriers, calculation of which are now underway.[16] Again, we note that ring formation is favorable, with little variation in Gibbs energy, in a number of charge states. However, the formation of neutral 4-rings is unlikely, not due to the energetics of the cyclization itself, but rather since neutral tetramers are unlikely to be present. In contrast, there is significant variation in the reaction free energies for further addition of silicate species (giving a pentamer), depending on the exact charge state.

Thus, from a consideration of the energetics of the reactions determined here, for formation of species up to tetramers, we would expect a large population of dimers, 3-rings, and 4-rings, primarily singly and doubly charged. However, further linear polymerization will be competing with condensation onto these smaller species, particularly the 4-ring. Thus, whilst formation of larger linear oligomers remains energetically favored, we do not expect such species to be present in large amounts, owing to the other, even more favored, competing processes. Indeed, internal cyclization of a pentamer is more likely to lead to the formation of a 4-1 unit rather than the 5-ring, in excellent agreement with experiment, where the former species is considered to be present, with little evidence of the formation of the 5-ring.[3] Similarly, the 6-ring is unlikely to form as a solution species (from a linear hexamer), since internal cyclization to form smaller rings is more favorable.

From these initial calculations we can draw a number of conclusions and inferences. Firstly, we find excellent agreement between the overall energetics of the processes considered and the experimental observations of small oligomers in solution. We find a pH dependence for polymerization and the formation of small rings. Thus, we may conclude, tentatively, that the methods selected, in which solvation is included (albeit as a continuum) and pH is treated by considering anionic silicate species, give a reasonable description of the system. Future work will establish whether more sophisticated (and necessarily more expensive) models are required: for example, the inclusion of explicit water to describe the mechanism of condensation and the solvation of counter ions such as $\mathrm{Na^+}$. Secondly, the formation of cyclic fragments is clearly favored—in agreement with experiment and with the expectation of the formation of zeolite-like nucleation species. Furthermore, the cyclization is driven by high pH—again well-known experimentally in silicate chemistry.[19,20] It is therefore unlikely that larger noncyclic oligomers play a significant role in either nucleation or crystal growth. Hence, growth is much more likely to occur by condensation of relatively small units, particularly those that lead to rings, in either nucleation species or in subsequent surface growth. We note that there is clear evidence that surfaces with complete (small) rings are prevalent from both high-resolution transmission electron microscopy and computational studies of siliceous zeolite surfaces.[21] Thirdly, it is clear that large single (>5- and even 5-) rings are not formed as free species in solution, although bridged species need to be considered, and result from the condensation of smaller units.

We are now considering larger species that are expected to form in solution (such as double-4-rings) and the mechanisms by which they may form (for example, double-6-rings can be constructed from 4-rings). Similarly, we are considering the reaction barriers for growth condensations and internal condensations. We believe that such studies will provide insight into the mechanisms of nucleation, assist the interpretation of experimental studies of nucleation phenomena, and also contribute to our understanding of subsequent crystal growth of siliceous zeolites.

Experimental Section

Theoretical method: All the calculations were performed using $\mathrm{DMOL^3}$, version 2.2,[22,23] using a numeric DNP basis set. All final structures were optimized using the BLYP functional. Water was considered by means of the COSMO solvation approach[13,24] and gas-phase structures were subsequently reoptimized in the presence of the solvation model. To avoid bias (as many of the fragments were taken initially from zeolite crystal structures) and to avoid local minima, a simulated annealing strategy was adopted to search for the lowest energy structures. Structures were subjected to a quantum molecular dynamics simulation run at 700 K for 3000 steps of 0.46 fs, using a low-cost basis set and the PWC functional. The final structure from such runs was then optimized at the BLYP/DNP level, first in the gas phase and then in COSMO. The Gibbs free energy was calculated by standard statistical mechanical methods; a temperature of 450 K was assumed, which is typical of zeolite synthesis.

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