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# New insights into zeolite formation from molecular modeling

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### Abstract

We review recent molecular modeling efforts to shed light on the mechanisms of zeolite formation. We focus on studies that model the early stages of silica polymerization and zeolite nucleation. Electronic structure calculations, classical molecular dynamics, atomistic Monte Carlo simulations and Monte Carlo simulations of lattice models have been used to probe the formation of zeolites and mesoporous materials. Results from these modeling studies predict that in early stages of formation, the silicate material is amorphous. Cluster growth is predicted to occur primarily through Ostwald ripening, and by aggregation of small fragments. © 2005 Elsevier Ltd. All rights reserved.

1. Introduction

Zeolites are nanoporous alumino-silicates used in industrial applications such as catalysis and separations [1]. Understanding how zeolites nucleate and grow is of fundamental scientific and technological importance. The formation of the siliceous zeolite silicalite (Fig. 1) is one of the most well studied cases. Such understanding could be used to optimize catalysis and separations by tailoring zeolite crystallite size and shape. In addition, controlled zeolite synthesis could open new fields of application such as optical electronics [2], bio-implants [3] and enantioselective separations [4]. Standard characterization techniques such as NMR and diffraction have produced few insights into this problem, because key zeolite nucleation and growth events likely occur at length scales above the NMR window and below the diffraction regime. In contrast, molecular simulations have the potential to shed light on zeolite nucleation and growth. Here we review a variety of recent efforts to use molecular modeling to elucidate the early states of silica polymerization and zeolite formation [5].

Generations of zeolite scientists have sought to understand how zeolites form, leading to the following questions [4]. What are the sizes and structures of critical zeolite nuclei? What is the role in zeolite growth of secondary building units such as rings or partial cages? What is the role of structure directing agents such as organic templates or hydrated alkali cations? Regarding precursor silica nanoparticles—which have been found to play a role in zeolite formation from clear solutions [6-11]—what are the structures of these nanoparticles? How do they lead to zeolite formation?

These questions touch on a range of themes, from local chemical reactivity to large-scale cooperative phenomena. As such, a range of molecular modeling techniques has been applied to investigate these questions. Electronic density functional theory calculations [12] on clusters have revealed gas-phase reactivity trends. Classical molecular dynamics [13] (MD) on gas-phase and solvated clusters have accounted for flexibility of clusters and their stabilization (or destabilization) from solvation. Classical MD and atomistic Monte Carlo simulations [13] on extended systems have revealed dynamical and equilibrium properties of silica polymerization. And finally, Monte Carlo simulations of lattice models [14] have yielded qualitative insights into the formation of precursor nanoparticles and mesoporous materials.

These studies have yielded a preliminary understanding of zeolite formation. A common theme from the quantum chemical studies is the importance of a template in maintaining the structural integrity of partial silica cages in a solvated environment. Another common thread coming from the largerscale simulations is the importance of Ostwald ripening [15] rather than multi-cluster aggregation in silica nanoparticle formation. We anticipate that computer simulations may be able to reproduce zeolite self assembly over much wider length

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Fig. 1. Framework structure of the siliceous zeolite silicalite (MFI), looking down the straight channels (b-axis).

and time scales. There is some distance to go before we reach that point.

# 2. Quantum mechanical cluster calculations

Silica polymerization occurs through the following generic condensation reaction:

$$\equiv Si - OH + \equiv Si - OH \Rightarrow \equiv Si - O - Si \equiv + HOH.$$
(1)

Pereira et al. [16,17] examined the structures and energetics of various silica clusters that are believed to arise from such condensation chemistry. These studies used electronic density functional theory to model the structures of linear silica clusters of the form  $Si_xO_{x-2}(OH)_{2x+2}$  for x up to five; three-, four-, five- and six-member rings; branched trimer and tetramer rings; branched linear clusters containing four and five silicons; and cubic octamer cages. It was found that for longer linear fragments, hydrogen bonding between terminal OH groups plays a significant role, causing these linear molecules to approach ring-like structures in their low-energy conformations. It remains unclear how relevant this is to solution chemistry. The computed condensation energies of cyclic clusters show a trend for larger rings to be more energetically favorable than smaller, more strained rings. It was also found that due to their symmetric arrangement, four- and six-member rings are more stable than the five-member ring. In general, linear clusters are more energetically stable than branched clusters consisting of the same number of silicons, and that cluster stability decreases with increasing degree of branching [18].

## 3. Atomistic simulations

Silica polymerization has been studied by classical molecular dynamics (MD) and Monte Carlo simulations that use interatomic potential functions [19–25]. Although these potential functions (forcefields) provide energies and forces very efficiently, accuracies vary strongly from one function to the next. Nonetheless, using forcefields provides a practical way to perform relatively large-scale and long-time simulations on atomistic systems.

## 3.1. Molecular dynamics

Catlow et al. performed MD simulations to study effects of environment on silica clusters [26,27]. Lewis et al. studied solvation effects by placing various silica fragments into a 15 Å radius sphere of water and minimizing the system energy [27]. Open structures, i.e., those not supported by rings or interconnects, were found to collapse, resulting in surface area reductions by as much as 50%. In contrast, fully-formed cages and rings were found to be self-supporting. Strong binding to templates was found to counteract this compressive effect of solvation [27]. For small fragments, the template (either 1aminoadamantane or *N*-methylquinuclidinium) has little effect, while for an open-cage structure the template helps maintain the fragment's structural integrity. Lewis et al. suggest that short-range van der Waals forces are important in the structure directing capability of the complexed system.

Catlow et al. also applied MD to study the dynamical properties of solvated silica-template clusters [26,27]. They found that Coulombic forces are crucial for binding the template and silica cluster for long enough time to allow subsequent growth. They found that neutral silica clusters and template molecules remain bound for only a few picoseconds, while anionic silica fragments and cationic template molecules remain bound for much longer times. Thus, while van der Waals forces control the structure of a silica cluster strong Coulombic attractions keep templates bound long enough for nucleation and growth to occur.

Rao and Gelb [28<sup>\*</sup>] studied the early stages of silica polymerization using the reactive interatomic potential developed by Feuston and Garofalini [19]. They simulated the polymerization dynamics of silicic acid monomers into large,

highly cross-linked silica polymers. Their simulations were initiated with 729 silicic acid monomers [Si(OH)<sub>4</sub>] at various temperatures, volumes, and mole fractions of water. Rao and Gelb found that at short times (nanoseconds), monomers quickly react to form a large population of dimers, which later become depleted as larger clusters appear. These findings are in qualitative agreement with experimental NMR results [29], and suggest that silica clusters grow through Ostwald ripening. Although the most likely cluster observed by Rao and Gelb is the dimer, they found an average cluster size (in number of silicons) of about 30, with the largest clusters containing close to 275 silicons (Fig. 2). At short times (<0.5 ns), they found four-member rings to be the most common ring size, while at longer times (>1 ns) five-member rings dominate the ring population, in contrast with quantum cluster calculations which find four- and six-member rings the most stable [16-18].

Rao and Gelb also simulated silica polymerization with low water content [28\*]. They found rapid polymerization kinetics, with more than half of the monomer population reacted within the first 100 ps. After this time the polymerization rate decreased, and the number of large clusters remained constant. However, the number of medium-sized clusters grew slowly at the expense of small clusters, again pointing to Ostwald ripening. At higher initial water content the reaction was found to proceed more slowly at short times; however, the rate increased with time. Rao and Gelb suggest that the continued growth of silica polymers at high water content points to both monomer incorporation and cluster–cluster aggregation as reaction mechanisms. Nucleation is generally a rare event, observed in molecular dynamics only at high temperatures, often outside of relevant experimental regimes. Indeed, when the MD simulations of Rao and Gelb were run at 300 and 600 K, no polymerization was observed [28<sup>\*</sup>]. Monte Carlo simulations have been used to overcome this time scale limitation, allowing the study of nucleation and growth under ambient conditions.

# 3.2. Monte Carlo simulations

Stable silica-template nanoparticles have been observed as a precursor to silicalite-1 crystallization from clear solutions [6,8-10,30-42]. These nanoparticles are believed to play an important role in the formation of the final zeolite [43]; however, their nanoscopic structures remain poorly understood. To address this, Wu and Deem reported an initial Monte Carlo study of the structure and nucleation properties of silica nanoparticles without template [44<sup>•</sup>]. They used Vashishta's silica potential [24] with explicit silicons ( $\leq 200$ ) and oxygens, and an implicit treatment of hydrogens, oxygen ions and a neutralizing background charge. Wu and Deem added a distance-dependent dielectric function to estimate shielding in aqueous solution, and altered the partial charge on terminal oxygens to account for deprotonation at high pH. Based on the assumption that cluster-cluster interactions are negligible during clear-solution zeolite synthesis, Wu and Deem sampled equilibrium structures of a single silica nanoparticle.

Equilibrium structures sampled by Wu and Deem were generally amorphous. Ring-size distributions were compiled for clusters containing 77 and 200 silicons. Ring sizes were



Fig. 2. Largest silica cluster observed in molecular dynamics simulations of Rao and Gelb [28\*]. Silica is modeled using the Feuston and Garofalini potential [19].

mostly between four and eight silicon atoms, with some large rings (up to 11) in the larger clusters. It was found in this system that four-and six-member rings are more likely than five-member rings, in accordance with quantum studies [16– 18]. By calculating cluster free energies as a function of cluster size for various silica concentrations, Wu and Deem predicted that critical nuclei for silica polymerization contain as few as 30-40 silicons (Fig. 3). They also predict that the nucleation barrier increases with the critical-nucleus size, giving further support to Ostwald ripening in nanoparticle formation.

While the Monte Carlo study by Wu and Deem allows for direct simulation of cluster formation under ambient conditions, the use of a detailed interatomic potential limits the system size to no more than 200 silicons. Experimental studies of these precursor nanoparticles estimate that, on average, nanoparticles contain 500–600 silicons [10,34], which is presently too large for free energy calculations using detailed atomistic approaches. To address this issue, we recently proposed a simplified model of silica [45], consisting of hard spheres and directional square wells representing silicon– oxygen bonds. This simple potential allows for the simulation of larger systems. In work underway we are using this simplified model to study the early stages of zeolite formation.

## 4. Lattice model simulations

Lattice models are computationally much simpler than atomistic models, and can provide qualitative insights into the workings of complex systems. This computational simplicity allows for simulations of larger systems than can be handled by atomistic methods. Jorge et al. [46<sup>\*</sup>] recently simulated silica-template nanoparticle formation using a "united atom" representation, where each molecule was



Fig. 3. Plot of free energy of a growing silica cluster calculated by Wu and Deem [44\*]. Quartz is the thermodynamically stable phase; however it has a high nucleation barrier which prevents it from forming. The nucleation barrier increases with critical-nucleus size, giving further support to Ostwald ripening. The different plots represent different concentrations of silica, units are in mol Si/L. The solid square dots are the free energy needed to form a quartz cluster at a concentration of 0.33 M.

represented by a single site on a three-dimensional simple cubic lattice. Three species were represented: neutral silica  $(Si(OH)_4)$ , ionized silica  $(Si(OH)_3O^-)$ , and template molecules (tetrapropylammonium=TPA ions); the remaining sites were occupied by implicit solvent. In agreement with the results of Rao and Gelb [28<sup>\*</sup>], Jorge et al. observed rapid depletion of monomers due to formation of small clusters. These small clusters fluctuated in size, providing nutrients for the growth of larger, more stable nanoparticles, again pointing to Ostwald ripening [46<sup>\*</sup>]. The alternative growth mechanism of cluster aggregation was not observed by Jorge et al., presumably because the high surface charge of silica at high pH prevents aggregation through electrostatic repulsion.

Jorge et al. found that nanoparticles spontaneously form in their canonical Monte Carlo simulations when neutral silica is present (Fig. 4). The simulated nanoparticles are composed of a core of neutral silica with negatively charged silica on the surface, surrounded by a layer of TPA. To address whether these nanoparticles are true equilibrium states, Jorge et al. performed parallel tempering Monte Carlo simulations [47,48], which more efficiently surmount barriers that prevent equilibration. Jorge et al. found that the parallel tempering simulations always produce one single cluster, suggesting that silica-template nanoparticles observed experimentally are actually metastable states. They then studied how the metastable cluster size distribution varies with pH, silica concentration, and template size. In qualitative agreement with the SAXS and SANS experiments of Fedevko et al. [34], Jorge et al. found that these metastable nanoparticles shrink with increasing pH, because of the greater concentration of TPA which serves to cap the nanoparticles. Also in agreement with experiment [34], Jorge et al. found that nanoparticle size is independent of template molecule size. While such a lattice model cannot provide atom istic structural data, it does generate qualitative insights into the metastable behavior of these silica-template nanoparticles.

Siperstein and Gubbins reported a lattice model consisting of silica, surfactant and solvent that demonstrates structure directing in the self-assembly of mesoporous MCM-41 [49,50,51]. Siperstein and Gubbins modeled the surfactant as a chain on a lattice with m hydrophilic head groups and nhydrophobic tail groups. Favorable interactions between the head groups and silica particles lead to a variety of phases. By varying the surfactant volume fraction they simulated the formation of lamellae and hexagonally packed cylinders, thus simulating structure direction and self-assembly of MCM-41. There are two factors present in the work of Siperstein and Gubbins that allow the simulations to form ordered phases as opposed to the nanoparticles formed in the simulations of Jorge et al. [46<sup>•</sup>]. First, the template model used is not spherically symmetric, it is a linear long-chain surfactant; secondly the lattice used by Gubbins et al. has a much higher coordination number than the simple cubic lattice used by Jorge.

### 5. Summary

We have reviewed recent molecular modeling studies of silica polymerization and early-state zeolite formation. At very



Fig. 4. Snapshots of lattice simulations of nanoparticle growth (a) no nanoparticles form in the absence of neutral silica; (b) canonical Monte Carlo produces several stable nanoparticles; (c) parallel tempering gives one large cluster.

early stages in silica polymerization, silica clusters are predicted to be amorphous in structure. These clusters appear to grow through Ostwald ripening, where smaller, more soluble particles dissolve and add their material to larger, more stable particles. Cluster–cluster aggregation is predicted to be an unlikely growth mechanism because of the strong negative surface charge on silica clusters under alkaline conditions. Template molecules were found to provide several functions, from stabilizing incomplete cages to capping the growth of nanoparticles.

Future studies will have to address how solvation impacts the chemistry of silica condensation, perhaps through the application of ab initio molecular dynamics [52,53]. In addition, future simulations of silica self-assembly will have to develop methods for computing the free energies of various three- dimensional network structures. While the ultimate goalcomputational self-assembly of a zeolite-remains some distance away, computer modeling promises to shed much further light on how zeolites form.

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