Magic Silica Clusters as Nanoscale Building Units for Super-(Tris)tetrahedral Materials

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For bridging between the building block and the bulk, we consider the assembly of highly stable $(SiO_2)_8$ "magic" clusters into inorganic framework materials. Our cluster building blocks are predicted to be strongly energetically preferred while also having the propensity to form intercluster siloxane (Si−O−Si) bridges. Silicate framework materials are thus proposed with their viability judged via state-of-the-art density functional calculations. All frameworks differ from known synthesized materials with the most stable frameworks lying in a thermodynamically accessible window shared by mesoporous silicas. A few frameworks also correspond to hypothetical frameworks discovered through top-down mathematical approaches providing a link between high-level searches and our bottom-up constructive approach. We predict that the gas-phase deposition of magic clusters will potentially allow the fabrication of new framework materials not readily achievable through traditional hydrothermal syntheses.

Introduction

Predicting synthetically viable new materials solely from the structure and properties of molecular-scale precursors provides an ongoing test of computational methodologies and the synthetic chemist's imagination. The bottom-up approach to the design and understanding of new materials also lies at the heart of the philosophy driving current nanotechnological research. From such a perspective chemistry has traditionally advanced through adroit manipulation of molecular species in solution. Of all materials formed in this manner, crystalline porous silicates (zeolites) have attracted much attention because of their proven rich possibilities in structural form and their subsequent application potential in fields as diverse as catalysis and microelectronics. The vast and complex structural space of hypothetical zeolite frameworks has been the subject of numerous recent studies which aim at a systematic evaluation of all such possible frameworks via the application of top-down methods based on recent advances in mathematical tiling and graph theory.[1−5] However, although an overall perspective of the landscape of both hypothetical and synthesized silicate frameworks is gradually emerging, there is still a large knowledge gap between actual materials and the identification of potential building blocks, which could suggest a route to their formation.

Recently, the assembly of well-defined rigid molecular building units has been put forward as a new experimental means for the bottom-up synthesis of metal−organic framework materials from solution[6] or co-condensation.[7] For silicate frameworks, through consideration of probable species present in the traditional hydrothermal synthesis mixture, some theoretical efforts have investigated ways in which cubic Si_8O_{12} double four-ring units may be combined into periodic structures.[8] An alternative rational for choosing such nanoscale building units is to consider small well-defined clusters, which intrinsically display unusually high stability in a vacuum.[9] It is often observed that, upon the production of cluster beams from bulk materials, the formation of certain cluster types is particularly favored over the formation of others. Such "magic" clusters typically display relatively high symmetry and a large excess energetic stability over other cluster isomers of the same and similar composition. Bottom-up synthesis based upon gas phase clusters requires precise control of (i) the cluster deposition/assembly process and (ii) the cluster species. Numerous experiments have already demonstrated the controlled depo-

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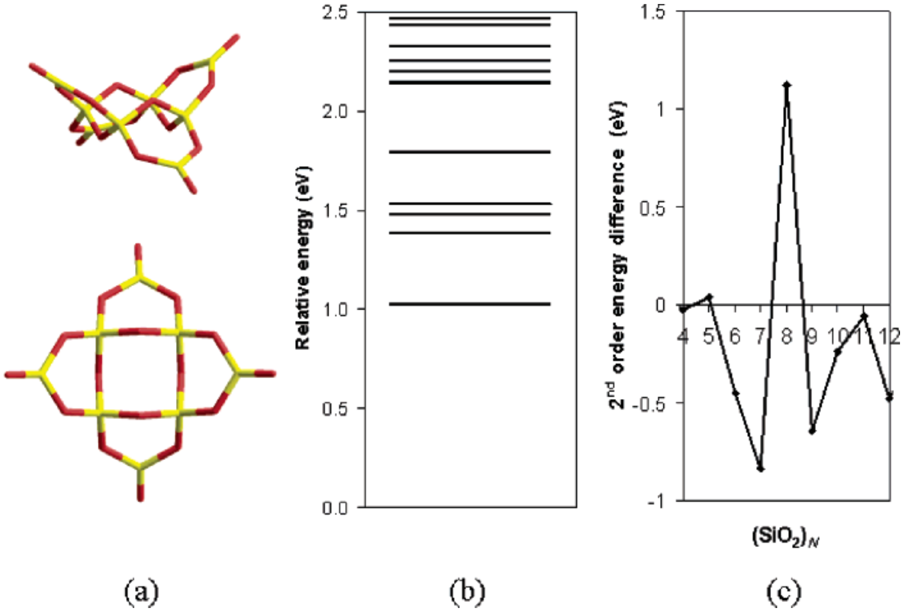

Figure 1. (a) Two views of the structure of the $(SiO_2)_8$ magic cluster showing its four opposing Si═O terminations (upper) and highly symmetric form (D_{2d}; lower); (b) the low energy spectrum of the bottom 13 $(SiO_2)_8$ cluster isomers (B3LYP/6-311+G(d) optimizations using the GAMESS-UK code)[15] showing a large (>1 eV) gap between the magic ground-state cluster and the next highest energy isomer (found to be a symmetrized version of that reported in ref 16 which was calculated at a B3LYP/6-31G(d) level); and (c) the second-order energy difference for clusters $(SiO_2)_N$ ($N = 4-12$), $E_{2nd}(N) = -2E(N) + E(N - 1) + E(N + 1)$, derived from ground-state cluster energies $E(N)$ calculated at a B3LYP/6-31G(d) level.[16]

sition of silica clusters, usually produced via vapor phase oxidation of silicon or silicon-containing species, to form silicate films.[10,11] In such experiments there is a wide distribution of silica cluster sizes/types, and the resulting deposited phase is amorphous. To exert some control over the synthesized material, self-elected magic clusters are particularly good candidates for nanoscale building blocks because of the relative ease with which they can, in principle, be selectively produced in large quantities. Examples of magic cluster building blocks experimentally realized in this manner are C_{60} fullerenes,[12] metallocarbohedrene clusters,[13] and $Al_{13}I_x^-$ clusters.[14] For silica, in Figure 1 we show an $(SiO_2)_N$ ($N = 8$) cluster which is markedly conspicuous with respect to two defining measures of "magic": (i) stability with respect to cluster isomers of the same composition and (ii) stability with respect to $N + 1$ and $N - 1$ ground-state isomers (the second-order energy difference).

We discovered this cluster and its magic status by detailed extensive global optimization searches of the low energy spectra clusters of $(SiO_2)_N$ ($N < 13$).[16] As far as we are aware, cluster beams have thus far produced well-defined pure $(SiO_2)_N$ clusters up to only $N = 4$,[17] and the stability and structure of our $N = 8$ magic cluster are a prediction for future experiments to confirm. It is encouraging, however, that hydroxyl-terminated $(SiO_2)_8$ magic clusters have been shown to exist in laser ablation experiments,[18] albeit with structure different from the $(SiO_2)_8$ magic cluster employed herein.[19] In the remainder of this paper we investigate magic-cluster-based bulk silica phases by exploring numerous ways in which our $(SiO_2)_8$ building blocks may be assembled into ordered materials.

Methodology

For all calculated energies and structures, periodic density functional (DF) calculations using the projected augmented wave[20] method for core states and a plane wave basis set were employed with the PW91 functional[21] and suitable k-point meshes generated via the Monkhorst−Pack scheme.[22] All calculations allowed both internal atomic positions and cell dimensions to vary freely to obtain the lowest energy structures. A relatively large energy cutoff of 800 eV was employed to minimize the spurious effects of basis set variability with changing cell size, and all final energies were checked by subsequent high-level single point calculations. The VASP[23] code was used throughout. Further details of the calculations and the optimized structures thus obtained can be found in Supporting Information.

The $(SiO_2)_8$ magic cluster (Figure 1) has two clear assets when viewed as a building unit, with respect to both its terminated structure and its overall topology. The cluster possesses four silanone (Si═O) terminations, which are

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known to be mutually reactive centers that undergo barrierless coalescence to form siloxane (Si—O—Si) bridges,[24,25] thus providing a natural means to link clusters together to form a bulk material. In a fully connected framework material possessing no defects, each Si═O termination in the original clusters should thus combine to form two Si—O—Si linkages between clusters. By noting typical energies of a Si—O bond (452 kJ/mol) and a Si═O bond (590 kJ/mol) and calculating the energy difference per cluster between a collection of free clusters and a cluster-based material ($4 \times 590 - 8 \times 452 = -1256$ kJ/mol) we can immediately see that, in this ideal scenario, the reaction of the clusters to form an extended material is strongly thermodynamically favored. The total energy of the $(SiO_2)_8$ magic cluster is found to be −17 040 kJ/mol (see Supporting Information for details). Adding to this the cohesive energy of optimally condensed material estimated above, we arrive at −18 296 kJ/mol of $(SiO_2)_8$ units (equivalent to −2287 kJ/mol of SiO_2 units). This energy in turn can be compared to the total electronic energy of α-quartz (−2307 kJ/mol of SiO_2 units, see Supporting Information for details), providing us with an approximate benchmark value of ~20 kJ/mol SiO_2 above quartz for an optimally condensed material comprised of magic clusters.

It is noted that the presently considered class of silicate frameworks all contain small rings (Si_MO_M; $M < 4$) which are inherently present as a result of the structure of the magic cluster (see Figure 1) and, in some cases, as a result of the nature of the connections between magic clusters. Although classical interatomic potentials have often been used to provide reasonable estimates of relative energetics of numerous hypothetical frameworks,[1−3,8] as such force fields are generally parametrized with respect to materials without such small rings, the validity of their application in such cases is unclear. In contrast, the present ab initio method of energetic evaluation, employing the gradient corrected PW91 functional, is known to be particularly applicable to accurately assessing the energetics of small-ring-containing silicate materials[26] and other strained silicate materials.[27] To demonstrate the potential magnitude of the discrepancies between our DF-based predicted framework energetics and those from calculations based upon classical potentials for small-ring-containing silicates, we have calculated the energy of an all-silica version of the OSO zeolitic framework,[28] which consists solely of connected Si_3O_3 rings. Our DF calculation gives an energy of 16 kJ/mol above α-quartz, which lies satisfyingly between the experimental formation enthalpy of hydrothermally synthesized non-three-ring-containing all-silica zeolites (upper limit ~14 kJ/mol SiO_2)[29] and that of the all-silica disordered three-ring-containing[30] mesoporous framework materials (lower bound ~19 kJ/mol SiO_2).[30] Our estimate contrasts sharply with the reported corresponding energy of ~55 kJ/mol SiO_2[8] for all-silica OSO calculated using classical potentials, indicating a breakdown of the empirical parametrization for such systems.

In the following section we investigate the various ways in which our magic $(SiO_2)_8$ clusters may be assembled into bulk crystalline silicate materials though the result of the siloxane bridge forming reaction (4[Si═O] → 8[Si—O—Si]) between clusters.

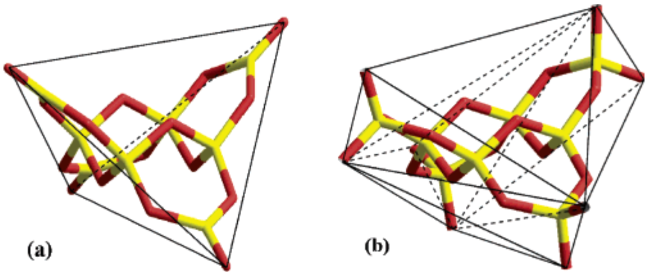

Figure 2. (a) $(SiO_2)_8$ magic cluster schematically encased by a tetrahedron whereby the vertexes show the fourfold tetrahedral bonding potential and (b) the $(SiO_2)_8$ magic cluster encased by a tristetrahedron with its vertexes indicating the eightfold bonding propensity.

Results

The four Si═O terminations of the magic cluster are distributed in a highly symmetric manner with each pointing in a mutually opposing direction. The resulting cluster topology can thus be thought of as a super-analogue of the basic SiO_4 tetrahedral silicate unit (see Figure 2a).

Extending this concept, the realization of materials employing this topological analogy is highlighted in Figure 3 showing how both corner-sharing and edge-sharing of SiO_4 tetrahedra can be mimicked in a meta-fashion using the magic clusters to form “super-tetrahedral” (ST) silicate structures. In Figure 3 four such ST silicates (ST1−ST4) are shown: (ST1) a ST version of the edge-sharing silica polymorph silica-W[31] and ST versions of the corner-sharing silicates quartz (ST2) and cristobalite (ST3). Additionally, the ST4 structure shows how two cristobalite-like frameworks can be interleaved with each other, forming a substantially denser material.

In each case the transformation of the usual silica polymorph to its ST form entails an inevitable increase in the unit cell size and also leads to relatively lower density silica materials. In particular in their ST versions the two-ring chains of silica-W become more akin to nanowires and the dense silica phases of cristobalite and quartz become open framework materials. A comparison of the experimental crystal parameters and framework densities of the SiO_4-tetrahedral-based silicate materials (where known) and the calculated values for our corresponding ST versions is given in Table 1.

To construct these ST silicates one must connect the Si═O terminations of distinct clusters in a one-to-one fashion whereby the resulting pairs of siloxane bridges lead to the formation of strained Si_2O_2 double rings. Examining the energies of the four ST silicates with respect to α-quartz (Table 1) we can see that the coalescence of clusters via

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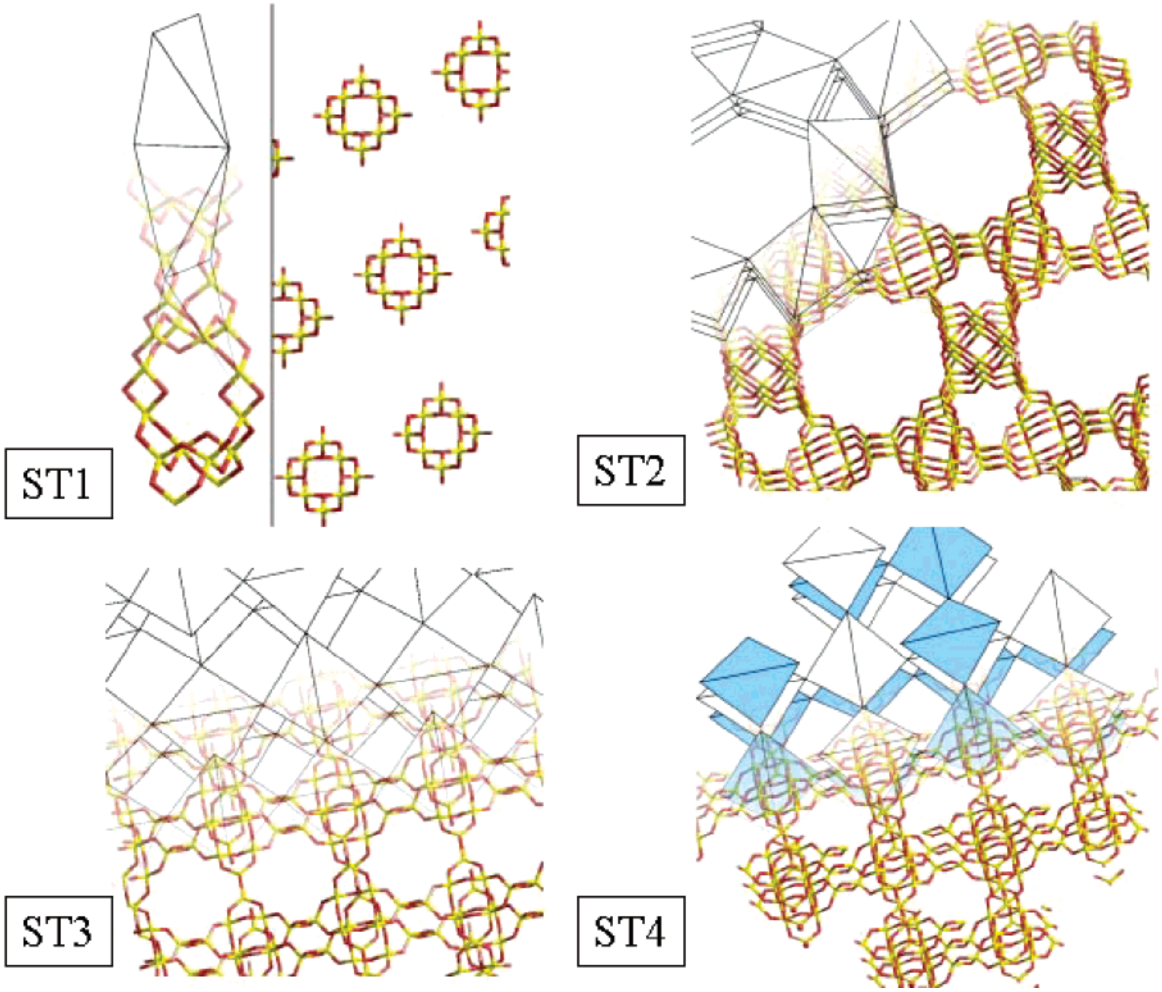

Figure 3. Magic-cluster-based ST frameworks showing an atomic representation and a schematic ST representation in each case. ST1: the edge-sharing ST version of the discrete-chain-based polymorph silica-W (left shows an individual superchain and right shows a view down the *c* axis of the material). ST2: a corner-sharing ST version of quartz. ST3: a corner-sharing ST version of cristobalite. ST4: a ST material formed from two interleaved cristobalite-like frameworks.

Table 1. Cell Parameters, Framework Densities (FD), and Energies with Respect to α-Quartz of the Four ST Framework Materials ST1−ST4[a]

	a	*b*	*c*	α	*β*	*γ*	FD (Si/1000 Å^3)	$\Delta E_{\alpha\text{-quartz}}$ (kJ/mol SiO_2)
ST1	12.96 (8.37)	10.12 (5.16)	13.12 (4.76)	95.7 (90)	86.3 (90)	88.4 (90)	9.4 (19.5)	72.9
ST2	17.39 (4.91)	17.39 (4.91)	13.04 (5.41)	90 (90)	90 (90)	120 (120)	7.0 (26.5)	59.2
ST3	17.81 (4.97)	17.67 (4.97)	17.83 (6.92)	90 (90)	90 (90)	90 (90)	5.7 (23.5)	55.4
ST4	13.50	13.50	5.43	95.7	84.3	91.6	15.2	57.0

[a] Comparison of the experimental cell parameters and densities (where available) of the corresponding SiO_4-tetrahedral-based silicates (i.e., ST1/silica-W,[31] ST2/quartz,[32] ST3/cristobalite)[33] are given in parentheses. For full coordinates see Supporting Information.

two-ring bridges appears to lead to relatively highly energetic materials. Compared to our estimated optimal benchmark energy above α-quartz of ∼20 kJ/mol for magic-cluster-based materials we see that these structures are a further ∼36−53 kJ/mol higher in energy and are thus probably not easily viable synthesis targets.

An alternative to joining the Si═O terminations of each cluster in a one-to-one manner is to consider a one-to-two type of connection. In this way each single Si═O termination opens to form two Si−O−Si links with two other magic clusters. With respect to our tetrahedral representation of the magic cluster we can regard this extended bonding mode as an addition of a single connection point (vertex) at each of the four faces of the tetrahedron. Topologically this leads to formation of a distorted Triakis tetrahedron (tristetrahedron)[34] geometry, which can be also viewed as a basic building unit (see Figure 2b).

Using this mode of assembly leads to framework materials having clusters that are connected to between two and eight neighbors (super-tristetrahedral (STT) materials), rather than between two and four as in the ST materials. This cluster bonding mode has the advantage that energetically unfavored two-ring linkages are naturally avoided thus allowing greater potential for lower energy materials. In Figure 4 we show six STT framework materials (STT1−STT6) in order of

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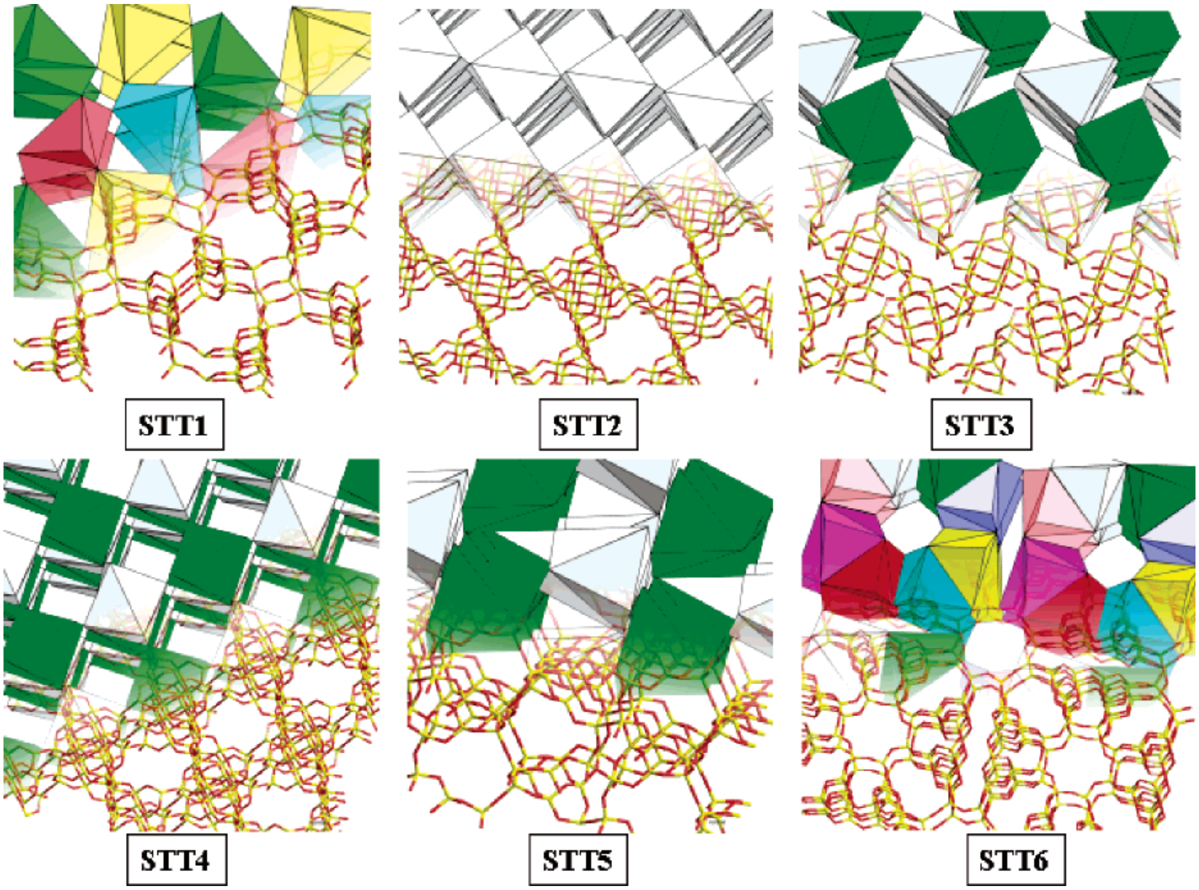

Figure 4. Magic-cluster-based STT frameworks showing an atomic representation and a schematic STT representation in case.

Table 2. Comparison of Calculated Cell Parameters, Framework Densities (FD), Energies with Respect to α-Quartz ($\Delta E_{\alpha\text{-quartz}}$), Tetrahedral Mismatches Δ_{TM}, and Space Groups and Largest Pore Sizes of the Magic-Cluster-Based STT Framework Materials[a]

	a	*b*	*c*	α	*β*	*γ*	FD (Si/1000 Å^3)	$\Delta E_{\alpha\text{-quartz}}$ (kJ/mol SiO$_2$)	Δ_{TM} (10^{-2})	space group	largest pore (no. Si atoms)
STT1	15.81	15.81	9.96	90	90	90	12.9	21.3	2.04	*P*4/*mbm*	12
STT2	18.31	18.30	5.11	90	90	90	18.7	23.6	2.12	*Amm*2	12
STT3	11.62	11.62	5.20	90	90	90	22.8	25.3	2.39	*P*21212	12
STT4	13.68	13.68	10.49	90	90	90	16.3	25.6	2.23	*I*4/m	12
STT5	14.17	12.73	10.31	90	90	90	17.2	26.2	3.16	*P*222	8
STT6	20.57	9.74	20.46	90	90	90	15.6	34.6	4.38	*Pmmm*	12

[a] For full coordinates see Supporting Information.

decreasing energetic stability, constructed by the connection of magic clusters in a one-to-two fashion. The cell parameters, framework densities, and energies with respect to α-quartz are given in Table 2.

Discussion and Conclusions

To evaluate the synthetic viability of the STT frameworks we have investigated both their topology and their energetics. An indication of the strain inherent within each STT framework can be assessed by calculating the tetrahedral mismatch (Δ_{TM}) of each framework.[35] Such a measure has been found to be instructive in suggesting limits on the viability of hypothetical framework to be synthesized through hydrothermal means ($\Delta_{TM} < 2.5 \times 10^{-2}$ Å^2) .[36] The tetrahedral mismatch for all six STT materials is given in Table 2. Four of the STT frameworks (STT1−STT4) have Δ_{TM} values that lay within the range shared by known synthesized frameworks suggesting that their bonding topology is not a barrier to their eventual synthesis. Although we do not expect our STT frameworks to be viable synthesis targets through hydrothermal means, the reasonable range of Δ_{TM} values for STT1−STT4 gives us extra confidence that there should exist an alternative route to their formation based on magic clusters as proposed herein.

The energies of the STT frameworks STT1−STT5 all lay in a narrow range between 21 and 26 kJ/mol above α-quartz with STT6 being a further 8 kJ/mol higher in energy (see Table 2). The relatively high energy and Δ_{TM} of STT6 is probably due to it exhibiting "super-edge-sharing" whereby some clusters are connected to only six out of a possible eight neighbors. Although all the STT energies are quite high compared to hydrothermally synthesized all-silica zeolites (7−14 kJ/mol),[29] in comparison with the range of experimentally determined enthalpies of formation for mesoporous

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silica frameworks (19−32 kJ/mol)[30] it is evident that our STT frameworks lay in a thermodynamically accessible window. The higher energies of mesoporous silicas relative to the all-silica zeolites have been attributed to the presence of Si_3O_3 three-membered rings.[30] The incorporation of small rings into zeolitic structures has also been topologically linked to the possibility of creating materials with the highly desirable property of possessing extra-large pores.[37,38] Although, thus far, hydrothermal syntheses have not managed to produce a three-ring-containing pure-silica zeolite, their presence in mesoporous silica frameworks[30] and in biosilicas[39] indicates that this is not a fundamental constraint on crystalline pure silica. All our cluster-based frameworks incorporate three rings from their intrinsic presence in the magic cluster (see Figure 1). For small nanoclusters three rings appears to be a relatively energetically favored motif,[16,40] and thus the formation of frameworks, perhaps possessing very large pores and/or channels, from such building blocks indicates a novel route to naturally incorporate Si_3O_3 three-membered rings into all-silica materials.

Except for the presence of three rings, the six STT frameworks do not appear to display physical characteristics that would be deemed particularly atypical of known silicate frameworks. Topologically, however, all STT frameworks (with the exception of STT5) have at least one 12-ring pore and are thus so-called large pore frameworks. Most also have 8- or 10-ring pores running in perpendicular directions making such materials potential attractive targets for catalytic and membrane applications. Furthermore, the utilization of a single type of cluster building block does not appear to significantly restrict the variability in framework type. The framework density of the magic-cluster-based materials goes from very open (STT1 with a framework density comparable to that of Faujasite) to very dense (STT3 with a framework density comparable to that of α-cristobalite). Similarly, the frameworks range from cage-type frameworks (STT5) via frameworks with pores in only one direction (STT2) to frameworks with pores extending throughout the structure in all three spatial directions (STT1 and STT4). Interestingly, the dense framework STT3 has a slitlike 12-ring pore (11.8 × 5.4 Å) running through it in one direction, in contrast with known frameworks of a similar density (e.g., α-cristabolite, tridymite), which are all nonporous. We note further that, although our entire range of frameworks was constructed via bottom-up design, we subsequently discovered that three of them (STT2, STT3, and STT4) also correspond to hypothetical frameworks independently generated through top-down methods based on graph theory.[41] This link between two different predictive approaches provides an important bridge between materials discovery and identifying potential building blocks for their fabrication, suggesting that there may be considerable benefits in combining both approaches.

Taking the energy with respect to α-quartz of our lowest energy framework (21 kJ/mol for STT1, which as of yet has not been found to correspond with a previously known hypothetical framework), we can see that the one-to-two mode of construction for STT frameworks can lead to an almost optimal assembly of our magic clusters into a material (with respect to our ideal estimate of ∼20 kJ/mol). Although this indicates that further searches into other modes of assembly of our particular magic cluster are unlikely to yield significantly more stable framework materials, it is hoped that our study will motivate experimental cluster-based approaches to inorganic materials synthesis (as a gas-phase extension to solution-based reticular synthesis)[6] and further stimulate theoretical searches for new viable materials employing other types of cluster building blocks.

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Supporting Information Available: Calculation details, optimized unit cell parameters, and fractional coordinates of all materials and complete ref 15 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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