

Absence of Limitations on the Framework Density and Pore Size of High-Silica Zeolites

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Through atomistic optimizations of recently enumerated hypothetical frameworks, we demonstrate that in contrast with the experimental observation by Brunner and Meier (Brunner, G. O.; Meier, W. M. *Nature* **1989**, 337, 146), there is theoretically no evidence for any topological, geometric, or energetic constraint on framework density and pore size in siliceous zeolites. More specifically, we show that there are numerous very low-density and/or very large-pore siliceous materials with comparable energetics to currently synthesized materials. The experimentally observed limitations thus seem instead to stem from a far from complete experimental exploration of the siliceous zeolite structural landscape and might be related to the lack of suitably large and rigid template molecules to fill the enormous void volume. Self-assembly of organic molecules to form nanosized templates might therefore hold the key to low density and/or extra-large-pore frameworks.

Introduction

Nanoporous zeolites are the workhorses of the petrochemical industry due to their high pore volume, thermal stability, and well-defined pore structure. The latter property, in particular, permits an unrivalled selectivity in catalysis (shape selectivity^{1,2}) and separation (molecular sieving³). However, the current zeolites are limited in pore dimensions and framework density: there are very few with pores larger than those circumscribed by 14 tetrahedral atoms and, similarly, few zeolites having a density lower than 12 T atoms per 1000 Å³, limiting the size and number of molecules that can enter.^{2,4} In 1989 Brunner and Meier performed a topological analysis on the underlying frameworks (so-called 4-connected nets) of all of the 70+ dense and porous silicate or aluminophosphate materials then synthesized (or found as minerals). They noticed that when the frameworks are grouped together based on the smallest ring present, the minimum FD_{Si} (the framework density calculated for an idealized SiO₂ composition) for each of the groups decreases with the smallest ring size.⁵ Consequently, this work sparked a great deal of interest in doping the zeolite synthesis mixture with elements empirically known to “stabilize” 3-rings (Be, Zn), as this seemed to hold the key to the lowest density

and possibly also the largest pore materials.^{6–8} Nearly 20 years later, Brunner and Meier’s empirical observation still stands, even though more than 100 new frameworks have been synthesized in the intervening period, including the supertetrahedral RWY framework, which is synthesized only as a sulfide or selenide material⁹ and the recently synthesized 18-ring pore materials ECR-34¹⁰ (ETR framework) and ITQ-33.¹¹ Novel nonzeolite materials lacking such limits^{4,12,13} have been developed (e.g., locally disordered mesoporous oxides and metal organic frameworks), but these generally do not possess the stability or the regular pore structure of zeolites.

It is often implied that this restriction observed by Brunner and Meier arises from some fundamental topological, geometric, or energetic constraints inherent to tetrahedral frameworks, something we can now test using databases of hypothetical frameworks^{14–23} that recently have become

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available. A search through these databases yields a variety of framework topologies that appear to be more open than would be expected on the basis of the observation by Brunner and Meier, but does not provide us with an answer to the question as to whether such low density structures are chemically reasonable, i.e., likely to be observed in hydrothermal synthesis. Using computational chemistry methods that allow us to characterize hypothetical frameworks in terms of their thermodynamic stability and compare them directly with experimentally known structures, we demonstrate that there is no theoretical constraint on framework density and pore size in siliceous zeolites. More specifically, there are potentially many very-low-density and/or very-large-pore materials of comparable thermodynamic stability to currently synthesized materials. The observed limitations thus seem to stem instead from a far from complete experimental exploration of the zeolite structural landscape.

Computational Methodology

The siliceous materials were studied using atomistic calculations in which the interaction between silicon and oxygen ions was described by the Sanders–Leslie–Catlow interatomic potential.²⁴ This potential has been shown to reproduce very accurately the experimentally measured energetic ordering of the different silica polymorphs^{25,26} and the corresponding quantitative enthalpy differences after rescaling.²⁶ All crystal structures were minimized without any symmetry constraints using a constant pressure optimization algorithm as implemented in the program GULP²⁷ (i.e., both atomic positions and cell parameters were optimized). A combination of the use of a rational function optimizer²⁸ (RFO) as enthalpy minimization routine, which guarantees that the optimized structure has only three zero and no negative frequencies at the gamma point, and a final phonon calculation (using a $4 \times 4 \times 4$ 32 k point sampling grid), to check for the absence of soft modes at other special positions in the Brillouin zone, was employed to guarantee that only true minima were found.

All enthalpies quoted for the siliceous materials are relative enthalpies compared to α -quartz (comparable to the experimentally measured enthalpies of transition), normalized to the number of T atoms per unit cell. Experimentally, the entropy differences between different crystalline siliceous polymorphs and α -quartz are known to be small and span a narrow range;²⁹ the calculated enthalpy differences are also a good approximation of the free energy landscape of crystalline silica.²⁶ To verify that this approximation

also holds for materials based on hypothetical frameworks, we determined the entropies for all the materials considered. These were calculated from the final phonon calculations, in which it is assumed that the vibrational motions in the solid can be described by independent quantized harmonic oscillators. The optimized structures were further analyzed using the ZEOTS³⁰ and GASP³¹ codes for, respectively, intertetrahedral (Si–O–Si) and intratetrahedral (O–Si–O) distortion. For the latter calculations, a reference Si–O bond length of 1.6 Å was applied, in line with our previous work.³²

Finally, to probe the thermal stability of the hypothetical materials at realistic synthesis and calcination temperatures, we explored the free energy landscape around the enthalpy minima by molecular dynamics (MD) runs at 400 and 800 K in GULP, for selected materials. Both the length of the MD runs (100 ps after 5 ps of initial temperature equilibration) and the choice of ensemble (NPT,³³ so cell parameters are allowed to change) were driven by a desire to give the materials freedom to collapse during the simulation into denser and lower free-energy phases, if kinetically possible. The MD was carried out with the same interatomic potentials as for enthalpy minimization, and using adiabatic dynamics,³⁴ in which the O shells are given a small mass (10% of the atomic mass) and their motion is integrated in the same way as that of the cores, by numerical integration of the classical equations of motion.

Results and Discussion

We first distinguish between three key criteria, which must all be met in order for a given framework to be likely to exist as a real material. These criteria, or “constraints” on the framework’s realizability, are based on the quite distinct concepts of topological, geometric, and energetic feasibility. We define these criteria using the following three questions:

(1) Can one conceive a 4-connected net with the desired openness and/or topological density?

(2) If so, can such a 4-connected net be realized as a framework material without chemically unfeasible distortions of local geometry?

(3) And if so, does the resulting material lie low in energy (enthalpy) compared with the global minimum structure for the given chemical composition?

Question (1) defines the topological constraint. At this stage of the evaluation we ignore any geometric details and consider only the connectivity of the net; in other words essentially those properties, such as ring size, that do not change upon compression or stretching.

Following on from this, although it might be possible, on topological grounds, to imagine a framework with the desired low density and/or large pores, it might only be realized as a real material at the expense of chemically implausible local geometries, e.g., strained T–O bonds and/or extreme O–T–O angles. We refer to this effect of embedding the abstract 4-connected net in three-dimensional Euclidean space, defined by question (2), as the geometric criterion.

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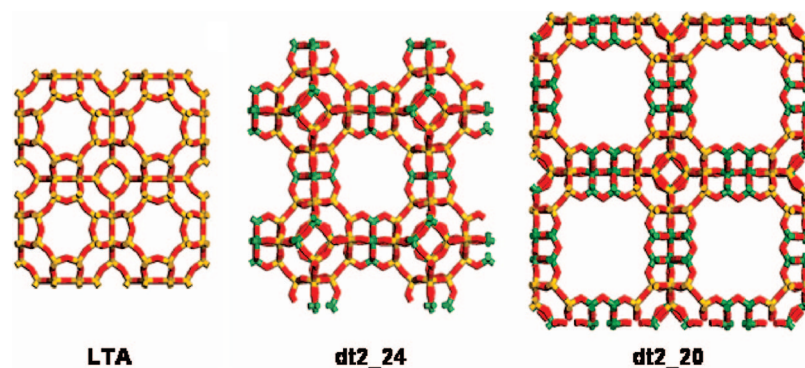


Figure 1. Illustration of the expansion of the LTA structure by consecutive insertion of double 4-rings between the sodalite cages (Si atoms between two double 4-rings in green, all other Si atoms in yellow, and O atoms in red).

Table 1. Number of Double 4-Rings between Two Sodalite Cages, Framework Density, Pore Size (PS), Average Si–O–Si Angle, Total Tetrahedral Distortion of the Si Atoms in the Sodalite Cage (TTD1), Total Tetrahedral Distortion of the Si Atoms between Two Double 4-Rings (green atoms in Figure 1, TTD2), and Relative Lattice Enthalpy Compared to Quartz for the LTA Framework and Two of Its Expansions, Optimized as Siliceous Structures (between brackets the rescaled enthalpies)

framework	no. D4R	FD _{Si} T atoms per 1000Å ³	PS	⟨Si–O–Si⟩ (deg)	TTD1 (Å)	TTD2 (Å)	ΔE _{quartz} (kJ/mol SiO ₂)
LTA	1	14.5	8	149.4	2.3 × 10 ⁻²		19(14)
Dt2_24	2	11.5	12	145.4	3.3 × 10 ⁻²	1.1 × 10 ⁻¹	41(28)
Dt2_20	3	9.0	16	143.4	3.1 × 10 ⁻²	1.1 × 10 ⁻¹	49(34)

Finally, defined by question (3), there is the condition of energetic feasibility, which refers to the thermodynamic stability of a particular structure. In the case of silicate materials, this is closely correlated to local atomic-scale geometry. However, we consider energy (enthalpy) as a clearly distinct criterion since its dependence on geometry will vary according to chemical composition. Only when a hypothetical framework fulfils all three of the criteria is it likely to be realized as a real material. The three criteria are therefore all necessary conditions for framework material feasibility. That, together, they may not be sufficient conditions to guarantee a successful experimental preparation, because of current limitations in experimental synthesis design, is a separate matter to which we allude later.

It is very easy to demonstrate that the limitations are not topological. This was illustrated most graphically by Smith and Dytrych, who showed that it is possible to construct infinite series of nets based on common structural units, for instance, the series derived from the AFI and VFI framework types.³⁵ Taking the more recent example of nets generated from tiling theory, we consider the LTA framework (zeolite A) consisting of sodalite cages interconnected by double 4-ring (D4R) cages. Now, as in Figure 1, one can replace the single D4R connecting two sodalite cages by a chain of two D4Rs (dt2_24²¹) or a chain of three D4Rs (dt2_20²¹). The process of adding a D4R into the chain linking the sodalite cages can in principle be repeated an infinite number of times, giving rise to hypothetical frameworks with any pore size and framework density. Moreover, one can show the same lack of topological limitations in a similar fashion for many other types of framework, e.g., by expanding the FAU structure with additional 6-rings (dt2_35, dt2_31²¹). As can be seen in Table 1, such frameworks are, however, not low enthalpy frameworks, mostly because of the severe

distortion of the SiO₄ tetrahedra³² lying between two D4Rs, and are as a result unlikely to be synthesized in a high silica form.

Shedding light on the other two constraints (geometric and energetic limitations) is considerably more difficult as they cannot simply be “proved by example”, as in the case of the topological construction. Therefore, we selected low FD_{Si} and large-pore hypothetical frameworks with only 4 and larger rings from the sources at our disposal (generated by either hand or computer) and evaluated their enthalpy computationally, using the energy minimization method based on atomistic potentials. The results are striking. Although the database of hypothetical frameworks corresponding to simple tiling (the so-called ST frameworks^{36,37}) by Delgado-Friedrichs et al.¹⁵ contains no appropriate low enthalpy frameworks (in line with simple topological arguments developed previously^{36,37}), the hypothetical low framework density frameworks from the AFI/VFI family proposed by one of us³⁸ (derived from the work of Smith and Dytrych discussed above) are all predicted to lie within 6 kJ/mol(SiO₂) of the synthesized all-siliceous versions of the FAU and LTA frameworks. The existence of these hexagonal, relatively low-enthalpy N(on)ST frameworks (see Figure 2 and Table 2 for example(s) with 20–30 Å pores and FD_{Si} values well below the minimum values predicted by Brunner and Meier for frameworks with only 4 and larger rings further inspired us to search the database of Treacy and co-workers^{14,18,39} (containing both ST and NST frameworks) for similar frameworks. This database is found to

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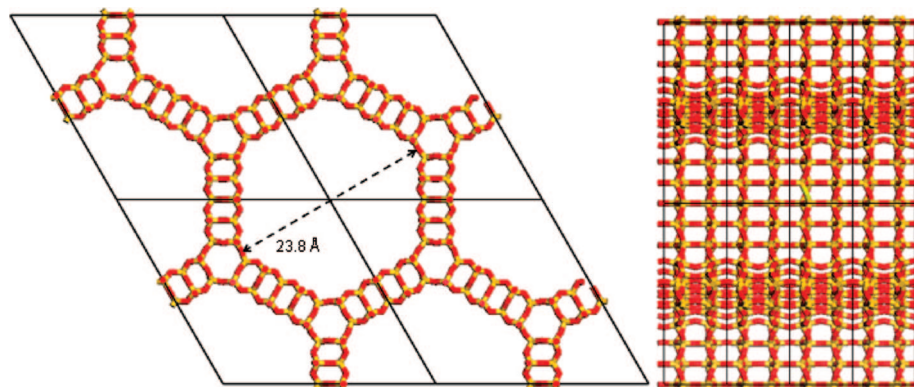


Figure 2. Views parallel and perpendicular to the pore direction of the ZM30 framework optimized as a SiO₂ structure, respectively showing the pore circumscribed by 30 Si atoms and the pore wall consisting of only 6-rings (Si atoms in yellow and O atoms in red). Note how the two layers of 6-rings that make up the pore are shifted relative to each other.

Table 2. Size of Smallest Ring^a (SR), Framework Density, Pore Size (PS), Total Tetrahedral Distortion (TTD), Smallest Pore Diameter (SPD), Largest Pore Diameter (LPD), Porosity, Schläfli Symbol of 3-Connected Nets Covering the Pore Surface and the Relative Lattice Enthalpy (between brackets rescaled relative lattice enthalpies) and Relative Entropy (both compared to quartz) for Some of the Hypothetical Frameworks with Large Pores and a Low Framework Density, Optimized as Siliceous Structures

framework	SR	FD _{Si} T atoms qaper 1000Å ³	PS	⟨Si–O–Si⟩ (deg)	TTD (Å)	SPD (Å)	LPD (Å)	porosity	pore surface	ΔE _{quartz} (kJ/mol SiO ₂)	ΔS _{quartz} (J (mol SiO ₂) ⁻¹ K ⁻¹) ^b	ref
FAU	4	13.5	12	143.3	3.62 × 10 ⁻²	9.8	9.9	0.5		19 (14)	1.9	
ZM30	4	10.8	30	144.5	4.86 × 10 ⁻²	21.1	23.8	0.6	6 ³	24 (17)	2.7	38
ZM36	4	8.8	36	146.7	2.57 × 10 ⁻²	24.8	28.3	0.7	4.6.8 + 6.8 ²	24 (17)	2.5	38
ZM42	4	8.5	42	143.9	4.74 × 10 ⁻²	30.1	34.6	0.7	6 ³	26 (18)	2.7	38
194_5_4713570	4+	8.3	42	148.8	3.47 × 10 ⁻²	30.5	33.1	0.7	6 ³	19 (13)	3.5	39
194_3_189	4	9.0	36	148.7	2.63 × 10 ⁻²	24.9	28.9	0.7	6 ³ + 4.6.8	20 (14)	2.9	39
191_4_9370	4	8.1	42	148.9	2.50 × 10 ⁻²	29.5	33.8	0.7	6 ³ + 4.6.8	20 (14)	2.9	39
194_4_6238	4	7.3	48	149.0	2.39 × 10 ⁻²	34.0	39.3	0.7	6 ³ + 4.6.8	20 (14)	2.9	39

^a In some frameworks, the size of the smallest ring is not the same at every T atom; such structures are indicated after Brunner & Meier⁹ with *n*+ (where *n* is the smallest ring in the whole framework). ^b ΔS_{quartz} calculated for synthesized frameworks: CHA, 3.3; ISV, 5.1; MFI, 4.7 (all in J (mol SiO₂)⁻¹ K⁻¹).

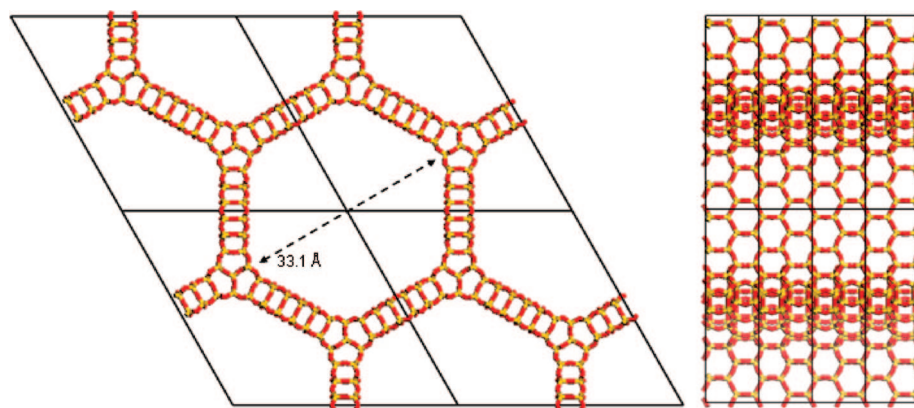


Figure 3. Views parallel and perpendicular to the pore direction of the 194_5_4713570 framework optimized as SiO₂ structure, respectively showing the pore circumscribed by 42 Si atoms and the pore-wall consisting of only 6-rings (Si atoms in yellow and O atoms in red).

contain a wealth of such (hexagonal) low-density and large-pore frameworks, many of which when optimized are only marginally higher or even similar in enthalpy to siliceous versions of FAU and LTA (see Figure 3 and Table 2 for example(s)), both of which have been prepared experimentally.^{40,41} Mesoporous siliceous zeolites are thus predicted to have energetics similar to those of currently synthesized siliceous zeolites. Moreover, as the Sanders–

Leslie–Catlow potential is known to overestimate the enthalpy differences compared to quartz²⁶ and as experimentally empty MCM-41, MCM-48 and SBA-15 all lie over 20 kJ/mol (SiO₂) above quartz⁴² (in contrast with zeolites, there appears to be no experimental measurement of the template framework interaction energy of mesoporous materials), all of the discussed hypothetical structures (including the AFI/VFI derivatives) are most likely more stable than the calcined amorphous mesoporous silica materials with similar pore size and pore volumes

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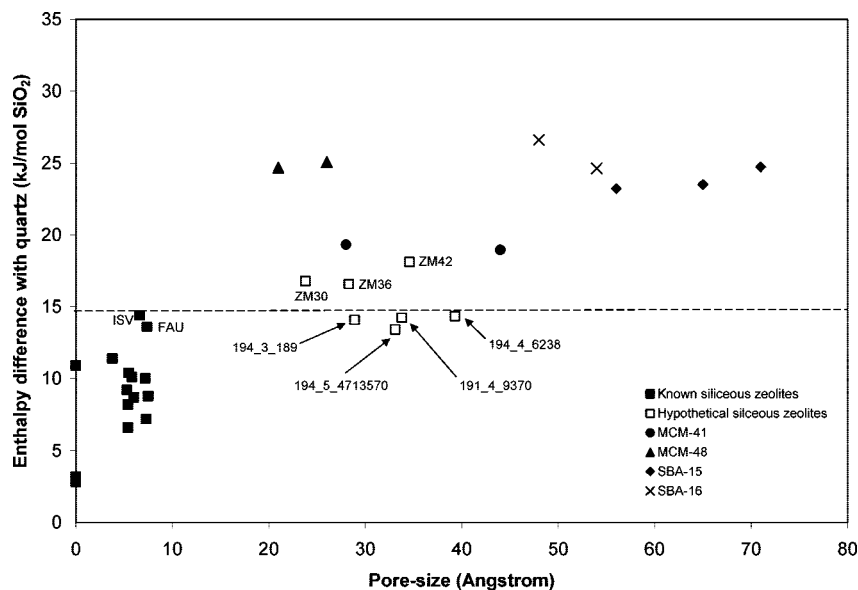


Figure 4. Relative enthalpies of siliceous zeolites and mesoporous materials as function of their pore size (experimental values for known siliceous zeolites⁴⁹ and mesoporous materials⁴² and rescaled²⁶ calculated values for the hypothetical siliceous zeolites; pore size of dense frameworks set to zero).

Table 3. Characteristics of the Si–O–Si Distribution for Some of the Hypothetical Frameworks with Large Pores and a Low Framework Density, Optimized as Siliceous Structures, and Three Experimental Structures (siliceous FER,⁴³ siliceous MWW (ITQ-1⁴⁴), and the aluminophosphate VFI (VPI-5⁴⁸))

	$\langle \text{Si-O-Si} \rangle$ (deg)	std. dev. Si-O-Si distribution (deg)	minimum Si-O-Si (deg)	maximum Si-O-Si (deg)	fraction Si-O-Si < 140	fraction Si-O-Si > 170	fraction Si-O-Si > 175
ZM30	144.5	12.7	126.6	157.0	0.40	0.00	0.00
ZM36	146.7	14.2	132.1	176.7	0.42	0.17	0.17
ZM42	143.9	13.5	126.6	157.5	0.43	0.00	0.00
194_5_471370	148.8	13.3	135.3	178.4	0.30	0.13	0.06
194_3_189	148.7	14.0	138.9	179.5	0.19	0.13	0.13
191_4_9370	148.9	14.5	138.9	179.6	0.22	0.16	0.16
194_4_6238	149.0	14.9	138.8	179.6	0.23	0.19	0.19
FER (exp)	153.0	9.5	138.3	170.7	0.11	0.11	0.00
MWW (exp)	153.0	4.2	137.2	180.0	0.04	0.04	0.04
VFI (ALPO, exp)	148.7	9.2	136.6	166.7	0.17	0.00	0.00

(see Figure 4). The latter is supported by the fact that all the rescaled enthalpy differences with quartz (in which the calculated enthalpy differences for the hypothetical frameworks are rescaled to the experimental range using a linear equation and parameters obtained from a least-squares fit between calculated and experimental enthalpy differences for a range of known siliceous structures²⁶), which can freely be compared with experiment, are all smaller than 20 kJ/mol (SiO₂). Finally, the calculated entropy differences in Table 2 strongly reinforce our assumption that the enthalpy differences employed here are a good approximation to the free energy landscape of crystalline silica and can be used to assess the thermodynamic stability of different polymorphs. The entropies of the already synthesized and hypothetical materials are comparable in magnitude and moreover, as has also been experimentally verified for the synthesized materials,²⁹ the calculated entropy differences for the hypothetical structures are small and span a narrow range. This is all perhaps not very surprising as Piccioni and co-workers²⁹ already noted that framework structures based on SiO₄ tetrahedra show a remarkably small spread of the length of the Si–O bond, and that therefore the vibrational density of states associated with Si–O bond stretching is expected to be relatively constant from polymorph to polymorph (something we also observe in our calculations) leading to almost constant room-temperatures entropies. They further noted that poly-

morphs do differ in the lower frequency region associated with bending of the Si–O–Si angle and the very low frequency range associated with so-called rigid unit modes, but that these vibrations contribute at very low temperatures (below 50 K²⁷) to the heat capacity and lead to significant differences only in the entropy of different frameworks in that temperature range.

In addition to the calculated heats of formation and entropy differences, Table 2 gives average Si–O–Si angles, tetrahedral distortion, FD_{Si} , porosity, and pore sizes for a number of example low-enthalpy hypothetical frameworks with the desired properties from both databases. In line with the absence of any observable energetic penalty, the calculated tetrahedral distortion values for all hypothetical materials considered lie in a range typical of high-silica zeolites such as CHA, FER ISV, and MFI (2E-2 to 8E-2 Å),³² although the average Si–O–Si angles and the Si–O–Si angle distribution for the hypothetical frameworks in Tables 2 and 3, respectively, also show behavior typical of high-silica zeolites. The AFI/VFI family frameworks are found to have relatively small minimum Si–O–Si angles (not unlike those predicted for a siliceous version of the VFI framework) but the four frameworks considered from the database of Treacy and co-workers have minimum Si–O–Si angles (135–139°) comparable to those found experimentally for siliceous

materials such as FAU,⁴⁰ FER⁴³ and MWW (ITQ-1⁴⁴). The maximum Si–O–Si angles for the four frameworks from the database of Treacy and co-workers are relatively large, tending but not equal to 180°. However, experimentally siliceous FER is found to have a maximum Si–O–Si angle larger than 170°, and siliceous MWW has one of 180°. For all frameworks the maximum and minimum Si–O–Si angles are found to occur in the pore wall. In contrast to the assertion of Hyde et al.,⁴⁵ the Si–O–Si angle distributions and tetrahedral distortion values thus suggest that the hypothetical frameworks considered can be realized with normal bond angles. With FD_{Si} values well below 10 T atoms per 1000 cubic Å and pores up to 40 Å in diameter, there is thus clearly no evidence of any geometric and energetic limitation on either the framework density or pore-size. In contrast to popular belief there is thus also no obvious need for the presence of 3-rings and doping of the zeolite synthesis mixture with either Be or Zn for achieving low density or large pore zeolites.

A possible next step in the analysis of the low-density hypothetical frameworks would be to demonstrate irrefutably that they are kinetically stable at realistic synthesis and calcination temperatures. In other words that the free energy barriers between the low-enthalpy, low-density hypothetical frameworks and more denser materials are high enough so as not to observe a collapse of one into the other at a given temperature (e.g., 400 K for synthesis) and time scale (e.g., months or years). As the number of structures a material can collapse into is very large and as such a collapse is likely to involve amorphous intermediates, the only tractable approach to study kinetic stability is NPT molecular dynamics, in which both cell volume and shape are allowed to change. The latter can, however, never give the desired irrefutable answer, as one is essentially trying to prove a negative (the nonoccurrence of a transformation into another (meta)stable structure) and the timescales which can be effectively sampled with MD are small compared with those that one would like to study (picoseconds vs months). Taking this all into account NPT MD can be useful to probe for the presence of almost barrierless transformations. We therefore decide to perform 100 ps NPT MD runs on two of the hypothetical materials: ZM30 with a unit cell containing 180 atoms and 194_5_4713570 with a unit cell containing 264 atoms, at both 400 and 800K. These MD runs show no sign of the hypothetical frameworks transforming into another structure (no dramatic changes in lattice parameters during the run and the framework topology, as analyzed by coordination sequence and vertex symbols, stays constant). On the basis of this observation and the fact that the bonding in silica is both strong and highly directional, we would expect the low-enthalpy, low-density hypotheti-

cal frameworks to be kinetically stable at realistic synthesis and calcination temperatures.

All the siliceous versions of the hypothetical frameworks discussed have the pore-sizes and framework densities required for catalysis and adsorption of molecules that are too large for the currently synthesized zeolites without the (hydro)thermal stability and pore structure issues that plague their nonzeolite analogs. Moreover, they are predicted to have a higher mechanical stability than locally amorphous mesoporous oxides with a similar porosity. For example, framework 194_5_4713570 is predicted to have a bulk modulus of 27 GPa and a Young's modulus of 44.5 GPa along the pore direction and 11.5 GPa perpendicular to the pore direction. These values are low compared with the considerably denser known siliceous zeolites⁴⁶ but an order of magnitude higher than those predicted for amorphous silica with a comparable porosity⁴⁷ (0.7, see Table 2). The low-density hypothetical frameworks therefore are especially suitable for applications in which a combination of large pores/low density and mechanical toughness is key. An example of the latter is the proposed application of nanoporous materials as ultralow k insulators in microchips,^{4,46} where mechanical strength is important to prevent crack formation during packaging.

In conclusion, our work illustrates the crucial importance of combining computational chemistry techniques with the study of hypothetical frameworks, in order to give an accurate assessment of their physical and chemical properties. Using such methods, we show for the first time that pore sizes and pore volumes that are currently still the exclusive realm of amorphous mesoporous materials, such as MCM-41 and SBA-15, and metal organic frameworks are not only topologically possible but more importantly lie thermodynamically well within the range of possibilities for zeolites. The only limitation preventing the synthesis of crystalline mesoporous silica is thus not topological, energetic or geometric in nature but much more likely the lack of suitably large and rigid template molecules to fill the enormous void volume. The key to low density and/or extra-large-pore zeolites thus probably lies with small organic molecules self-assembling to form nanostructures that can act as templates.⁴⁰

Conclusion

Using computational chemistry methods to study examples of recently enumerated hypothetical frameworks, we demonstrate that at variance with the experimental observation by Brunner and Meier there is theoretically no constraint on framework density and pore size in siliceous zeolites. More specifically, we show that there are potentially many very low-density and/or very large pore materials of comparable thermodynamic stability to currently synthesized materials.

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The experimentally observed limitations thus seem to stem instead from a far from complete experimental exploration of the siliceous zeolite structural landscape.

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