

GEOMETRIC SIMULATIONS

A lesson from virtual zeolites

Although computational methods are generating a bewildering number of hypothetical zeolite structures, the selection of candidates for synthesis remains problematic. The presence of a flexibility window in the structure may turn out to be a useful criterion.

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The name zeolite means boiling stone in ancient Greek. It stems from the fact that when this mineral is heated, water boils out of the pores. Thus porosity is the defining property of zeolites, giving them a dizzying variety of uses (petrochemical catalysis, molecular sieving, water purification, soil treatment and many more). There are 48 naturally occurring zeolites and 167 synthetic ones, not a small number in absolute terms. But considering the large host of applications, we should like to be able to generate more, with prescribed pore size and shape, so that they can ensnare specific molecules. Unfortunately, zeolite synthesis is a difficult process and we don't know *a priori* which ones will actually be achievable. Asel Sartbaeva and colleagues, writing in this issue, evaluate real zeolite frameworks and find a criterion that may be useful to predict which hypothetical structures are realizable¹. In addition their geometric computations based on empirical data offer insights into the very fundamental question of why zeolites have pores.

Compared with the practically infinite number of synthesizable organic molecules, the number of zeolites available is miniscule, although the number of hypothetical zeolites obtained through energy minimization methods is growing at a tremendous rate. Mike Treacy, one of the authors of the paper in question, 15 years ago spearheaded a project to compute a census of all possible zeolites. The project is one of enormous complexity, as efficient generation and analysis of hypothetical zeolites turns out to use much of modern mathematics, computer science and of course chemistry. It is still gathering speed (the interested reader can marvel at the results at <http://www.hypotheticalzeolites.net>) and the article in this issue is one of the fruits borne by this project.

The crystalline structure of zeolites consists of tetrahedral units, the so-called T-sites, which are 4-valent atoms, typically silicon or aluminium, connected to O-sites, which are oxygen atoms. So, for each of the 230 crystallographic groups there are four

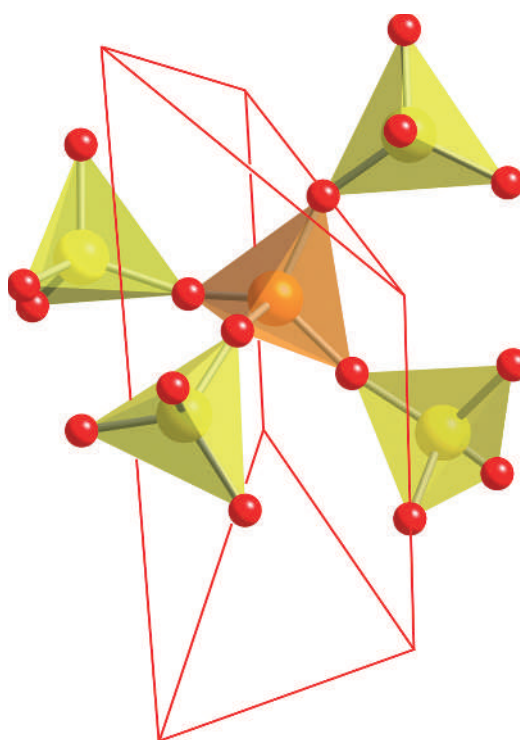


Figure 1 Faujasite tile. A representation of how the SiO_4 tetrahedra are arranged with respect to one another in faujasite. The larger spheres at the centre of the tetrahedra are silicon atoms, the red spheres are the corner-sharing oxygen atoms. The orange SiO_4 tetrahedron is the basic tetrahedron and lies within the fundamental tile, whereas the green ones are the neighbouring tetrahedra that lie outside the tile. The red lines are the edges of the tile.

regular frameworks, which admit a physical realization with low energy. Every crystallographic group Γ has a fundamental region — a tile whose image, repeated under the action of Γ , fills all the space. In each particular structure the number of T-sites in the tile is always the same. These are the 'unique T-sites'; the hypothetical zeolite database consists of structures with a small (but growing) number of unique T-sites. But why do all materials made of these building blocks form porous frameworks?

Sartbaeva and colleagues observe that whereas most materials appear to want to be as dense as possible, zeolites are just the opposite. All of the viable frameworks examined have low energy (that is, they can exist) over a wide range of densities but they seem to prefer a lower-density state. This is quite different from what happens in most classes of materials, from amorphous networks to metallic close-packed

lattices. However, a situation similar to zeolites has been observed for some ionic liquids². In fact, Sartbaeva *et al.* suggest that the underlying reason for this behaviour might be electrostatic repulsion.

In the geometrical models of zeolites computed by Sartbaeva and colleagues, the frameworks of interconnected tetrahedra can budge, and the extent of movement that does not cause distortions in the geometry of the tetrahedra constitutes a window of flexibility. Within this window the material's density changes because the twisting or turning of tetrahedra makes the pores wider, but from the energy standpoint the material remains viable.

The authors modelled all 14 real framework structures and focused in detail on simulating the annealing process of faujasite (the fundamental tile for faujasite is shown in Fig. 1), the most used catalyst in the petroleum refining industry. In each case, they found this flexibility window and discovered that the real structures always lie at the low-density end of this window. The authors' explanation for this is based on considerations of electrostatic repulsion between oxygen atoms on adjacent tetrahedral, which has the effect of making the pores as large as possible. They also conjecture that the flexibility window may actually be a necessary condition for zeolite synthesis to be possible. Although this is plausible, the existence of the flexibility window is rather enigmatic, but it is likely that the explanation for it is purely geometric.

A remarkable observation in the paper is that some structures with a narrow (or non-existent)

flexibility window might undergo a phase transition to a less symmetric form (as illustrated in Fig. 2). Such a transformation may result in a small increase in density but it can give the framework more degrees of freedom to significantly expand (or create) the flexibility window. It is surprising to see how badly the structure wants to decrease its density, even at the cost of losing symmetry. This geometric phase transition strikes me as a very interesting and beautiful event, which is closely connected philosophically to the way mathematicians now study three-dimensional manifolds (following ideas on distortion, which also inspired the recent resolution of the Poincaré conjecture by Perelman). The fact that this occurs in the physical world is extremely satisfying.

Currently, computational experiments are the only way for us to get insight into the basic questions of the physics and chemistry of zeolites. The article by Sartbaeva and colleagues seems to uncover some basic ingredients necessary for realizing the synthesis of yet undiscovered zeolites, which may one day lead us to designer zeolites. This is particularly exciting as we might be witnessing the birth of a new chemical technology era where we can imagine producing a zeolite with the precise pore shape needed to accommodate a specific molecule, and so facilitate completely new types of chemical processes.

REFERENCES

1. Sartbaeva, A., Wells, A. S., Treacy, M. M. J. & Thorpe, M. F. *Nature Mater.* 5, 962–965 (2006).
2. O'Keeffe, M. *Acta Cryst.* A33, 924–927 (1977).

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In this News & Views article, Fig. 2 was missing; it should have appeared as shown here. Both Figs 1 and 2 should also be credited to M. M. J. Treacy.

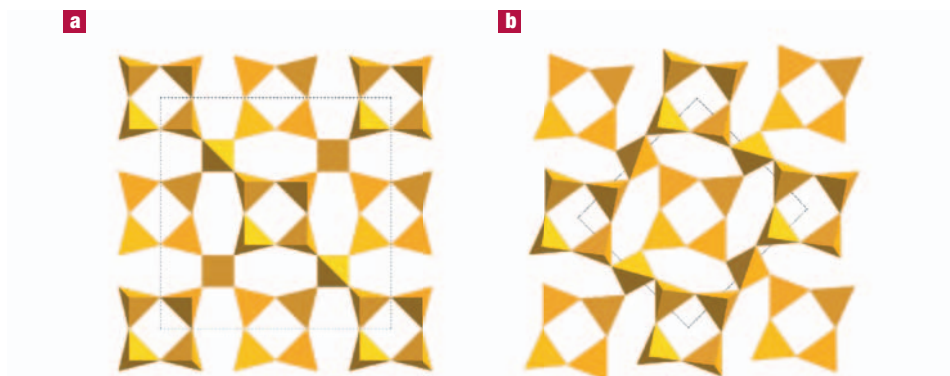


Figure 2 Zeolites that don't like symmetry. The framework of a zeolite known as AST. **a**, The idealized cubic form with the corner-sharing tetrahedra visible. **b**, The framework relaxes into a tetragonal framework (with lower symmetry) by tilting the tetrahedra. For both **a** and **b**, the view is down the tetragonal c axis and the tetragonal unit cell is outlined. The tetragonal form has a wider flexibility window than the cubic.