The flexibility window in zeolites

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Today synthetic zeolites are the most important catalysts in petrochemical refineries because of their high internal surface areas and molecular-sieving properties[1,2]. There have been considerable efforts to synthesize new zeolites with specific pore geometries[3,4], to add to the 167 available at present. Millions of hypothetical structures have been generated on the basis of energy minimization[5], and there is an ongoing search for criteria capable of predicting new zeolite structures. Here we show, by geometric simulation[6–8], that all realizable zeolite framework structures show a flexibility window over a range of densities. We conjecture that this flexibility window is a necessary structural feature that enables zeolite synthesis, and therefore provides a valuable selection criterion when evaluating hypothetical zeolite framework structures as potential synthetic targets. We show that it is a general feature that experimental densities of silica zeolites lie at the low-density edge of this window—as the pores are driven to their maximum volume by Coulomb inflation. This is in contrast to most solids, which have the highest density consistent with the local chemical and geometrical constraints.

Zeolites are crystalline microporous frameworks consisting of corner-sharing nearly perfect tetrahedra, connected by soft hinges at the oxygen atoms[9]. The strongest forces in silica networks are those holding the rigid structural units (SiO_4 tetrahedra) together and also those forces bridging these tetrahedra through the twofold coordinated oxygen atoms to form a framework, as shown in Fig. 1 for the framework of faujasite (FAU) zeolite. Today, more than 40% of oil conversion is achieved using catalysts based on faujasite (Zeolite Y)[3]. Zeolite frameworks contain pores with the larger oxygen anions lining the insides of the pores. Structurally, a perfectly coordinated silica network of this type would be considered 'well balanced' (if the tetrahedra had ideal geometry), as the number of degrees of freedom exactly matches the number of constraints[10,11]. Each of the tetrahedra in silica networks can be considered to be a rigid body and so has six degrees of freedom. The shared corners of tetrahedra each require three constraints that are shared between the two joining tetrahedra. As there are four corners, this leads to a total of six constraints per tetrahedron, exactly balancing the degrees of freedom, and leading to a rigid but stress-free network that is referred to as isostatic[12]. This is known to be a particularly favourable situation, leading to a free-energy minimum where the strain (enthalpy) is minimized as the network remains intact[10]. What was not clear until the present study was that such globally isostatic networks could exist over a range of densities leading to the flexibility window, which is the subject here.

The flexibility window, for a framework of interconnected structural units, is a range of densities in which the structural units (for example, tetrahedra) can retain their ideal shape. As we shall see, the limits of the window are defined by steric clashes under compression and stretching of bonds on expansion. All of the real silicate frameworks we studied and discussed in this work show this flexibility window, which suggests that this is a pervasive property of tetrahedral-framework minerals, and of zeolites in particular. As the limits of the window depend on the specific geometry and topology of a particular framework, no general theory on the existence of the flexibility window has yet emerged. We have investigated the flexibility window in zeolite frameworks using geometric modelling (see the Methods section).

We present the results for the faujasite framework in most detail. The simulated bond lengths and tetrahedral angles are shown in Fig. 2a,b. We observe a surprisingly wide range of densities in which the bond lengths and tetrahedral angles retain their ideal values, which defines the flexibility window. Outside this range the tetrahedra are deformed. Not only do the mean bonds and angles deviate from perfect values, but also the variation around the average values increases. Within the flexibility window, the bridging Si–O–Si angles (Fig. 2c) change monotonically. Three angles co-rotate, decreasing as density increases, and one antirotates in the sense that it rotates in the opposite direction[13]. On expansion, none of the Si–O–Si angles reaches 180°, and the minimum density in the flexibility window is achieved when the framework reaches a jammed (locked) state, where further expansion is impossible without distorting the tetrahedral units. This jamming is a cooperative global effect[14] in which attempts are unsuccessful in increasing the volume beyond this minimum density at the low-density edge of the flexibility window. In rare cases, the minimum density occurs when the distance between some adjacent tetrahedral centres is a maximum (linear Si–O–Si bond angle). Incidentally, minimum density does not necessarily mean that the pore apertures widen. Hinging effects can readily decrease their width. The maximum density in the flexibility window corresponds to contacts between codimeric oxygen atoms, that is second-neighbour oxygen atoms. The experimental framework density of pure-silica faujasite lies right at the low-density edge of the flexibility window, as shown in Fig. 2, indicating that the real structure is maximally expanded, consistent with minimal distortion of the tetrahedral units (Fig. 2b). This is in contrast with the commonly held view that, as Bernal[15] put it, 'In all coherent structures there is a tendency to arrive at minimal volumes', as is most apparent in close-packed structures
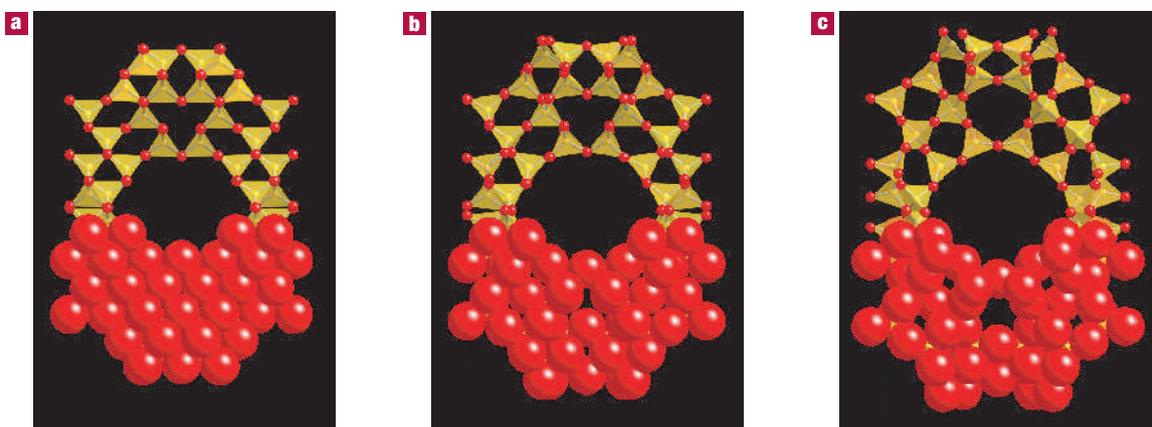
Figure 1 Structural fragment of faujasite (FAU) zeolite with a pure silica composition at different densities, viewed down the cubic [110] direction. The upper half of each fragment shows the rigid SiO_4 tetrahedral units, with small spheres representing the corner-sharing oxygen anions. The lower halves show the oxygen anions drawn with their nominal van der Waals radius of 1.35 Å (ref. 3). **a**, At high density (16.3 T/1,000 Å³), with codimeric oxygen atoms in contact. **b**, In the middle of the flexibility window (density 14.8 T/1,000 Å³). **c**, At low density, with codimeric oxygen atoms mutually repelling (density 13 T/1,000 Å³). The structure can expand no further without distorting the tetrahedral units. Panels **a** and **c** are at the extrema of the flexibility window.

such as metals. Here, however, we have a class of structures that tend towards maximal volume consistent with the framework constraints. A similar situation has been described for some ionic solids[16].

These results for faujasite lead to two questions. First, is the flexibility window a universal property for zeolite frameworks? Second, are all silica frameworks maximally extended in nature? In Fig. 3a, we present results for zeolites that exist as pure silica. This includes the industrially important catalyst for dewaxing and isomerization—MFI (ref. 2). We show that all these structures do indeed possess a flexibility window. In addition, the experimentally observed density is very near to the low-density edge of the flexibility window. In Fig. 3b, we present results for all 14 cubic zeolite frameworks, modelled as pure silica and indexed by effective framework density[9,17]. We use effective framework density (see the Supplementary Information) because not all the cubic zeolites exist as pure silica, and often contain some Al or other cations, which substitute for the Si cations. It therefore seems that framework structures are maximally extended consistent with maintaining undistorted tetrahedral connected units, and this could expedite the search for new zeolites for industrial purposes.

Three mechanisms that prevent 'collapse' of zeolite frameworks—limitation by antirotating angles, steric limitation by channel contents and repulsion between oxygen atoms—have been suggested previously by Baur[18]. In Fig. 2c, the bridging angles of faujasite have an antirotating behaviour. The set of structures we studied includes frameworks with both antirotating and co-rotating angles (see the Supplementary Information), and both classes show a flexibility window. Steric limitation by channel contents (for example, water molecules) may well be a factor, but some frameworks can be dehydrated but remain stable[19,20]. The experimental densities given in Fig. 3a include structures refined with channel content, for example, MTN (ref. 21), and without, for example, FAU (ref. 22).

The most general mechanism to explain the extension of the framework is Coulomb repulsion between the oxygen anions, producing an overall inflation of the structure. Considering the codimeric oxygen atoms (second-neighbour oxygen atoms whose steric contacts limit the folding mechanism at high density), the effect of increasing density is to bring these oxygen atoms closer together; clearly, this would incur a considerable cost in Coulomb energy. Thus, Coulomb inflation provides the internal driving force that decreases the density to the edge of the flexibility window. There is experimental evidence for structural flexibility in aluminosilicate zeolite frameworks, for example analcime (ANA), that is shown on dehydration[23,24].

It is hard to attach a significance to the high-density end of the flexibility window, as it corresponds to the hard-sphere collisions of codimeric oxygens. However, hydrostatic compression to such densities should lead to a change in the structure. Either the cell will change to a lower symmetry that allows further compression (for example, cubic to tetragonal) or, if no such change is possible, then rebonding may occur (as in the pressure-induced amorphization of quartz and cristobalite[25,26]) with the associated onset of irreversible behaviour. For example, the AST framework shows flexibility windows in both its cubic (Fig. 3b) and tetragonal (Fig. 3a) forms. The high-density limit of the cubic form (17.79 T/1,000 Å³) corresponds to the low-density limit of the tetragonal form (17.80 T/1,000 Å³), where the experimental tetragonal structure is found[27]. Similarly, the ANA framework shows a very narrow window in the cubic form (Fig. 3b) and is experimentally observed to transform to a triclinic form with a small increase in density at about 1 GPa (ref. 24).

The actual variations in bond lengths and angles observed in crystallographic refinements of silica zeolites exceed slightly those allowed by our definition of 'perfect' tetrahedra. Some of this variation may be due to the difference between crystallographic average positions and instantaneous atomic positions, whereas some is due to thermal motion. The key point, however, is that distortions of the tetrahedra are not required by the topology of the structure. The existence of the window is related to the mathematics of framework flexibility[28]; however, flexibility analysis generally assumes a starting structure in which all constraints are satisfied, whereas we are studying whether such a structure exists at a given density.

It might be concluded from this survey of framework structures that any tetrahedral network structure can be relaxed to form a network of perfect tetrahedra, given the right density and boundary conditions. However, this is not the case. Many low-energy hypothetical zeolite structures[5] cannot be made perfect
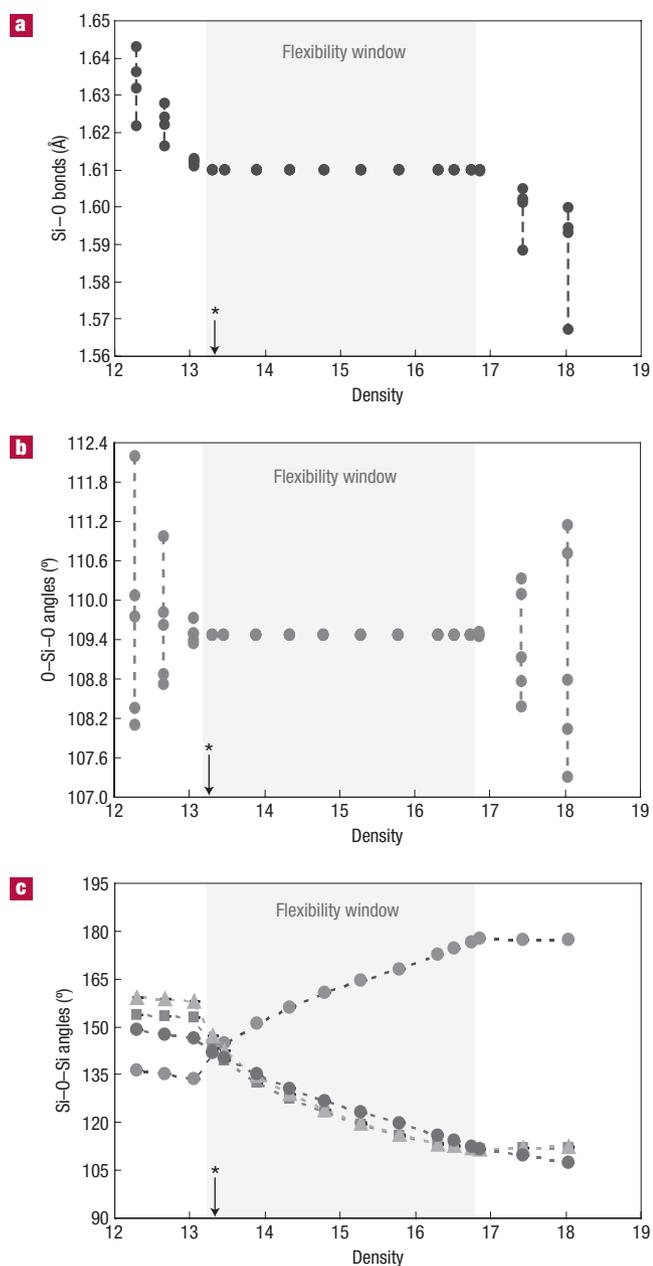
Figure 2 The flexibility window, shown as a shaded region, for FAU with pure silica composition. **a–c**, Outside this window, structural distortions develop rapidly as shown by bond lengths (**a**), tetrahedral angles (**b**) and bridging angles (**c**), for various framework densities. The framework density of a zeolite is defined as the number of tetrahedral units per 1,000 Å^3. The experimental density of FAU is marked by an asterisk in each panel.

Figure 3 Flexibility window for zeolites depending on densities. **a**, Flexibility window for silica zeolites with cubic, hexagonal and tetragonal unit cells depending on experimental densities. Here, the density is the zeolite framework density, which is defined as the number of tetrahedral units per 1,000 Å^3. In all cases the experimentally observed density lies at the lower edge of the flexibility window. **b**, Flexibility window for cubic frameworks simulated as pure silica composition depending on the effective density computed by distance-least-squares, (DLS; see the Supplementary Information). Cristobalite, quartz and amorphous silica also show the existence of flexibility windows of various sizes.

inflation, that is repulsion between the codimeric oxygen atoms. The ability of zeolites to support large open channels and pores, even when dehydrated, seems less surprising from this point of view. Whereas energy minimization methods[5] are generating hypothetical structures at a tremendous rate, this has not been matched by a corresponding increase in the actual synthesis of new zeolite structures. This indicates a bottleneck related to the selection of candidate structures for synthesis. The degree of tetrahedral distortion[29] does seem to be a significant factor, and we are at present preparing a systematic survey of millions of hypothetical zeolites[5] in search of flexibility-window-possessing candidates for synthesis as potential novel catalytic materials. The presence of a flexibility window in silica zeolites, including industrially important ones such as FAU and MFI, suggests that this

using geometric simulation at any density and so there is no flexibility window (see example in Supplementary Information).

All of the real cubic zeolite frameworks, and other non-cubic silica zeolite frameworks (with six hexagonal and tetragonal unit cells) that we have studied, can be made perfectly tetrahedral over a range of densities that defines the flexibility window. Known pure-silica zeolite structures exist at the low-density end of this window, indicating that the frameworks are maximally extended. This maximal extension is nicely accounted for by Coulomb
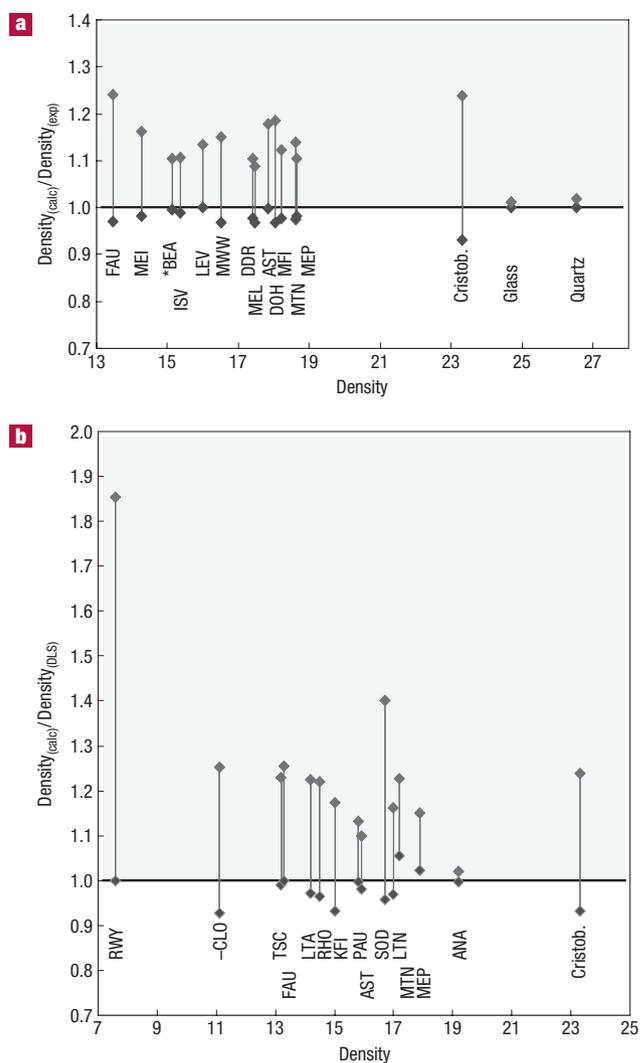
is an important property for any hypothetical zeolite framework if it is to be a viable synthetic target.

METHODS

We used the geometric analysis of structural polyhedra (GASP) method, previously applied successfully to model quartz structures[7,8] and zeolite compression mechanisms[6,30], to idealize the SiO_4 units. In this method, we tether the atoms in a SiO_4 tetrahedron by springs to the vertices of a template having ideal tetrahedral geometry, and adjust the positions of the atoms and templates during relaxation to minimize the distortion of these springs (see Supplementary Information for details). We have investigated all 14 realizable cubic zeolite frameworks, modelled as pure silica. As not all of these frameworks exist as pure silica, we have also modelled several orthorhombic, tetragonal and hexagonal frameworks that do exist as pure silica, to give additional perspective. We have also simulated several computer-generated hypothetical frameworks[5] so as to compare real and hypothetical structures. We relaxed each structure while retaining the same number of atoms in the unit cell, and the atomic positions were not constrained to crystallographic sites. In addition, we note that cubic unit cells have a single variable cell parameter, whereas tetragonal and hexagonal cells have two. The oxygen atoms were given a hard-sphere radius of 1.350 Å (ref. 9), and the tetrahedra were given a bond length of 1.610 Å as in silica. We have defined tetrahedra to be perfect, with the very strict criteria that they have bond lengths within the range 1.610 ± 0.001 Å and bond angles within the range $109.471 \pm 0.001°$.

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Competing financial interests

The authors declare that they have no competing financial interests.