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Flexibility windows in faujasite with explicit water and methanol extra-framework content

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We present geometric simulations on a zeolite framework (faujasite) with extra-framework methanol and water contents explicitly present. We distinguish the intrinsic flexibility window of the framework from the newly defined extrinsic window limited by host-guest steric interactions. The extrinsic flexibility window can be limited not only in compression, but also in expansion, as the beta-cages in a maximally expanded framework lack the flexibility to adapt to bulky contents such as a combination of methanol and water molecules. Our simulations suggest a reinterpretation of extra-framework content nominally refined as water sites in compression experiments.

1 Introduction

Zeolites, alumino-silicate minerals with meso- and nano-porous framework structure, have found numerous industrial applications as catalysts, molecular sieves and ion-exchange materials in oil production, refining, production of domestic chemicals and many other industries[1–4]. The framework of zeolites consists of SiO_4 and AlO_4 tetrahedral units connected through oxygen atoms. Many zeolites have very open frameworks consisting of cages, channels and pores large enough to accommodate not only ions but also water and small molecules. Framework flexibility, arising from collective motions of the framework polyhedra, can be significant in tetrahedral silicate frameworks[5] and gives rise to striking effects such as negative thermal expansion.

Geometric simulation, implemented in the program GASP (Geometric Analysis of Structural Polyhedra) is a specially suitable method to study the flexibility of polyhedral framework structures including zeolites[5–8] and perovskites[9]. This method models the most local bonding and steric interactions, using a system of templates to represent bonding in the tetrahedral units, while neglecting weaker long-range interactions. During a "geometric relaxation" of a structure, the positions of atoms and the positions and orientations of bonding templates are adjusted together, so as to minimise the mismatch between atoms and template vertices (thus improving bonding geometry) and the steric overlap of atomic spheres.

Investigations using geometric simulation have shown that zeolite frameworks display a geometric property termed a 'flexibility window'[7]. Over a range of densities, it is in principle possible for the framework to be made geometrically 'stress-free'; that is, the structural tetrahedra can in principle have perfectly regular geometry without distortions or steric clashes. Outside the flexibility window, distortions of the polyhedra are inevitable, even in the absence of long-range or host-guest interactions. In this case the framework is geometrically 'stressed'.

Recent studies have demonstrated a strong connection between the flexibility window and the physical behaviour of the framework in compression. The analcime group — analcime, wairakite, leucite and pollucite — of zeolites with **ANA** framework topology are among the densest zeolites, with framework densities between 19-20 tetrahedral units per cubic nanometer (T/nm^3). These zeolites undergo structural phase transitions under pressure with anomalous softening of the framework[10–13]. For all four of these zeolites, the phase transition occurs at a density coinciding with the edge of the flexibility window.

Intriguingly, a more open silicalite zeolite (**MFI** framework topology) shows different flexibility behaviour with and without penetrating pressure media. When compressed with a non-penetrating silicone oil, the structure starts to undergo PIA (pressure induced amorphization) even while the crystalline framework remains within its flexibility window. With penetrating media (Ar or CO_2), the silicalite framework is forced outside its flexibility window[14] and does not undergo PIA[15,16].

Previous investigations of zeolite flexibility windows have modelled the empty framework without explicitly including extra-framework content in the geometric simulations. The flexibility windows thus obtained may be termed "intrinsic". In this work we extend the flexibility window concept to

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frameworks with explicit extra-framework content, by modelling the effect of water and methanol beta-cage content in siliceous zeolite Y (**FAU** framework topology). We make use of experimental data on extra-framework sites from the high-pressure studies and Rietveld analysis of Colligan *et al.*[17]. Our results suggest a novel interpretation of the data involving beta-cage occupation by methanol as well as water molecules.

2 Method

In our simulations we make use of geometric simulation[5,6,8] implemented in the program GASP[5–7]. This approach is adapted to study the flexibility of zeolite framework structures using a simplified physical model which takes account of only the strongest and most local forces — tetrahedral bonding and steric exclusion. A full description of the method and its applications in zeolites is given in the recent review by Wells and Sartbaeva[8]. In this study we make use of a new revision of GASP with an improved numerical algorithm for geometric relaxation.

The input is an all-atom crystal structure in $P1$ symmetry, in this case a single unit cell of the **FAU** framework containing 192 tetrahedral units (192 Si and 384 framework oxygen atoms). The structure is modeled with fixed cell parameters and periodic boundary conditions. Inter-atomic bonding in the SiO_4 unit is represented using a tetrahedral template[8] with Si–O bond length of 1.61Å. Framework oxygen atoms are assigned a steric radius of 1.35Å[18]. Although the geometric simulation method is capable of modelling both SiO_4 and the larger AlO_4 tetrahedra, our input structure is in this case refined as a purely siliceous SiO_2 structure, and so only SiO_4 units are used in the modelling. The siliceous faujasite structure is described by Colligan *et al.*[17] as neutral, hydrophobic and without cations present, thus providing "an ideal opportunity to examine the effects of pressure without complications due to charge-balancing cations and their interactions with framework oxygen atoms . . .".

In previous studies[7], the criteria to consider the tetrahedral units effectively undistorted were (i) for all tetrahedral bond lengths to be within 0.001Å of their ideal value, and (ii) for all internal angles of the tetrahedra to be within $0.01°$ of the geometrically ideal value ($\arccos(-1/3)$). In this study we make use of a unified measure made possible by the new revision of GASP; our criterion is for all mismatches between atomic positions and template vertices to be less than 0.001Å.

A major point of interest for our study is the steric limitation of beta-cage occupancy by water and methanol molecules. Given the simplified nature of the geometric simulation we represent these molecules using a united atom approach. Water molecules are represented as a molecular sphere with a radius 1.39Å based on the inter-oxygen distance in water[19]. The larger methanol molecule is represented as a diatomic molecule consisting of a 'methyl' sphere of radius 2.0Å and a 'hydroxy' sphere of radius 1.39Å, connected by a bond of 1.4Å[20,21].

For input structures we make use of the experimental data obtained on siliceous zeolite-Y (**FAU**) under pressure by Colligan *et al.*[17] using methanol/ethanol/water (16:3:1) and silicone oil as penetrating and non-penetrating pressure transmitting fluids. The behaviour of porous materials under compression can be strikingly different when the pressure transmitting medium contains small molecules capable of penetrating the pores and channels of the structure, compared to the case when the medium consists of larger molecules (such as silicone oil) which cannot occupy void spaces within the material[22]. Since the beta-cages in faujasite are much more confined than the "supercages" making up the main channel network, we focus on occupation of the beta-cages and neglect supercage content.

We can impose a cell parameter on the framework, either from theory or from experimental data, and populate the extra-framework sites with a chosen distribution of molecules. Geometric relaxation of the structure reveals whether the framework can accommodate the extra-framework content without distortion of the tetrahedral units. In this case the structure is 'stress-free' within our simplified physical model, lying within its flexibility window. If the structure cannot accommodate without distortions, then it is intrinsically stressed. We explore to a precision of 0.01Å in the a parameter, e.g. a reported window edge on expansion of 23.46Å signifies that the structure relaxes at this value but not at $a = 23.47$Å.

3 Results

3.1 Intrinsic flexibility window in FAU

We begin with the flexibility window of the empty framework of siliceous faujasite, to establish comparability between the new revision of GASP and previous work. Starting from the empty structure as refined by Colligan *et al.*[17] at ambient pressure ($a = 24.24$Å), we explore greater cell volumes by increasing the a cell parameter to identify the point at which overextension of the Si–O bond becomes inevitable, thus defining the upper limit of the flexibility window. We likewise explore lower cell volumes by decreasing the a parameter to identify the point at which collisions between codimeric framework oxygen atoms can no longer be resolved without distortions of the tetrahedral geometry, thus defining the lower limit of the window. The intrinsic window thus obtained lies between $a = 24.46$Å and $a = 22.50$Å. The wide range of the flexibility window, and the position of the cell parameter under ambient conditions near the expanded edge, are fully consistent with earlier results[7]. These data are plotted in figure 1 along with the experimental ranges of compression observed experimen-
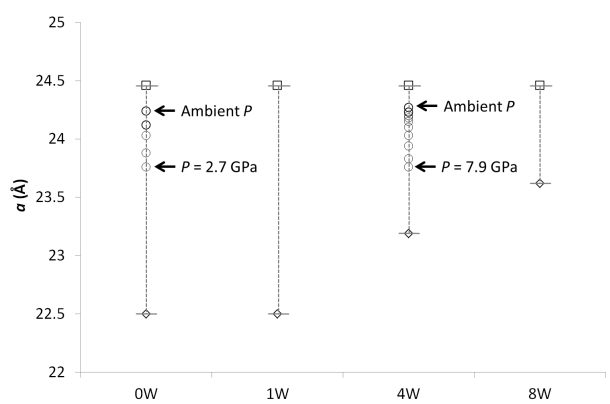
Fig. 1 Flexibility windows of the **FAU** framework with varying water content in the beta-cages: zero, 1, 4 or 8 water spheres per cage. The upper (squares) and lower (diamonds) limits of the flexibility window for each case are shown and the extent of the window is shown with a dashed bar. For the zero water case, circles show experimental data points during compression in silicone oil; for the 4 waters case, circles show experimental data points during compression in methanol/ethanol/water. The upper and lower pressure limits of the experimental data are indicated by labelled arrows.

tally.

During compression experiments without penetrating media, the structure starts to display significant peak broadening at pressures above 2.2GPa[17], which is interpreted as the onset of amorphization. At this stage the framework lies well within the theoretical limits of the flexibility window, with $a = 23.76$Å at 2.7GPa. This observation matches a recent result on silicalite[14], with amorphization occurring while the framework lies within the flexibility window. During compression in our modelling, steric contacts between codimeric framework oxygen atoms first occur when the a parameter reaches 23.00Å. This indicates that, experimentally, amorphisation in the empty framework sets in well before the framework oxygens would be forced into contact.

In the geometric simulations, Si–O–Si bridging angles are not explicitly constrained. However, in practice zeolite structures do display a preference for angles in the vicinity of 145 degrees[18] and substantially smaller angles would indicate a degree of strain in the framework. We have therefore examined the angular geometry of the input crystal structure, and of the structure geometrically relaxed under ambient conditions ($a = 24.24$Å) and at the experimental onset of amorphisation ($a = 23.76$Å). Four crystallographically distinct populations of bridging angles are identifiable in siliceous faujasite. The input structure displays bridging angles of 137, 149, 126 and 148 degrees (all values reported to an accuracy of 1 degree) with a mean around 140 degrees; essentially the same values are tabulated by Colligan *et al.*[17]. When the structure is geo-

metrically relaxed under ambient conditions, the four populations become much more similar, with values of 144, 142, 139 and 141 degrees. This suggests that the low (strained) values in the crystal structure may be an artefact of the refinement. At the onset of amorphisation the values in the relaxed structure are 154, 129, 127 and 132 degrees, with a mean around 135 degrees, indicating that considerable angular strain would exist in the structure by this point and may be the driver of amorphisation.

In the case of silicalite, the framework becomes geometrically stressed during compression with penetrating media. In faujasite, however, the framework remains within its intrinsic flexibility window even with penetrating pressure media, as the smallest cell parameter recorded ($a = 23.76$Å at 7.9GPa) lies well above the limit of the intrinsic window at $a = 22.50$Å. This difference maybe due to the lower framework density of faujasite compared to silicalite (13.3T/nm^3 vs. 18.4T/nm^3).

3.2 Steric limits on water occupancy in beta-cages

In the experimental investigation[17], extra-framework content was notionally modeled as 'water' sites. At various stages of compression, the beta-cage was refined with one, four or eight water sites, though with partial occupancies less than 1. At low pressures there is a single extra-framework site, Ow(1), at the center of the beta-cage, located at the special symmetry position $(1/8, 1/8, 1/8)$. At pressures from 2.7GPa upwards, this primary site moves off the special position and becomes a tetrahedron of partially occupied sub-sites, Ow(4). As thermal factors could not be refined for these sites[17] we should not overinterpret their exact positions; rather, they represent a zone of extra-framework density. At pressures from 3.2GPa upwards a second extra-framework site, Ow(5), in the beta-cage is also occupied. Full population of all extra-framework sites in our modelling corresponds to placing eight water spheres in each beta-cage, a level of cage occupation which exceeds that observed experimentally. We have modelled the structure with beta-cage contents of one, four and eight water molecules initially placed on extra-framework "water" sites. The flexibility windows thus obtained are shown in Figure 1.

A single water molecule per beta-cage can be accomodated without affecting the intrinsic flexibility window. As water occupancy increases, the flexibility window narrows, giving an extrinsic flexibility window controlled by host-guest interaction in the beta-cages. The sum of partial site occupancies seen experimentally at higher pressures corresponds roughly to occupation by four water molecules per beta-cage. However, even with eight water molecules per cage, the extrinsic flexibility window is wider than the experimentally observed range of cell parameters, indicating that cage occupancies greater than those observed experimentally are sterically possible.

Colligan *et al.*[17] treat all extra-framework sites as water sites, and make the following comment: 'There are distances shorter than the van der Waals contacts between Ow(4) and Ow(5) sites in the beta-cages ... but given the partial occupancies these will not be simultaneously occupied.' However, there is more to be said about the occupations of these sites. In the case of primary sites, the distance between the sub-sites is approximately 1.6Å, and the partial occupancy of these sub-sites is 0.5 or higher for pressures from 2.7 to 5.7GPa. These partial occupancies imply that at least two of the sub-sites in each cage are occupied; and yet the 1.6Å distance between sub-sites is quite incompatible with a water–water contact distance of 2.8Å. Indeed, the inter-sub-site distance is closer to a typical value for an inter-atomic bond.

The sites as refined within the beta-cage form a central tetrahedron of Ow(4) subsites spaced 1.6Å apart, surrounded by a complementary outer tetrahedron of Ow(5) subsites lying in the 6-ring apertures connecting the beta-cage to the supercage. The Ow(4) sites are in steric clashes among themselves while the Ow(5) sites are in a steric clash with framework oxygen atoms in the six-ring. Four water molecules in the simulation, lying initially on the Ow(4) subsites, sterically repel each other to a contact distance of 2.8Å. Eight water molecules lying initially on the Ow(4) and Ow(5) subsites resolve their steric clashes in the simulation, taking up an almost cubic arrangement within the beta-cage. The geometry of the beta-cage in this case is illustrated in figure 2. The contrast between the refined extra-framework site positions in panel 2a and those that are geometrically possible, panel 2b, is very evident.

3.3 Steric limits on methanol occupancy in beta-cages

The results of section 3.2 make it doubtful that water molecules in the beta-cage can fully account for the extra-framework density observed in the experiments. The presence of a methanol molecule in the beta-cage, however, would provide a natural explanation for the presence of two closely adjacent non-hydrogen atoms (C and O) on two of the Ow(4) sub-sites during compression with a methanol/ethanol/water pressure-transmitting fluid. We have therefore investigated the capacity of the beta-cages to accommodate methanol molecules as well as water molecules. When introducing methanol molecules into the cage, we initially place the 'hydroxy' and 'methyl' spheres on two Ow(4) subsites in the centre of the cage.

Placing a single methanol molecule in one beta-cage and leaving the others empty allows the framework to relax over a window from $a = 24.46$Å to $a = 23.10$Å. Placing a single methanol molecule within each of the eight beta-cages in the unit cell also allows the framework to relax over an only slightly narrower window, with the lower limit at $a = 23.29$Å.
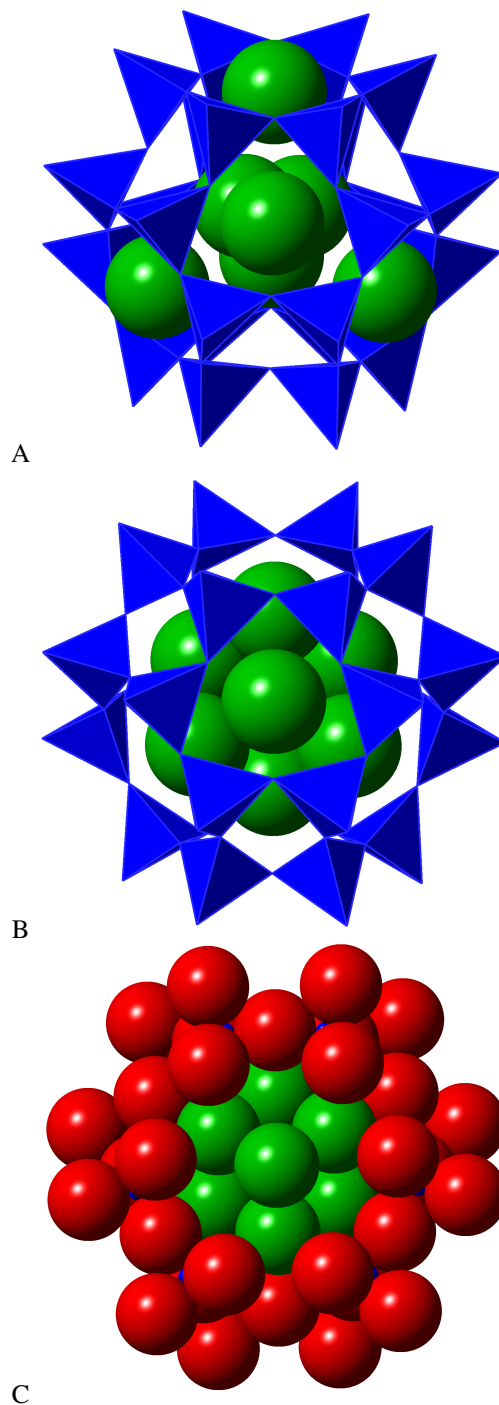
Fig. 2 Panel A: beta-cage of faujasite from the crystal structure (tetrahedral framework view), showing the locations of the eight 'water' sites (spheres). Panel B: beta-cage after geometric relaxation, showing the tetrahedra of the framework and the relaxed locations of eight 'water' spheres. Panel C: as panel B, with the atoms of the framework shown in space-filling representation; one six-ring of the beta-cage has been removed to show the occupation of the interior. The view is in all cases along a crystallographic [1$\bar{1}$1] direction.

A structure with one methanol molecule in one cage and four waters in each of the others relaxes down to $a = 23.24$Å. These data suggest that a single methanol molecule is almost interchangeable with four water molecules in terms of beta-cage contents.

Two methanol molecules cannot be placed in a single beta-cage without introducing stress into the framework. However, some water molecules can share a cage with a methanol molecule. Placing a single methanol molecule and two water molecules in one beta-cage and leaving the others empty allows the framework to relax over a window from $a = 24.43$Å to $a = 23.57$Å. Here we see an interesting effect, with cage content causing the flexibility window to become narrower at both the extended and compressed edges; a structure at the limit ($a = 24.46$Å) of the empty framework is unable to accomodate the cage contents, and must contract slightly to allow the cage to adapt. A similar but much more marked effect is seen if a single methanol molecule and two water molecules are placed in each of the eight beta-cages in the unit cell. In this case the window narrows to the range from $a = 24.41$Å to $a = 24.18$Å. This dramatic narrowing illustrates the collective nature of framework flexibility. The beta-cages do not accomodate their contents in isolation, but rather through collective motions of the framework polyhedra, which are transmitted to adjacent cages. This behaviour can be considered as a form of 'internal auxetic' effect; near the expanded edge of the flexibility window, expansion of the entire framework effectively contracts the beta-cages, preventing them from accomodating bulky contents.

The flexibility windows obtained with methanol in beta-cages are shown in Figure 3. The geometry of the beta-cage containing one methanol and two water molecules is shown in Figure 4. Note particularly the substantial reorientations of the framework tetrahedra in panel 4a compared to panel 2b, illustrating the importance of framework flexibility in adapting the cage geometry to bulky contents.

4 Discussion

We suggest that the experimental data of Colligan et al.[17] provide evidence for the entry of methanol molecules into the beta-cages of the **FAU** framework during compression. This would account for several features of the beta-cage occupancy which are difficult to explain if water is the only molecule occupying the beta-cage. One of these features is the 50% partial occupancy of the Ow(4) subsites lying only 1.6Å apart. This concentration of heavy-atom (non-H) sites is sterically forbidden for water molecules but is easily explained by the methanol C and O atoms effectively occupying two adjacent Ow(4) sub-sites. Another is the location of the Ow(5) subsite in an apparent clash with framework oxygen atoms in the 6-ring, and a net occupation of extra-framework sites in the beta-
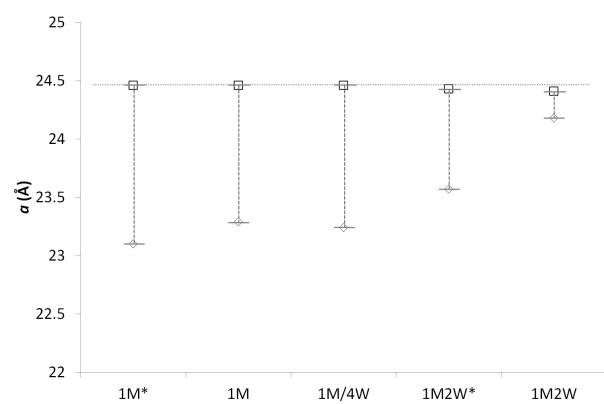

Fig. 3 Flexibility windows of the **FAU** framework with varying methanol and water content in the beta-cages. 1M*=1 methanol in one cage, other cages empty; 1M=1 methanol in each cage; 1M/4W=1 methanol in one cage, four waters in all other cages; 1M2W* = 1 methanol and 2 waters in one cage, other cages empty; 1M2W= 1 methanol and 2 waters in each cage. The upper (squares) and lower (diamonds) limits of the flexibility window for each case are shown and the extent of the window is shown with a bar. A finely dotted line highlights the contraction of the upper edge of the window in the latter two cases.

cage corresponding to around four 'water' molecules, when sterically up to eight water molecules could be accomodated without clashes. A disordered arrangement with methanol molecules in some beta-cages and varying numbers of water molecules in others would account for these data. Steric limitations mean that no more than one methanol molecule is able to occupy a beta-cage, as two methanol molecules would inevitably cause geometric stress in the framework.

4.1 Access to the beta-cage through the six-ring pore

A final question to be addressed is that of the accessibility of the beta-cage interior to methanol molecules, as the relatively large methyl group must pass through the small radius of the six-ring aperture. In general the available aperture depends on the local geometry of an individual six-ring, which may vary considerably; the statistics of such apertures across large structural models can be investigated using Delaunay triangulation[23]. However, the maximum free aperture will be displayed when the six-ring has regular hexagonal geometry, as any deviation will bring some pair of opposing oxygens closer together, and we therefore investigate this limiting case. We can consider the aperture as a hexagon of oxygen sites whose edge length is the edge length of the regular SiO_4 tetrahedron, which (for an Si–O bond length of $l_b = 1.61$Å) is $l_E = 2.63$Å. The distance between opposite oxygen centres will be twice the edge length, and the free aperture is this distance less twice the radius of a framework oxygen atom,
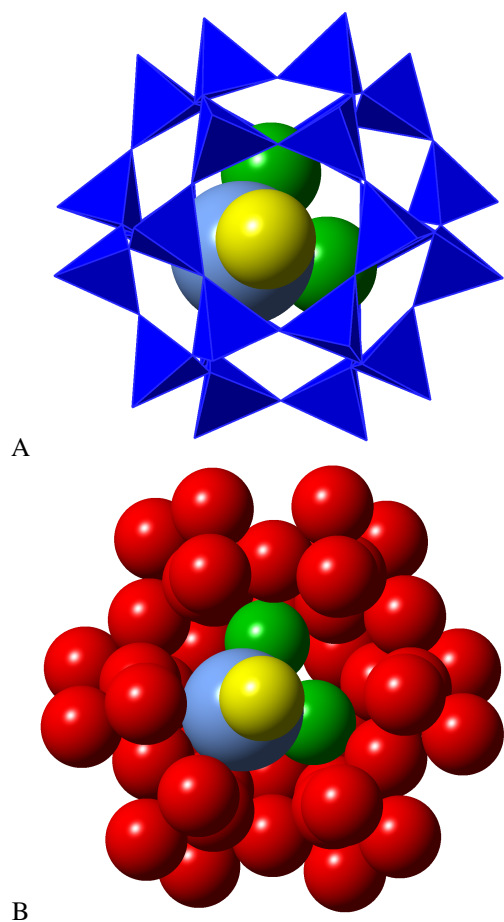
Fig. 4 Panel A: beta-cage of faujasite, showing the tetrahedra of the framework after relaxation with cage contents of one methanol and two water molecules (spheres) The methanol hydroxy group is the sphere nearest the centre of the image. Panel B: as panel A, showing the oxygen atoms of the framework in space filling representation. One side of the cage has been removed to view the interior. Both panels are viewed along a crystallographic [1$\bar{1}$1] direction.
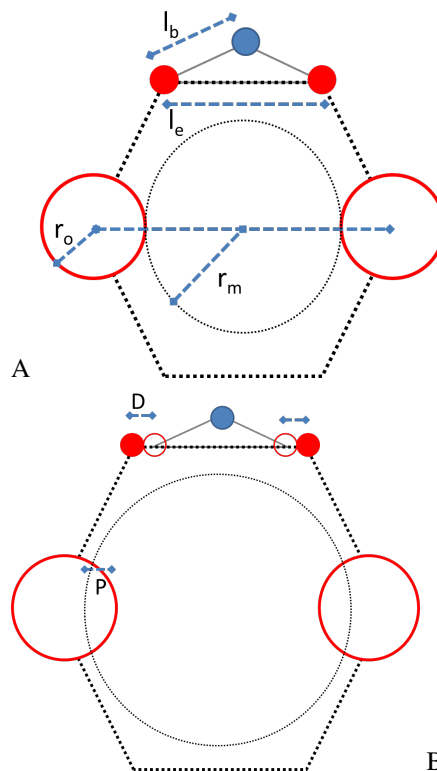
Fig. 5 (A) Relationship between Si–O bond length l_b, six-ring aperture edge length l_E, framework oxygen radius r_O and the radius, r_M, of the largest molecule that can pass through an unstrained six-ring aperture. (B) distortions in tetrahedral bonding, D, and steric overlap, P, when larger molecules pass through.

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r_O; this is $5.26 - 2.7 = 2.56$Å, the diameter of the largest molecule that could pass without strain in the 6-ring (see Figure 5a). Comparing this to the diameters of our water group (2.78Å) and of our methyl group (4.0Å) we can see that both molecules would be excluded from passage through an unstrained six-ring aperture. We must therefore consider what degree of strain is required to permit molecules to pass.

Two parameters will be needed to describe this situation: the tetrahedral strain D involved in stretching the O-O distance to increase the tetrahedral edge length, and the overlap P as atoms approach more closely than the sum of their radii. If D is the displacement of a framework oxygen atom from its ideal vertex in the tetrahedron, the edge length is now $l_E^* = l_E + 2D$, and the distance between opposite oxygen vertices in the strained six-ring will now be given by $2l_E^*$. If a molecule with a radius r_M is passing through the aperture, this distance must be equal to $2r_O + 2r_M - 2P$. These parameters are illustrated in Figure 5b.

We estimate the strain required by equating D and P, so that all deviations from ideal geometry, steric or bonding,

are equal in magnitude. Setting P=D we find $2l_E + 4D = 2r_O + 2r_M - 2D$, hence $D = (1/3)(r_O + r_M - l_E)$. The passage of a water group with $r_M = 1.39$Å requires a distortion of $D = 0.03$Å. Using the methyl radius $r_M = 2$Å, we obtain a required strain of $D = 0.24$Å. This degree of compression requires the methanol and framework oxygen groups to approach to about 90% of their contact distance, presenting a significant but not insuperable barrier to entry. The appearance of the multiple Ow(4) site within the beta-cage at a pressure of 2.7GPa may thus mark the point at which the pressure is sufficient to drive methanol, the major component of the pressure-transmitting medium, into the beta-cages of faujasite.

5   Conclusions

We have extended the "flexibility window" concept for zeolites to address the influence of explicitly present extra-framework content. Low loadings of water within the faujasite beta-cage do not affect the flexibility window, which on compression is limited by collisions among codimeric framework oxygen atoms, as in the empty framework. Higher loadings of water or methanol lead to a different behaviour in which the flexibility window on compression is limited by collisions between framework oxygens and extra-framework content. We can thus distinguish between the intrinsic flexibility window of the empty framework and the extrinsic window at higher loadings.

An unexpected feature of the extrinsic window is that it can be narrower than the intrinsic window not only in compression, but also in extension. It is intuitive that the presence of extra-framework content should naturally impose a steric limit on the window in compression. The effect on extension is more subtle; near the expanded edge of the window, the cages in the structure lack the freedom to adapt to the shape of bulky contents such as a combination of methanol and water molecules.

Analysis of structural data on the siliceous faujasite framework under compression, using geometric simulation, indicates that the framework remains within its flexibility window over a wide range of pressures, with or without penetrating pressure-transmitting media. The onset of amorphization during compression without penetrating media occurs while the framework is well within its flexibility window, as has also been observed in silicalite. Our geometric simulations indicate that the distribution of extra-framework content in faujasite

within the beta-cages at higher pressures (2.7GPa and above) may be accounted for by the presence of methanol molecules within some of the beta-cages.

Acknowledgements

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