

Synthesis of 'unfeasible' zeolites

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Zeolites are porous aluminosilicate materials that have found applications in many different technologies. But although simulations suggest that there are millions of possible zeolite topologies, just over 200 zeolite frameworks of all compositions are currently known, of which about 50 are pure silica materials. This is known as the zeolite conundrum - why have only so few of all the possible structures been made? Several criteria have been formulated to explain why most zeolites are unfeasible synthesis targets. Here we demonstrate the synthesis of two such 'unfeasible' zeolites, IPC-9 and IPC-10, through the assembly-disassembly-organisation-reassembly mechanism. These new high-silica zeolites have rare characteristics, such as windows comprising odd-membered rings. Their synthesis opens up the possibility of preparing other zeolites that have not been accessible by traditional solvothermal synthetic methods. We envisage that these findings may lead to a step change in the number and types of zeolites available for future applications.

Computer enumeration suggests that there are millions of possible zeolite topologies,¹⁻³ yet only about 200 have so far been prepared, primarily using solvothermal procedures.^{4,5} This is the zeolite conundrum³ and several researchers

have formulated criteria as an explanation, suggesting that zeolites which do not obey certain rules are unfeasible synthesis targets, and so that many of the hypothetical zeolites simply cannot be made.⁶⁻⁸ These criteria include a measure of how far a hypothetical zeolite lies away from the energy-density correlation of known zeolites, measured by a so-called feasibility factor, θ ,⁶ and a realisation that the known zeolites are generally flexible over a significant range of densities – the flexibility window.⁷ The most recent criteria postulated are those based on local interatomic distances (LID) where feasible zeolite targets are only those that obey strict criteria describing limits on the values of the interatomic distances and angles.⁸ All previously known zeolites obey all five of the local interatomic distance criteria (for details of the criteria please see the supplementary information section 5).

It has long been recognised that the known zeolites show a strong correlation between framework energy and density, a finding that was predicted computationally^{9,10} and confirmed experimentally.¹¹ Nevertheless, the largest sets of hypothetical zeolites, postulated simply by connecting SiO_4 tetrahedra in as many ways as possible, do not show such a correlation and indeed the potential structures cover a large region in energy-density space.¹² However, it has also been noted that the known zeolites can all be found at the low-density edge of the energy-density distribution of hypothetical zeolites.^{12,13} This suggests that known zeolites all obey the correlation not because of the properties of the zeolites formed but because of kinetic limitations of the synthesis procedure (or at the very least a combination of the two).¹³ This means that solvothermal synthesis is the limiting factor in determining which zeolites are feasible or not. This all suggests that the development of new synthetic pathways could overcome the limitations of solvothermal synthesis and prepare zeolites that are currently thought to be unfeasible.

In addition, the topological features of zeolites are not evenly distributed in energy-density space, and in particular odd-membered rings (loops in the structure containing odd numbers of tetrahedral units) are rare at the low density edge of the

distribution but more common away from this edge, which explains why odd rings comprising 7- and 9- tetrahedra are so rare in the known zeolite structures.^{13,14}

Here we present the structures of two new silica zeolites, IPC-9 and IPC-10. Neither material obeys all the local interatomic distance criteria and so would be considered unfeasible. Both new zeolites also contain unique two-dimensional channel systems containing odd-membered rings. The work opens up the possibility that the majority of hypothetical zeolites, which were once thought not to be feasible synthetic targets, are potentially accessible. We believe that this outcome could revolutionise the types of zeolitic solids available in the future.

Results and Discussion

To obtain 'unfeasible' zeolites the traditional method of synthesis should not be used. In particular the reversibility present in solvothermal synthesis, which will always allow the final structure to avoid any high-energy configurations, should be avoided. Figure 1 shows one such new synthetic pathway for zeolites that is not limited in the same way as solvothermal synthesis; the ADOR (Assembly-Disassembly-Organisation-Reassembly) mechanism.¹⁵⁻¹⁸ This recent development in zeolite synthesis allows one to selectively disassemble a parent germanosilicate zeolite, in this case one with the UTL structure,^{19,20} to produce a material called IPC-1P²¹ comprising layers of known structure, which can then be reconnected to produce new pure silica zeolites.

If the orientation/arrangement of the layers with respect to each other is the same as it was in the parent UTL zeolite then reconnecting the layers produces zeolites that obey all the local interatomic distance criteria and would be described as feasible zeolite targets, irrespective of which units link the layers (such as IPC-2,¹⁵ IPC-4¹⁵ and IPC-6¹⁶). This is not surprising, as since the layers come from a fully connected zeolite they are geometrically perfectly matched to each other and can be reconnected through the different units without introducing any strain into the new materials. To produce 'unfeasible' zeolites we predicted that the relative arrangement of the layers would need to be changed so as to introduce a small geometric mismatch between them. The slight mismatch means reassembly can only

happen by introducing a small amount of strain into the final framework, ending up with a configuration of higher energy than if there was no geometric mismatch.¹⁴ Unlike in solvothermal synthesis, the final reassembly step in the ADOR mechanism is an irreversible, entropy-driven reaction that offers no opportunity to avoid any particular high-energy arrangement.

The key to success of this approach is to control the organisation step of the ADOR process so that the layers are shifted with respect to each other. To achieve this any strong hydrogen bonding between the layers must be broken, and the layers moved relative to each other into a new orientation.²² This can be done in two ways. A two-step method where a large surfactant molecule is intercalated into the structure, followed by de-swelling the structure in the presence of an organic structure directing agent (SDA) that favours the desired relative arrangement of the layers. Alternatively, a one-step method where the conditions are basic enough to deprotonate the silanol groups that cover the surface of the layers while simultaneously intercalating the SDA between the layers.

Choline cations work extremely well as the SDA, and favour the desired 'shifted' orientation of the layers. The IPC-1P layers have groups of four silanols, which we call quadruplets. DFT studies on the optimum interactions between choline cations and single layers of IPC-1P predict that the cation will preferentially locate between quadruplets (See Supplementary information). The computational studies indicate that the most favourable arrangement of multiple layers is likely to depend on exactly how much choline is incorporated in between the layers. At low levels of choline (1 choline cation per four silanols) the layers will be shifted from their original IPC-1P positions by half the unit cell vector in the crystallographic *b* direction. This arrangement is favoured over the unshifted arrangement by 103 kJ mol⁻¹ and over any other layer arrangement by 21 kJ mol⁻¹. In contrast, when the amount of choline intercalated is greater, with a choline:silanol ratio of 1:2, the most favoured arrangement involves a shift of half a unit along the crystallographic *c* direction (favoured by 165 and 82 kJ mol⁻¹ over the unshifted IPC-1P and the *b*-shifted arrangements respectively). Our successful experimental results involve a

large excess of choline in the intercalation step, and X-ray diffraction of the intermediates is consistent with that predicted for the *c*-shifted, high choline content material. It is also consistent with the final structure of IPC-9, which has the same relative shift in the layers.

Calcination of the materials at temperatures above 500 °C leads to thermal elimination of the SDAs and reassembly of the layers into fully condensed zeolite structures. This can also be done in two ways. If one simply calcines the materials as they are then the layers are joined through only oxygen bridges, leading to IPC-9. However, if extra silicon is added (in the form of dimethyldiethoxysilane) intercalated between the layers, then the extra silicon can form a bridge between the layers, resulting in a structure with an added single-four-ring unit (S4R), leading to IPC-10.

A great advantage of the ADOR mechanism is that the final structure of new zeolites is relatively easy to predict computationally. The structures of IPC-9 and IPC-10 (Figure 3) can be recognised as those expected from our predictions simply by comparing the calculated and experimental powder X-ray diffraction patterns.^{23,24} The structures are then confirmed by whole pattern (Le Bail type) refinement of the unit cells against the X-ray diffraction data. In the case of IPC-9 the structure was further confirmed by Rietveld refinement of the structural model against the X-ray diffraction data.

The structure of IPC-9 consists of the UTL-type layers linked together as shown in Figure 3a. The material has a two-dimensional channel system comprising 10 x 7 rings. IPC-10 has the same layer arrangement as IPC-9 but in this case they are linked via single-four-rings (S4Rs). This leads to a slightly more complex structural arrangement because there are two possible ways in which the S4Rs can form with the same basic layer arrangement. DFT calculations indicate that the two possibilities are very close in energy (separated by only 2 kJ mol⁻¹ TO₂⁻¹) and therefore it is likely that both are present in the material, leading to some disorder in the interlayer region (Figure 3). The disordered nature of IPC-10 can be confirmed using transmission electron microscopy. The channel system in IPC-10 comprises

orthogonal 12 x 9 rings, irrespective of which type of S4R is present. See the supplementary information for further details of the structures. Both IPC-9 and IPC-10 show two dimensional ring systems, joining a class of multidimensional zeolites, the importance of which has recently been reviewed by Corma and coworkers.²⁵ The framework energies (using the established SLC force field²⁶) of the two structures can be calculated as described in the Supplementary Information (Section 3) and compared with those for all the known silica zeolites. Figure 4a shows the energy-density plot for all the silica zeolites and demonstrates that IPC-9 lies at the edge of the region where known zeolites can be found. However, unlike all other previously prepared zeolites IPC-9 fails two of the five rules and by virtue of this would not be a feasible synthesis target using traditional methods (please see the Supplementary Information, section 5, for the full discussion). IPC-10 has an even higher energy for its density, lying well outside of the region populated by the known zeolites and clearly does not obey the correlation between framework energy and density. IPC-10 fails three of the five local interatomic distance criteria and so would also be termed as an 'unfeasible' synthetic target. The slight geometric mismatch needed to form frameworks that do not follow the energy-density correlation can be seen in a reduction of the product of the unit cell parameters *b* and *c* corresponding to the intralayer directions – a small contraction in IPC-9 (about 3.2% compared to the analogous IPC-4 material) and a larger one in IPC-10 of almost 5% compared to IPC-2 (Figure 4b).

As remarked earlier, both IPC-9 and IPC-10 contain odd-numbered rings; seven-rings in the case of IPC-9 and nine-rings for IPC-10. This confirms the view that structures containing odd –membered rings are more prevalent away from the energy-density correlation.¹³ Given that the utility of zeolites is intimately connected with their structural architectures by virtue of the high surface area and size/shape selectivity that their porous structure imparts, new topologies with rare ring sizes may be extremely important in determining new applications. An important feature of the ADOR process is that because the intermediates have come from a fully connected parent zeolite, the silanols groups are geometrically pre-arranged to be reassembled

into a fully connected zeolite without any remaining silanols groups. This means that both IPC-9 and IPC-10 are true zeolites with fully-connected tetrahedral centres.

The other important aspect of zeolites that determines their applicability is their chemistry, and particularly the possibility of substituting other elements into the materials to produce active sites. The most common way of doing this is to substitute aluminium for a small proportion of the silicon atoms, producing a negative charge on the framework that can be balanced by an extraframework proton, leading to the acidity that is so commonly used in catalysis. As with other zeolites prepared using the ADOR mechanism¹⁴ it is straightforward to introduce aluminium into IPC-9 and IPC-10 by starting the process with Al-substituted UTL. The aluminium remains present throughout the ADOR process and into the final solids (at least if low acidity conditions are used to limit any dealumination). Further details on this can be found in the supplementary information (section 6).

Conclusion

The most important feature of the results we give here is not the materials themselves but the realisation that most of the hypothetical zeolite structures are not, as previously thought, unfeasible, but may be realizable by designing new synthetic routes that avoid the limitations of solvothermal synthesis. We have shown that two of the previously 'unfeasible' zeolites are now realisable synthesis targets. We believe that this truly opens up any of the hypothetical zeolites as feasible targets as long as any strain introduced in the frameworks can be accommodated without breaking of the silicon-oxygen bonds. This advance gives hope that the zeolite conundrum is solved, and that in the long term the number of accessible zeolites will be vastly increased. Given the undoubted importance of zeolites in many aspects of industry and the clear recognition that new architectures and chemical properties are the key to opening up new technological applications, such an increase in the number of accessible materials may well be a vital disruption to our current thinking in zeolite science.

Methods

The synthesis of the germanosilicate parent zeolite with the UTL topology and hydrolysis into the IPC-1P layered materials are described in the supplementary information (Section 1).

Synthesis of IPC-9 zeolite

The layered precursor to IPC-9 was prepared by intercalation of choline hydroxide into the IPC-1P layered material. It was performed in two ways: by direct intercalation and by de-swelling method.

Direct intercalation was performed using 50% water solution of choline hydroxide. The choline hydroxide was prepared by ion-exchange of choline chloride 50% water solution using Ambersep® 900 resin (100 g of resin per 100 g of solution). Then, 1 g of zeolite precursor IPC-1P was mixed with 30 g of choline hydroxide solution and stirred for 4 h at room temperature. The resulting solid was centrifuged, washed with water, centrifuged again, and dried in oven at 60 °C.

The de-swelling method involves exchange of intercalate in between layers. First step of the preparation is swelling of IPC-1P with CTMA-OH 25% solution with w/w ratio of 1/30 for 16 h at room temperature. Solid product was centrifuged, washed with water and dried. Next step is choline-assisted de-swelling of swollen layered precursor (IPC-1PSW). A 0.62 g of IPC-1PSW was introduced into choline chloride (16 g) solution in absolute ethanol (40 g). The mixture was stirred for 10 h at room temperature, zeolitic powder was separate by centrifugation, decanted, washed once with absolute ethanol (~15 ml) and centrifuged again, then decanted and dried in oven at 60 °C. Repeating of the de-swelling ensures more complete exchange. To form IPC-9 the choline incorporated materials were calcined at 550 °C for 8 h with temperature ramp of 2 °C min⁻¹.

Synthesis of IPC-10 zeolite

A 0.1 g sample of IPC-1P intercalated with choline (prepared as above) was introduced into a 25 ml PTFE - lined autoclave. Then, 0.05 g of diethoxydimethylsilane and 10 ml of 1M HNO₃ was added. The autoclave was kept in the oven without agitation for 16 h at 175 °C. The product was filtered, washed with water (100 ml) and dried in oven at 60 °C. IPC-10 was then formed through calcination at 550 °C for 8 h with temperature ramp of 2 °C min⁻¹.

Computational details

Calculations were performed at the density functional theory level, using the VASP program package.²⁷ For the assessment of feasibility using the local interatomic distance criteria optimisation of the structure and energy calculations were completed exactly as described in reference 8. Full details of characterisation and computational modelling are given in the Supplementary Information – this includes

crystallographic information files for the two structures and movie files showing the orientation of the layers in IPC-1P and IPC-9P.

Figure Captions

Figure 1. Synthesis of ‘unfeasible’ zeolites. The ADOR process involves (i) the selective disassembly of a germanosilicate with, in this particular case, the UTL structure, to form a layered material (called IPC-1P) followed by (ii) the use of the choline cation (shown as a blue circle containing a +ve charge) as a structure directing agent to shift the layers with respect to each other (IPC-9P). The layers can then be reassembled in two ways, (iii) by calcination to form IPC-9 and (iv) calcination after intercalation of diethoxydimethylsilane to form IPC-10. Colour key: Blue atoms denote the tetrahedrally coordinated silicon or germanium atoms while red circles denote the oxygen atoms.

Figure 2. The role of choline cations in organising IPC-1P layers. Starting from the unshifted, most favourable arrangement of IPC-1P layers after initial hydrolysis (bottom left panel), calculations reveal the most favourable position for choline cations interacting with a single IPC-1P layer (top left panel). The results show that the choline cations locate between the silanol quadruplets that line the surface of each layer (negative charge -1 per silanol quadruplet ($\text{Si}_4(\text{OH})_3\text{O}^-$) was used to maintain charge balance). The effect of the choline intercalation on the arrangement of multiple layers is dependent on the amount of choline occluded. If the choline:silanol ratio is 1:4 the most favourable layer shift is along the crystallographic *b* –axis (top right panel). If the choline:silanol ratio is 1:2 the most favourable layer arrangement involves a shift along the crystallographic *c*- axis (bottom right panel). Each panel shows two crystallographic views (parallel to the *b*– and *c*- crystallographic axes) except for the top left panel, which shows a single IPC-1P layer. The choline cation is shown schematically as a blue circle.

Figure 2. Role of the choline cations in organising IPC-1P layers. (a), The unshifted, most favourable arrangement of IPC-1P layers after initial hydrolysis (Si and O atoms depicted in red and blue, respectively). (b), Calculations reveal the most favourable position for the choline cations interacting with a single IPC-1P layer: between the silanol quadruplets that line the surface of each layer (a negative charge of -1 per silanol quadruplet ($\text{Si}_4(\text{OH})_3\text{O}^-$) was used in the calculations to maintain

charge balance). A single IPC-1P layer is shown for clarity (Si, O, and H atoms shown in red, blue, and white, respectively, using a ball and stick mode for surface silanols, tube mode for Si and O atoms on the IPC-1P surface and stick mode for the rest of the atoms; the choline cation is depicted in ball and stick mode with N, C, O, and H atoms in light blue, grey, red, and white, respectively. (c) and (d). The effect of the choline intercalation on the arrangement of multiple layers depends on the amount of choline occluded. For a choline:silanol ratio of 1:4 (c), the most favourable layer shift is along the crystallographic *b* axis. For a choline:silanol ratio of 1:2 (d), the most favourable layer arrangement involves a shift along the crystallographic *c* axis. In panels (a), (c) and (d) two crystallographic views are shown, parallel to the *b* (left) and *c* (right) crystallographic axes); In panels (c) and (d) the choline cation is schematically shown as a positively charged blue circle.

Figure 3. Structure of IPC-9 and IPC-10 (a) the structure of IPC-9 viewed parallel (010 direction) to the seven-ring channels (marked as 7MR) in the structure (left) and parallel (001) to the 10-ring (10MR) channels (right). (b) The structure of idealized IPC-10 viewed in the (010) direction parallel to the nine-ring (9MR) channels (left), and parallel to the 12-rings (12MR) (right). Note there are two possible connections in the IPC-10 structure, marked (i) and (ii) in the diagrams, which are likely to be randomly disordered (For further detail see Supplementary Information section 4).

Figure 4 The energetics of IPC-9 and IPC-10. (a) The position of IPC-9 and IPC-10 (squares) in energy-density space showing that they both lie away from the correlation calculated from the position of all other known silica zeolites (circles). IPC-9 lies on the edge of the region of known zeolites while IPC-10 lies much further away from the correlation, which is shown by the black line. (b) Comparison of the 2D unit cell area parallel to the UTL-like layers, calculated from the product of the *b* and *c* unit cell dimensions. The figure shows the parent zeolite UTL, the feasible zeolites IPC-4 and IPC-2, and the 'unfeasible' zeolites IPC-9 and IPC-10, showing the contraction of the layers in the latter two zeolites.

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Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for information should be addressed to R.E.M. (rem1@st-and.ac.uk).

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Competing financial interests

The authors declare no competing financial interests.

