

A family of zeolites with controlled pore size prepared through a top-down method

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Abstract

The properties of zeolites, and thus their suitability for different applications, are intimately connected with their structures. Synthesizing specific architectures is therefore important but has remained challenging. Here we report a top-down strategy involving the disassembly of a parent zeolite, UTL, and its reassembly into two zeolites with targeted topologies, IPC-2 and IPC-4. The three zeolites are closely related, adopting the same layered structure and differing only in how the layers are connected. Choosing different linkers gives rise to different pore sizes, enabling the synthesis of materials with predetermined pore architectures. The structures of the resulting zeolites were characterized by interpreting the X-ray powder diffraction patterns through models using computational methods; IPC-2 exhibits orthogonal 12- and 10-ring channels, IPC-4 is a more complex zeolite comprising orthogonal 10- and 8-ring channels. We describe how this method enables the preparation of functional materials and discuss its potential for targeting other new zeolites.

Environmentally friendly and economically beneficial industrial applications of zeolites in catalysis, adsorption, and ion-exchange processes are well known. This success of zeolites drives fundamental research and a continuing effort towards synthesis and manipulation of their structures. The reactivity, selectivity, and utility of zeolites are intimately connected with their structural architecture and so much of this effort is focussed on preparing materials with new framework types.¹⁻⁵ In particular, it is advantageous to target materials with different pore sizes and structures as this controls accessibility to the internal surface of the zeolites. Recent years have seen many new solids with interesting properties discovered using solvothermal synthesis methods,⁶⁻¹² but the goal of pre-determining zeolite architecture and pore size remains elusive. In this contribution we report the synthesis of two complex zeolites, IPC-2 and IPC-4 with targeted pore sizes based on a top-down, chemically selective disassembly of a parent zeolite, UTL,^{13,14} into its constituent layers followed by reassembly into the new zeolites (note that zeolite structures and topologies are named using three-letter codes; see the International Zeolite Association website, <http://www.iza-structure.org/databases/> for further details).

The most important feature of this process is that control of the linkers used in the reassembly leads to predictable structures with pre-determined pore sizes, leading in turn to a family of zeolites with closely related structures but different channel systems (Figure 1). All three zeolites, the parent UTL, IPC-2 and IPC-4 contain the same layer structure connected by units of different size; double four ring (D4R), single four ring (S4R) and oxygen units, respectively. Importantly, this strategy allows zeolites with particular pore systems to be targeted. For example, the parent zeolite UTL has a

channel system comprising two orthogonal channels delineated by windows containing 14 and 12 tetrahedral atoms respectively (a so called 14 x 12 ring system). Replacing the D4R unit that connects the layers in UTL with a S4R results in the smaller 12 x 10 ring channel system of IPC-2 and replacing the D4R unit with only an oxygen linker results in the even smaller 10 x 8 ring channel system of IPC-4 (Figure 2). The significance of this work is that we demonstrate that it is possible to target specific ring sizes in a material by replacing one size of unit in the structure with alternative units of a different size.

Results

Synthesis

Recently, it has been shown that the germanosilicate zeolite UTL^{13,14} can be selectively disassembled via the chemically selective removal of germanium-rich D4R units in the structure leaving a material with UTL-like layers connected only by hydrogen bonding through silanol groups (a material known as IPC-1P).¹⁵ The Si/Ge ratio in the starting UTL was ~ 4, but after hydrolysis this had increased to between 25 and 30, depending on the exact sample, indicating that significant amount of Ge had been removed during the hydrolysis.

Our hypothesis in this work was that fully connected zeolite materials with different pore sizes could be reformed by replacing the D4R with other units. Using this approach IPC-2 was prepared by replacing the D4R with a S4R unit by intercalating diethoxy dimethyl silane between the layers and then calcining at 540 °C or 750 °C in air to remove the organic groups and condense the silanols. The geometric arrangement of the silanol

groups on the UTL-like layers is such that, on condensation of the diethoxy silyl units with the layers, the methyl groups on the silicons are brought close enough to facilitate the formation of the Si-O-Si bonds in the S4R unit.

For the synthesis of IPC-4, the hydrolysed UTL was treated with neat octylamine, which intercalated between layers. Calcination and accompanying fusion of the layers through silanol group condensation produced an ordered framework, which we call IPC-4. The presence of the octylamine is necessary for the successful preparation of IPC-4 as calcination without organic present results in only poorly ordered layers (a material we call IPC-1). The final Si/Ge ratios were in the range 28 to 32 and 25 to 30 for IPC-2 and IPC-4 respectively. Full details of the synthetic procedures for IPC-2 and IPC-4 are found in the methods section below and in the supplementary information.

Structure Solution

A great advantage of the above synthetic procedure is that, in principle, the layers formed from the hydrolysis of the parent UTL remain intact throughout the whole process (see the discussion below). Assuming this to be the case the structure solution problem becomes much more tractable because the number of ways layers can be connected through any one linker is very limited and the structures are predictable. In the case of the UTL-derived layers, there are only four possible ways to connect them to form a zeolite (i.e. to yield a solid with no unconnected silanol groups). Therefore there are only four possible structures each for IPC-2 and IPC-4. These can be readily assessed for their feasibility computationally (by calculating lattice energies) and verified

against experimental powder diffraction patterns. Each of the models was built and their calculated X-ray powder diffraction patterns compared with experimental data. In both cases the correct structure was obvious on visual comparison of the patterns.

The IPC-4 model was obtained by reconnecting adjacent IPC-1P layers (formation of Si-O-Si inter-layer link and removing H₂O) in a periodic manner; adjacent layers were moved together along the normal of the IPC-1P plane (*bc* plane). This connection results in the formation of a 3D zeolite with two-dimensional intersecting channel system; 10-ring channels parallel to *c* (projection in *ab* plane) and 8-ring ones parallel to *b* (Figure 1). The structure of the formed 3D zeolite was fully optimized (optimizing fractional coordinates and the unit cell volume and shape) at the DFT level using VASP.^{16,17} The monoclinic *Cm* space group with following unit cell parameters was obtained: *a* = 2.036, *b* = 1.417, *c* = 1.246 nm and $\beta = 114.09^\circ$; the corresponding simulated XRD powder pattern closely matched the experimental one, and Le Bail refinement against the X-ray data confirmed the unit cell parameters. Finally, the IPC-4 structure obtained at the DFT level was used in subsequent Rietveld refinement against the experimental X-ray diffraction data. The refinement proceeded successfully and resulted in a structural model that agrees with the calculated one (Figure 3b). The framework structure of IPC-4 has been assigned the code **PCR** by the International Zeolite Association (<http://www.iza-structure.org/databases/>).

The model for IPC-2 was built in a similar way, but this time the layers were connected through a S4R unit. The structure of the zeolite was fully optimized as above and resulted in a model with P-1 symmetry with the following unit cell: *a* = 1.252, *b* = 1.389, *c* = 1.397 nm, $\alpha = 118.75^\circ$, $\beta = 90.17^\circ$, $\gamma = 107.09^\circ$. The computed X-ray diffraction

pattern closely matched the experimental Le Bail and Rietveld refinements against the X-ray diffraction data, confirming that the structures were correct. Comparisons of the observed and Rietveld-calculated X-ray diffraction patterns are shown in Figure 3. Full details of the computational work and the structural refinements are given in the supplementary information.

The structural characterisation confirms that IPC-2 and IPC-4 both comprise exactly the same layer topology as the parent UTL zeolite (Figure 1). In IPC-2 the layers are linked by S4R units to form a 12 x 10 ring channel system with relatively spherical windows of 6.6 x 6.2 Å for the 12-ring and 5.3 x 5.5 Å for the 10-ring (Figure 2). For comparison the parent UTL material has a 14 x 12 ring system with elliptical window sizes of 8.6 x 7.6 Å for the 14-ring and 8.2 x 5.7 Å for the 12-ring.

In IPC-4 the layers are linked to form orthogonal channels delineated by 10-rings parallel to the *c*-axis and 8-rings parallel to the *b*-axis. IPC-4 joins a small family of zeolites with orthogonal 10 x 8 ring channel systems, which includes the highly important commercial zeolite ferrierite (FER). The 10-ring windows into the channels in IPC-4 are slightly elongated compared to those in FER. The 10-ring has openings of 5.8 x 3.8 Å (cf 5.4 x 4.2 Å in FER). The ellipsoidal shape of the 10-ring apertures may be more beneficial for selective isomerisation of hydrocarbons. In contrast the 8-ring windows are slightly rounder than in FER (4.5 x 3.6 Å compared to 4.8 x 3.5 Å). As one might expect, the density of IPC-4 and FER are broadly similar, the structures containing 18.3 and 17.8 tetrahedral atoms per 1000 Å³ respectively.

The zeolitic porosity of IPC-2 and IPC-4 was confirmed using nitrogen adsorption experiments at 77 K. The experimental isotherms (Figure 3c) demonstrate beautifully

the difference in micropore volumes caused by the different sized channel systems. The magnitudes of the micropore volumes in the order UTL ($0.190 \text{ cm}^3 \text{ g}^{-1}$) > IPC-2 ($0.146 \text{ cm}^3 \text{ g}^{-1}$) > IPC-4 ($0.106 \text{ cm}^3 \text{ g}^{-1}$) matches perfectly with the decreasing size of the pores in the series. IPC-2, with the larger channel system, has a BET surface area of $334 \text{ m}^2 \text{ g}^{-1}$ while IPC-4 exhibits a BET surface area of $236 \text{ m}^2 \text{ g}^{-1}$. The adsorption isotherm for IPC-2 shows some hysteresis at higher P/P_0 values, indicative of some mesoporosity caused by interparticle adsorption. This is much less pronounced in the other two samples.

Solid-state NMR further confirmed that both materials comprise almost fully condensed silicate species, consistent with the X-ray diffraction data described above and with the designation of the materials as true tetrahedrally-connected zeolites. The conventional ^{29}Si MAS NMR spectrum shows only slight evidence for Q^3 defects in both structures (resonances at around -100 ppm). $\{^1\text{H}\}^{29}\text{Si}$ cross-polarisation (shown in Figure 3d and in Figure S5 in the supplementary information) confirm that these are silanol defects. In IPC-2 there is also evidence for a very minor amount of T-type silicon (CH_3SiO_3 , $\sim -60 \text{ ppm}$) presumably from a very small proportion of defects where the S4R units have not fully condensed. This is only visible in the cross-polarisation spectra, which will be very sensitive to this type of defect, and not in the conventional ^{29}Si spectra. Calcining at higher temperatures (e.g. $750 \text{ }^\circ\text{C}$) removes this signal.

Discussion and Conclusion

The overall synthetic strategy used to prepare the materials, the initial removal of a structural unit from a preformed zeolite, followed by replacement with an alternative unit to form a zeolite with a different, targeted pore size is shown in Figure 4. We call this strategy ADOR (Assembly, Disassembly, Organisation, Reassembly). To target a particular pore size one must have good control over the resulting linkages, and the two examples described here illustrate the two possibilities. For zeolite IPC-4 the fully connected zeolitic material is prepared by condensation of the IPC-1P layers. The key to this process is therefore the organisation of the layers by the octylamine. Without it only poorly ordered materials are formed on calcination. DFT calculations (see supplementary information) indicate an energetic preference for IPC-4 over the other possible structures (Fig. S5). The calculations show that a small energetic preference in favour of a layer arrangement suitable for the formation of IPC-4 is further enhanced by the addition of octylamine (see supplementary information); one could describe it as a structure directing agent (SDA), akin to those used in the hydrothermal synthesis of zeolites. That being the case other species of similar size and chemistry may also be good organising agents, and indeed the ionic liquid 1-ethyl, 3-methyl imidazolium bromide, a previously known zeolite SDA,¹⁸ can replace the octylamine successfully. In contrast, IPC-2 is prepared by adding an S4R to replace the D4R unit. Here the key to successful synthesis of a zeolite is the choice of a linker that matches the geometry of the layers in order that calcination can give a fully condensed structure. The chemistry of the diethoxy dimethyl silane is important here, in that the ethoxy groups are available to condense with the silanols of the layers, leaving the methyl groups to form the Si-O-Si linkages of the S4R on calcination at high temperature.

Pivotal to the success of the ADOR process is that the layers originate from the disassembly of a fully connected zeolite, which means the geometry of the layers is ideal for the condensation into a fully condensed zeolite. Previous attempts to link directly synthesised zeolite-like layers using silylating agents have all failed to form true zeolites, always leaving uncondensed silanols in the final structure.¹⁹⁻²³

In this work, because we have started from the disassembly of a fully connected zeolite, the reassembly of layers can lead to a family of fully connected zeolites with targeted pore sizes. Other methods to target specific structures have been investigated, either starting from layers like those cited above or those that begin with a known zeolite, such as the remarkable inverse sigma transformation recently reported by Verheyen et al,²⁴ which makes a material probably isostructural to IPC-2. So far however, they have not led to the synthesis of a family of structurally related zeolites. A fascinating potential of the ADOR process is that it may be possible to use longer silylating agents to expand the size of the zeolite pores. Again, it will be the fact the layers are geometrically compatible with a fully connected structure that will be key in targeting true zeolites. Of course the utility of any zeolite relies on the possibility of incorporating functionality into the material, and for the ensuing material to have sufficient stability to complete its function. An important point to note in this work is that we have taken a hydrolytically unstable UTL zeolite, and transformed it into a much more stable family of microporous solids. Measurements in water at 99 °C show that the stability of the three zeolites follow the trend IPC-4 > IPC-2 >>> UTL, and that both IPC-2 and IPC-4 have sufficient stability to be useful zeolites. In addition we have also shown that aluminium can be incorporated into IPC-2 and IPC-4 by applying the ADOR process to Ge/Al-UTL to

produce catalytic materials (Al)IPC-2 and (Al)IPC-4. Previous work has suggested that unlike Ge, aluminium sites are preferentially within the 'layers' of UTL²⁵ and so would not compete with the ADOR process. Figure S8 shows the infrared spectra of hydroxyl region of (Al)IPC-2 and (Al)IPC-4 and also the areas of vibrations of deuterated acetonitrile used as probe molecule indicating the presence of both Lewis and Brønsted acid sites. The activity and selectivity of the zeolites in toluene alkylation using isopropyl alcohol was examined and shows that the activity of (Al)IPC-2 was similar to MFI, but lower than both zeolite-beta, which has a highly accessible three dimensional 12 x 12 x 12 ring system, and UTL (14 x 12 ring). However, selectivity to cymenes was higher than MFI and similar to beta and UTL, although selectivity to p-cymenes was similar to MFI. The activity of (Al)IPC-4 was much lower, consistent with the smaller channels in this structure (supplementary information, Figure S9).

There are obvious questions regarding whether the ADOR strategy bears any relationship to the real mechanism of the process. For example, an important question is whether the UTL-like layers remain intact throughout the whole process or whether they dissolve and reform during the manipulations. At one level it does not matter to the outcome of the process (the preparation of the zeolites) and it is beyond doubt that the intermediate solids (from previous electron diffraction¹⁵) and the final zeolites (from the current crystallographic studies) all contain the same UTL-like layer topologies.

However, we believe that the layers remain intact for two reasons. Firstly, it is extremely unlikely, under the different conditions used to form IPC-2 and IPC-4 that the UTL layers would dissolve and then recrystallize in the same topologies. Secondly, and even more

convincingly, the conditions used to form IPC-4 (octylamine intercalation at 70°C) are conditions that do not dissolve silica. One can see that significant dissolution does not take place during the course of the intercalation and attempts to synthesise high silica zeolites from other starting materials under these conditions fail. Therefore the chemistry of the process strongly suggests that the schematic representation shown in Figure 4 does indeed have validity. This opens us the possibility that this type of approach might not be restricted to the UTL-type layers but that it is more general. More than 10% of all zeolites known contain D4R units,²⁶ and many of these have been prepared using germanium. Several of these zeolites look particularly suitable targets for this strategy – zeolites IWW,²⁷ ITH,²⁸ ITR,²⁹ IWR,³⁰ and IWV³¹ as well as UTL all have layer-like topologies linked by D4R units, and have all been prepared with significant Ge content. In fact, in our laboratory we have already shown how zeolite IWW can be disassembled in the same manner as UTL. Therefore it looks very likely that ADOR will be a general process for several different zeolite classes, offering to expand the number of known zeolites considerably. However, a great advantage of beginning the process with a fully assembled zeolite such as UTL is that it is guaranteed, at least geometrically, that the resulting disassembled layers can be reassembled into a zeolite with the desired target structure. This is not necessarily the case for other, directly synthesised, layers.

As far as the particular system reported here goes, we have successfully replaced one set of structural units with others of a different size to make two zeolites with different pore sizes. We believe that this is the first time that any one has targeted a family of zeolites with controlled pore sizes in this manner.

Methods

Full details of the materials and methods can be found in the supplementary material.

Synthesis and hydrolysis of zeolite UTL. The starting UTL zeolite was prepared as previously REF. Calcined UTL was hydrolyzed in 0.1 M HCl with w/w ratio of about 200/1 at temperature near boiling in a plastic bottle, for overnight. The solid, called IPC-1P, was isolated by filtration and centrifugation, washed with water and dried in air for overnight.

Synthesis of zeolite IPC-2 A 0.5 g sample of IPC-1P in 10 ml of 1 M HNO₃ solution containing 0.1 g of Si(CH₃)₂(OCH₂CH₃)₂ was heated at 170°C for 16 hr. The product was isolated by centrifugation, washed and calcined at 540 °C for 2 hrs.

Synthesis of zeolite IPC-4 A 0.3 g sample of the precursor IPC-1P was mixed with 20 g of octylamine, heated at 70 °C for several hours and then stirred at room temperature for overnight. The solid was isolated by centrifugation, decantation of the supernatant and drying in an open tube in air at 90 °C.

X-ray Diffraction The crystallinity of samples under study was determined by powder X-ray diffraction on a Bruker AXS D8 Advance diffractometer with a Vantec-1 detector in the Bragg-Brentano geometry using CuK α radiation. All samples were gently ground to limit the effect of preferential orientation of individual crystals.

Adsorption isotherms Adsorption isotherms of nitrogen at –196 °C were determined using an ASAP 2020 (Micromeritics) static volumetric apparatus. Before adsorption experiments the samples were degassed under turbomolecular pump vacuum at the temperature of 250 °C for 8 h.

FIGURE CAPTIONS

Figure 1. The structures of zeolites UTL, IPC-2 and IPC-4. The diagram shows the layer topology that is common to all three materials (in red) together with the different sized linkers (shown in blue) that lead to the different pore sizes in the materials.

Figure 2. The pore windows and sizes for zeolites IPC-2 and IPC-4. The diagrams illustrate the 10-rings (a) and 12-rings (b) in IPC-2, and the 8-rings (c) and 10-rings (d) from IPC-4. The dimensions of the pores are measured from the centre of the opposite oxygen atoms minus the van der Waals diameter of an oxygen atom (2.7\AA) as described in reference 26. Key: Grey spheres are silicon atoms, red spheres are oxygen.

Figure 3 Characterisation of zeolites IPC-2 and IPC-4. Rietveld plots for the refinement of the structural models against X-ray powder diffraction data for IPC-2 (a) and IPC-4 (b). The figures show the measured diffraction data (black dots), the calculated X-ray diffraction pattern (red line) and the difference between the two (black line). The calculated positions of the diffraction lines are shown by the tick marks. (c) Nitrogen adsorption data (77 K) for IPC-2 (blue) and IPC-4 (red). The data for UTL (black) are shown as a comparison. Adsorption data are shown as open circles, desorption as closed circles. (d) ^{29}Si magic angle spinning spectra (black) and ^{29}Si CP MAS NMR spectra (red) for IPC-2 (bottom) and IPC-4 (top).

Figure 4. The ADOR (assembly-disassembly-organisation-reassembly) strategy for the preparation of zeolites. Stage A is the assembly of a zeolite from the starting materials; D is the controlled disassembly of the zeolite; O is an organisation step whereby a new linking unit or a structure directing agent (blue oval) is incorporated and R is the final reassembly step. In the case of zeolites IPC-2 and IPC-4 there is no direct synthesis route yet available. The colour key is as for Figure 1, with the layers common to all materials shown in red and the different linkers shown in blue.

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Author contributions

W.J.R., P. C. and O.S. completed the synthesis work, P.N., L.G. and M.P. the calculations, P.S.W. the Rietveld refinement, V. R. S. and S. E. A. the NMR and A.Z. the adsorption. W.J.R. P.N., J.C and R.E.M wrote the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permission information is available online at <http://www.nature.com/reprints>.

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Competing financial interests

The authors declare no competing financial interests.