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ITQ-12: a new microporous silica polymorph potentially useful for light hydrocarbon separations†

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The new synthetic form of microporous crystalline silica, denoted as ITQ-12, shows a high potential for the separation of propane and propene from its mixtures.

Crystalline pure silica polymorphs of microporous nature are attractive materials for applications based on hydrocarbon adsorption, because they combine the hydrophobic nature of a defect-free SiO_2 framework with the molecular sieve properties of a zeolite. In particular, the small pore DD3R has been proposed for separation of propene and propane,[1] and indeed all high and pure silica materials are candidates for this kinetic based process.[2] For this separation, a high selectivity for light hydrocarbons, a low affinity for water and the appropriate small pore size giving rise to a large difference in the rate of adsorption of both hydrocarbons are required. However, until quite recently small pore pure silica microporous materials were scarce and only the development of new synthetic pathways has allowed the discovery of a few new silica polymorphs presenting these features.[3] Here we report on the synthesis of ITQ-12,[4] a new microporous, crystalline pure silica polymorph and on its potential for the energy efficient separation of propene and propane, an industrially important separation currently realized by an energy intensive cryogenic distillation.

Zeolite ITQ-12 can be prepared in pure silica form by the combined use of fluoride anions and any of two different organic derivatives of the imidazole ring: 1,2,3-trimethylimidazole, or 1,3,4-trimethylimidazole.‡ The fluoride anion acts both as a catalyst for the breaking and formation of Si–O–Si bonds and also to some extent as a structure directing agent.[5] This is suggested by the presence in the structure of double 4-member ring cavities (see below) that have never been encountered in pure SiO_2 materials synthesized without the use of fluoride. Actually, a single resonance at -40 ppm in the ^{19}F MAS NMR spectrum of the as-made ITQ-12 material (not shown) demonstrates the fluoride anions are located exclusively inside these small cavities in the structure.[6] Chemical analysis points to a nearly complete occupancy by fluoride of these cavities (1.97 F per unit cell, compared to 2 double 4-member rings per unit cell). On the other hand, the organic cation acts as a structure directing agent (SDA).[7] Because of its size, the organic cation must be occluded in the relatively large cavities in the structure (see below) and chemical analysis suggests nearly full occupancy of those cavities (1.90 cations per unit cell, compared to 2 cavities per cell). Fluoride and organics can be removed by calcination in air at temperatures of 600 °C yielding a pure SiO_2 material of microporous nature (0.13 $cm^3\ g^{-1}$ as measured by N_2 adsorption using the *t*-plot method). It is noteworthy that thermogravimetric analyses (TGA) of as-made ITQ-12 indicate no weight loss below 500 °C. This is consistent with the hydrophobic character expected for ITQ-12 and suggests that there are no connectivity defects in the as-made solid. Moreover, the comparatively high temperature before the onset of weight loss in the TGA data supports the constrained entrapment of fluoride and organics within its cavities. The absence of connectivity defects in ITQ-12 is further supported by ^{29}Si MAS NMR spectroscopy, which showed no -105 ppm resonance indicative of Si–OH connectivity defects either before or after calcination. In the spectrum of the as-made material there are two single resonances at -106.9 and -115.8 ppm (intensity ratio 3 : 1), assigned to $Si(OSi)_4$ species in different crystallographic environments. As found before in other silica phases in which F^- is occluded in a double 4-member ring, such as AST and ISV, there are no resonances due to pentacoordinated $Si(OSi)_4F$ species which by contrast appear when fluoride is occluded in slightly larger cavities.[8] After calcination, the spectrum shows five resonances (approximate relative intensities 1 : 1 : 1 : 1 : 2) in the -108 to -118 ppm region (Fig. 1), corresponding to $Si(OSi)_4$ species in different crystallographic sites.

From conventional low resolution X-ray diffraction powder data of calcined ITQ-12 we obtained a fully connected three-dimensional structure using direct methods. The structure was then refined with soft T–O constrains in two different space groups. Due to the relatively poor quality of the data and the structural complexity, the details of the structure, although generally correct, were not fully satisfactory: in one space group with 12 inequivalent T–O distances one short T–O distance (1.536 Å) was found, while in the other space group one low OTO angle (93.2°), out of 36, was encountered. Thus, while the topology must be fully correct, some precise details will require

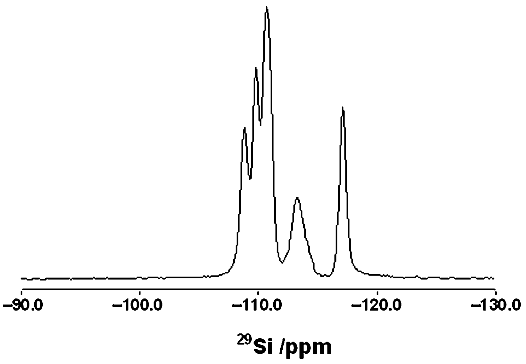

Fig. 1 ^{29}Si MAS NMR spectrum of calcined SiO_2 ITQ-12.

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† Electronic supplementary information (ESI) available: details of the structure solution, Rietveld refinements in space groups *C*2/*m* and *Cm* and energy minimisation calculations in *C*2/*m*, *Cm* and *C*2. See http://www.rsc.org/suppdata/cc/b3/b306440a/

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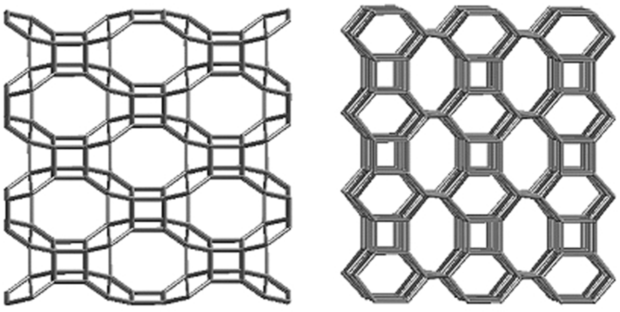
a refinement using high quality synchrotron X-ray diffraction data. Details of the refinements and energy minimisation calculations in different space groups are available.†

This new zeolite topology contains a two dimensional system of channels (Fig. 2) accessed *via* 8-ring windows. Along (100) the channel elongated 8-ring windows appear too narrow (2.4 × 5.3 Å) to allow the passage of even the smallest hydrocarbons. The channels along (001) are open through more circular windows (3.8 × 4.1 Å). The windows give access into a larger cavity with a flat shape that resembles that of both imidazolium derivatives, which share in common the planar shape derived from the aromaticity of the ring. Between these large cavities there are small double 4-member rings where fluoride is located in the as-made material. Considering the crystal structure and cage types contained therein, we believe it is reasonable to infer that a combination of structure directing effects from fluoride and either of the two isomers of the SDA afforded the discovery of this new silica polymorph.

The size and shape of the pores in ITQ-12 suggest the potential application for the separation of small hydrocarbons with very similar size, such as propene and propane. With the current technology, using cryogenic distillation, this separation is one of the most energy intensive separation processes in the petrochemical industry. A kinetic based process such as pressure swing adsorption could clearly have large economic and environmental benefits due to a much lower consumption of energy. For such a process, which is based on kinetics rather than on equilibrium, the adsorbent must have large differences in diffusion rate for these two gases. In order to discriminate between molecules with very similar sizes the adsorbent must have pore sizes very close to the size of these gases. High silica zeolites with eight member ring pores are candidates for such adsorbents and a material named DD3R[1] and, more recently, silica chabazite and ITQ-3 have been investigated.[2,9] For a given structure type and inherent diffusion parameters, the adsorption times are governed primarily by the crystal size of the particular preparation and operating temperature. In this preliminary investigation, the ITQ-12 used showed large differences in these diffusion coefficients (the ratio of diffusion coefficients for propene and propane at 30 °C is 9500) and also had a crystal size giving rapid adsorption of propene, as shown in Fig. 3, where it can be seen that in one minute at 30 °C ITQ-12 is close to propene equilibrium while in this time interval propane is only 3% of its expected saturation value.


[001]

[100]

Fig. 2 The topology of pure silica ITQ-12 (oxygen atoms have been omitted for clarity). The minimum channel apertures are defined by rings of 8 (Si–O) units.

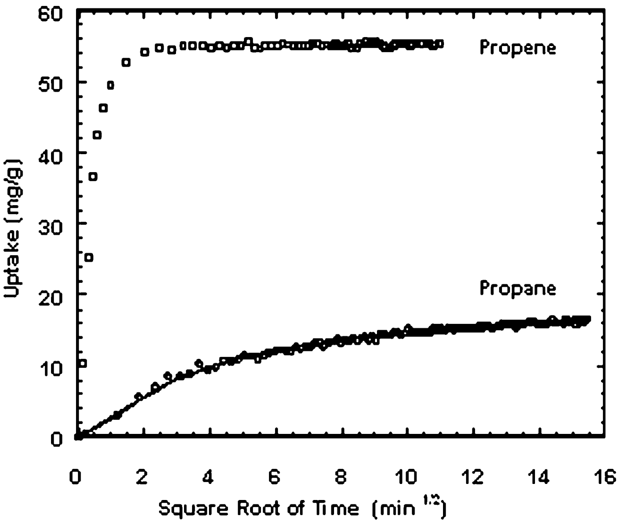


Fig. 3 Sorption of propene and propane on ITQ-12 at 30 °C.

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Notes and references

‡ Gels of composition SiO_2 : 0.56 R^+OH^- : 0.62 HF : 7.0 H_2O, where R^+ is one of the trimethylimidazolium isomers, were crystallised at 175 °C for 10 days in Teflon lined stainless steel autoclaves. The trimethylimidazolium isomers were synthesised by reacting methyl iodide with the parent imidazole (4-methylimidazole or 2-methylimidazole) for six days at room temperature in the presence of $K_2CO_3{\cdot}1.5H_2O$. The as-synthesised iodides were converted into hydroxides by anion exchange.

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