

ITQ-15: The first ultralarge pore zeolite with a bi-directional pore system formed by intersecting 14- and 12-ring channels, and its catalytic implications†

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The pore topology of ITQ-15 zeolite consists of an ultra-large 14-ring channel that is intersected perpendicularly by a 12-ring pore; acid sites have been introduced in its framework and this unique structure shows advantages over unidirectional ultra-large pore zeolites for diffusing and reacting large molecules.

There is much interest in finding molecular sieves with extralarge pores that allow diffusion of bulky reactants. Despite the great efforts made up to now by industrial and academic laboratories, only a few zeolitic materials with more than 12-ring channels (12-R) have been synthesized. Among them, we can highlight UTD-1,¹ CIT-5,² SSZ-53, SSZ-59,³ ECR-34⁴ and OSO-1.⁵ These have enlarged the preexisting pore diameter of zeolites from a maximum of 0.74 nm for Faujasite (12-R) to 1.01 nm (ECR-34).

Catalytic results have shown the benefit of the ultralarge pore zeolites when reacting bulky molecules. However, they also present diffusional limitations and catalyst deactivation due to the fact that, for practical purposes, all the above microporous materials act as unidirectional pore zeolites.⁶ It appears, then, that the potential of ultralarge pore zeolites could be improved if materials with multidirectional channel systems could be synthesized. In 2000, we described the synthesis of a new zeolite that was named as ITQ-15,^{7,8} that here we show to possess an interconnected ultralarge (14-R) and large pore system (12-R). We have succeeded in introducing active acid sites in the structure and the catalytic results show the benefit of its pore topology when compared with unidirectional pore zeolites (UTD-1).

ITQ-15 was prepared using 1,3,3-trimethyl-6-azonium-tricyclo-[3.2.1.4^{6,6}]dodecane as structure directing agent (see ESI† for its structure), which was added to a synthesis gel having the following molar composition:

0.91 SiO₂ : 0.09 GeO₂ : 0.01 Al₂O₃ : 0.5 [C₁₄H₂₆N]OH : 10 H₂O

In a typical synthesis, 0.60 g of GeO₂ were dissolved in 52.95 g of a 0.60 M solution of 1,3,3-trimethyl-6-azonium-tricyclo-[3.2.1.4^{6,6}]dodecane hydroxide. Then, 12.60 g of tetraethyl orthosilicate (TEOS) and 0.27 g of aluminium isopropoxide were added and left under stirring until the alcohol and the amount of water necessary to reach the final composition were evaporated. The final gel was homogenized and autoclaved at 448 K for 18 days. After cooling down to room temperature, the solid was recovered by filtration and washed. Finally, the solid was calcined in air at 813 K for 3 hours. The X-ray diffraction pattern of the calcined ITQ-15 material is shown in Fig. 1 (experimental details are given as ESI).

The structural elucidation was achieved by combining TEM, XRD techniques and energy minimization calculations. A preliminary examination of the Electron Diffraction (ED) pattern of the main zone axis shows an intense streaking, particularly in some diffraction rods and in the vicinity of some diffraction peaks. The

above observations are valid for several examined crystals, and that led us to the conclusion that several overlapping domains are co-existing in the same crystallite. It was possible to obtain the symmetry and cell dimensions through the analysis of the ED patterns of several zone axes, and careful tilting around main zone axis. This leads to a monoclinic space group symmetry, being $a = 2.863$ nm, $b = 1.38$ nm, $c = 1.231$ nm and $\beta = 99^\circ$. The observed systematic absences in the ED patterns were consistent with a space group $I2/m$ (No: 12).

The high resolution electron microscopy (HREM) image corresponding to the [001] axis shows clearly the existence of several domains in the structure, with a size of several tenths of nanometres. In the noise filtered image (see Fig. 1 of ESI) and near the edge of the crystal (where structural interpretation is more reliable due to thickness effects) one can clearly see elongated (ellipse-like) pores of maximum size 0.8 nm, in accordance with the pore size diameter calculated from the Ar adsorption isotherm using the Horwath–Kawazoe formalism (see ESI). HREM observation of the [101] zone axis also confirms the existence of domains of several nanometres (see Fig. 2 of ESI).

With this information, we carried out the structure solution using the image processing of different zone axis HREM images, by direct method refinements using the measured intensities for the reflections observed in the ED patterns collected along eight different zone axes. First, through HREM image processing, the positions of 8 independent Si atoms were selected. Then, this model was confirmed by direct method refinements using the ED patterns collected along 8 different zone axes (430 reflections). The SHELX97 refinement shows a reasonable agreement between the calculated model (considering the $I2/m$ space group) and the observed intensities ($R = 32\%$). The remaining T atoms were extracted from the Fourier map and then, the following step for the structural elucidation of the ITQ-15 structure was to introduce the oxygen atoms in between each two neighbouring T atoms,

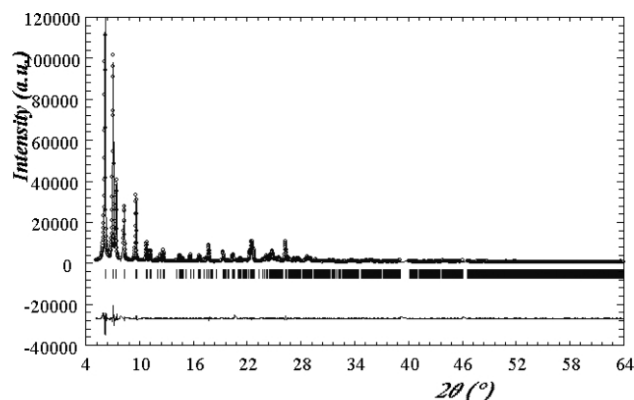


Fig. 1 Rietveld refinement of ITQ-15. Experimental (circles) and calculated (lines) XRD patterns as well as the difference profile (bottom). The short tick marks below the pattern give the positions of the Bragg reflections. $R_w = 0.062$, $R_{exp} = 0.034$, $R_{Bragg} = 0.02$ and $\chi^2 = 6.8$.

† Electronic supplementary information (ESI) available: SDA plot, further experimental details, TEM images, atomic coordinates and adsorption results. See <http://www.rsc.org/suppdata/cc/b4/b406572g/>

considering the approximate atomic coordinates obtained by TEM techniques. Then, energy minimisation calculations were carried out on this preliminary structure by means of the ZeoTsites Program.⁹ This gives a close model that was further refined and confirmed from the Rietveld analysis of the XRD pattern of the calcined ITQ-15 sample. A good agreement between the experimental and the calculated XRD patterns can be seen in Fig. 1. The Rietveld analysis of the XRD pattern has allowed us to find that Ge atoms preferentially occupy T1 and T2 positions, which are those sites forming the D4R units. Therefore, this is a new example in which Ge directs the synthesis towards zeolites that contains D4R units in their structures.^{10–13} It should be noticed that, as in other cases, this could be achieved in a fluoride free synthesis medium.^{12,14,15} The atomic coordinates and T occupations of the refined ITQ-15 structure are given as ESI.

The structure and pore topology of ITQ-15 are shown in Fig. 2. There, it can be seen that this new microporous material possesses a unique 12- and 14-R bidirectional pore system, in which both pores intersect with one another. The largest 14-R pore system runs along the *c* axis (Fig. 2a) having a pore entrance of 1.00×0.67 nm, while the 12-R can be viewed along the *b* axis with a channel dimension of 0.84×0.58 nm. (Fig. 2b). On the contrary, the ITQ-15 does not possess any microporosity along the normal axis to the previous projections (Fig. 2c). This pore topology can also be described as a nearly circular pore system in which the channels are surrounding the D4R units with pore openings of 14 and 12 rings. It is noteworthy that the structure of ITQ-15 resembles a lamellar phase (T sites as blue atoms in Fig. 2) in which the two neighbouring layers are linked through the T1 and T2 sites (red atoms in Fig. 2) giving rise to the formation of D4R units.

For catalytic applications, aluminium was introduced in the framework to produce Brønsted acidity. Indeed, step-wise pyridine desorption experiments show that Al-containing ITQ-15 zeolite is able to retain pyridine up to 623 K under vacuum, which indicates the presence of strong acid sites, and therefore, its suitability as an acid catalyst.

The benefit of combining the extralarge and large channels, together with the presence of acid sites, can be evidenced by carrying out dealkylation experiments of two molecules with different sizes, *i.e.* triisopropylbenzene (TIPB) and diisopropylbenzene (DIPB). The first molecule is hindered from entering into the 12-R pore system, but can easily diffuse through the 14-R channel.⁶ On the other hand, diisopropylbenzene can also diffuse into the 12-R pores. Taking into account the above, the kinetic

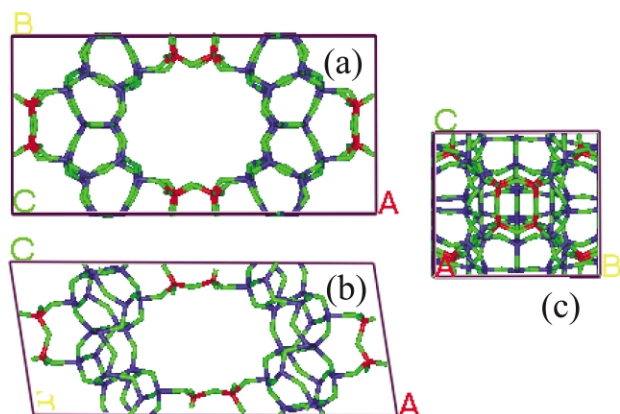


Fig. 2 Perspective view of the unit cell of ITQ-15. Projections along the (a) *c* axis, (b) *b* axis and (c) *a* axis.

Table 1 Kinetic rate constants for the dealkylation of tri- and diisopropylbenzene (K_{TIPB} and K_{DIPB} , respectively) on ITQ-15 and UTD-1^a

Catalyst	$K_{\text{DIPB}}/\text{g g}_{\text{cat}}^{-1} \text{s}^{-1}$	$K_{\text{TIPB}}/\text{g g}_{\text{cat}}^{-1} \text{s}^{-1}$	(Si + Ge)/Al
ITQ-15	8.8	9.5	67
UTD-1	5.5	9.9	80

^a Reaction conditions: $T = 773$ K; time on stream = 60 s; amount of catalyst = 0.200 g. The Si/Ge ratio of ITQ-15 catalyst was 7.6.

reaction rate constants for dealkylation of di- and triisopropylbenzene with ITQ-15 and UTD-1 are given in Table 1. The values for the bulkier TIPB are similar for ITQ-15 and UTD-1, since this molecule can only diffuse through the 14-R channel present in both zeolites. On the contrary, the rate of DIPB dealkylation is significantly higher with ITQ-15, since DIPB can diffuse through both 14- and 12-R pores, while in UTD-1 it diffuses only through the unidirectional 14-R channel. These results show the catalytic benefit of the bi-directional channel system of ITQ-15 with respect to the unidirectional pore topology in the case of UTD-1.

In conclusion, ITQ-15 is the first zeolite with a structure containing interconnected ultralarge and large pores. It has been possible to introduce acid sites in its framework and it is able to react molecules whose diffusion is hindered in large pore zeolites.

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Notes and references

- R. F. Lobo, M. Tsapatsis, C. C. Freyhardt, S. Khodabandeh, P. Wagner, C. Y. Chen, K. J. Balkus, S. I. Zones and M. E. Davis, *J. Am. Chem. Soc.*, 1997, **119**, 8474.
- P. Wagner, M. Yoshikawa, M. Lovallo, K. Tsuji, M. Tsapatsis and M. E. Davis, *Chem. Commun.*, 1997, **22**, 2179.
- A. Burton, S. Elomari, C. Y. Chen, R. C. Medrud, I. Y. Chan, L. M. Bull, C. Kibby, T. V. Harris, S. I. Zones and E. S. Vittoratos, *Chem. Eur. J.*, 2003, **9**, 5737.
- K. G. Strohmaier and D. E. W. Vaughan, *J. Am. Chem. Soc.*, 2003, **125**, 16035.
- T. Cheetham, H. Fjellvag, T. E. Gier, K. O. Kongshaug, K. P. Lillerud and G. D. Stucky, *Stud. Surf. Sci. Catal.*, 2001, **135**, 788.
- J. Martínez-Triguero, M. J. Díaz-Cabanas, M. A. Cambor, V. Fornes, Th. L. M. Maesen and A. Corma, *J. Catal.*, 1999, **182**, 463.
- A. Corma, M. J. Díaz-Cabanas and F. Rey, *Sp. Pat.* ES2186487, 2000.
- A. Corma, M. J. Díaz-Cabanas and F. Rey, *PCT Int. Appl.* WO0203820, 2002.
- G. Sastre and J. D. Gale, *Microporous Mesoporous Mater.*, 2001, **43**, 27.
- A. Corma, M. T. Navarro, F. Rey, J. Rius and S. Valencia, *Angew. Chem., Int. Ed.*, 2001, **40**, 2277.
- A. Corma, M. J. Díaz-Cabañas, J. Martínez-Triguero, F. Rey and J. Rius, *Nature*, 2002, **418**, 514.
- A. Corma, F. Rey, S. Valencia, J. L. Jorda and J. Rius, *Nat. Mater.*, 2003, **2**, 493.
- R. Castaneda, A. Corma, V. Fornes, F. Rey and J. Rius, *J. Am. Chem. Soc.*, 2003, **125**, 7820.
- A. Corma, M. T. Navarro, F. Rey and S. Valencia, *Chem. Commun.*, 2001, **16**, 1486.
- A. Corma, M. J. Díaz-Cabañas and F. Rey, *Chem. Commun.*, 2003, **9**, 1050.