

ITQ-16, a new zeolite family of the beta group with different proportions of polymorphs A, B and C

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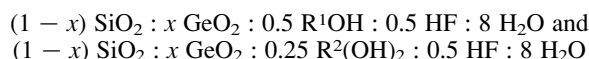
ITQ-16 is a new zeolite family formed by polymorphs A, B and C of the beta intergrowth in which the proportion of polymorph C can be controlled by changing the organic structure directing agent and/or by changing the Ge content of the synthesis gel; ITQ-16 can be synthesised either in fluoride or fluoride-free medium and Al can be introduced in the framework giving a material with very strong Brønsted acidity.

Beta is the only high silica zeolite with a three-dimensional system of 12-membered ring pores (MRP) that has found commercial applications up to now.¹ Zeolite beta is formed by an intergrowth of polymorphs A and B which gives the typical XRD pattern of this zeolite (Fig. 1).

Over 20 years ago, Newsam *et al.*² predicted that a third polymorph with a closely related structure should also exist. We have showed that polymorph C not only exists, but can be synthesised as a unique phase by working in either fluoride³ or in OH⁻ fluoride free media.⁴ The structure of polymorph C is formed by a three-dimensional system of rectilinear 12 MRP channels, and the corresponding XRD pattern is shown in Fig. 1.

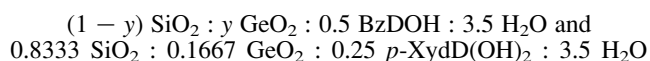
In the present work, we show that it is possible now not only to synthesise the pure polymorph of C (ITQ-17), but also a new family of materials (ITQ-16) can be prepared where the three polymorphs A, B and C exist and the ratio C/(A + B) can be varied as desired. This can be achieved by using different organic structure directing agents (OSDAs) in the synthesis, and also by working in different ranges of gel compositions and crystallization conditions. It will be shown here that ITQ-16 can be synthesised in fluoride as well as in a fluoride-free media.

The general synthesis conditions employed in this work for the experiments in fluoride media were as follows:



where R¹ and R² are the OSDAs shown in Scheme 1 and x was varied between 0.0196 and 0.1667. The OSDAs were prepared

according to methods reported in the literature.⁵ ITQ-16 zeolite was also synthesised in alkaline media, starting with the following gel compositions:



where y was 0.0625 and 0.1667. For ITQ-16 synthesised by the alkaline route, 3 wt% (with respect to the total weight of SiO₂ and GeO₂) seeds of pure ITQ-17 zeolite were added to the synthesis gel in order to promote crystallisation.

The gels were autoclaved at 150 °C for different crystallisation times and the solids were recovered by filtration and then were extensively washed with distilled water and dried at 100 °C, overnight. Table 1 shows the synthesis conditions studied in this work as well as the crystalline phase obtained in the final solids.

Syntheses 1–5 show that the level of polymorph C present in the final solid obtained from the same starting synthesis gel can be varied by using different organic structure directing agents. In this way, p-XydD²⁺ (sample 2) and BzD⁺ (sample 1) give pure polymorph C, while BzQ⁺ (sample 3) gives a mixture of the three polymorphs (Fig. 2). ITQ-16 can also be obtained with other OSDAs, such as dPyrrP²⁺ and in this case a different ratio of C/(A+B) polymorphs is observed (Fig. 2, sample 4). It is noted that polymorph C is not detected when using TEA⁺ (sample 5) as the OSDA in the same synthesis conditions.

The ratio of the three polymorphs in ITQ-16 can also be controlled by modifying the cation composition of the synthesis gel. For instance, when using BzD⁺ as the OSDA, it can be seen in Fig. 3 that the proportion of polymorph C increases when increasing the Ge content of the synthesis gel (Table 1; samples 1, 6–9).

ITQ-16 can also be synthesised in fluoride-free alkaline media. In this case, highly concentrated gels and longer crystallisation periods are required for the synthesis of ITQ-16 (Table 1; samples 10–12). The formation of ITQ-16 in alkaline

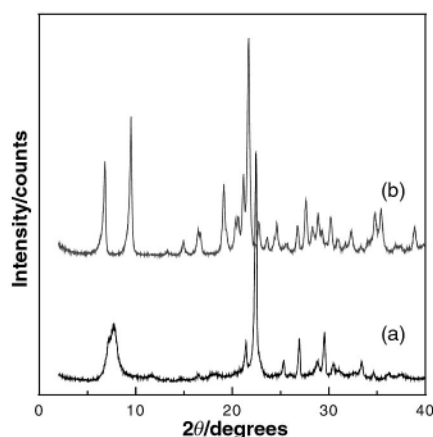
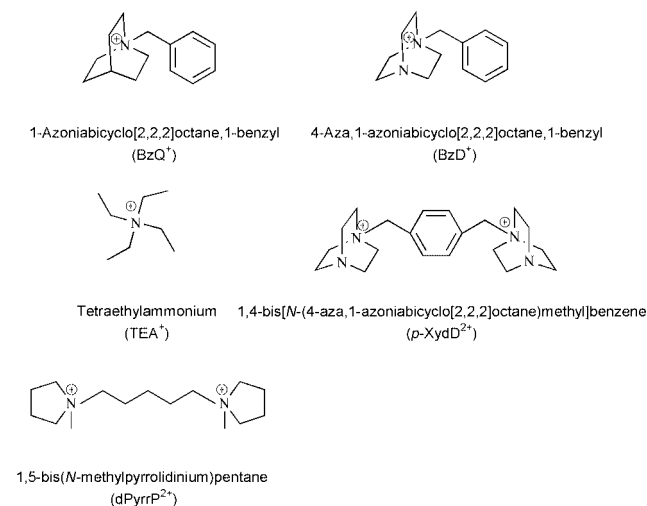


Fig. 1 X-Ray diffraction patterns of as-prepared zeolite beta (a) and pure polymorph C (ITQ-17) (b).

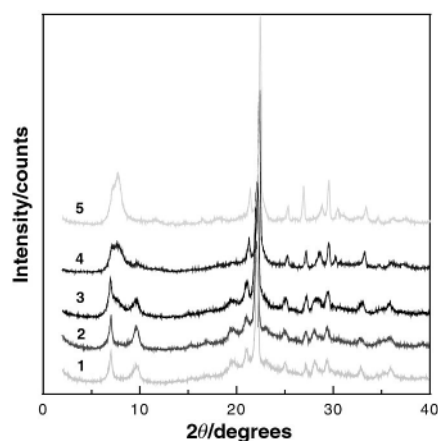
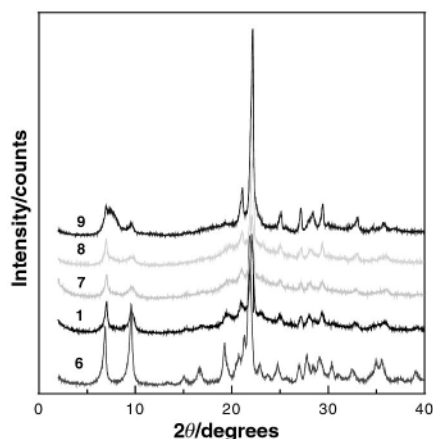


Scheme 1

Table 1 Synthesis conditions and zeolitic structures obtained using different OSDAs and Ge contents in the crystallisation gel

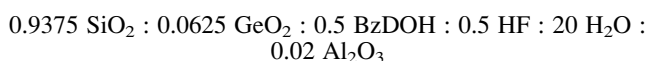
Sample	Crystallisation time	OSDA	Ge/(Si + Ge)	Structure	Percentage of polymorph C ^a
1	13 h	BzD ⁺	0.0625	ITQ-17	100
2	19 h	<i>p</i> -XydD ²⁺	0.0625	ITQ-17	100
3	20 h	BzQ ⁺	0.0625	ITQ-16	46
4	12 d	dPyrrP ²⁺	0.0625	ITQ-16	31
5	24 h	TEA ⁺	0.0625	Beta	0
6	14 h	BzD ⁺	0.1667	ITQ-17	100
7	15 h	BzD ⁺	0.0385	ITQ-16	85
8	48 h	BzD ⁺	0.0278	ITQ-16	52
9	13 h	BzD ⁺	0.0196	ITQ-16	27
10 ^b	5 d	<i>p</i> -XydD ²⁺	0.1667	ITQ-16	66
11 ^b	6 d	BzD ⁺	0.1667	ITQ-16	48
12 ^b	7 d	BzD ⁺	0.0625	ITQ-16	40

^a The percentage of polymorph C was estimated from the XRD patterns as the integrated area below the characteristic peaks at *ca.* 7.0 and 9.5° with respect to the total area in the range 5–12°. ^b Syntheses carried out in alkaline fluoride-free gels.

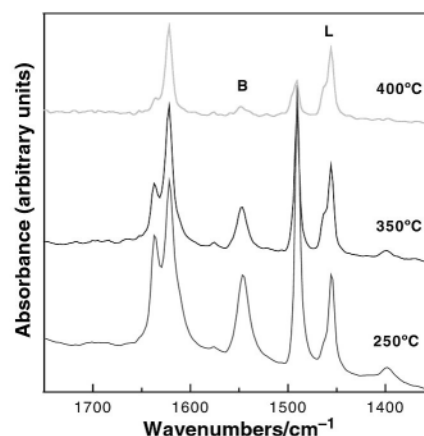
**Fig. 2** X-Ray diffraction patterns of as-prepared ITQ-16 zeolites synthesised with different OSDAs (samples of Table 1).**Fig. 3** X-Ray diffraction patterns of as-prepared ITQ-16 zeolites synthesised from gels with different Ge content (samples of Table 1).

media requires lower Si/Ge ratios than when the synthesis was carried out in fluoride media. Thus, it appears that Ge plays a very important role in driving the synthesis towards the formation of polymorph C between the other possible polymorphs which constitute the beta zeolite intergrowth.

For practical catalytic uses it is interesting to introduce acidity in the samples. We have succeeded in incorporating isomorphically Al into the ITQ-16, and one of the possible synthesis gel compositions is given below.



An Al-ITQ-16 material was obtained after 10 days of crystallisation at 150 °C. The resulting Al-ITQ-16 shows a

**Fig. 4** IR spectra of adsorbed pyridine of the Al-ITQ-16 sample at different desorption temperatures (B and L indicate the characteristic IR bands of pyridine adsorbed on Brönsted and Lewis acid sites, respectively).

unique resonance peak at 53 ppm in the ²⁷Al MAS NMR spectrum assigned to the presence of Al in tetrahedral coordination.

Acidity was measured after calcination of the sample at 500 °C, by means of pyridine adsorption–desorption. The IR spectra of adsorbed pyridine (Fig. 4) indicate the formation of pyridinium ions (*ca.* 1545 cm⁻¹) associated with the presence of Brönsted acid sites, as well as a band of pyridine coordinated to extraframework or partially dislodged Lewis acid Al atoms generated upon calcination (*ca.* 1450 cm⁻¹). It can be seen in Fig. 4 that Brönsted acid sites have been generated by the introduction of framework Al, and some of these sites can retain pyridine upon desorption at 350 and 400 °C and 10⁻² Torr, indicating the presence of very strong acid sites in Al-ITQ-16.

In conclusion, ITQ-16 is formed by polymorphs A, B and C, and the proportion of polymorph C in the sample can be controlled by changing the organic structure directing agent and/or by changing the Ge content of the synthesis gel. ITQ-16 can be synthesized either in fluoride or fluoride-free medium and Al can be introduced in the framework giving a material with very strong Brönsted acidity.

Notes and references

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