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Synthesis of a New Zeolite Structure ITQ-24, with Intersecting 10- and 12-Membered Ring Pores

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The use of zeolites for shape-selective catalytic processes is likely to be expanded by the synthesis of new structures formed by pores of different dimensions. In this sense, SSZ-33, SSZ-26, and CIT-1 were the first materials reported presenting a multidirectional pore system formed by intersecting 10MR (member ring) and 12MR channels that provide access to the internal network through both type of pores.¹ These structures can be thought as members of a family of disordered materials wherein the two end members denoted as polymorphs A and B are formed by the same periodic building unit, but with different stacking sequences. The zeolite structure formed by the ABAB... stacking sequence corresponds to polymorph A of orthorhombic symmetry, while that formed by the ABCABC... stacking sequence corresponds to polymorph B with monoclinic symmetry.^{1,2} CIT-1 material corresponds to the pure polymorph B,³ while SSZ-26 and SSZ-33 would be faulted structures formed by approximately 15% and 30% of polymorph B and 85% and 70% of polymorph A, respectively.^{1,2}

It was reported that a hypothetical structure, denoted as polymorph C,^{1,2} would be formed by 12MR and 10MR pores with a space group *Cmmm* by stacking the layers of polymorph A in an AAA... stacking sequence. It has been a challenge to obtain this hypothetical zeolite, but the synthesis of a pure polymorph of intergrowth structures is not a simple task, and only in a very few cases has it been successfully done.^{3–6} As a notorious difference, the proposed structure of the polymorph C of the SSZ-33/SSZ-26/CIT-1 family contains double-four-membered rings (D4MR) as secondary building units. Recently, we have shown that it can be possible to direct the syntheses toward D4MR containing zeolites by the isomorphic incorporation of Ge atoms into the siliceous zeolite frameworks.^{3–10} Thus, it may be feasible to obtain the elusive structure of polymorph C of the SSZ-33/SSZ-26/CIT-1 family by following this synthesis approach.

In the present work, a new zeolite (named ITQ-24) with intersecting 12MR and 10MR channels has been synthesized in OH[−] media and using hexamethonium cation as SDA. A typical synthesis gel for preparation of Al-ITQ-24 materials has the following molar composition: 5.0 SiO₂:1.0 GeO₂:0.15 Al₂O₃:1.5 R(OH)₂:30 H₂O, where R(OH)₂ is hexamethonium dihydroxide. The gel was prepared by dissolving GeO₂ (1.46 g from Aldrich) in a solution of R(OH)₂ (0.499 M, 42.0 g). Tetraethyl orthosilicate (14.54 g from Aldrich) and aluminum triisopropoxide (0.856 g from Aldrich) were then hydrolyzed in the solution, and the mixture was stirred gently until complete evaporation of the alcohols formed. After 15 days of crystallization at 448 K in a PTFE-lined stainless steel rotating (60 rpm) autoclave, a crystalline solid was obtained by filtration, exhaustively washed with water and acetone, and dried at 373 K for 12 h. This synthesis procedure allows the direct

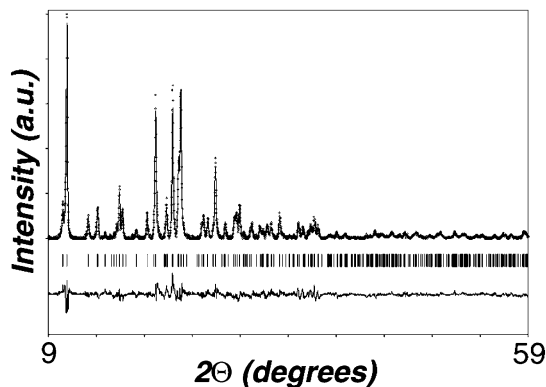


Figure 1. Observed (crosses) and calculated (line) X-ray powder diffraction patterns of calcined Al-ITQ-24 zeolite as well as the difference profile (bottom). The short tick marks below the pattern give the positions of the allowed Bragg reflections.

incorporation of Al in the framework and generates catalytically active acid sites. It is also possible to synthesize the corresponding titanasilicate ITQ-24 material wherein Ti occupies framework positions (see Supporting Information).

The structure of ITQ-24 has been determined and is topologically coincident with that proposed for the hypothetical polymorph C of the SSZ-33/SSZ-26/CIT-1 family.^{1,2} Indeed, the XRD pattern of the calcined ITQ-24 material was indexed according to an orthorhombic unit cell with the following unit cell parameters: $a = 21.254$, $b = 13.521$, $c = 12.609$ Å. The Rietveld refinement of the crystal structure was successfully performed in the space group *Cmmm*. The refined atomic coordinates are given as Supporting Information, while Figure 1 shows the good agreement between the observed and calculated XRD patterns.

The details of the Rietveld refinement are given as Supporting Information. The projections of the ITQ-24 structure along the different crystallographic axes are shown in Figure 2.

There, the presence of a tridirectional pore system of intercrossing 12MR and 10MR channels is shown. The first set of 12MR straight channel runs perpendicularly to the *ab* plane with a pore aperture of approximately 7.7×5.6 Å. A second set of 12MR sinusoidal channels is placed along the *a* axis with a pore aperture of 7.2×6.2 Å. Finally, there is a third 10MR channel system that intersects perpendicularly to both 12MR channel systems with a pore opening of 5.7×4.8 Å. In contrast to polymorphs A and B, the sinusoidal 12MR channel of polymorph C, that surrounds the D4MR cages, lies parallel to the plane *ab*. Meanwhile, in the polymorphs A and B, this channel system is also sinuous along the *c* direction. By taking advantage of the high contrast of the scattering power between Si and Ge, it is possible to calculate the Ge distribution among the different T sites. It was observed that the highest Ge

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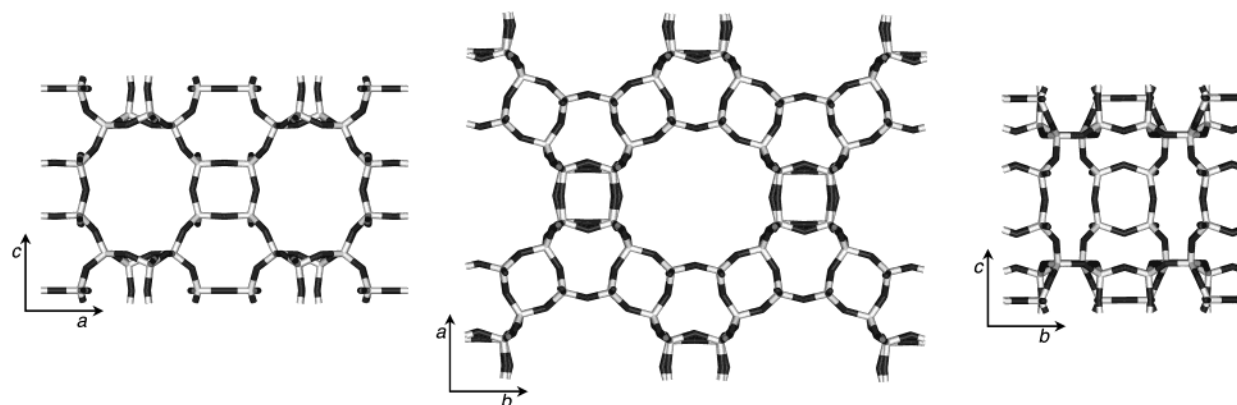


Figure 2. Projections of the ITQ-24 structure along the crystallographic axes.

concentration between the different crystallographic positions is found at the T1 site (31%), that corresponds to those sites placed at the D4MR units of the ITQ-24 structure, while the other T sites contain a much lower concentration of Ge (<10%). The preferential occupation of T1 sites is further supported by the observed lengthening of the averaged T1–O distance (1.663 Å) with respect to the other T–O distances (1.587, 1.625, and 1.601 Å for T2–O, T3–O, and T4–O bonds, respectively). These results clearly indicate the preferential occupation of Ge atoms in the D4MR cages, in good agreement with other previously reported Ge containing zeolites^{4,7–10} and our hypothesis of the preference of this cation for such secondary building units. Noticeably, Al containing ITQ-24 materials have been synthesized by following a one-step synthesis procedure. It has been stated by means of ²⁷Al-MAS NMR spectroscopy that the Al was isomorphically incorporated into the framework and mostly remains there upon calcination as deduced from the presence of the resonance at 55 ppm in both as-prepared and calcined ²⁷Al-MAS NMR spectra (given as Supporting Information). The acid properties of the calcined Al-ITQ-24 have been evidenced by the infrared spectra of the OH region, and by stepwise pyridine desorption of the Al-ITQ-24 sample. Indeed, the calcined Al-ITQ-24 shows an absorption at 3618 cm^{−1} attributed to an acid bridging hydroxyl groups that disappears when adsorbing pyridine. Meanwhile, pyridinium cations are formed, as deduced from the characteristic band at 1545 cm^{−1} (see Supporting Information). Thus, we can conclude that Al^{IV} was isomorphically incorporated into framework positions and has generated acid sites in ITQ-24 structure.

Also, the synthesis of Ti containing ITQ-24 materials was successful as is indicated by the presence of the intense charge-transfer UV–vis band in the spectrum of the calcined material at 217 nm characteristic of Ti in framework positions (see Supporting Information).^{11–13}

Finally, the Al containing ITQ-24 zeolite has been found to be catalytically active and selective for alkylation of benzene with propylene at 398 K and 3.5 MPa of pressure using a benzene-to-propylene ratio of 3.4 and a spatial velocity (WHSV) referred to the olefin of 12 h^{−1}. Under these experimental conditions and 30 min of time on stream, the conversion was 59.7% with a selectivity to cumene of 99.2%.

In conclusion, a new 10MR and 12MR zeolite, named ITQ-24, has been synthesized, and it has been found that its structure is coincident to that predicted for the hypothetical polymorph C of the CIT-1/SSZ-26/SSZ-33 family. More importantly, stable acid and redox ITQ-24 materials can be prepared, that open new possibilities for catalysis with zeolites, overcoming some drawbacks of zeolites of the SSZ-33/SSZ-26/CIT-1 family for industrial applications, such as the nature of the organic structure directing agents (OSDA) and the difficulty of introducing catalytically active heteroatoms in framework positions.¹⁴

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Supporting Information Available: Experimental details, atomic coordinates of ITQ-24 structure, NMR, IR, and UV–vis spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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