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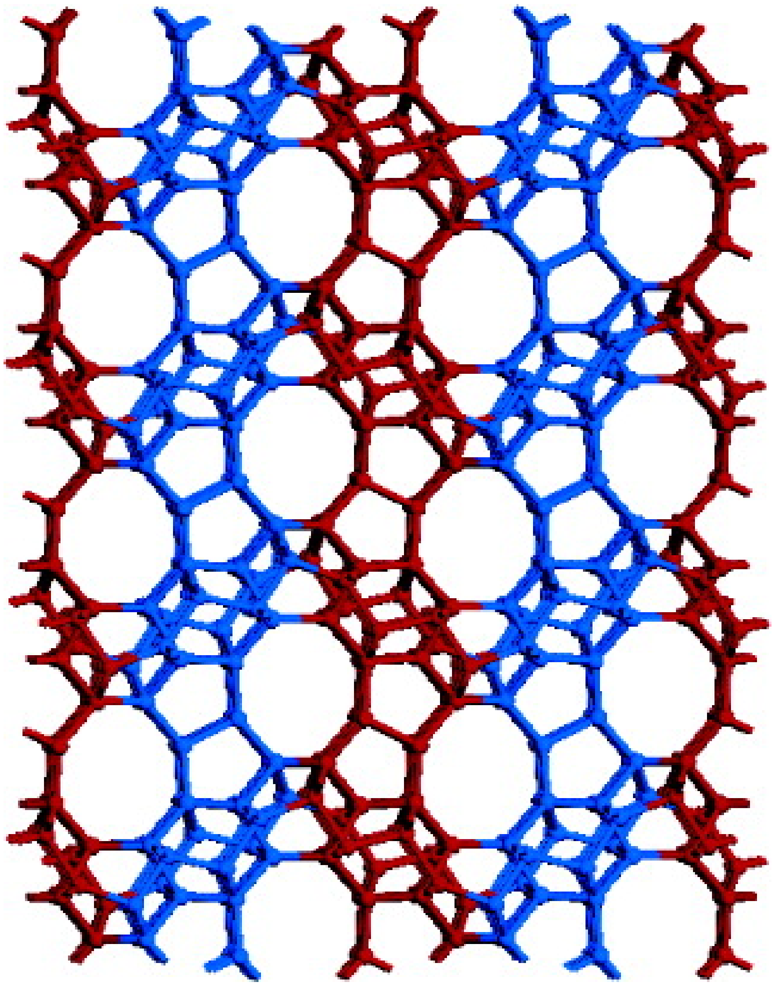

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Synthesis and Structure of the Bidimensional Zeolite ITQ-32 with Small and Large Pores

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In the last years, several groups have been involved in the synthesis of low framework density and/or ultralarge pore zeolites[1−5] that may open new possibilities for catalysis. However, separation and purification of gas mixtures by selective adsorption of one or more of their components, today, is a matter of enhanced interest owing to exploitation of large gas fields. Then, it is not surprising that the number of patents dealing with gas separation by adsorption and adsorption of air for pollution control is growing very rapidly[6−10] due to the development of new zeolitic materials as well as to the advances in zeolitic membranes.[11] Indeed, zeolites offer the possibility of changing the pore diameter, cavity and channel sizes, framework Si/Al ratios, and amount and type of exchanged cations, allowing their use in gas separation through size or steric exclusion, thermodynamic, and kinetic selectivity. More specifically, silica-rich small-pore eight-membered ring zeolites offer new possibilities for gas separation in the field of natural gas, propylene−propane separation,[7−10] and linear and branched olefins.[12] These zeolites, by being highly thermally and hydrothermally stable and resistant to acids and other impurities, can offer some advantages over more conventional aluminosilicates for certain separations.

In this work, we present the synthesis and structure determination of a new bidimensional eight-membered ring zeolite, denoted as ITQ-32, which presents a relatively large pore volume (0.16 cm^3/g) and pore apertures of 3.5 × 4.3 Å.

Two organic structure directing agents (SDA's) were found to be able to direct the synthesis toward ITQ-32 structure, whose structures are given as Supporting Information. The first SDA was *N*,*N*,*N'*,*N'*-tetramethyldecahydrocyclobuta[1,2-*c*;3,4-*c'*]dipyrrolidinium (SDA-1) and was prepared by means of a photochemically induced [2 + 2] cycloaddition reaction of *N*-methylmaleimide followed by a reduction with $LiAlH_4$ and quaternization with methyl iodide. The second SDA was 4-cyclohexyl-1,1-dimethylpiperazinium (SDA-2) and was prepared by alkylation of *N*-cyclohexylpiperazine with methyl iodide. The iodide salts were transformed into the corresponding hydroxide by using an anionic exchange resin (detailed synthesis procedures are given as Supporting Information).

The crystallization of ITQ-32 zeolites was performed in PTFE-lined stainless steel autoclaves at 175 °C under continuous tumbling from gels of the following molar compositions:

$$SiO_2{:}x\ Al_2O_3{:}0.25\ \text{SDA-1}(OH)_2{:}0.5\ HF{:}7\ H_2O$$

$$SiO_2{:}x'Al_2O_3{:}0.5\ \text{SDA-2}(OH){:}0.5\ HF{:}7\ H_2O$$

where x was varied between 0.01 and 0.033 (for SDA-1), and x' was varied between 0 and 0.033 (for SDA-2).

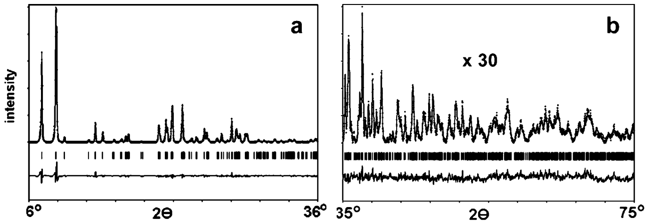

Figure 1. Low-angle (a) and high-angle (b) X-ray powder diffraction patterns of essentially pure silica ITQ-32 zeolite in the calcined form as well as the difference profile (bottom). The short tick marks below the pattern give the position of the allowed Bragg reflections.

This synthesis procedure allowed the direct incorporation of Al in the zeolite framework, generating acid sites, as well as the essentially pure silica analogue (detailed synthesis procedures are given as Supporting Information).

The structure of ITQ-32 has been determined from powder X-ray diffraction data. The synchrotron XRD pattern of the calcined ITQ-32 sample with Si/Al = 32 was indexed according to an orthorhombic unit cell with the following unit cell parameters: a = 13.692(2), b = 24.064(8), c = 18.187(3) Å. From the observed systematic absences, two space groups were possible: *Cmca* (No. 64) and the noncentrosymmetrical *C2cb* (No. 41). By assuming the most probable centrosymmetrical space group, *Cmca*, the application of a slightly modified version of direct-methods origin-free modulus sum function to the intensity data extracted from the calcined pattern[13] showed the positions of 7 of the 9 symmetry-independent Si atoms. The remaining two positions showed up in the Fourier synthesis after a Rietveld refinement cycle. This result is consistent with the ^{29}Si MAS NMR spectrum of the nearly pure silica ITQ-32 (see Figure 4 in the Supporting Information) that shows the presence of at least six different resonances, but it can be fitted using nine different signals that correspond to the nine T sites proposed for the ITQ-32 structure. Finally, the position of the oxygen atoms was found by interpolation. This topology was further confirmed by Rietveld refinement using the laboratory X-ray diffraction data of the essentially pure silica ITQ-32 zeolite (details of the Rietveld refinement and the atomic coordinates for the pure silica ITQ-32 are given as Supporting Information). Figure 1 shows the very good agreement between experimental (crosses) and calculated (line) X-ray diffraction patterns.

A convenient description of the ITQ-32 structure can be made by considering the building unit formed by two fused [4^15^8] cages (see Figure 6 of Supporting Information) sharing a common four-ring and contains all the T atoms except T9. This site (shown as blue atoms in Figure 2a) is bridging two building units to give rise to the formation of chains that contains 12-ring windows located between the two basic units.

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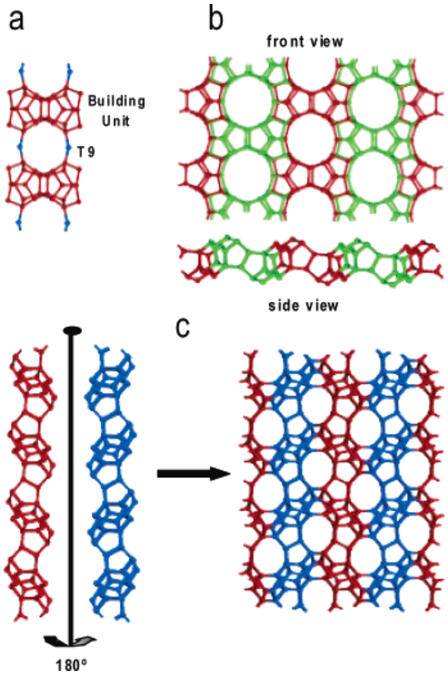

Figure 2. Structure of ITQ-32 zeolite. (a) Chain formation by the linkage through T9 atoms (blue) of characteristic building units of ITQ-32 zeolite (shown in red). (b) Layer formation by subsequent packing of adjacent chains (shown as green and red). (c) Stacking of different layers (red and blue) to build up the ITQ-32 structure.

The connectivity between adjacent chains is made by linking T9 sites to T6 atoms and T5 positions with T4 atoms, as it is shown in Figure 2b (front view). This yields to the formation of a corrugated layer (side view in Figure 2b).

The full structure can be obtained by generating a new layer by applying the 2-fold axis along the *b* direction and then connecting these layers through T2−T2, T5−T5, and T8−T9 linkages, as it is schematically shown in Figure 2c.

The pore topology of ITQ-32 zeolite exhibits a unidirectional small 8R channel system along the *a*-axis, with a pore aperture of 3.5 × 4.3 Å (see Figure 2c). The 8R pore system is perpendicularly crossed by relatively short 12R channels, which interconnect two neighbored 8R channels along the *c* direction. These bridged 12R channels have a diameter of 6.3 and 16.2 Å in length. A figure showing the cross-section of the 12R channel is given as Supporting Information. Therefore, all of the 8R pores are interconnected through bridging 12R channels, resulting in a bidirectional pore structure.

This pore topology is consistent with the micropore volume determined from the N_2 adsorption isotherm (0.16 cm^3/g). The relatively large micropore diameter obtained by applying the Horvath−Kawazoe formalism to the Ar isotherm (5.3 Å) can be explained by considering that straight 8R channels are frequently crossed by large pores.

According to the X-ray diffraction results and to the refined ITQ-32 structure, the center of the SDA-1 molecule is most probably placed at (0,0,0). This site corresponds to the 4*a* lattice complex with 2/*m* point symmetry. This symmetry is compatible with the SDA molecule in chair conformation and also nicely fits with the size and shape of the elongated cavities. Additionally, ^{19}F MAS NMR spectroscopy sheds light on the fluoride location. Indeed, the NMR spectrum shows a main resonance at −78 ppm, which is very similar to that reported for nonasil,[14] indicating that fluoride anions in ITQ-32 are probably located close to the four-ring unit of the $[4^15^8]$ cage, as occurs in pure silica nonasil zeolites. Also, ^{13}C MAS NMR spectra and elemental analyses of the as-prepared ITQ-32 materials indicate that the SDA remains intact inside the pores of the zeolite (see Supporting Information).

ITQ-32 zeolite was successfully synthesized as a silicoaluminate, yielding to the formation of acid sites after SDA removal. SDA-1 allows the incorporation of Al within a range of Si/Al ratios from 13 to 32, while with SDA-2 samples with Si/Al > 300 can be obtained (chemical analyses of the zeolites are given as Supporting Information). The incorporation of Al in framework positions was proven by means of ^{27}Al MAS NMR spectroscopy that shows a resonance at 54 ppm in the as-prepared form, which is assigned to Al in tetrahedral coordination. After calcination, the signal of tetrahedrally coordinated aluminum remains and only a very minor band at 0 ppm (assigned to octahedral aluminum in extra framework positions) appears. Acidic properties of the Al−ITQ-32 sample of Si/Al ratio of 17 was studied by pyridine adsorption followed by IR spectroscopy and by TPD-MS of ammonia. Pyridine adsorption experiments did not show any acidity due to the small pore opening of the channels that precludes the diffusion of pyridine molecules inside the zeolite pores. However, ammonia TPD-MS experiments indicate that Al−ITQ-32 zeolites possess strong acid sites able to retain ammonia at temperatures as high as 416 °C.

In conclusion, a new bidirectional zeolite with 8R pores connected by 12R channels, termed ITQ-32, has been synthesized and its structure solved. This zeolite can be prepared as a nearly pure silica zeolite and as aluminosilicate. In the latest case, acidic properties are developed.

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Supporting Information Available: Experimental procedures for preparation and chemical analyses of the SDA's and ITQ-32 zeolites, the ^{13}C and ^{29}Si MAS NMR spectra of ITQ-32 zeolite, figure of a cross-section of the ITQ-32 structure showing the 12R pores, and X-ray data collection and Rietveld refinement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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