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Synthesis and Structure of the new bi-dimensional 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 is today 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 8-membered ring zeolites offer new possibilities for gas separation in the field of natural gas, propylene-propane separation,[7-10] and lineal 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 8 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 x 4.3 Å.

The synthesis of high quality ITQ-32 samples was successfully carried out using two different organic structure directing agents (SDA's), whose structures are given as supporting information. The first SDA was N,N,N',N'-tetramethyl-decahydro-cyclobuta[1,2-*c*;3,4-*c'*]dipirrolidinium (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-dimethyl-piperazinium (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 175ºC 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).

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 by means of X-Ray diffraction analyses. The High-resolution XRD synchrotron 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 non-centrosymmetrical *C2cb* (No. 41). By assuming the most probable centrosymmetrical space group *Cmca*, the application of the slightly modified 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 were shown 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 2 of supporting information) that shows the presence of at least six different resonances. Nevertheless, the spectrum required 9 different signals to be fitted, and these correspond to the 9 T sites proposed for the ITQ-32 structure. Finally, the position of the oxygen atoms were found by interpolation. This topology was further confirmed by Rietveld refinement of the laboratory X-Ray diffraction data obtained on 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 a very good agreement between experimental (crosses) and calculated (line) X-Ray diffraction patterns.

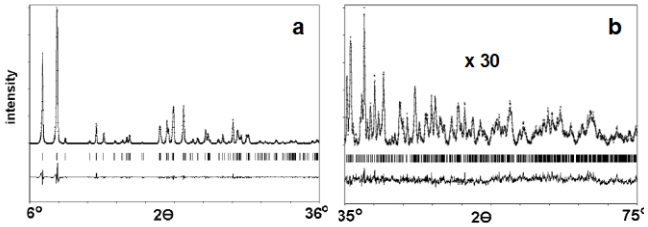

Figure 1. Low angle (a) and high angle (b) X-ray powder diffraction patterns of essentially pure silica ITQ-32 zeolite in the calcined form as well as the difference profile (bottom). The short tick marks below the pattern give the position of the allowed Bragg reflections.

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 4 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.

The connectivity between adjacent chains is made by linking T9 sites to T3 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 twofold axis along *b* direction and then connecting these layers through T2-T2, T5-T5 and T8-T9 linkages, as it is shown in Figure 2c.

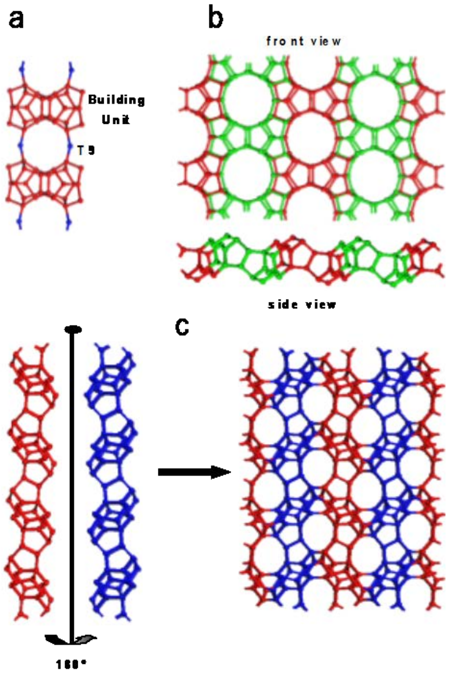

Figure 2. Structure of ITQ-32 zeolite. a) Chain formation by the linkage through T9 atoms (blue) of characteristic building units of ITQ-32 zeolite (shown in red). b) Layer formation by subsequent packing of adjacent chains (shown as green and red). c) stacking of different layers (red and blue) to build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

The pore topology of ITQ-32 zeolite exhibits an unidirectional small 8R-channel system along *a* axis, with a pore aperture of 3.5 by 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 *c* direction. These bridged 12R-channels have a diameter of 6.3 Å and 16.2 Å in length. A figure showing the cross-section of the 12R-channel is given as supporting information. Then, all the 8R-pores are interconnected through bridging 12R-channels, resulting in a bi-directional 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 *4a* 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 probably Fluoride anions in ITQ-32 will be located close to the 4-ring unit of the [4^15^8] cage as occurs in pure silica nonasil zeolites.

ITQ-32 zeolite was successfully synthesized as silico-aluminate yielding to the formation of acid sites after SDA removal. SDA-1 allows the incorporation of Al from a Si/Al ratio of at least 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 proved 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 extraframework 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 ºC.

In conclusion, a new bidimensional zeolite with 8R and 12R pores, named 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 ^{29}Si-MAS-NMR spectrum 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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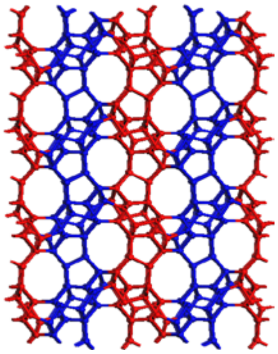

A new bidimensional zeolite containing 8R and 12R pores, denoted as ITQ-32, has been synthesized and its structure solved by means of X-Ray diffraction analyses. This zeolite presents a relatively large pore volume (0.16 cm^3/g) and pore apertures of 3.5 x 4.3 Å and can be prepared as a nearly pure silica zeolite and as aluminosilicate. In the latest case, acidic properties are developed.