A New Microporous Polymorph of Silica Isomorphous to Zeolite MCM-22

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Zeolites are microporous materials useful in a number of processes, including heterogeneous catalysis, separation, ion exchange, and sorption applications. While their microporous features are characteristic of each zeolitic structure, generally the chemical composition can be varied in some extent by synthesis. However, there seems to be a range of preferred chemical compositions for almost any zeolite, and frequently, trying to go beyond this range results in the crystallization of a different phase. Thus, it appears to be difficult to crystallize pure silica polymorphs of most zeolites, and no pure-silica polymorph containing two independent systems of channels, one of them consisting of interconnected large cages, has been reported. Such a kind of structure is present in the intermediate Si/Al ratio zeolites MCM-22[1] and SSZ-25[2] which can be easily crystallized in a range of Si/Al ratios of about 15 to 50. Attempts to synthesize them with higher Si/Al ratios failed.[3,2] The conclusion was drawn that this phase cannot spontaneously nucleate when the Si/Al ratio is too high.[3] The structure of these zeolites comprises two independent void spaces: a sinusoidal 10MR channel plus large 12MR supercages connected to each other through 10MR windows, which form a second independent system of 10MR channels.[4] In addition to its importance from a fundamental point of view, the synthesis of microporous phases with very low heteroatom content is of importance when looking for applications where hydrophobic properties are required or when the active centers are wanted to be far apart from each other. For example, MCM-22 has been shown to be a good cracking catalyst,[5] but for its application as an FCC additive it would be convenient to prepare the material with Si/Al ratios above those presently available by direct synthesis. Here we report on the synthesis of a new polymorph of silica with zeolitic nature,

referred to as ITQ-1,[6] which belongs to this family of zeolites. Such a material is formed after calcination of a layered precursor containing a high concentration of not randomly distributed connectivity defects. Our synthetic procedure allows us also to prepare aluminosilicates with high Si/Al ratios.

The synthesis was done in the absence of aluminum and alkali cations by using *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAda⁺OH⁻): 1.125 g of silica (Aerosil 200, Degussa) was added to 15.874 g of a 0.29 M solution of TMAdaOH. The mixture was heated for 17 days at 423 K in a PTFE-lined stainless steel autoclave under rotation (60 rpm). The final pH of the reaction mixture was 11.2 with no signs of TMAda⁺ decomposition. The crystalline product had a Si/Al ratio >3000. Al can also be incorporated into ITQ-1 using the above procedure, but a decrease in the crystallization rate is observed in contrast to the reported synthesis of MCM-22 zeolite, where the higher the Al content, the faster the crystallization rate.[3] Interestingly, the rate of crystallization of pure silica ITQ-1 can be greatly enhanced by the combined use of 1-TMAda⁺ and a secondary amine (dipropylamine or, preferably, hexamethyleneimine), using the procedure described above and an amine/1-TMAda⁺ molar ratio of 1.2. The reason for the beneficial effect of using two organic additives is unclear at present, although the stabilization of two types of void spaces could be best accomplished by the cooperative use of the amine (to stabilize the 10MR channel) and 1-TMAda⁺ (to stabilize the 12MR cage). Although we found evidence for the presence of both TMAda⁺ and HMI in the as-made material (¹³C MAS NMR and C, N, H elemental analysis), this does not necessarily support a "cooperative templating effect". A mere effect of the amine on the gel chemistry or as a loose pore-filling stabilizer cannot be ruled out.

The X-ray powder diffraction pattern of the as-synthesized material is similar to that of as-synthesized SSZ-25 and most likely corresponds to a layered precursor such as those already proposed for the borosilicate ERB-1[7] and the aluminosilicate MCM-22.[8] After calcination at 580 °C the occluded organics are removed and the 3D framework is formed by condensation of SiOH groups in site T1 of the proposed structure.[4] The changes observed in the XRD pattern of ITQ-1 upon calcination are consistent with those already described by Lawton et al. for MCM-22 materials.[8] The powder X-ray diffraction pattern of calcined ITQ-1 is indicative of a highly crystalline material and is coincident with those of calcined MCM-22 and SSZ-25. N₂ adsorption of calcined ITQ-1 reveals a 0.17 cm³/g micropore volume, similar to those of MCM-22 (0.17) and SSZ-25 (0.18).[9] This is the first reported example of the synthesis of this type of zeolite with Si/Al > 50. In the typical MCM-22 synthesis conditions increasing the Si/Al ratio causes coprecipitation of MFI or MTW zeolites,[3] while in the

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Table 1. Assignment of ^{29}Si MAS NMR Lines for As-Made and Calcined Pure-Silica ITQ-1^a

as-made ITQ-1			calcined ITQ-1			
δ	I	assignment	δ	I	assignment	population
−91.8	2.4	Q^2				
−94.2	17.6	Q^3	−98.6	4	Q^3	
−102.3	1.0	Q^3	−102.6	0.9	Q^3	
−105.0	1.6	Q^4	−105.5	11.2	Q^4, T2	12
−110.1	24.3	Q^4	−111.1	21.5	Q^4, T8 + T7	24
−113.8	2.6	Q^4	−113.4	11.4	Q^4, T3	12
−115.5	17.8	Q^4	−116.3	14.5	Q^4, T6 + (T4 or T5)	16
−119.5	4.7	Q^4	−120.1	8.5	Q^4, T1 + (T4 or T5)	8

^{a} Chemical shifts (δ) in ppm from TMS; relative intensities (I) normalized to account for 72 T atoms per unit cell; T sites numbering and population according to ref 4; $Q^n = Si(OSi)_n(OH)_{(4-m)}$.
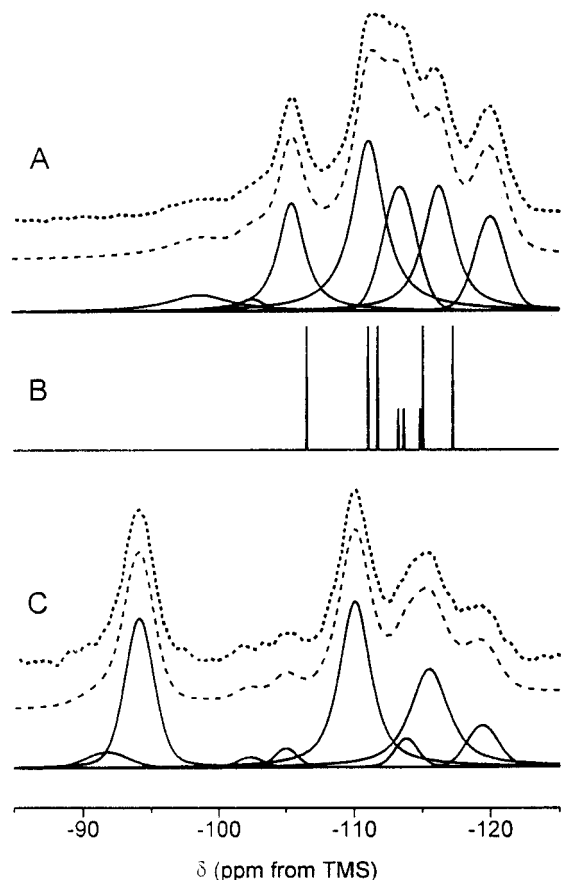

Figure 1. ^{29}Si MAS NMR spectra of calcined (A) and as-made (C) pure silica ITQ-1; experimental (···), simulated (- - -) and deconvoluted components (—). Experimental spectra recorded at 5 kHz spinning rate using a Varian VXR-400S WB spectrometer at 79.5 MHz, with 3.0 μs pulse of $3\pi/8$ rad and 60 s recycle delay. Trace B is the spectrum calculated with experimental correlation of Thomas et al.[11] by using TOT angles derived from the proposed hexagonal structure.[4]

SSZ-25 synthesis conditions SSZ-24 crystallizes for pure-silica compositions.

The ^{29}Si MAS NMR spectrum of calcined pure silica ITQ-1 (Figure 1A) shows, together with a small fraction of Si−OH defect groups (6.9% of total Si), the presence of at least five $Si(OSi)_4$ sites with relative intensity ratios of 3:6:3:4:2 (Table 1). Resolution of $Si(OSi)_4$ resonances must be ascribed to crystallographic inequivalence. According to the proposed structure for MCM-22, there are 8 sites in the hexagonal model with multiplicity ratios of 3:3:3:3:3:1:1:1 and 13 sites in the orthorhombic model with multiplicity ratios of 1:1:1:1: 2:2:1:1:2:2:1:1:2.[4] Our five $Si(OSi)_4$ lines can be considered as having intensities of 3:(3+3):3:(3+1):(1+1) (in the hexagonal model) or 3:(2+2+2):3:4:2 (in the orthorhombic one), i.e., there are several crystallographic sites with overlapping resonances. As expected, the spectrum shown in Figure 1A matches almost perfectly in shape, number of lines, and relative intensities the spectrum previously published for MCM-22 with Si/Al ≈ 50.[10] On the other side, the ^{29}Si MAS NMR spectrum agrees well with the simulation calculated from average TOT angles[11] (Figure 1A,B), taking into account both the empirical nature of the relationship used and the limitations of the Rietveld refinement of powder X ray data with respect to the accuracy of Si−O distances and Si−O−Si angles, as well as to the real symmetry of the refined structure. Very recently Kennedy et al. showed the ^{29}Si MAS NMR of deboronated MCM-22 and made a tentative assignment of the peaks in favor of the orthorhombic form of the proposed structure.[12] We shall not discuss here about which symmetry represents better the true structure as this would make no difference regarding the basic topology of the framework and our NMR data can support both models equally well. We will adhere, however, to the simpler hexagonal description of the structure as it reasonably matches our spectrum.

Interestingly, the number of connectivity defects in the as-made ITQ-1 sample (that is, the layered precursor) is very high and exceeds the minimum concentration required in the layered precursor according to the mechanism proposed for the formation of ERB-1[7] and MCM-22.[8] According to this mechanism, the as-made layered precursor transforms into the 3D framework upon calcination by condensation of T1OH groups (where T1 is tetrahedral site 1 in the proposed hexagonal structure of MCM-22). T1 sites are 5.6% of total tetrahedral sites. As shown in Figure 1C, the as-made sample presents a concentration of Q^3 (i.e., $Si(OSi)_3OR$, R = H, TMAda$^+$) of 29.2%. Obviously, connectivity defects are also needed to balance the organic cation charges, and as shown by Koller et al.,[13] connectivity defects appear usually in larger concentration than needed from charge balance considerations when the synthesis is carried out with OH$^−$ as the mineralizer. Interestingly, a comparison of the ^{29}Si MAS NMR spectra of the as-made and calcined ITQ-1 reveals that in addition to T1−OH defects, other connectivity defects

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occur between well-defined crystallographic sites, i.e., the defects are not randomly distributed but occur between two distinct crystallographic sites with relative populations of 3:3. A close inspection of the structure proposed for calcined MCM-22 shows that these sites could be any of the couples (T2−T3), (T3−T6), (T6−T7), or (T7−T8). Couple T7−T8 can be disregarded if the proposed mechanism for MCM-22 is assumed to work for ITQ-1, because a systematic lack of connectivity between these sites would destroy the intralayer 10MR sinusoidal channel, which has been shown to be already present in MCM-22 layered precursors.[8] We think it is between T2 and T3 where the systematic defect of connectivity exists, because of two reasons. First, the T2−O−T3 angle is 136.2°, and thus this connection must be rather stressed for a pure-silica material. This would explain the high specificity of the connectivity defects. It could be argued that there are also very stressed TOT angles of 180° in the hexagonal description of MCM-22.[4] However, these angles are very unlikely to exist in the localized environment and could be an artifact imposed by the average hexagonal symmetry detected by XRD. Actually, in the orthorhombic description of the structure these linear TOT angles become 157° and 161°. Anyway, these angles involve sites with a relative abundance of 1 (sites T1, T4, and T5) which could not account for the whole concentration of defects. Second, sites T2 and T3 would resonate very close to the "missing lines" in the spectrum of the as-synthesized material (−105 and −113 ppm observed, −106 and −112 ppm expected). Our proposed assignment of the ^{29}Si MAS NMR lines is presented in Table 1.

Finally, in addition to differences in synthesis procedures and composition of the materials, ITQ-1 differs from MCM-22 and SSZ-25 in two other significant features: first, the high quality and sharpness of the XRD patterns of the as-made and calcined ITQ-1 (supporting information). There is an apparent contradiction between that sharpness (compared to MCM-22 or SSZ-25) in the pattern of as-made ITQ-1 and its high concentration of defects. The enhanced sharpness can be due either to a higher thickness of ITQ-1 crystals (≈0.15 μm compared to ≈0.03 μm for MCM-22[14] and ≪0.1 μm for SSZ-25[9]) or to the nonrandom distribution of the defects. While we have no definitive answer to this question, it should be noted that apparent contradictions between NMR data (sensible to local environments) and XRD (which averages and promediates the long-range order) have been seen before;[15] second, the presence of the very strong resonance at −94.2 ppm in the ^{29}Si MAS NMR spectrum of as-made ITQ-1. We have detected this line (with much lower intensity) only for SSZ-25 and MCM-22 materials with Si/Al > 25. A plausible reason for this is overlapping with Si(3Si,Al) or Si(2Si,2Al) lines and splitting of the line due to the presence of Al in Si(2Si,Al,OH) species. A different concentration of defect sites due to the presence of Al is also possible.

Calorimetric[16] and theoretical[17] studies on the stability of silica polymorphs show that dense and microporous pure-silica frameworks all fall in a narrow range of stability. Then, crystallization of microporous silica materials must be controlled by kinetic factors or by the stabilizing effect of the interaction between the silica framework and the organic molecule residing in its cavities. Interestingly, under otherwise identical synthetic conditions using TMAda⁺, the presence of alkali-metal cations (either Na⁺ or K⁺) leads to the crystallization of SSZ-24 when the autoclaves are rotated during heating. When the synthesis is carried out in static conditions, K⁺ and Na⁺ lead to SSZ-24 and SSZ-31, respectively, and no crystalline phases appear in the absence of alkali cations.[18] This shows the large structure-directing effect that alkali cations can have in the synthesis of zeolites and opens a possible new route to synthesize new materials using known templates, as the absence of alkali cations can prevent the formation of otherwise kinetically favored phases.

Supporting Information Available: X-ray powder diffraction patterns of as-made and calcined MCM-22, SSZ-25, and ITQ-1 (1 page). Ordering information is given on any current masthead page.

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