Chiral Zeolites

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A Pure Silica Chiral Polymorph with Helical Pores**

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Since the discovery of the complex structure of zeolite Beta in the late 1980s,[1] which comprises a disordered intergrowth of several polymorphs, one of them being chiral, the synthesis of zeolite materials with a chiral framework has been a very challenging goal.[2] Indeed, it can be argued that, when proper spatial conditions are met, a chiral zeolite could transfer its chirality to the product of a chemical or physical process occurring within its pores. The importance of stereochemical control arises from the fact that chiral molecules typically provoke a different response in living beings depending on their chirality, a phenomenon already recognized by Pasteur over 150 years ago.[3] Despite an early report claiming a minor enantiomeric excess (*ee* ca. 5%) in a reaction catalyzed by a zeolite Beta synthesized using a chiral structure-directing agent (SDA),[4] there have only been significant advances in the last few years. The chiral nature of several zeolites had passed unnoticed until very recently, and calorimetric measurements on a natural zeolite indeed suggested a potential for use in processes that entail enantiomorphic molecular discrimination.[5] However, those chiral zeolites contain non-helical pores, and it can be expected that these pores will impose less severe steric restrictions. Recently a germanosilicate zeolite[6] (structure type code STW) with a helical channel was reported, but its stability is severely limited by its very high germanium content ($Ge/Si > 1$): amorphization occurs above 673 K, and it is likely that even at room temperature, ambient humidity could degrade the structure to a large extent.[7] This limited stability is also observed in the case of a mesoporous chiral zeolite-like material with an -ITV interrupted framework, which cannot withstand ambient humidity at room temperature without fast structural collapse.[8] None of the known chiral zeolites has been synthesized in a pure homochiral form to date. The synthesis of a chiral silica-based, as opposed to germania-based, zeolite with helical channels would be thus highly desirable. Herein we present HPM-1,[9] the first pure silica chiral zeolite with a helical pore, STW structure type, and having the high stability of silica-based zeolites.

The chiral zeolite HPM-1 was synthesized by using achiral 2-ethyl-1,3,4-trimethylimidazolium cations as the SDA. Under the reaction conditions reported for silicogermanate SU-32 using diisopropylamine as SDA and with Ge/Si ratios exceeding unity, there is a strong competition for crystallization between SU-32 and SU-15 (an achiral germanosilicate, framework type SOF, currently unknown in pure silica composition); frequently crystals of both phases along with unreacted GeO_2 are found in the final solid product.[6] By contrast, no framework type SOF or amorphous silica are found using our conditions.

Calcination of HPM-1 at 973 K affords the removal of fluoride anions and organic cations without structural degradation. Furthermore, HPM-1 withstands calcination up to at least 1173 K, and it is not affected by ambient humidity. This outstanding stability is due to the SiO_2 composition and the lack of connectivity defects of HPM-1: After calcination, ^{29}Si magic-angle spinning (MAS) NMR spectroscopy reveals four resonances with approximate 1:2:1:1 relative intensities in the Q^4 region, with no hints of Si−OH or $Si{-}O^-$ defects in the region around $\delta = -102$ ppm (Figure 1). This essentially perfect SiO_2 network has a micropore volume of 0.22 $cm^3\,g^{-1}$.

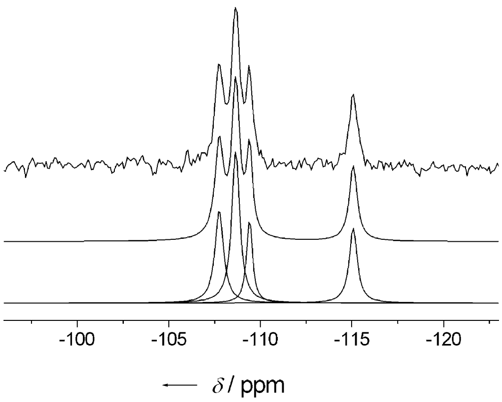

Figure 1. ^{29}Si MAS NMR spectrum of calcined pure silica HPM-1 (top to bottom: experimental, simulated, and deconvoluted components). The four $Si(OSi)_4$ resonances are assigned to (left to right) Si2, Si1 + Si3, Si4, and Si5, based on the order of decreasing chemical shifts (increasing SiOSi average angles), see the Supporting Information, Table 4S.

Rietveld refinement of a $P6_122$ model based on the STW structure type went smoothly with no restraints on bond lengths or angles in the final stages (see the Supporting Information). The refined structure contains Si−O bonds and O-Si-O angles (1.578–1.630 Å, average 1.599 Å and 106.6–114.0°, average 109.5°, respectively) in the usual ranges for silica zeolites, while the Si-O-Si angles are more spread and tend to be slightly sharp, although still within typical ranges (139.7–170.7°, average 150.6°). The small Si-O-Si angles of calcined HPM-1 are confirmed by inspection of its ^{29}Si MAS

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NMR spectrum (Figure 1): Three of the four distinct resonances observed (4/5 of the total Si) appear at quite low fields ($\delta = -107.7$ to --109.4 ppm) and are assigned to Si in double four-ring units (D4R). The remaining resonance appears at a chemical shift of $\delta = -115.1$ ppm, which is in a more typical range for $Si(OSi_4)$ species in tectosilicates and is assigned to the only crystallographic site that does not belong to D4R units. A calculation of the Si-O-Si average angle of each crystallographic Si site by using the empirical equation of Thomas et al. and the chemical shifts observed in Figure 1[10] is in good agreement with the refinement results, although the angles are always sharper when calculated from the ^{29}Si spectrum (Supporting Information).

The main pore in HPM-1 consists of an helical arrangement of $[4^6 5^8 8^2 10^2]$ cavities with access through windows of 10 tetrahedra, 10-membered ring (10MR), with minimum and maximum crystallographic free diameters of 5.36 and 5.80 Å, respectively. Figure 2 shows the helical arrangement of 10MR windows in the main pore. Two smaller 8MR pores (3.29–4.56 Å) run perpendicular to the screw axis. From powder XRD data it is not possible to discern the relative proportion of $P6_122$ and $P6_522$ crystals. Although no chiral reagent was used in the synthesis spontaneous resolution cannot be ruled out: Spontaneous chiral symmetry breaking during the crystallization of chiral crystals from achiral units has been reported,[11] and, according to recent findings, may be more frequent than thought.[12] This may provide the basis for synthetic strategies toward a purely homochiral STW zeolite.

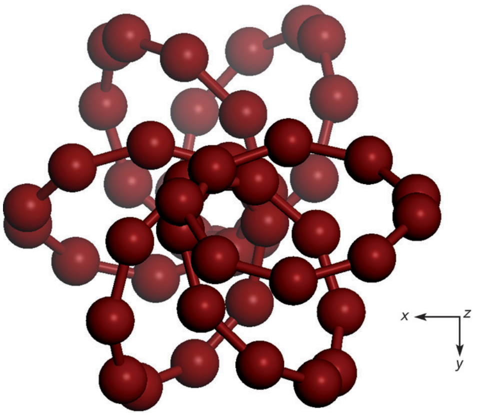

Figure 2. The helical arrangement of the rings of ten Si–O pairs that limit diffusion through the main pores of HPM-1. Space group $P6_122$; viewed along [001], oxygen atoms omitted for clarity.

We would like to suggest one point for reflection regarding the feasibility of silica zeolites. Silica-STW has no "flexibility window",[13] and its feasibility has been explicitly ruled out on the basis of molecular mechanics calculations.[14] The existence of a flexibility window has been very convincingly proposed as a useful discriminating parameter for the real existence of hypothetical frameworks,[15] and it was recently proposed that the existence of a broad flexibility window would increase the likelihood of a good matching between an organic structure-directing agent and the framework, thus increasing the probability of a favorable stabilization energy.[16] Conversely, the lack of such a window would translate into a low probability for finding favorable host–guest interactions unless a particularly suitable SDA could adequately fit into the voids of the rigid framework. On the other hand, molecular mechanics calculations have concluded that, owing to the existence of SiOSi angles that are stressed for a pure silica composition, pure silica STW is an unfeasible material (see Table 3 in reference [14]). Herein we want to stress that criteria or calculations applied on a calcined zeolite may eventually fail, because the synthesized zeolite is in fact a host–guest complex. It has been recently demonstrated that fluoride occluded in pure silica D4R affords a flexibilization of the whole framework by polarization of the Si–O bond.[17] Thus, rigid-tetrahedra models may fall short in their predictions if host–guest interactions provide an enhanced flexibility relaxing an otherwise strained framework.

In summary, we have synthesized a chiral SiO_2 zeolite, HPM-1, with helical channels that may offer the possibility to test asymmetric processes on zeolites if the next step, namely obtaining a homochiral solid or selectively blocking homochiral pores,[18] is realized.

Experimental Section

In a typical synthesis, tetraethylorthosilicate was hydrolyzed in a hydroxide solution of 2-ethyl-1,3,4-trimethylimidazolium (ROH), and the mixture was stirred while allowing ethanol and some water to evaporate. HF (48% aq., Aldrich) was then added. The mixture with a composition SiO_2:0.5 ROH:0.5 HF:4.5 H_2O was heated to 175 °C for 11 days in teflon vessels inside stainless steel bombs tumbled at 60 rpm. The structure of the pure SiO_2 material was refined by using laboratory powder diffraction data (Cu $K\alpha_1$ radiation); details are given in the Supporting Information.

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