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Communications

Distribution of Fluorine and Germanium in a New Zeolite Structure ITQ-13 Studied by ^{19}F Nuclear Magnetic Resonance

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The synthesis of novel zeolite structures is a very active research field in material science and catalysis. The ultimate goal is to develop new zeolites that possess tailor-made pore systems and chemical properties to closely fit specific applications. Among the hypothetical zeolite structures, those possessing three-directional medium-size pores are specially attractive because of its potential interest in the petrochemistry and refining industry. Recently, our group has reported the crystal structure of a new zeolite named ITQ-13 (International Zeolite Association code ITH),[1] shown in Figure 1, formed by three sets of interconnecting medium-pore channels: one 9-ring system along the *a* axis with an aperture of 4.0 × 4.9 Å and two 10-ring channel systems along the *c* and *b* axis of dimensions 4.8 × 5.7 and 4.7 × 5.1 Å, respectively. At present, this is the only zeolite possessing 9- and 10-ring intercrossing channels.

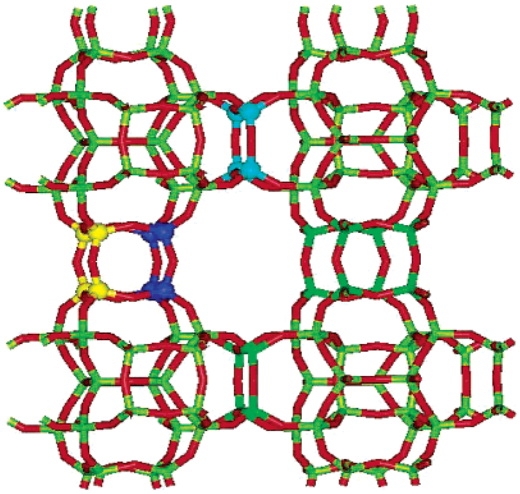

Figure 1. View along the axis [1 0 1] of the ITQ-13 structure. Circles indicate crystallographic T2 (dark blue), T5 (yellow), and T7 (light blue) positions, which are involved in the formation of the cages where fluoride anions are located. Sites T2 and T5 are forming the double four-membered ring cage, and T7 is constituting the four-membered ring shared by the fused $[4^15^26^2]$.

Another peculiarity of zeolite ITQ-13 is the simultaneous presence of two sets of fluoride anions located into two type of cages to compensate the doubly positively charged hexamethonium (HM^{2+}) cations used as structure-directing agents (SDAs).[1] The first set of fluorides is placed at the center of double four-membered rings (D4R) and the second close to the four-membered (4R) ring shared by two fused $[4^15^26^2]$ cages (sites T7 in Figure 1), producing a short Si−F distance.[1] Fluoride locations analogous to the latter have been reported for [F, TPA]-MFI and [F,DMBAO]-STF zeolites.[2,3] In this way, fluoride may also act as a structure-directing agent by stabilizing the four-membered ring and the small D4R cages with constrained T−O−T angles below

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Table 1. Chemical Composition and the Main Results Derived from the ^{19}F NMR Spectra of Ge-Free and Ge−ITQ-13 Zeolites

sample	unit cell volume (Å^3)	chemical analysis				NMR data			
		Si/Ge^a	Ge/u.c.^{b}	F/N^a	SDA/u.c.^{b}	Si/Ge$_{D4R}$^{a,c}	Ge$_{D4R}$/u.c.^{b,c}	$I_{F(D4R)}$^{d}	$I_{F(4R)}$^{d}
SiO_2−ITQ13	3143	∞	0	1.0	1.98	∞	0	1	0.8
25Ge−ITQ13	3160	25	2.2	0.8	1.91	25.9	2.1	0.96	0.63
10Ge−ITQ13	3199	11	4.8	0.7	1.94	11.2	4.6	0.85	0.30
5Ge−ITQ13	−	6	8.0	0.6	1.92	9.4	5.4	0.70	0.30

^{a} Molar ratios. ^{b} Number of atoms or molecules per unit cell. ^{c} $Ge_{D4R}/u.c. = 2 \times \sum nI_{F(nGe)}$, $I_{F(nGe)}$ being the intensity of the NMR signals (normalized to 1) of ^{19}F anions at D4R cages containing n Ge T atoms; $n = 0$, 1, and 3 for the signals at −38, −20, and −8 ppm, respectively. $Si/Ge_{D4R} = (56 - Ge_{D4R})/Ge_{D4R}$. ^{d} Intensity of the signal of ^{19}F within the D4R ($I_{F(D4R)}$) and the [$4^15^26^2$] cages ($I_{F(4R)}$) referred to that of ^{19}F inside D4R in siliceous ITQ-13 (signal at −38 ppm in spectrum of Figure 3a).

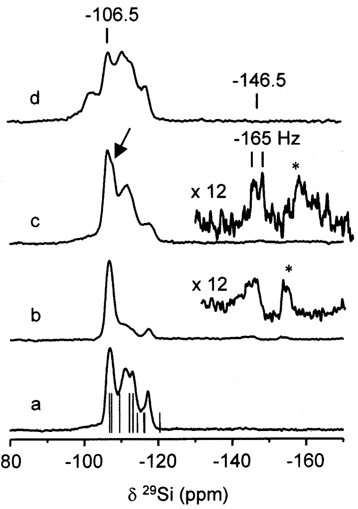

Figure 2. ^{29}Si MAS NMR spectra of sample SiO_2−ITQ13 (a−c). (a) Comparison with the chemical shift predicted for crystallographic sites: T2, T5, T7, T6, T3, T8, (T1, T9), and T4 (from left to right) indicated with lines; (b) the ^{19}F to ^{29}Si CP spectrum (contact time 5 ms and a recycle delay 80 s); (c) the ^{1}H to ^{29}Si CP spectra recorded at 170 K (lower) and 220 K (upper) (contact time 5 ms and recycle delay 3 s). (d) The ^{29}Si MAS NMR spectrum of sample 25Ge−ITQ13. The asterisks indicate spinning sidebands.

140°.[4,5] Since T−O−T angles close to 130° are the preferred for Ge−O bonds,[6] isomorphous substitution of Ge for Si constitutes an alternative way to direct toward the ITQ-13 structure, as proposed for other Ge-containing zeolites, such as ITQ-7, ITQ-17, and ITQ-21.[4,5,7]

For samples synthesized in a fluoride medium, ^{19}F within the D4R units acts as an NMR probe of the local composition, as its chemical shift depends on the amount of Ge atoms incorporated at the D4R sites.[4,5] Here, ^{19}F MAS NMR spectroscopy is used to investigate the distribution of F and Ge atoms in D4R and fused [$4^15^26^2$] cages in zeolite Ge−ITQ-13.

Samples were synthesized following the procedure described firstly,[8] from gels with the following molar composition

$$(1-x)SiO_2{:}xGeO_2{:}0.28HM(OH)_2{:}0.56HF{:}7H_2O$$

where x was adjusted to obtain solids with the Si/Ge ratios of ∞, 25, 11, and 6. The crystallization was performed at 135 °C for 24 days. The magic-angle spinning (MAS) NMR spectra were recorded with a Bruker AV 400 spectrometer, using a 2.5-mm Bruker probe for ^{19}F and BL7 and Doty XC4 probes for ^{29}Si.

The X-ray diffraction (XRD) patterns of the samples are characteristic of pure ITQ-13 zeolites. The isomorphous substitution of Ge for Si in Ge−ITQ-13 is proved by the expansion of the unit cell volume because of the larger ionic radii of Ge (see Table 1). The XRD peaks broaden as the Ge content increases (see Figure 1 of Supporting Information), according to the diminution of the crystal size observed by scanning electronic microscopy. Interestingly, the broadening is larger for the (0 0 l) reflections, suggesting that the structural disorder along the c axis of ITQ-13 increases with the Ge content.

The chemical analysis of the samples, shown in Table 1, indicates that the occluded structure-directing agent remains intact after the hydrothermal treatment. In the Ge-free zeolite, the charge of the SDA is fully compensated by the fluoride anions. However, the amount of fluoride in Ge−ITQ-13, specially at high Ge contents, is insufficient to compensate the positive organic charge, which must be balanced by SiO^-, generating connectivity defects.

Figure 2a shows the ^{29}Si MAS NMR spectrum of SiO_2−ITQ-13, consisting of four bands of Si (4Si) at −106.5, −111.1, −113.0, and −117.2 ppm, which is in fairly good agreement with that predicted for the ITQ-13 structure, with nine nonequivalent crystallographic sites.[1,9] The comparison with the calculated chemical shift, drawn in Figure 2a, suggests the assignment of the signal at −106.5 to sites T2 and T5, forming the D4R units in ITQ-13, whereas the peak intensity is 29% of the total as expected from the site multiplicity: (8 T2 + 8 T5)/56 T sites. The signal at −106.5 ppm dominates the ^{19}F to ^{29}Si cross-polarization (CP) spectrum of Figure 2b, supporting its assignment to (T2 + T5) Si positions close to fluorine. Two components for T2 and T5 sites are resolved in the ^{29}Si spectrum acquired at 170 K (Figure 2c, lower part).

The shortest Si−F distance in ITQ-13 is associated with fluoride linked to silicon atoms at the 4R in the fused [$4^15^26^2$] cages. Similar fluoride locations in other zeolite structures have been reported to give a high-field ^{29}Si NMR signal attributed to five-coordinated

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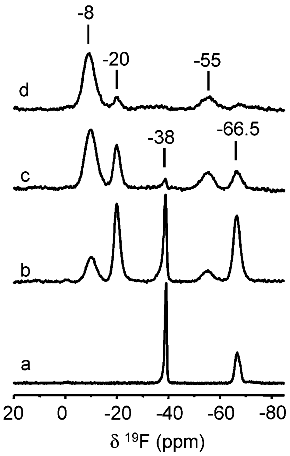

Figure 3. ^{19}F MAS NMR spectra of zeolites: (a) SiO_2−ITQ13, (b) 25Ge−ITQ-13, (c) 10Ge−ITQ-13, and (d) 5Ge−ITQ13. The acquisition conditions are as follows: spinning rates of 25 kHz, $\pi/2$ pulses of 4 μs, and recycle delays of 80 s.

silicon $[SiO_{4/2}F]^-$.[2,3,10,11] The detection of this site is not easy in ITQ-13 because of its low population (3.6% of the total silicon, according to the crystal structure), the ^{29}Si−^{19}F couplings, and the broadening derived by the disorder in fluoride location.[2,3,10,11] Even though, a band at −146 ppm is observed in the spectrum 2b registered under cross polarization from ^{19}F to ^{29}Si. This band is split into a doublet by a *J*-coupling with ^{19}F of 165 Hz, typical of $[SiO_{4/2}F]^-$ units in the ^{1}H to ^{29}Si CP spectrum recorded at 220 K (Figure 2c).[3,11] The changes in the ^{29}Si MAS NMR spectra by the presence of Ge are illustrated in Figure 2d for sample ITQ-13 with a Si/Ge = 25. The decrease of the Si (4Si) signals and the appearance of low field components, more prominent for samples richer in Ge, are consistent with the incorporation of Ge into the second coordination shell of Si.[4,12]

Figure 3 shows the ^{19}F MAS NMR spectra of Ge-free and Ge-containing ITQ-13 zeolites. The spectrum of sample SiO_2−ITQ-13 consists of a sharp signal at −38 ppm typical of ^{19}F within D4R,[13] and a broader one at −66.5 ppm, attributed to fluoride in the $[4^15^26^2]$ cages.[2,3] The intensities ratio, 1 (−38 ppm):0.8 (−66.5 ppm), is close to the site occupancy found by XRD, with some deficient fluoride content in the larger cages.[1] In Ge−ITQ-13, new ^{19}F signals emerge at −8, −20, and −55 ppm. As was stated in previous publications, the peaks at −8 and −20 ppm are attributed to ^{19}F anions within D4R formed by (7 Si, 1Ge) and (5 Si, 3Ge) or (4 Si, 4Ge), respectively.[4,5] On the basis of the low field shift observed when Ge is incorporated into the close environment of fluoride, we attribute the new signal at −55 ppm to ^{19}F within Ge-containing $[4^15^26^2]$ cages. Figure 3 shows that the relative intensity of the signals of ^{19}F inside the cages with Ge atoms increases with the Ge content. Following the procedure described in previous publications,[4,5] we have calculated the amount of Ge at the D4R units from the ^{19}F spectra. The results, collected in Table 1, clearly indicate that Ge preferentially occupy crystallographic sites (T2 and T5) at the D4Rs.

The quantitative analysis of the ^{19}F MAS NMR spectra shows a decrease in the fluoride content in Ge−ITQ-13, in agreement with the chemical analysis (see Table 1). For the sample richer in Ge (5Ge−ITQ13), the fluoride inside the D4R and $[4^15^26^2]$ cages decreases, approximately, 30% and 70%, respectively. Since the number of fused pair $[4^15^26^2]$ cages containing T7 sites equals that of D4R, it comes out that fluoride prefers to occupy D4Rs despite the formation of F−Si bonding with T7 sites.

To summarize, in Ge−ITQ-13, (i) Ge preferentially occupy crystallographic sites at D4R; (ii) as the Ge content increases, fewer fluoride anions are incorporated; (iii) fluoride is preferentially lodged within the smaller D4R cages.

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Supporting Information Available: X-ray diffractograms of the Ge−ITQ-13 zeolites (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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