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**Preferential location of Ge atoms in polymorph C of Beta zeolite (ITQ-17) and their structure directing effect: A computational, XRD and NMR study\*\***

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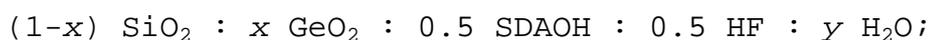
## Synthesis and characterization of Ge-ITQ-17

The exact synthesis, particularly the  $H_2O / (Si+Ge)$  ratio and crystallization time, were selected to produce pure ITQ-17 materials and are depicted in Table 1.

Tetraethylammonium hydroxide was commercially available and used as received. The BD cation was obtained as chloride by reacting 18.99 g (0.15 mol) of benzyl chloride with 25.75 g (0.225 mol) 1,4-diazabicyclo[2,2,2]octane (DABCO) in 200 ml of ethylacetate at room temperature, overnight. The resulting solid was filtered, exhaustively washed with ethyl acetate and diethylether and dried under vacuum for 12 hours. The elemental analysis and  $^1H$  NMR spectroscopy indicate that the mono N-benylation of DABCO occurs, being the purity of the BDCl over 98%. The BDCl was transformed into the hydroxide form by contacting an aqueous solution of BDCl (1 M) with a fourfold excess of an anion exchange resin (Amberlite IRN-78 supplied by Supleco). This exchange protocol was carried out twice in order to achieve 100% exchange. The final hydroxide solution was used as  $OH^-$  and SDA source simultaneously into the synthesis gel.

A typical ITQ-17 synthesis was carried out by mixing the tetraethylortosilicate (TEOS from Aldrich) with the above mentioned BDOH solution and appropriate amount of germanium

oxide (from Aldrich) until a clear solution is obtained. The ethanol formed during the hydrolysis of TEOS was evaporated at room temperature under continuous stirring. Then, the amount of water was adjusted to the gel composition shown below and hydrofluoric acid was added to the reaction mixture. The final gel composition was:



where  $x$  and  $y$  were chosen to give the ratios shown in Table

The crystallization was carried out at 150°C under autogenous pressure in Teflon-lined stainless-steel autoclaves and static conditions. The solids were filtered, washed with distilled water and dried at 100°C, overnight. Samples were withdrawn for each synthesis composition at different crystallization times until crystalline materials were collected. Crystalline materials were obtained at the crystallization times given in Table 1.

The organic elemental analysis indicates no decomposition of the occluded SDA during the hydrothermal synthesis as can be deduced from the C/N ratio (Table 2). The high crystallinity of the Ge-ITQ-17 samples can be clearly seen from the measured XRD patterns (Figure 1) and from micropore volume determinations (see Table 1 of article).

In-situ calcination of the as-prepared samples was performed in an Anton Parr HTK-16 High Temperature chamber attached to the diffractometer using a Pt sample holder as heating element. The sample was heated under air at 500°C and then, was evacuated under high vacuum ( $10^{-5}$  torr) and cooled down to 35°C. The diffraction measurements were carried out at room temperature under high vacuum to avoid any structural damage of the ITQ-17 samples.

**Table 1.** Synthesis conditions of Ge containing ITQ-17 samples

Sample	SDA	Gel composition				Temp (°C)	Time (h)
		Si/Ge	SDA/T(IV)	HF/T(IV)	H <sub>2</sub> O/T(IV)		
17Ge	TEA <sup>[a]</sup>	0.5	0.5	0.5	8	150	16
11Ge	BD <sup>[b]</sup>	2	0.5	0.5	8	150	15
7Ge	BD <sup>[b]</sup>	5	0.5	0.5	8	150	18
6Ge	BD <sup>[b]</sup>	7.5	0.5	0.5	8	150	26
4Ge	BD <sup>[b]</sup>	10	0.5	0.5	16	150	72

<sup>[a]</sup> Tetraethylammonium

<sup>[b]</sup> 1-benzyl-4-aza-1-azoniacyclo[2,2,2]octane

**Table 2.** Chemical analysis of ITQ-17 samples.

Sample	%C	%N	%H	%F	C/N <sup>[c]</sup>	C/N <sup>[d]</sup>
17Ge <sup>[a]</sup>	9.44	1.32	1.98	1.05	8.4	8.0
11Ge	13.69	2.47	1.87	1.22	6.5	6.5
7Ge	13.51	2.34	1.66	1.14	6.7	6.5
6Ge	14.28	2.56	1.84	0.87	6.5	6.5
4Ge <sup>[b]</sup>	12.48	2.19	1.67	1.37	6.6	6.5

<sup>[a]</sup>ITQ-17 obtained using TEA as SDA.

<sup>[b]</sup>includes amorphous material (approximately 15 wt%)

<sup>[c]</sup>calculated

<sup>[d]</sup>expected

### Computational details

Figure 2 shows the different atom types in the SDA and the charges obtained were:  $q(\text{C2})=-0.19$  (7 atoms),  $q(\text{C6})=-0.19$  (5 atoms),  $q(\text{C6}')=-0.03$  (1 atom),  $q(\text{N3})=-0.50$  (1 atom),  $q(\text{N4})=-0.56$  (1 atom),  $q(\text{H})=+0.23$  (19 atoms); where C2 is secondary carbon, C6 is aromatic carbon, N3 and N4 are tertiary and quaternary nitrogen atoms respectively, and H is hydrogen.

The orientation of BD is defined by the short range interactions with the micropore structure of ITQ-17 and in order to find the minimum energy conformation, the pure

silica structure was considered. In this way the complexity of handling the multiple possibilities for the Ge location is avoided. On the other hand, the positions of the fluoride anions are clear, since the presence of two F<sup>-</sup> and two D4Rs in the unit cell suggests one F<sup>-</sup> in each D4R. This point is further supported by means of NMR techniques as will be discussed later. With this initial setup a random set of 50 valid configurations for the organic template molecule have been generated, and the coordinates of all the atoms of the system, as well as the unit cell parameters, have been optimized by searching for the minimum energy configuration. The final optimized location of the SDA is shown in Figure 3.

#### **XRD Refinement on the as-prepared Ge-ITQ-17 material.**

In order to study the Ge distribution on the ITQ-17 non-calcined samples, the XRD pattern of the sample 7Ge (Si/Ge=1.8) was collected in an X'PERT PHILIPS diffractometer with Bragg-Brentano geometry and Graphite secondary monochromator. Intensity data obtained with a fixed divergence slit (1/2). Cu K $\alpha_{1,2}$  radiation ( $\lambda=1.5406$  and  $1.5444$  Å). Tube voltage and intensity: 50 KV and 40 mA. Scan range from 12 to 60° 2 $\theta$ . Step scan size and time 0.01° 2 $\theta$  and 15s.

After checking that the space group is the same than that found in the calcined sample (P42/mmc) by means of the program AJUST, a new refinement of the structure was performed by using the program FULLPROF99.

Si, Ge and O coordinates found for the corresponding calcined sample was used as starting positions for the as-prepared one.

F atoms were placed at the center of each D4R, assuming that these sites are fully occupied, as suggested by chemical analysis and  $^{19}\text{F}$  NMR data.

Two SDA were introduced per unit cell, as suggested by elemental analysis, but due to the high complexity of the occluded organic cations, they were modeled as single peaks containing all the electronic density of each template molecule.

The refinement was carried out by adjusting 8 profile parameters and 30 structural parameters, as in the corresponding calcined sample.

The calculated Ge distribution among the three symmetry independent T sites in the as-prepared sample is close to that found for the calcined sample (Table 3), clearly indicating a preferential occupation of D4R positions (T1 sites) by Ge. Moreover, a similar behavior is found in the T-O bond lengths; in this case, T1-O distance is 1.68(1) Å, and T2-O and T3-O distances are equal to

1.65(1) Å, confirming the preferential occupation of Ge in T1 sites.

**Table 3.** T sites Ge occupation of as-prepared and calcined Ge-ITQ-17 (7Ge) samples.

Sample	Ge occupation		
	T1*	T2**	T3**
As-prepared	8.6	2.0	0.7
Calcined	7.2	2.3	1.8

\* total number of T1 sites = 16

\*\* total number of T1 sites = 8

The minor differences found between the as-prepared and calcined samples occupation can be caused by the presence of the template molecules, due to the error introduced by modeling them as a single electronic density peak. These differences are not so large, specially at the T1 sites, suggesting that there are not significant changes in Ge distribution during calcinations. However, results obtained from calcined samples are usually more accurate, due to the lack of template and fluoride ions in the material, that results in a reduction of the number of parameters to be refined, and avoiding the requirements for a proper simulation of the organic component.

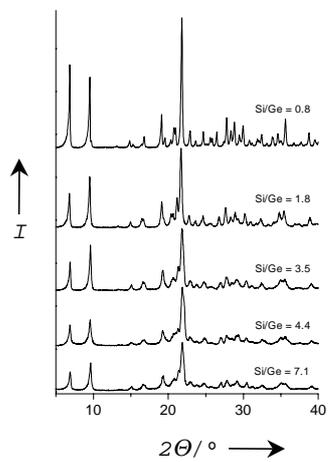


Figure 1\_Supporting information\_Corma et al

**Figure 1.** XRD patterns of the as-prepared ITQ-17 materials obtained with different Si/Ge ratios in the synthesis gel (see also Table 1).

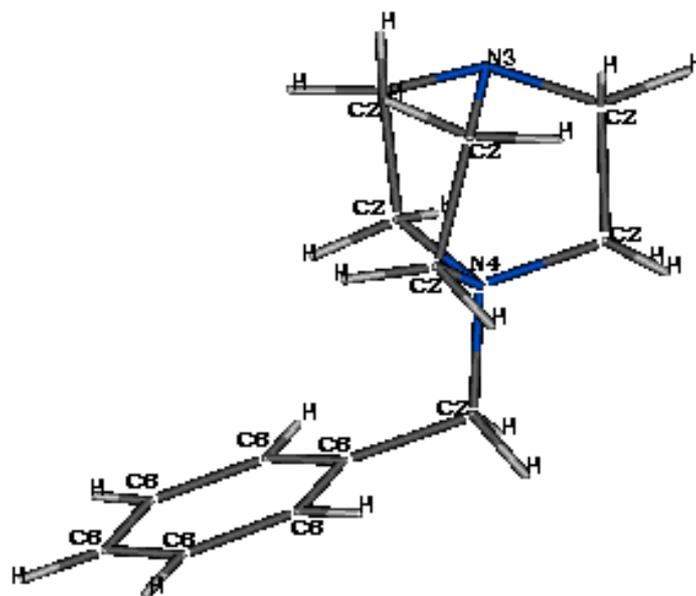


Figure 2\_Supporting information\_Corns et al

**Figure 2.** Structure and atom labelling of the organic structure directing agent used in the synthesis of ITQ-17,  $C_{13}H_{19}N_2OH$ : 1-benzyl-1,4-diazabicyclo[2.2.2] octane hydroxyde (BD).

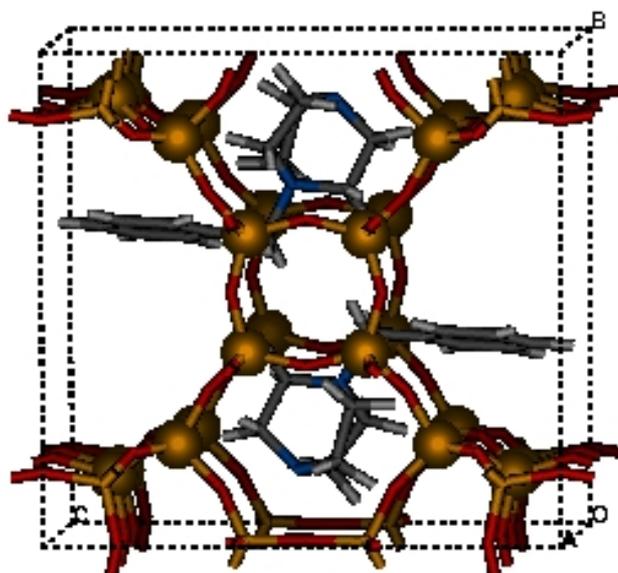


Figure 3\_Supporting information\_Cornas et al

**Figure 3.** Optimised location of the two SDA cations in the unit cell of ITQ-17. A pure silica composition ( $\text{Si}_{32}\text{O}_{64}$ ) has been used and the coordinates of all the atoms of the system have been optimised. Two fluoride anions have been introduced in the D4Rs (not shown).