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Pure Polymorph C of Zeolite Beta Synthesized by Using Framework Isomorphous Substitution as a Structure-Directing Mechanism[**]

Avelino Corma,[*] Marie T. Navarro, Fernando Rey, Jordi Rius, and Susana Valencia

Zeolites are crystalline tectoaluminosilicates, whose structure is formed by TO_4 tetrahedra (T = Al, Si) and each apical oxygen atom is shared between two adjacent tetrahedra. The main interest of these materials lies on the fact that the TO_4 tetrahedra are organized in such a way that micropores of regular dimensions are formed giving these materials molecular-sieve properties. The regular and shaped pores and cavities could act as microreactors selecting the transition state that better fits to a given particular structure. However, an important prerequisite for supramolecular inorganic host – guest chemistry will be production of tailor-made host systems with designed topologies and adapted surface properties.[1] Important advances towards this direction have been made by introducing organic cations into the synthesis media. The very relevant work carried out on this field by the groups of Davis and Zones[2–4] have allowed these authors to conclude that while organic cations play an important role as structure directing agents during the synthesis, very seldom they act as true templates, at least in the sense that this term is used in biological systems.[5] Therefore, it is not surprising that only in very few cases it can be claimed that the organic cations act as true templates.[6–8] This implies that, despite the important attempts to carry out "a priori design of zeolites",[9, 10] the synthesis of new zeolitic structures advances by accumulating knowledge on the influence of the different synthesis variables.

A more sophisticated achievement would be to direct the synthesis of zeolites, which are formed by an intergrowth of polymorphs, towards the production of a single, pure polymorph. As far as we know, this has been done in the case of SSZ-33, which corresponds to an intergrowth of two polymorphs, and one pure polymorph could be obtained by choosing the appropriate organic structure-directing agent (SDA).[8, 11, 12]

Zeolite Beta is accepted as a highly faulted intergrowth of two polymorphs, A and B, which are normally found in a 60:40 ratio.[13] However, it has been proposed that a third polymorph (polymorph C) should also exist even if has not been detected experimentally.[13] The structure of the proposed polymorph C of Beta is closely related to those of polymorphs A and B and could be generated from polymorph A simply by the recurrent application to the building layers of a shear operation along both a and b axes. In this way, the space group of polymorph A ($P4_122$) is transformed into the more symmetrical polymorph C ($P4_2/mmc$).

What is interesting is that the hypothetical structure of polymorph C has a three-dimensional pore topology, in which all three 12-membered-ring channels are linear, while in the case of the other two polymorphs one of the channels is sinusoidal.[13] An additional important structural difference between the different polymorphs is that polymorph C contains double four-membered-ring (D4MR) cages as secondary building units, namely two D4MR cages per unit cell (u.c.), while polymorphs A and B do not contain such secondary building units. If one takes into account that the D4MR cages should be under high tension in this structure, thereby introducing a certain instability, it is not surprising that polymorph C has been elusive under the synthesis conditions of zeolite Beta.

By means of theoretical calculations, we have found (see Supporting Information) that stability is gained in D4MR cages when germanium replaces silicon in the TO_4 tetrahedra.[14] Indeed, the isomorphous substitution of Si by Ge does not introduce any framework charge but allows angles and distances to vary and thereby stabilizing such a secondary

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[*] Prof. A. Corma, Dr. M. T. Navarro, Dr. F. Rey, Dr. S. Valencia
Instituto de Tecnología Química
UPV-CSIC Universidad Politécnica de Valencia
Avda. de los Naranjos, s/n, 46022, Valencia (Spain)
Fax: (+34) 96-3877809
E-mail: acorma@itq.upv.es

Dr. J. Rius
Institut de Ciència de Materials de Barcelona (CSIC)
Campus de la UAB, 08193-Bellaterra, Catalunya (Spain)

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building block. This, together with the observed fact that F⁻ ions located within the D4MR cages increases their stability,[15] made us to think that it could be possible to synthesize the polymorph C by introducing F⁻ ions and Ge in the synthesis gel. If our hypothesis were correct, both factors (or even only one of them) should be enough to discriminate polymorph C from polymorphs A and B during the synthesis of zeolite Beta regardless of the organic SDA used in the synthesis media. We will see that indeed this has been the case, and that pure polymorph C can be obtained with a large variety of SDAs which, in the absence of Ge in the media, gives the typical intergrowth of polymorphs A and B of zeolite Beta or even other zeolite structures.

A germanium-containing polymorph C was synthesized by using 1-benzyl-1,4-diazabicyclo[2.2.2]octane (benzyl-DABCO; BD$^+$) as an SDA. The resultant calcined sample with a Si:Ge molar ratio of 1.8:1 exhibits the X-ray powder diffraction (XRD) pattern given in Figure 1. This pattern was indexed according to a tetragonal unit cell with the following optimized unit cell parameters: $a = 12.823$ and $c = 13.345$ Å. The Rietveld refinement of the crystal structure of the Si:Ge = 1.8:1 form of polymorph C was successfully performed in space group $P4_2/mmc$, the same space group which has been proposed by Newsam et al.[13] for the aluminosilicate form (Si:Al = 10:1) of polymorph C of Beta. From the chemical analysis of the sample and assuming that all T sites are filled, the unit cell composition of the calcined sample is close to $Si_{20.6}Ge_{11.4}O_{64}$. Its refined unit cell volume is larger by 61 Å^3 than the volume calculated for the aluminosilicate form. This result is consistent with the larger ionic radius of Ge compared to Si and clearly indicates that Ge is located at framework sites replacing isomorphically Si atoms in the structure. The refined atomic coordinates are listed in Table 1, and Figure 1 shows the very good agreement between observed and calculated XRD patterns. The details of the Rietveld refinement are given in the Experimental Section and the averaged values of some relevant distances and angles are compared to those proposed for the aluminosilicate form in Table 2.[13, 16]

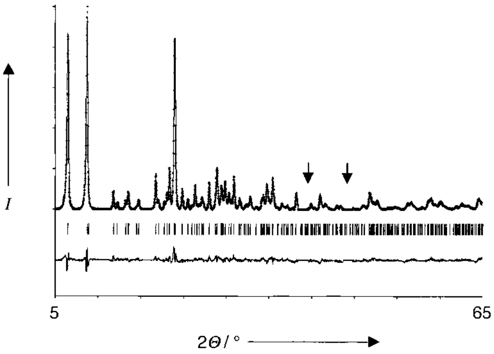


Figure 1. Observed (crosses) and calculated (lines) XRD patterns of polymorph C as well as the difference profile (bottom). The short tick marks below the pattern give the positions of the Bragg reflections. The arrows indicate the two small regions excluded from the Rietveld refinement containing the diffraction lines of the platinum sample holder ($Cu_{K\alpha 1,2}$ radiation).

Table 1. Fractional atomic coordinates[a,b] for polymorph C (Si:Ge = 1.8:1).

Atom	x	y	z	Number of positions	Wyckoff notation
T1[c]	0.3777(4)	0.1259(4)	0.1143(3)	16	r
T2[c]	0.1915(8)	x	¼	8	n
T3[c]	0	0.1229(7)	0.1160(8)	8	o
O1	0	0	0.1303(16)	4	g
O2	0.0994(6)	0.1764(9)	0.1705(6)	16	r
O3	0.3486(12)	0	0.1278(12)	8	o
O4	½	0.1481(14)	0.1555(11)	8	p
O5	0.3010(6)	0.1772(8)	0.1954(6)	16	r
O6	0.3543(12)	0.1583(11)	0	8	q
O7	0	0.1635(17)	0	4	l

[a] As obtained from Rietveld refinement (space group $P4_2/mmc$; $a = 12.823(2)$, $c = 13.345(3)$ Å). [b] Estimated standard deviations given in parentheses. [c] Refined atomic occupations for site T1: 0.54(2) Si + 0.46(2) Ge; T2: 0.72(2) Si + 0.28(2) Ge; T3: 0.77(2) Si + 0.23(2) Ge.

Table 2. Comparison of relevant averaged distances (d) and angles (∢) between the refined polymorph C structure (Si:Ge = 1.8:1) and the corresponding simulated one (Si:Al = 10:1) from a least-squares refinement on distance.

	Si:Ge = 1.8:1 experiment	Si:Al = 10:1 simulated
d (T–O) [Å]	1.614(23)	1.616(1)
∢ (O-T-O) [°]	109.4(3.7)	109.47(3)
∢ (T-O-T) [°]	151.4(8.2)	150(15)

Figure 2 shows the arrangement, along one 4_2 screw axis, of the two structural building units of polymorph C, namely the [5^4] cage consisting of four five-membered rings and the

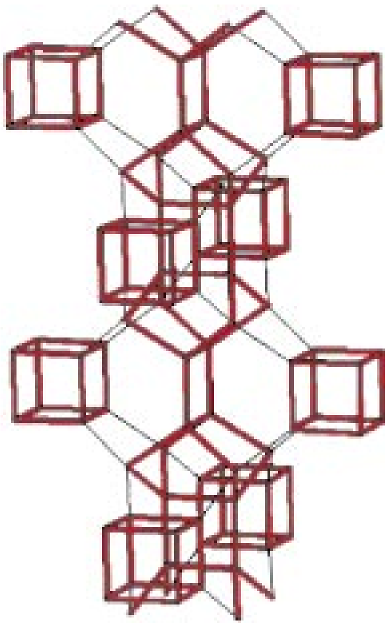


Figure 2. Arrangement along the 4_2 screw axis of the two structural building units of polymorph C, cage [5^4] formed by four five-membered rings and cage D4MR formed by double four-membered rings. The mirror-related [5^4] cages are connected forming four-membered rings and are linked to the [5^4] cages of the neighboring unit cells through the D4MR cages, which are preferentially occupied by Ge. The D4MR cages consist only of T1 sites while each [5^4] cage contains sites of type T2 and T3. To visualize the D4MR building units, the links between T1 and T2 sites have been depicted as single lines.

D4MR cage. The complete structure is plotted in Figure 3 and agrees well with that of polymorph C postulated by Newsam et al.[13]

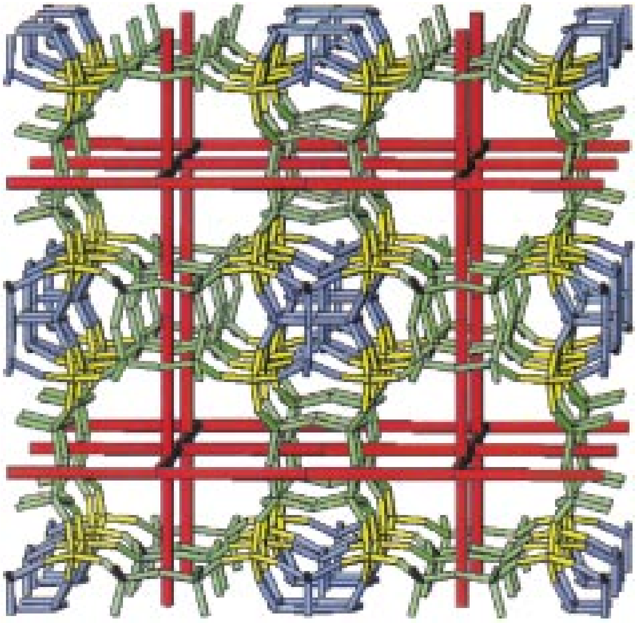
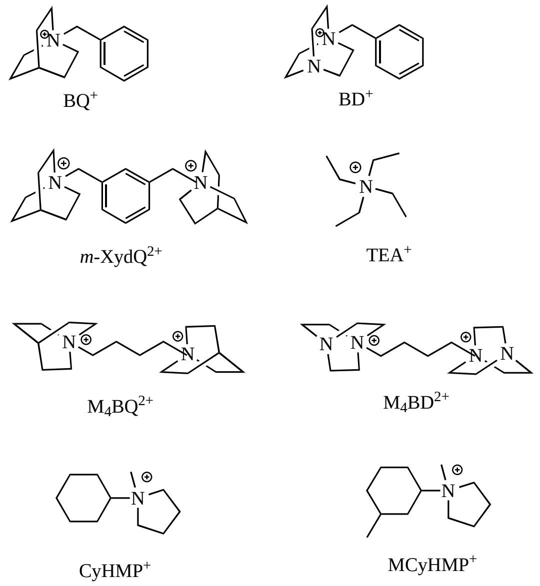


Figure 3. A [001] perspective view of the crystal structure of the calcined polymorph C of zeolite Beta showing the three-dimensional pore system formed by linear channels of nearly circular 12-membered rings intersecting at different heights as indicated by the bars. The pore diameter of the channels calculated from the crystallographic data ranges from 6.3 to 6.6 Å, which is very close to the experimental value of 6.9 Å calculated from the Ar adsorption isotherm by using the Horvath–Kawazoe formalism.

Due to the high contrast in scattering power between Si and Ge, one simple way to determine the distribution of Ge among the different T sites consists on the least-squares refinement of the effective number of electrons at each site. This refinement yields for site T1 a Ge occupancy of 46 % while for the two remaining sites T2 and T3 the respective occupancies are 28 % and 23 % (Table 1). This Ge distribution is also reflected in the mean T–O distances: $\langle T1{-}O\rangle = 1.632$; $\langle T2{-}O\rangle = 1.596$; $\langle T3{-}O\rangle = 1.615$ Å. As expected, the longest average T–O distance corresponds to site T1, which is preferentially occupied by Ge and is the only one located in D4MR cages.

The preferential occupancy of D4MR cages by Ge is further supported by ^{19}F MAS-NMR spectroscopy and chemical analysis of the noncalcined polymorph C sample. Indeed, the ^{19}F MAS-NMR spectrum of the polymorph C sample with a Si:Ge ratio of 1.8:1 shows an unique resonance at $\delta = -6.6$ (CCl_3F as reference), which is very close to that observed for the purely Ge-octadecasil material synthesized as reported before[17] and exactly at the same position and with very similar broadening than the band observed for the ITQ-7[18] structure with a similar Si:Ge ratio (see Supporting Information). In both materials, octadecasil and ITQ-7, fluoride has been unambiguously located into the D4MR cages.[18, 19] It is noteworthy that the chemical analysis of polymorph C yielding 1.95 F^- per unit cell also closely corresponds to the presence of fluoride anions into the small cavities (2 D4MR/u.c.). Consequently, all the experimental results support the assignment of F^- inside the Ge-rich D4MR cavities of polymorph C.

To check the structure-directing effect of Ge, a series of syntheses were carried out using different organic SDAs (Scheme 1). The synthesis procedure was the same as described in the Experimental Section and the gel compositions were $(1-x)\,SiO_2:x\,GeO_2:0.5\,SDAOH:0.5\,HF:w\,H_2O$ and $(1-x)\,SiO_2:x\,GeO_2:0.25\,SDA(OH)_2:0.5\,HF:w\,H_2O$. The results from Table 3 indicate that all SDAs produce, in absence of germanium, zeolite Beta with a typical intergrowth polymorphs A and B, as well as other zeolite structures. However, if germanium is introduced, all of them give pure polymorph C in a very wide range of Ge contents. The



Scheme 1. Structure-directing agents essayed in this work.

Table 3. Synthesis conditions and zeolitic structures obtained by using different SDAs with and without germanium in the crystallization gel.

SDA	H_2O [w]	Si/Ge	T [°C]	Time [h]	Ge zeolite	SiO_2 zeolite
BQ^+	8	1–10	150	15–120	polymorph C	ITQ-4
BD^+	8–24	0.5–30	135–175	15–120	polymorph C	ITQ-4
m-$XydQ^{2+}$	8	5	150	16–96	polymorph C	Beta
M_4BQ^{2+}	7.5–15	2–10	175	24–96	polymorph C	Beta, ZSM-12
M_4BD^{2+}	15	2–20	175	24–96	polymorph C	ZSM-12
$CyHMP^+$	7.25	5	135–175	15–96	polymorph C	ZSM-12
$MCyHMP^+$	7.25	5	135–175	15–96	polymorph C	Beta
TEA^+	7.5	2	140	96	polymorph C	Beta

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structure-directing effect of Ge becomes evident from these results since, in absence of Ge, no polymorph C was obtained despite the fact that F^- was used in all syntheses. Furthermore, we have found that polymorph C also grows in absence of F^- (OH^- media) when Ge is present (see Supporting Information).

Finally, various syntheses have been carried out using BD^+ as SDA and different Si:Ge ratios in the gel. It has been found that pure polymorph C is obtained for Si:Ge ratios of up to at least 30:1; these samples are highly stable upon calcination in air and after exposure to moisture.

A sample of polymorph C with a Si:Ge = 5:1 was calcined in air and a micropore volume of 0.21 $cm^3 g^{-1}$ was calculated from the N_2 adsorption isotherm using the t-plot method. This value corresponds very well with the value predicted by the structural parameters given in this work (0.23 $cm^3 g^{-1}$).

In conclusion, we have shown that the pure polymorph C of zeolite Beta can be synthesized using germanium for stabilizing the structure. Germanium has a greater tendency to occupy the positions at the double four-member ring cages which can be responsible for stabilizing this structure. We have found that this is a general effect, since germanium also facilitates the formation of all the high-silica zeolites reported up to now having D4MR cages in their structures (ITQ-7[18] and octadecasil[19]). In both materials, a selectivity for the occupancy of D4MR by germanium has been observed (see Supporting Information).

Experimental Section

Synthesis: A Ge-containing polymorph C was synthesized by using the hydroxide form of benzyl-DABCO (BD^+) as SDA. A series of synthesis gels were prepared with the following molar compositions:

$0.666\,SiO_2 : 0.333\,GeO_2 : 0.5\,BDOH : 0.5\,HF : 8\,H_2O$ **1**

$0.833\,SiO_2 : 0.166\,GeO_2 : 0.5\,BDOH : 0.5\,HF : 8\,H_2O$ **2**

$0.937\,SiO_2 : 0.062\,GeO_2 : 0.5\,BDOH : 0.5\,HF : 8\,H_2O$ **3**

The gels were autoclaved at 150 °C for 15 h in Teflon-lined stainless steel autoclaves under static conditions. The three synthesing gels resulted in pure polymorph C, with final Si:Ge atomic ratios of 1.8:1, 5.0:1, and 11.6:1, respectively.

XRD: The sample was calcined at 400 °C in air for 1 h. The air was purged at this temperature by several cycles of pumping and filling the high-temperature chamber with N_2. Subsequently, the sample was cooled under the inert atmosphere. The pattern was measured at room temperature in N_2 within the high-temperature chamber attached to an diffractometer (Philips X'Pert) with Bragg – Brentano geometry using a Pt sample holder and graphite secondary monochromator. Intensity data obtained with variable divergence slit. $Cu_{K\alpha 1,2}$ radiation ($\lambda = 1.5406$, 1.5444 Å). Tube voltage and intensity: 45 kV and 40 mA. Step scan size and time: 0.02° 2θ and 10 s.

Rietveld refinement:[20] The Rietveld refinement with LSP7 was performed using a 2θ range from 5.00 to 65.00° with two excluded regions, 39.04° – 40.53° and 45.45° – 46.77°, due to the appearance in these regions of the (111) and (200) Pt diffraction peaks of the sample holder. The transmission coefficient at the Pt(111) Bragg position is 0.20, which was used for correcting the finite thickness of the sample. Number of contributing reflections: 247. Number of geometric restraints of type $d(\text{T–O}) = 1.62(3)$ Å: 12. Number of structural parameters: 24. Number of profile parameters: 8, including unit cell parameters and zero shift (−0.095° 2θ), with visually estimated background. Profile function used was Pearson-VII. Refined overall thermal coefficient: $B = 2.4$ Å^2. The residuals of the refinement were: $R_{wp} = 0.081$; $R_{exp} = 0.032$; $R_p = 0.062$; $R_I = 0.117$ (see Supporting Information).

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