Zeolites

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Synthesis and Characterization of the All-Silica Pure Polymorph C and an Enriched Polymorph B Intergrowth of Zeolite Beta**

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Zeolite beta was first reported by Mobil Oil in 1967 and was the first example of a tridirectional large-pore zeolite with low aluminum content.[1] This work initiated further research in the synthesis of zeolitic structures with large and extralarge pores.[2–6] The structure of zeolite beta was only determined in 1988 by Treacy and Newsam,[7] as an intergrowth of two closely related polymorphs, named polymorphs A and B, which are present in a ratio of 60:40. A third polymorph (named polymorph C) was also proposed, which, in contrast to polymorphs A and B, contains double 4-ring (D4R) cages as secondary building units and a 3D intersecting channel system formed by straight 12-ring pores (see Supporting Information). This hypothetical material remained elusive until recently when Conradsson et al. and our group reported the synthesis of pure polymorph C of zeolite beta (International Zeolite Association (IZA) code: BEC) as the pure germanate (FOS-5)[8] and as a silicogermanate (ITQ-17).[9] Later, pure silica with the polymorph C structure was detected by high-resolution TEM as an overgrowth on zeolite beta.[10] However, the X-ray diffraction pattern of this material, named ITQ-14, was similar to that of pure silica zeolite beta, as polymorph C appears as a minor impurity in the beta intergrowth.[11]

The preparation of siliceous and silicoaluminate analogues of pure polymorph C of zeolite beta will open new possibilities for applications.[12] It will also allow us to rationalize differences in stability between this polymorph and zeolite beta.[13]

We show herein that it is possible to obtain the all-silica, pure polymorph C of zeolite beta by using the cation 4,4-dimethyl-4-azoniatricyclo[5.2.2.$0^{2,6}$]undec-8-ene as a structure-directing agent (SDA) and that the presence of K^+ ions and relatively high ratios of OH^- ions to silicon atoms greatly favor the crystallization of the pure silica polymorph C structure. Furthermore, depending on the synthesis conditions, this SDA allows the production of a material that corresponds to a new intergrowth of zeolite beta, which is enriched in polymorph B.

In a first set of synthesis experiments, it was found that the crystallized product consisted of zeolite beta with 20% polymorph C. Attempts to increase the yield of polymorph C in this mixture gave variable results depending on the batch of the SDA used for the synthesis; some reactions gave pure polymorph C. Careful analyses of all the experiments undertaken showed that K^+ ions were present in the synthesis gel, and that the synthesis gel containing the most K^+ ions yielded the material with the highest proportion of polymorph C. The K^+ ions were not deliberately introduced, but originated from the $KHCO_3$ used to deprotonate the secondary amine during its quaternization by ICH_3 (see Supporting Information). At this point, careful recrystallization of the SDA was performed, and in all subsequent cases, the absence of K^+ ions was specifically verified.

A systematic study of the SDA:K^+ ratio was performed by adding controlled amounts of K^+ ions to the syntheses. The parameters screened by high-throughput (HT) synthesis were the ratios of SDA:Si, K^+:Si, H_2O:Si, OH^-:Si, and F^- (from NH_4F):Si, temperature, and time of crystallization.[14] The phases identified by powder X-ray diffraction are given in Figure 1. Pure polymorph C was obtained when K^+ ions were present in the synthesis gel and crystallization was carried out at relatively high ratios of OH^-:Si. It is noticeable that polymorph C always formed with an impurity, which was

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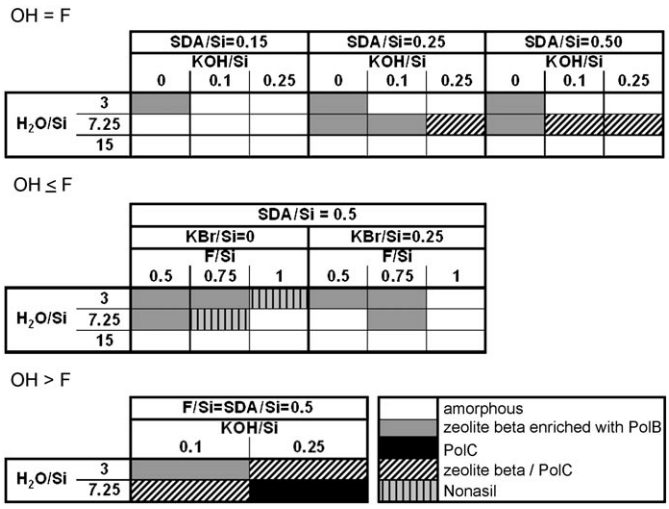

Figure 1. Phase diagram obtained by means of HT synthesis. The crystallization conditions for this set of data were 175 °C and 14 d. PolB/C = polymorph B/C. The SDA was introduced in the hydroxide form. $[OH^-] = [SDA] + [KOH]$.

identified as K_2SiF_6 by X-ray diffraction and ^{19}F magic-angle spinning (MAS) NMR spectroscopy. The impurity was easily removed by washing the product with boiling water for 15 min, and the remaining solid was the all-silica form of pure polymorph C of zeolite beta.

Rietveld analysis of the X-ray diffraction pattern (Figure 2)[15] unambiguously confirms that the all-silica polymorph C of zeolite beta was synthesized. The tetragonal unit cell ($P4_2/mmc$) of $a = 12.6241$ and $c = 13.1255$ Å is consistent with that for the germanium-containing material ITQ-17,[9] but the superlattice reported for FOS-5 is not observed.[8] This point is confirmed by the ^{29}Si MAS NMR spectrum of the calcined sample, which shows three very narrow resonances at

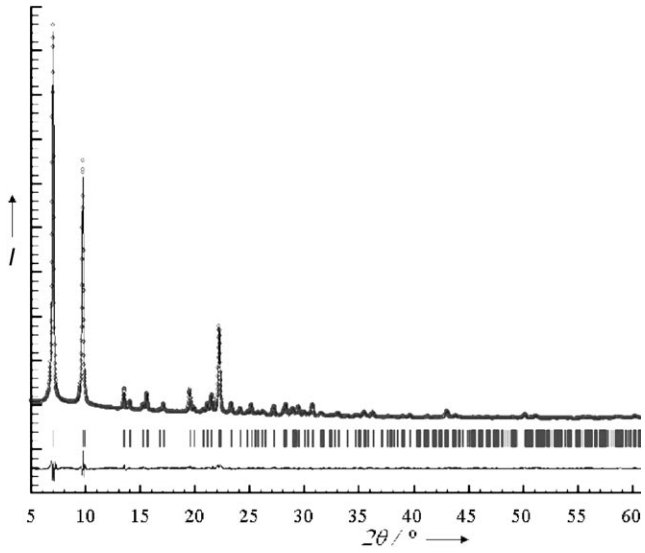

Figure 2. Observed (circles) and calculated (line) powder X-ray diffraction patterns of polymorph C of zeolite beta (top), and a difference profile (bottom). The short bars below the patterns give the positions of the Bragg reflections.

−110, −112, and −116 ppm that correspond to the three crystallographic positions described for ITQ-17 and not to the nine sites expected for FOS-5. Moreover, the ^{19}F MAS NMR spectrum of the as-synthesized material shows a single signal at −38.3 ppm (see Supporting Information). This resonance is assigned to the presence of F^- ions encaged within D4R units,[17] which are uniquely present in the C polymorph of those described for the beta family.

When the syntheses were carried out in absence of K^+ ions or at lower ratios of OH^-:Si, a new material that closely resembles zeolite beta was obtained. This new zeolite is a form of zeolite beta enriched with polymorph B. Simulation of the diffraction patterns of zeolite beta with different ratios of polymorphs A:B, using the program DIFFaX,[18] indicates that the material is formed by an intergrowth ratio (A:B) of 35:65, instead the 60:40 ratio present in zeolite beta (see Supporting Information). During the growth of polymorph B-enriched zeolite beta, some polymorph C was frequently detected under all the synthesis conditions studied. Indeed, a kinetic study shows that the first phase observed is the polymorph B-enriched zeolite, which evolves towards the polymorph C structure.

This observation has been further confirmed by carrying out an experiment in which polymorph B-enriched zeolite was used as the silica source for the synthesis. The initial zeolite transformed into polymorph C, which indicates that polymorph C is thermodynamically more stable than polymorph B of zeolite beta under these conditions. Therefore, the main conclusions arising from the HT syntheses are: 1) The all-silica polymorph C of zeolite beta can be synthesized as a pure phase. 2) A new zeolite closely related to zeolite beta, but enriched in polymorph B has been synthesized. 3) The presence of K^+ ions and high OH^-:Si ratios in the synthesis gel strongly favors the crystallization of the pure-silica polymorph C of zeolite beta.

The role of K^+ ions in the crystallization media was investigated on the basis of two different hypotheses. In the first hypothesis, K^+ ions are incorporated into the final polymorph C because of the relatively small size of the K^+ ion with respect to the organic SDA. Thus, more positive charges are incorporated with a corresponding increase in the number of F^- counterions. A higher number of F^- ions should favor the structure with the most D4R units,[19] which is polymorph C. This hypothesis was easily tested by analyzing the amount of K^+ ions incorporated into polymorph C. The results showed that K^+ ions are found in the pure polymorph C only at trace levels, and therefore, this hypothesis was rejected as an explanation of the role of K^+ ions in the crystallization of the polymorph C structure.

In the second hypothesis, we considered that owing to the formation of K_2SiF_6, which was detected in conjunction with polymorph C of zeolite beta, the concentration of F^- ions during crystallization is strongly reduced with respect to those of syntheses performed in the absence of K^+ ions. In principle, this effect should stop or at least strongly decrease the crystallization rate of the zeolite, as a large fraction of the mobilizing agent (F^- ion) is removed from the synthesis media. However, we also found that the synthesis of polymorph C requires high ratios of OH^-:Si (Figure 1),

which suggests that the initial mobilizing agent of the silica is the OH^- ion rather than the F^- ion.

Consequently, a picture of the crystallization of polymorph C of zeolite beta could be as follows. In the first stage, fluorosilicate species formed from the amorphous silica evolve towards the polymorph B-enriched zeolite. The zeolite then accommodates F^- ions in high concentration in the $[4^15^4]$ cages, as it contains 12 of such units per 64 SiO_2 groups. These anions provide the possibility of compensating the occluded organic cations and also introduce flexibility in establishing the pairs of charge-compensated organic-cation/F^--anion pairs within the structure. At this stage of the process, no K_2SiF_6 was detected in our experiments. The transformation of the polymorph B-enriched zeolite beta into polymorph C of zeolite beta is accompanied by the formation of K_2SiF_6 (note that a small quantity of this salt implies a large consumption of F^- ions from the synthesis gel). This observation suggests that polymorph C grows in media that are defective in ions with respect to the synthesis gel, but crystallizes in a fluoride-buffered medium produced by the presence of K_2SiF_6. If this is the case, shifting the equilibrium constant of SiF_6^{2-} should not produce polymorph C of zeolite beta. This hypothesis was supported by experiments in which Na^+ ions were added instead of K^+ ions. Na_2SiF_6 is much less soluble than K_2SiF_6, and therefore, no polymorph C was formed.

In conclusion, we have shown that it is now possible to synthesize the all-silica pure polymorph C of zeolite beta. A new beta-type material enriched with polymorph B has also been synthesized, and this material evolves to form polymorph C with time. Polymorph C has been obtained by using an organic SDA in the presence of K^+ ions. A hypothesis has been put forward to explain the role of the K^+ ions. We propose that OH^- ions are the silica-mobilizing agents and that a small but continuous supply of F^- ions allows the synthesis of the all-silica polymorph C of zeolite beta.

Experimental Section

The steps involved in the synthesis of the SDA are presented as Supporting Information. The general gel composition was SiO_2:*x* SDA:*y* KOH:*z* NH_4F:*w* H_2O, and the synthesis parameters studied were the values of *x*, *y*, *z*, and *w*. The synthesis gel was prepared by mixing the silica source with alkaline solutions of the SDA and KOH. When the mixture was homogeneous, a solution of aqueous NH_4F was added to give a thick gel. This gel was transferred to teflon-lined stainless-steel autoclaves, which were heated at different crystallization temperatures for different periods of time. The solids were recovered by filtration, extensively washed with boiling water, and dried at 373 K overnight.

A typical synthesis of the all-silica polymorph C of zeolite beta is given in the Supporting Information.

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[15] Crystal data: SiO_2, tetragonal, $P4_2/mmc$, $a = 12.6241(5)$, $c = 13.1255(6)$ Å, $V = 2091.79(16)$ Å^3, $Z = 32$. The intensity data were collected on an X'Pert Philips diffractometer using $Cu_{K\alpha1,2}$ radiation ($\lambda_1 = 1.5406$, $\lambda_2 = 1.5444$ Å) at 303 K in a Bragg–Brentano geometry (tube voltage and intensity: 45 kV and 40 mA; divergence slit: fixed (1/16); scan range (2θ): 3–75°; step size (2θ): 0.017°, time per step: 600 s). The structure was refined using the Rietveld method with the FullProf program.[16] $R_{wp} = 0.09$, $R_{exp} = 0.05$, $\chi^2 = 3.24$, $R_B = 0.04$, $R_F = 0.06$. Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the deposition number CSD-416768.
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