Synthesis and characterization of the all-silica pure polymorph C, and the enriched polymorph B intergrowth material of Beta zeolite.

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1.- Synthesis of Structure directing agents.

1.1. 4,4-dimethyl-4-azonia-tricyclo[5.2.2.0²,6]undec-8-ene Iodide

A toluene solution (350 mL) of the corresponding diene (103 mmol) and maleimide or N-methylmaleimide (103 mmol) was refluxed for 4 days. After cooling, the resulting precipitate was filtered and washed with hexane to give the Diels-Alder product in quantitative form. (see scheme 1).

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\text{Scheme 1}
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\text{To a suspension of LiAlH}_4 \text{ (127 mmol) in anhydrous diethyl ether or THF (250 mL) was slowly added the Diels-Alder adduct (51 mmol) under N}_2 \text{ and at 0° C. When the addition was finished the mixture was refluxed for 5 hours and stirred at room temperature overnight. Then, the reaction was quenched by addition of H}_2\text{O (10 mL), 15% aqueous solution of NaOH (10 mL) and distilled H}_2\text{O (10 mL). After 30 min stirring at room temperature the solution was filtered and then extracted with diethyl ether. The combined organic extracts were washed with brine, dried and concentrated to dryness providing the corresponding reduced product (89%).}
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\text{Scheme 2}
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Finally, to a solution of the secondary amine (33.5 mmol) in MeOH (85 mL) was added KHCO$_3$ (0.5 mol) and CH$_3$I (1.7 mol). The mixture was stirred 7 days at room temperature. Then it was filtered washing with CH$_2$Cl$_2$. The resulting solid after evaporation was recrystalized with Hexane-CH$_2$Cl$_2$ providing the desired quaternary salt (87 %). (see scheme 3).

![Scheme 3](image-url)

2.- Synthesis of zeolites

A typical synthesis of the all-silica polymorph C was obtained from a gel containing the structure directing agent SDA having the following molar composition: SiO$_2$ : 0.54 SDA(OH) : 0.25 KOH : 0.54 NH$_4$F : 7.25 H$_2$O, using Ludox AS-40 from Aldrich as the silica source. This gel was heated for 14 days at 175ºC, yielding to a white solid, after filtration and extensive washing with boiling water and drying at 373 K overnight, that possesses a X-ray pattern characteristic of pure polymorph C.

The elemental analysis of the resulting sample is given below:

C = 14.77 wt%; N = 1.39 wt% and H = 2.18 wt%.

Form these values, it is possible to conclude that the SDA is stable under the synthesis conditions employed here, since the C/N molar ratio is 12.3 very close to that of the native SDA (C/N = 12). Also, the Si/SDA molar ratio of the final sample, which is 13.7, indicates that there are two SDA moieties per unit cell (32 T atoms). This value of SDA molecules accommodated within the pores of pure silica ITQ-17 is very close to the number of D4R cages present in BEC structure, suggesting that charge compensation of the SDA cations is carried out by the Fluoride anions located in these small D4R cages. This is further supported by the presence of a single resonance in the $^{19}$F MAS-NMR spectrum of the pure silica BEC zeolite at -38 ppm ascribed to flouride anions entrapped in D4R cages as it is shown in figure B of this supplementary material.
Figure A: Framework structure of polymorph A (a), polymorph B (b), and polymorph C (c) of Beta zeolite, showing the different stacking order
Figure B: A) $^{29}\text{Si}$ MAS NMR spectra of the calcined material. B) $^{19}\text{F}$ MAS NMR spectra of the as made polymorph C of Beta zeolite.
Figure C: Application of the program DIFFaX to simulate the diffraction patterns of zeolite Beta with different BEA/BEB ratios indicates that the material is formed by an intergrowth of polymorphs B (65%) and A (35%), instead of 40% and 60%, respectively, present in Beta.