Synthesis of All-silica Zeolite Beta

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Synthesis of pure zeolite boron beta with Si : B ratios from 20 to infinity is possible when dibenzyldimethylammonium hydroxide is used as the template, with subsequent removal of the template by ozone at 110 °C.

Zeolite beta is the only high-silica zeolite with a three-dimensional pore system containing large 12-membered ring apertures,[1] which makes it very suitable as a regenerable catalyst in organic reactions. So far, no all-silica beta has been obtained;[2] usually the Si : Al ratio is claimed to be between 5 and 200.[3] Recently Rubin obtained zeolite beta with Si : Al ratios up to 500, upon synthesis in the presence of triethanolamine.[4] Our interest is aimed at the preparation of zeolite beta in which aluminium is isomorphously substituted by boron. Provided that no chelating agent such as triethanolamine is used, this synthesis can be further modified to allow direct incorporation of transition metals. In an effort to vary the density of the boron sites, we found the dibenzyldimethylammonium cation, which was reported by Rubin[5] to be particularly suitable for the synthesis of zeolite beta containing relatively low amounts of aluminium, could be used to make the all-silica form of zeolite beta.

Zeolite boron beta was synthesized under hydrothermal conditions at 135–140 °C in stirred autoclaves. Table 1 gives a summary of the gel compositions used. All gels were seeded with 5% m/m (based on SiO₂) deboronated Al-free zeolite beta (prepared according to de Ruiter *et al.*[6]). A 22.55% m/m aqueous solution of template hydroxide free of alkali metals was used. Low pressure argon adsorption isotherms were measured on a Micromeritics ASAP 2000M.

In all cases, a fully crystalline zeolite beta was obtained, sometimes accompanied by small amounts of impurities (see Fig. 1 and Table 1). Examination of the XRD patterns (Fig. 1) indicates that the fault probability as defined by Newsam *et al.*[1] is independent of the boron content. A highly crystalline all-silica zeolite beta was obtained from a sodium-free preparation (sample B6). The crystallization of an all-silica beta is apparently hindered by the presence of sodium ions, which appear to promote the crystallization of unwanted phases. In the presence of sodium ions the impurities were ZSM-12 and to a lesser extent ZSM-5, cristobalite and magadiite; in the absence of sodium ions only a trace of ZSM-12 was formed, which agrees with the observation by Goepper *et al.* that the formation of ZSM-12 is enhanced by sodium ions.[7] In contrast to syntheses carried out in the presence of sodium, relatively more boron than silicon is incorporated during the sodium-free syntheses (see Table 1). This is

probably due to the high alkalinity (OH⁻ : Si = 0.5), which keeps a relatively large amount of silicon in solution.

In a DTG experiment with zeolite boron beta (sample A1), carried out in dry air, a weight loss of 21% (at 700 °C), due to loss of template and boron, was observed. This corresponds to 4.0 template ions per 64 T-atoms, in accordance with molecular mechanics calculations.[8] However, after calcination at 400 °C a substantial amount of coke was still present. The higher temperature necessary to remove this coke gave rise to a substantial loss of XRD-crystallinity, accompanied by loss of boron. The use of high temperatures can be avoided by calcination in 1% ozone in oxygen at 110 °C followed by a hot acetone wash, which was found to completely remove the template with full retention of XRD-crystallinity.

The incorporation of boron into the zeolite framework is confirmed by the presence of a single sharp peak at δ −23.2 in the ^{11}B MAS NMR spectrum and a band at 905 cm⁻¹ in the FT-IR spectrum.[9] This was further confirmed by a linear relation between the interplanar spacing (indexed as 600 for polytype A[1]) and the boron content. ^{11}B MAS NMR shows that boron is fully retained in the framework after the mild ozone treatment. If an as-synthesized all-silica zeolite beta is treated in exactly the same way, a small second resonance at δ −103 (Q³), well separated from the Q⁴ resonance (δ −108 to
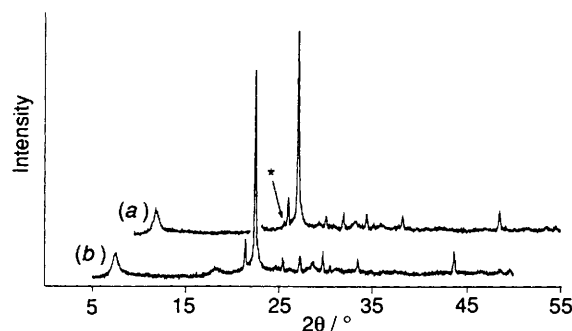

Fig. 1 XRD-diffractograms of as-synthesized zeolite beta. (*a*) All-silica zeolite beta (sample B6), (*b*) zeolite boron beta, Si : B 72 (sample B3). (*) Indicates the position of strongest ZSM-12 peak (2θ *ca.* 20.5).

Table 1 Gel compositions used for synthesis of zeolite boron beta

Sample[a]	Si : B (gel)	OH⁻ : Si (gel)	Na⁺ : Si (gel)	Q⁺[b] : Si (gel)	Si : B zeolite	Relative crystallinity (%)	Beta (%)[c]
A1	20.3	0.15	0.15	0.147	21.6	100[d]	100
A2	31.2	0.15	0.15	0.147	30.8	116	97
A3	41.4	0.15	0.15	0.147	39.2	97	93
A4	45.4	0.15	0.15	0.147	n.d.	95	92
A5	65.7	0.15	0.15	0.147	n.d.	88	84
B1	40	0.50	—	0.50	29	74	100
B2	80	0.50	—	0.50	59	101	100
B3	120	0.50	—	0.50	72	103	100
B4	200	0.50	—	0.50	108	109	92
B5	400	0.50	—	0.50	220	109	92
B6	∞	0.50	—	0.50	>1000[e]	106	>98

[a] Synthesis times and temp. of crystallization: A1–A5, 3 days, 140 °C; B1–B6, 7 days, 135 °C. [b] Q⁺ = dibenzyldimethylammonium cation. [c] Impurities are ZSM-12, ZSM-5, cristobalite or magadiite. [d] Reference zeolite. [e] Si : Al >5000.

−119) is observed in the ^{29}Si MAS NMR spectrum. It is assumed that this signal originates from structural defects already present in the as-synthesized material, probably as $SiO^-/SiOH$ pairs which are thought to be necessary for template charge compensation.[10] The observed $Q^3/(Q^3 + Q^4)$ ratio of 0.16 is not far from the expected value of 0.125, assuming a template content of 4 molecules per unit cell.

The ozone-treated all-silica zeolite has a micropore volume of 0.266 ml g^{-1} against 0.25 ml g^{-1} and 0.226 ml g^{-1} reported for zeolite aluminium beta[11] and zeolite boron beta,[6] respectively. The low micropore volume of 0.177 ml g^{-1} for the high-temperature calcined zeolite sample agrees with the observed loss of XRD-crystallinity. The Horvath–Kawazoe plot (Fig. 2) shows a bimodal pore size distribution with maxima at 5.6 and 7.0 Å. These values agree with the description of the channel system by Higgins et al.,[1] who reported average diameters of 5.5 and 7.0 Å for the tortuous and the straight channels, respectively. In contrast, a unimodal distribution is reported by de Ruiter et al.[6]

As a measure of hydrophobicity, the adsorption of water and toluene onto all-silica zeolite beta (ozone-treated) was measured at 50 °C. In sharp contrast to an H-[Al]-beta (Si : Al 11.2) the ozone-treated all-silica zeolite hardly adsorbed any water (8 mg g$^{-1}_{zeolite}$ vs. 74 mg g^{-1} for H-[Al]-beta), whereas toluene adsorption was somewhat higher (210 vs. 170 mg g$^{-1}_{zeolite}$). This clearly shows the increased hydrophobic character of the all-silica zeolite.

In conclusion, the synthesis of zeolite boron beta with dibenzyldimethylammonium is possible within a very wide compositional range (Si : B 20–∞). Not only can this synthesis
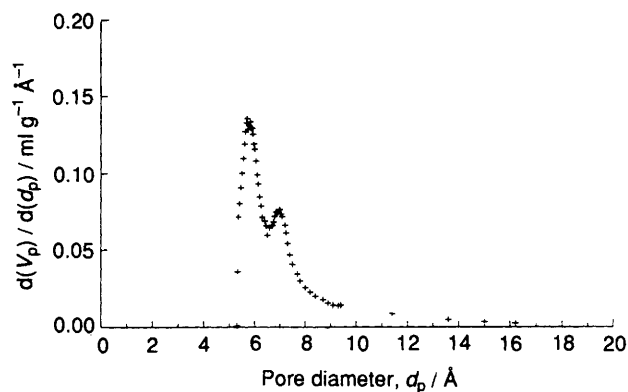
serve as a starting point in the synthesis of an aluminium or boron-free titanium-containing zeolite beta in analogy with the well known titanium silicalite 1 (TS-1) system[12] and the recently described [Al,Ti]-beta system,[13] but it is also suitable for the synthesis of well defined materials with high Si : B ratios, which can be used as precursors for transition metal containing materials.[6,14]

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Fig. 2 Horvath–Kawazoe pore size distribution plot of ozone-treated all-silica beta