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HIGH RESOLUTION SOLID STATE MAS ^{11}B-NMR EVIDENCE OF BORON INCORPORATION IN TETRAHEDRAL SITES OF ZEOLITES

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High resolution solid state MAS ^{11}B-NMR was used to detect quantitatively variously coordinated BO_x structural units in zeolites. Boron stemming from Pyrex autoclaves is progressively incorporated into the tetrahedral sites of ZSM-5 and mordenite frameworks during synthesis. The final crystalline zeolite phases may contain up to 0.8 B atoms in their unit cells.

Although isomorphous substitutions in compact or layered aluminosilicates are quite common, few partial or total substitutions of Si and/or Al atoms for boron in open zeolitic frameworks were reported. 1) In contrast, a number of syntheses of borosilicate molecular sieves with a structure similar to the one of the related Si-rich aluminosilicate zeolites ZSM-5, ZSM-11, Silicalite, Beta and Nu-1, were reported in the recent patent literature. 2-4) These materials showed acidic and catalytic properties different from those of their Al-analogues, due to a probable framework substitution of Si by B, during synthesis. It was also demonstrated that the catalytic (shape selective) properties of ZSM-5 zeolites could be deeply modified through their impregnation with B-containing chemicals5) but little information is available concerning the structural state of boron in the so formed compounds (mixtures). 6)

Solid state (essentially wide line) ^{11}B-NMR was used to study tetrahedrally coordinated boron nuclei in various salts 7) and borosilicate glasses8) but not in zeolites. The aim of this paper is to demonstrate the advantage to use high resolution solid state magic angle spinning (HRMAS) ^{11}B-NMR to detect the relative amount of various boron-oxygen structural units either incorporated in zeolitic frameworks or admixed with the zeolites as separate BO_x species.

Three methods were used to introduce boron in zeolites : direct synthesis of borosilicates in presence of H_3BO_3 following the procedure described in the patent literature, 2) impregnation of crystalline H-ZSM-5 with $H_3BO_3$5) and synthesis of mordenite 9) and ZSM-5 10,11) in Pyrex tubes. Pyrex, a borosilicate glass, is partly destroyed in high alkaline medium with a release of,

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among other species, various amorphous boron oxides, which are supposed to contaminate the growing zeolite particles. Boron was analyzed by HRMAS ^{11}B-NMR in a Bruker CXP-200 spectrometer. The spectra were obtained by a "one-cycle" type measurement : resonance frequency : 64.17 MHz, r.f. field : 9.6 G (45° pulses) ; repetition time:3 s, sweep width : 31.25 kHz, with 4 K data points. 200 to 2000 free induction decays were accumulated per sample. MAS was at 3.1 kHz, using conical Delrin rotors. The chemical shifts were determined from $BF_3.OEt_2$, used as external reference.

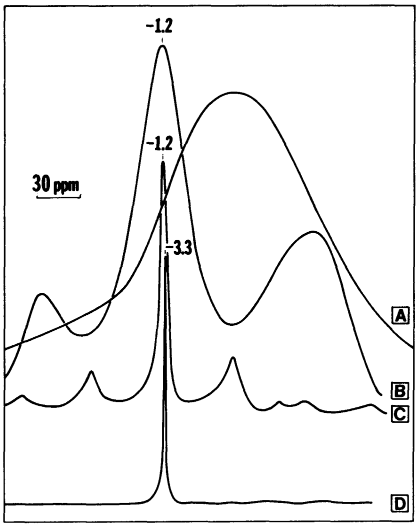


Fig. 1. High resolution solid state ^{11}B-NMR spectra of
(A) H_3BO_3, without MAS,
(B) Pyrex glass, without MAS,
(C) Pyrex glass, with MAS,
(D) ZSM-5 type borosilicate, with MAS.
Chemical shifts (from $BF_3.OEt_2$) of the principal lines, as indicated.

Figure 1 shows the ^{11}B-NMR spectra of compounds containing variously coordinated BO_x units in their structure : trigonal BO_3 and tetrahedral BO_4 units randomly dispersed in a Pyrex glass structure and tetrahedral BO_4 units packed in an ordered ZSM-5 type borosilicate structure. The line characterizing boron tetrahedrally coordinated to oxygens is generally narrow and symmetric in shape, because of the very small quadrupole coupling constant.[8)] It appears in the (+2)-(-3) ppm range (vs. $BF_3.OEt_2$) for various compounds.[8,12)] MAS further narrows this line but produces a complex sideband pattern for the broad line belonging to the trigonal BO_3 units, which undergo a strong quadrupolar splitting of the second order. The presence of these lines only qualitatively accounts for the existence of BO_3 entities and, in the particular case of zeolites, it was checked that they do not affect either the shape or the intensity of the central BO_4 resonance line.

A systematic investigation by ^{11}B-NMR of various compounds showed that the tetrahedral BO_4 units can be characterized by two different resonance lines. When randomly distributed in a structure (Pyrex, aluminosilicate gels), they give rise to an NMR line located at about -0.3 ppm. (This value is approximate as no correction was introduced for the quadrupolar line broadening). If these units are located in a more ordered structure (boron positioned on T sites in zeolites), this NMR line is shifted to higher fields by about 3 ppm. In a mixed (zeolite + gel) phase, both resonances are present and clearly resolved. The variation of their relative intensity appears to be related to the amount of crystalline zeolite present in the intermediate phase isolated after variable crystallization times of the precursor gel phase (Fig. 2) and this confirms their tentative assignment.

Figure 3 shows the parallel variation of the intensity of the ^{11}B-NMR line located at about -3.3 ppm with the % crystallinity of an intermediate phase containing ZSM-5 (procedures A and B)[10)] and mordenite, admixed with their respective gel precursors.

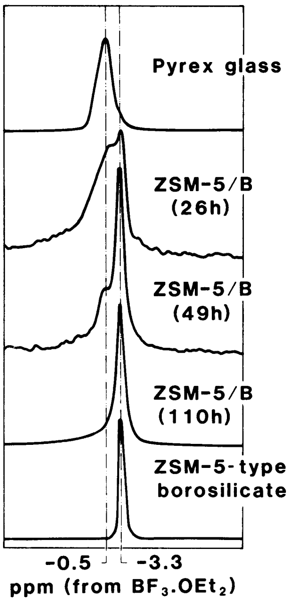


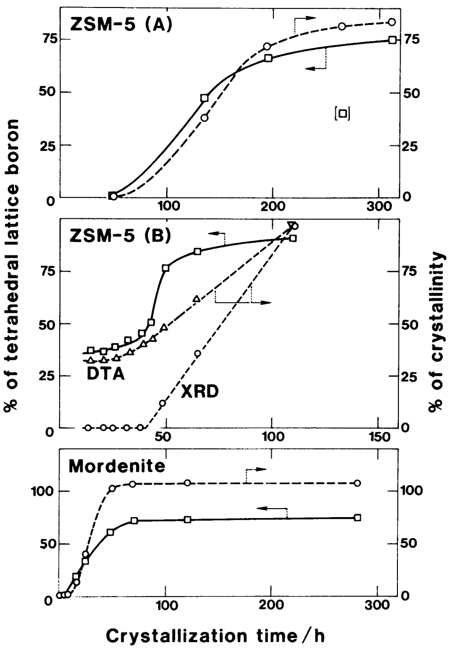
Fig. 2. HRMAS ^{11}B-NMR spectra of various phases containing tetrahedral BO_4 structural units, illustrating the progressive incorporation of boron in ZSM-5 lattice during synthesis in Pyrex tubes.

It clearly appears that the incorporation of boron in T zeolitic sites only occurs during crystallization and stops as soon as the growth is achieved. The presence of a residual line at -0.5 ppm indicates that the zeolite still contains some amorphous aluminosilicate gel-phase with distorted BO_4 units, confirming the XRD crystallinity data : 84% for ZSM-5 type A and 95% for ZSM-5 type B.[11)] For a 100% crystalline ZSM-5, the line at -0.5 ppm completely disappears. By contrast, for a 100% crystalline mordenite, the -3.3/-0.5 ppm line intensity ratio is about 3 : 1, suggesting that about 25% of non-zeolitic amorphous aluminosilicate gel (and containing BO_4 units) is occluded within the pore volume of the mordenite crystals.[13)]

Fig. 3. Parallel evolution of the amount of tetrahedral boron incorporated from the amorphous gel into the crystalline zeolitic lattice (full line) and the amount of crystalline zeolite formed (dotted line), as a function of synthesis time, for ZSM-5 type A, ZSM-5 type B, and Mordenite.

○ ; Crystallinity measured by XRD,

△ : crystallinity measured by DTA, as described in Ref. 10.



A quantitative determination of the total amount of tetrahedral boron in each phase could be derived by measuring the intensity of the two central NMR lines, provided a calibration curve is established. This curve relates the NMR intensity to the total boron content measured by proton induced γ-ray emission (PIGE) technique[14)] in various pure, 100% crystalline ZSM-5 type borosilicates, having only tetrahedral BO_4 units in their structure, used as standards. However, such a proportionality is not always observed with compounds having trigonal BO_3 units, as the latter, although totally detected by PIGE, may not be quantitatively determined by ^{11}B-NMR because the NMR lines of highly asymmetric species may be broadened beyond detection. Using such calibration curves, it is determined that each intermediate phase contains between 2 and 3 wt. % boron, about 25% of which being in tetrahedral coordination. From the relative -3.3/-0.5 ppm line ratio and taking into account the crystallinity of each phase, it is possible to estimate the actual amount of tetrahedral boron incorporated in the lattice of one unit cell in each zeolite. The average values obtained are 0.12, 0.8, and 0.25 B/u.c. for the as-synthesized final phases of ZSM-5 type A, type B, and mordenite, respectively. Very long heating times neither change the crystallinity of ZSM-5 type B nor lead to more boron incorporated in its T sites. A classical impregnation by H_3BO_3 of a ZSM-5 zeolite synthesized in a teflon-coated stainless steel autoclave, results in the incorporation of 0.2 boron atoms in the zeolitic lattice, the remaining boron (about 95 wt. %) being present in amorphous phases, either as distorted tetrahedral BO_4 or trigonal BO_3 units.

These preliminary observations show that HRMAS ^{11}B-NMR must be considered as another new powerful technique of structural investigation of zeolites. Traces of boron in various coordinations (tetrahedral in lattice, tetrahedral out of lattice or trigonal) can be accurately detected. In particular, our data demonstrate that tetrahedral boron can be very easily incorporated into the growing zeolitic particles during syntheses in Pyrex tubes, procedure which is widely used to obtain a variety of zeolitic materials.

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