^{1}H MAS NMR studies of hydroxyl groups in aluminium-free H-boralites

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Received 31 March 1993; accepted 5 November 1993

^{1}H MAS NMR spectra of H-boralites contain seven lines at 1.0, 1.4, 1.7, 2.3, 2.6, 4.7 and 6.7 ppm with intensities dependent on the activation temperature. The lines at 6.7, 4.7 and 1.7 ppm are assigned to residual ammonium ions, residual water and terminal Si–OH groups, respectively. The prominent line at 2.3 ppm comes from bridging Si–O(H)–B hydroxyls. The lines at 1.0, 1.4 and 2.6 ppm are tentatively assigned to B–OH, B–OH···O and Si–OH···O protons, respectively. The assignment has been assisted by the proton spectra of partially hydrated B_2O_3 and SiO_2, and by infrared measurements.

Keywords: Zeolite ZSM-5; boralite; solid-state NMR

1. Introduction

Many crystalline synthetic borosilicates and boroaluminosilicates with the structure of zeolite ZSM-5, known as "boralites", have been prepared and characterized by spectroscopic techniques and X-ray diffraction [1–13]. Although boralites are catalytically less active than aluminosilicate ZSM-5 zeolites, they favour certain desirable catalytic routes [11,14]. For example, boralite was found to be more selective for the production of light olefins from methanol than the aluminosilicate H-ZSM-5 [14]. The lower catalytic activity of boralites in comparison with their aluminium counterparts is due to the lower acid strength of the bridging Si–O(H)–B hydroxyls (Brønsted acid sites) than of Si–O(H)–Al groupings [3,7,10,12–14].

The substitution of boron into the zeolitic framework is reflected in: (i) the gradual decrease of the unit cell volume and the increase of intensity of the infrared (IR) band at 920 cm^{-1} (the B–O–Si symmetric stretching observed in both hydrated and dehydrated samples) with increasing boron content; and (ii) the sharp ^{11}B NMR line in the chemical shift range from −3 to −4 ppm relative to $BF_3 \cdot Et_2O$ found in magic-angle-spinning (MAS) NMR spectra of hydrated samples. The latter is characteristic of framework boron in BO_4 tetrahedra. In dehydrated samples boron occupies centers of trigonal BO_3 units and gives, even under MAS, a typical quadrupolar pattern, which in partly dehydrated samples overlaps with the line from tetrahedral boron [5,10]. There are two characteristic IR bands which can be used to monitor the coordination of framework boron: at 1150 cm^{-1} in hydrated samples, assigned to BO_4 asymmetric stretching vibration, and a doublet with maxima at 1380 and 1405 cm^{-1} in dehydrated samples, assigned to the asymmetric stretching vibration of the BO_3 unit [8,12,13]. The characteristic IR bands in boralite have been assigned [12,13] as follows: silanol groups, which are "free" or form hydrogen bonds as proton donors (3740 and 3460 cm^{-1}, respectively), bridging Si–O(H)–B hydroxyls (3720 cm^{-1}) and B–OH hydroxyls with the oxygen atom acting as a proton acceptor in the B–(H)O···H–O–Si hydrogen bond (3680 cm^{-1}).

Published ^{1}H MAS NMR studies of the hydroxyl groups in boralites are not extensive [3,10] and the interpretation of the spectra is uncertain, with the two groups reporting different assignments for the same line. Thus Scholle et al. [3] found two lines in Al-free boralites. The line at 2 ppm was assigned to "fast exchanging groups of protons of water clusters at the silanol groups". A higher frequency line, the position of which changes with water content (3.5 ppm in a partly hydrated sample), was assigned to bridging Si–O(H)–B hydroxyl groups involved in hydrogen bonding with water. On the other hand, Brunner et al. [10] detected an extra line at 2.1–2.4 ppm in dehydrated boralites with a substantial Al content. Since this line grew with boron incorporation, it was also assigned to bridging Si–O(H)–B hydroxyls. We report ^{1}H MAS NMR spectra of dehydrated and partly hydrated aluminium-free boralites, and interpret them in the light of IR results [12,13].

2. Experimental

Samples of boralite with a unit cell formula $(NH_4)_{1.0}(BO_2)_{1.0}(SiO_2)_{95.0}$, used in earlier studies [12,13], were shallow-bed activated in glass ampoules (3 mm inner diameter with the layer of boralite 8 mm deep) under vacuum at 200 and 500°C for 1 h. The ampoules were then sealed and NMR spectra recorded. Rehydrated samples were prepared by equilibration over a saturated solution of NH_4Cl for 48 h. B_2O_3 was prepared by calcining boric acid (Fisons) in vacuum at 300°C for 1 h. SiO_2 (fisons silica gel) was dehydrated in vacuum at 300°C for 1 h. Both B_2O_3 and SiO_2 samples were exposed to air for ca. 2 min prior to recording the spectra, which were then acquired using tightly closed MAS rotors.

^{1}H MAS NMR spectra were recorded at 400.13 MHz at room temperature using a double-bearing probehead and zirconia rotors spinning at ca. 3 kHz. Chemical shifts are given in ppm from external tetramethylsilane (TMS). The magic angle was set precisely by observing the ^{79}Br resonance of KBr.

3. Results and discussion

^{1}H MAS NMR spectra of H-boralites (fig. 1) contain seven lines at 1.0, 1.4, 1.7, 2.3, 2.6, 4.7 and 6.7 ppm with intensities and positions dependent on the activation temperature and the degree of hydration (see also table 1). The line from the glass capsule at 0.2 ppm was used as an internal standard. In accordance with earlier studies [16] we assign the line at 6.7 ppm to residual ammonium ions. This line disappears upon heating of the sample, because of the thermal decomposition of ammonium. The intensity of the line at 4.7 ppm increases dramatically after rehydration (see fig. 1), and we assign it to residual water. Although small, this line is clearly seen in the spectrum of the sample activated at 200°C, but is hardly noticeable in the sample activated at 500°C (fig. 1). We conclude that the sample activated at 200°C is still partially hydrated. According to literature [16] the line at 1.7 ppm should be assigned to terminal Si–OH silanol groups. Indeed, the spectrum of SiO_2 contains a silanol line at 1.9 ppm (fig. 1a).

We believe that the lines at 1.0, 1.4, 2.3 and 2.6 ppm all correspond to hydroxyl groups adjacent to boron atoms. Thus the line at ca. 2.3 ppm, the most prominent in the spectra of H-boralites, was assigned to bridging Si–O(H)–B hydroxyl groups [3,10]. This is in agreement with the intensity increase of this line with increasing

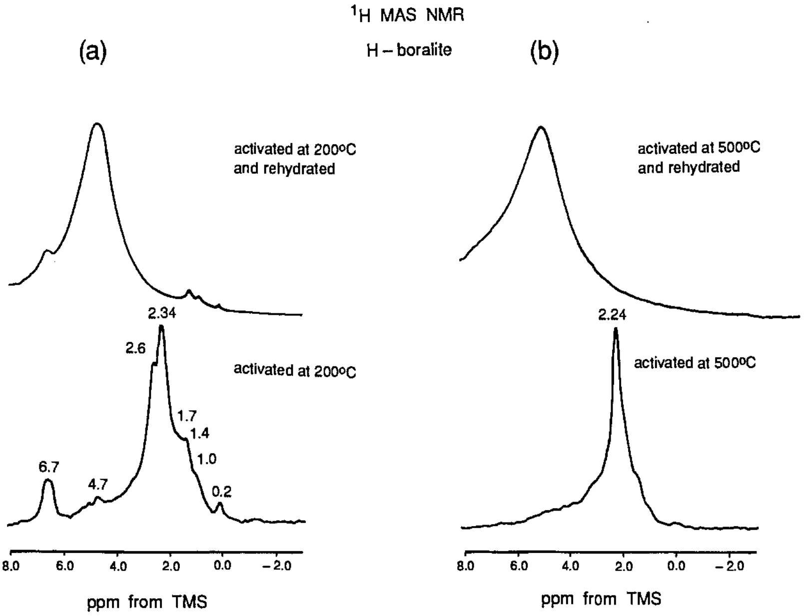

Fig. 1. ^{1}H MAS NMR spectra of H-boralite activated at (a) 200°C and (b) 500°C before and after rehydration. The spectra of activated samples are not on the same scale as those of rehydrated samples, the vertical axis in the latter being scaled down due to the very high intensity of the 4.7 ppm line.

Table 1
Chemical shifts of ^1H MAS NMR lines in the spectra of H-boralite (ppm from TMS). Abbreviations: w = weak; sh = shoulder

Activated at 200°C		Activated at 500°C		Assignment
activated	rehydrated	activated	rehydrated	
0.2	0.2	0.2	0.2	glass capsule
1.0	1.0	1.0 (w)	–	B–OH
1.4	1.4	1.4 (w)	–	B–OH···O
2.7 (sh)	–	1.7 (sh)	–	terminal Si–OH
2.34	–	2.24	–	bridging Si–O(H)–B
2.6	–	2.6 (w)	–	Si–OH···O
4.7	4.7	–	4.7	residual H_2O
6.7	6.7	–	–	residual NH_4^+

activation temperature (fig. 1). This is not surprising, as new Brønsted acid sites are generated as a result of decomposition of ammonium cations. Furthermore, the chemical shift decreases from 2.34 to 2.24 ppm with increasing temperature of activation, while the IR band of bridging Si–O(H)–B hydroxyls shifts from 3700 to 3720 cm^{-1} [12,13]. This further justifies the assignment of these NMR lines and suggests that acid properties of these hydroxyls depend on the activation temperature.

The chemical shift of the 2.3 ppm line from Si–O(H)–B groups is considerably smaller than that from Si–O(H)–Al groups (3.9–5.6 ppm) [7], which can be explained by the lower acid strength of Si–O(H)–B hydroxyls in boralites in comparison with Si–O(H)–Al hydroxyls in zeolites. The same conclusion can be drawn from temperature-programmed desorption [8] and IR [12,13] studies. It seems that the low acid strength of Si–O(H)–B hydroxyls in boralites is a consequence of the small size of a boron atom and the large O···B distance which make the Si–(H)O···B interaction rather weak. Thus the Si–O(H)–B hydroxyls are only slightly more acidic than the terminal Si–OH silanols (chemical shifts of 2.3 and 1.7 ppm, respectively), and therefore the Si–O(H)···B notation for the former is more appropriate. However, we shall continue to describe these sites as Si–O(H)–B in order to avoid confusion with the hydrogen bond.

The ^1H MAS NMR spectrum of H-boralites also contains lines at 1.0, 1.4 and 2.6 ppm, coming from other types of hydroxyl groups. The intensity of all of these decreases with increasing activation temperature. IR indicates that H-boralites also contain hydrogen-bonded SiOH···O(H)–B units [13,17]. Therefore, apart from the silanol (Si–OH) and bridging Si–O(H)–B groups, there are two further kinds of hydroxyls: silanol groups donating protons to hydrogen bonds and B–OH groups, with oxygen atoms as proton acceptors. IR also shows that the concentration of SiOH···O(H)–B (i.e. SiOH···O and B–OH) units sharply decreases with increasing activation temperature as a result of dehydroxylation:

$$\mathrm{SiOH\cdots O(H)-B \rightarrow Si-O-B + H_2O}\,.$$

It is possible that the 1.0, 1.4 and 2.6 ppm lines, the intensities of which also markedly decrease with increasing activation temperature, are associated with Si–OH and B–OH groups involved in mutual hydrogen bonding. Note that the 1.3 ppm proton line is present in the spectrum of B_2O_3 and the 3.29 ppm line in the spectrum of SiO_2 (fig. 2), both materials being partially hydrated and thus containing hydroxyl groups involved in hydrogen bonding with water. This gives us approximate values of the B–OH and Si–OH chemical shifts when these groups donate protons to hydrogen bonds with oxygen atoms. It follows that the 1.0 and 1.4 ppm lines can be tentatively assigned to B–OH groups (possibly "free" as in Si–OH···O(H)–B and hydrogen-bonded as in Si–(H)O···HO–B, respectively), and the line at 2.6 ppm to silanols participating in the hydrogen bonding in Si–OH···O(H)–B units. We note that a line at 4.0 ppm has been previously assigned to Si–OH···O hydroxyl groups in silica [17].

We have monitored the effect of sample hydration on the spectra of H-boralites activated at 200 and 500°C. Hydration results in the appearance of a strong water line at 4.7 ppm and the disappearance of almost all of the hydroxyl lines (fig. 2).

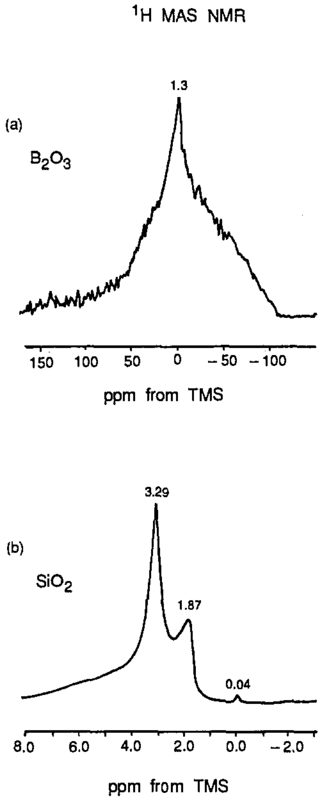

Fig. 2. ^1H MAS NMR spectra of partially hydrated (a) B_2O_3; (b) SiO_2.

Only in H-boralite activated at 200°C and rehydrated do the lines at 1.0 and 1.4 ppm, believed to correspond to B–OH, remain, suggesting that some of the B–OH groups are not accessible to water. All other hydroxyls form hydrogen bonds with H_2O. The fact that the B–OH lines do not reappear upon rehydration of H-boralite activated at 500°C (fig. 1) indicates that dehydroxylation is irreversible, i.e. that SiOH···O(H)–B and Si–(H)O···HO–B groupings are not reconstituted.

Acknowledgement

We are grateful to Unilever Research, Port Sunlight, and to Cambridge Colleges' Hospitality Scheme for East European Scholars, for support.

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