

IR STUDIES OF ACID PROPERTIES OF H-BORALITES ACTIVATED AT VARIOUS TEMPERATURES*

Jerzy DATKA and Marek KAWALEK

School of Chemistry, Jagiellonian University, Karasia 3, 30-060 Kraków, Poland

Received September 13, 1991

Accepted October 22, 1991

Four kinds of hydroxyls are present in H-boralite: $3\,450\text{ cm}^{-1}$ ($\text{Si}-\text{OH}\cdots\text{O}$), $3\,670\text{ cm}^{-1}$ ($\text{B}-\text{OH}$), $3\,700-3\,720\text{ cm}^{-1}$ ($\text{Si}-\text{OH}\cdots\text{B}$) and $3\,740\text{ cm}^{-1}$ ($\text{Si}-\text{OH}$). Only $3\,700-3\,720\text{ cm}^{-1}$ ($\text{Si}-\text{OH}\cdots\text{B}$) hydroxyls are Brønsted acid sites. Their concentration, as well as the concentration of Lewis acid sites, was found to be independent of the activation temperature (in the range $473-873\text{ K}$). On the other hand, both $3\,450$ and $3\,670\text{ cm}^{-1}$ hydroxyls are very prone to dehydroxylation which starts at as low temperature as 473 K . This is due to a reaction: $\text{Si}-\text{OH} + \text{O}(\text{H})-\text{B} \rightarrow \text{SiOB} - \text{H}_2\text{O}$. It has been found that the stretching frequency of $\text{Si}-\text{OH}\cdots\text{B}$ groups (Brønsted acid sites) depends on the activation temperature ($3\,700\text{ cm}^{-1}$ at 573 K and $3\,720\text{ cm}^{-1}$ at 773 K) suggesting a variation of the properties of Brønsted sites with temperature. We explain it by the loss of $\text{Si}-\text{OH}\cdots\text{O}$ and $\text{B}-\text{OH}$ hydroxyls situated in close vicinity of $\text{Si}-\text{OH}\cdots\text{B}$ ones.

Isomorphically substituted zeolites have been recently extensively studied because of their interesting properties and because of potential industrial applications (for a review see ref.¹). Boron substituted zeolites (boralites) draw a special attention because they show properties not observed in zeolites such as: (i) low acid strength of Brønsted acid sites²⁻⁵; (ii) the presence of tricoordinated B in dehydrated boralites (it becomes four coordinated after the sorption of electron-donor molecules^{2,3,5,6}); (iii) loss of boron during the $\text{Na}^+/\text{NH}_4^+$ ionic exchange and activation of NH_4 -boralites⁷; (iv) presence of some types of hydroxyls not observed in H-zeolites, characterized by the bands $3\,450$ and $3\,670\text{ cm}^{-1}$. These hydroxyls have been assigned^{5,8} to $\text{Si}-\text{OH}\cdots\text{O}$ and $\text{B}-\text{OH}$ groups in $\text{Si}-\text{OH}\cdots\text{O}-\text{B}$ units.

H

We are mostly interested in the properties of Brønsted acid sites ($\text{Si}-\text{OH}\cdots\text{B}$) groups and the ways how to modify their concentration and properties. Our previous study concerned H-boralites of various B content⁹. Now, we have followed the effect of activation temperature on the acid properties of H-boralite and the influence

* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis"*, Prague, September 8-13, 1991.

of the presence of $\text{Si}-\text{OH}\cdots\text{O}$ and $\text{B}-\text{OH}$ groups on the properties of Brønsted acid sites ($\text{Si}-\text{OH}\cdots\text{B}$).

EXPERIMENTAL

NaNH_4 -boralite was synthesized by Dr A. Cichocki from the School of Chemistry of Jagiellonian University. Its composition corresponded to a formula $\text{Na}_{0.02}(\text{NH}_4)_{0.97}[(\text{BO}_2)_{0.99}(\text{SiO}_2)_{95.1}]$. For IR experiments, the boralite was pressed into thin wafers ($3-6 \text{ mg cm}^{-2}$) and activated in situ in an IR cell in vacuum ($1 \cdot 10^{-4} \text{ Pa}$) at various temperatures (473–973 K) for 1 h. IR spectra were recorded using SPECORD 75 IR spectrometer (Carl Zeiss Jena) working on line with an Amstrad PC minicomputer.

RESULTS AND DISCUSSION

The spectra of hydroxyl groups in H-boralites activated at 473, 573, 673, 773, 873 and 973 K are shown in Fig. 1. Four OH bands are present in the spectra: 3 450, 3 670, 3 720, 3 740 cm^{-1} . The band at 3 740 cm^{-1} is due to terminal $\text{Si}-\text{OH}$ groups present in all zeolites and boralites. The band 3 720 cm^{-1} (well seen only in the spectra of H-boralites activated at 673 K and above this temperature) is assigned⁵ to $\text{Si}-\text{OH}\cdots\text{B}$ groups (Brønsted acid sites). The bands at 3 450 and 3 670 cm^{-1} were assigned⁸ to $\text{Si}-\text{OH}\cdots\text{O}$ and $\text{B}-\text{OH}$ groups in $\text{Si}-\text{OH}\cdots\text{O}-\text{B}$ units.

|
H

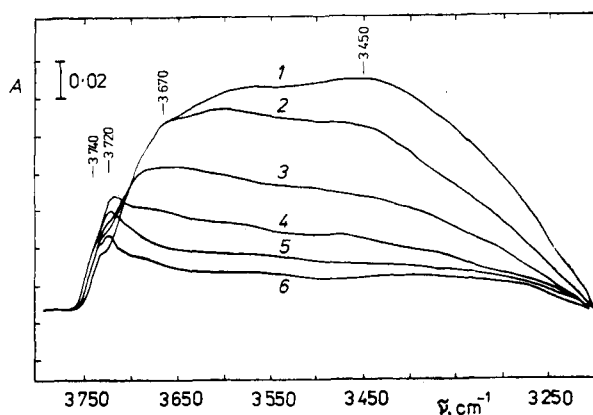
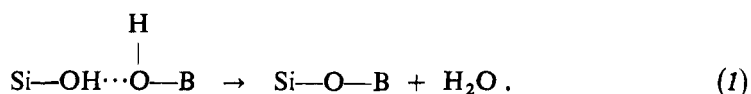


FIG. 1

The IR spectra of OH groups in H-boralite activated at 473 K (1), 573 K (2), 673 K (3), 773 K (4), 873 K (5), 973 K (6)

The data presented in Fig. 1 show that the bands at 3 450 and 3 670 cm^{-1} decrease distinctly with the activation temperature. The dehydroxylation process starts at as low temperature as 473 K. Normally, the dehydroxylation of hydroxyls in zeolites or on oxide surfaces starts at higher temperatures. The very low stability of $\text{Si}-\text{OH}\cdots\text{O}$ and $\text{B}-\text{OH}$ groups at higher temperature may be explained by the reaction:



The fact that these hydroxyls are so much prone to dehydroxylation is most probably

due to low energy barrier of splitting off H^* proton from $\text{Si}-\text{OH}^*\cdots\text{O}-\text{B}$, formation of $\text{SiO}^- \text{H}_2\text{O}^+-\text{B}$ and finally $\text{Si}-\text{O}-\text{B} + \text{H}_2\text{O}$.

As already mentioned, our attention was mostly focused on the properties of Brønsted acid sites ($\text{Si}-\text{OH}\cdots\text{B}$ groups). Their concentration was measured by pyridine sorption. Pyridine molecules when reacting with Brønsted acid sites form pyridinium ions (PyH^+) for which an IR band 1 545 cm^{-1} is characteristic. The intensity of this band expressed per 1 g of boralite A_{HPy^+}/m (measured after the saturation of all acid sites by pyridine) was taken as the measure of the amount of Brønsted acid sites. The values of A_{HPy^+}/m in the case of H-boralite activated at 473–873 K are presented in Table I.

The sorption of pyridine on H-boralite results also in the appearance of the 1 460 cm^{-1} band characteristic for pyridine complex bonded to Lewis acid sites (PyL). The intensity of PyL band expressed per 1 g of boralite (taken as the measure of the amount of Lewis acid sites) is also presented in Table I.

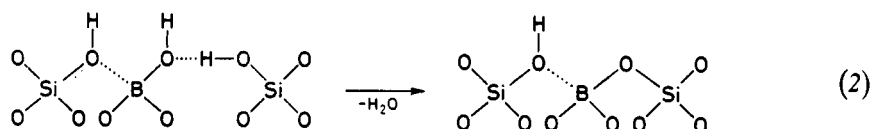
TABLE I

Intensities (expressed per 1 g of boralite) of 1 545 cm^{-1} (PyH^+) and 1 460 cm^{-1} (PyL) bands in H-boralite activated at various temperatures

Activation temperature, K	Intensity, g^{-1}	
	PyH^+	PyL
473	1.80	0.9
573	1.50	0.8
673	1.65	1.2
773	1.72	0.8
873	1.64	0.7

Both A_{HPy}/m and A_{PyL}/m values are practically independent of the activation temperature indicating that neither the loss of Brønsted acid sites nor creation of Lewis sites occurs up to 873 K. It means that the Si—OH···B groups being Brønsted acid sites are much more resistant to dehydroxylation than Si—OH···O and B—OH ones. It should be noted, that the dehydroxylation of Brønsted acid sites in HY zeolites starts at lower temperature (673 K) (ref.¹⁰). The fact, that Brønsted acid sites in H-borolite are more resistant to dehydroxylation than in HY zeolite is due to lower concentration of these sites in H-borolite if compared with HY.

It was interesting to follow the influence of the presence of both Si—OH···O and B—OH groups on the properties of Si—OH···B groups (Brønsted acid sites), according to the equation:



The presence of Si—OH···O and B—OH groups is expected to influence the acid properties of Si—OH···B groups situated in close vicinity. Their loss (by dehydroxylation — Eq. (2)) is expected to modify the properties of Brønsted sites. In order to obtain more data on this subject the frequencies of Si—OH···B band were compared in the spectra of H-borolites activated at 573 and 773 K. Figure 2 shows difference spectra of OH groups in H-borolite interacting with pyridine (a) and ammonia (b). The difference spectra were obtained by the subtraction of the spectrum of activated borolite from the spectrum of borolite with pyridine (or ammonia) sorbed. A minimum in the difference spectrum corresponds to OH groups consumed by reaction

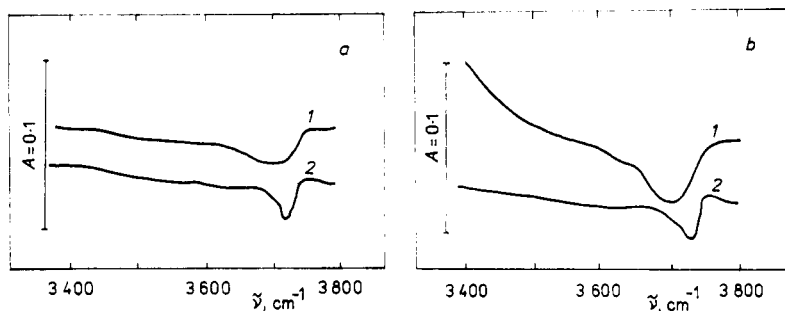


FIG. 2

The difference spectra of OH-groups in H-borolite interacting with pyridine (a) and ammonia (b). These spectra are subtraction result — spectrum recorded after pyridine (or ammonia) sorption minus spectrum of activated borolite: 1 H-borolite activated at 573 K, 2 H-borolite activated at 773 K

with pyridine (or ammonia) i.e. to Brønsted acid sites. The data presented in Fig. 2 show that in the case of H-boralite activated at 573 K, the Brønsted acid sites are OH groups vibrating at $3\,700\text{ cm}^{-1}$. In the case of H-boralite activated at 773 K this band shifts to $3\,720\text{ cm}^{-1}$. Such a change of stretching frequency of Si—OH \cdots B groups may be due to a variation of acid properties of these hydroxyls because of the loss of $3\,450$ and $3\,670\text{ cm}^{-1}$ groups (Si—OH \cdots O and B—OH) by dehydroxylation. A direct study of the effect of activation temperature on the acid strength and catalytic activity is planned in the future.

The authors thank Dr A. Cichocki from Jagiellonian University for the sample of NaNH_4 -boralite.

REFERENCES

1. Tielen M., Geelen M., Jacobs P. A.: *Proc. Int. Symp. Zeolite Catal., Siofok, 1985*, p.1.
2. Scholle K. F. M. G. J., Kentgens A. P. M., Veeman V. S., Frenken P., van der Velden G. H. P.: *J. Phys. Chem.* **88**, 5 (1984).
3. Coudurier G., Viedrine J. C.: *Pure Appl. Chem.* **58**, 1389 (1986).
4. Ratnasamy P., Hedge S. G., Chandwadker A. J.: *J. Catal.* **102**, 467 (1986).
5. Datka J., Piwowska Z.: *J. Chem. Soc., Faraday Trans. 1* **85**, 47 (1989).
6. Scholle K. F. M. G. J., Veeman W. S.: *Zeolites* **5**, 118 (1985).
7. Cichocki A., Łasocha W., Michalik M., Sawłowicz Z., Buś M.: *Zeolites* **10**, 583 (1990).
8. Datka J., Piwowska Z.: *J. Chem. Soc., Faraday Trans. 1* **85**, 837 (1989).
9. Datka J., Cichocki A., Piwowska Z.: *Surface Science and Catalysis 65* (G. Öhlmann, H. Pfeifer and R. Fricke, Eds). Elsevier, Amsterdam 1991.
10. Datka J.: *J. Chem. Soc., Faraday Trans. 1* **77**, 2877 (1981).