MAS NMR AND IR STUDIES ON ZSM-5-TYPE BOROALUMINOZEOLITES

E. BRUNNER, D. FREUDE, M. HUNGER, H. PFEIFER
Sektion Physik der Karl-Marx-Universität Leipzig, DDR-7010 Leipzig, German Democratic Republic

W. RESCHETILOWSKI
Sektion Chemie der Karl-Marx-Universität Leipzig, DDR-7010 Leipzig, German Democratic Republic

and

B. UNGER
Sektion Chemie der Technischen Hochschule "Carl Schorlemmer" Leuna-Merseburg, DDR-4200 Merseburg, German Democratic Republic

Received 20 April 1988

^{11}B MAS NMR proves that incorporation of boron into ZSM-5 zeolitic frameworks takes place when boric acid is present in the reaction mixture. The incorporated boron is removed by subsequent calcination, ion exchange, deammoniation, pelletization and time on stream. ^{1}H MAS NMR and IR spectroscopy show that OH groups introduced into the framework by boron substitution are non-acidic.

1. Introduction

Isomorphous substitution of framework atoms by boron in pentasil-type zeolites and the consequences of this for the catalytic properties, pore size and shape selectivity of these so-called SABO zeolites have recently been investigated [1–5]. Ref. [6] shows that catalyst deactivation is reduced by boron substitution. ^{11}B magic-angle-spinning NMR is capable of probing the short-range order of boron atoms [7] and can easily and accurately determine the concentration of boron in the framework [5]. We demonstrate how boron incorporated during synthesis is removed by subsequent calcination, ion exchange, deammoniation, pelletization and finally by the time on stream.

2. Experimental

SABO zeolites were prepared by hydrothermal crystallization with *n*-propylamine as template [6]. Boric acid was added to the reaction mixture. After calcination at 600°C and ion exchange with aqueous NH_4NO_3, H-SABO was produced by deammoniation at 500°C. The structure and crystallinity of the material were monitored by X-ray diffraction. NMR measurements were performed on a home-made spectrometer HFS 270 and a Bruker MSL-300 spectrometer at resonance frequencies of 270, 70 and 96 MHz for ^{1}H, ^{27}Al and ^{11}B, respectively. The rate of magic-angle spinning was 3–4 kHz. The concentrations of OH groups, framework aluminium and framework boron were determined by comparison with samples of an aqueous solution, of a well-characterized zeolite ZSM-5 and of a well-characterized boron glass for ^{1}H, ^{27}Al and ^{11}B, respectively. The experimental error was $\pm 10\%$. For ^{1}H NMR shallow-bed activation glass tubes of 5.5 mm inner diameter containing a 10 mm deep zeolite layer were used. The temperature was increased at a rate of 10 K/h. After maintaining the samples at the final activation temperature of 400°C and a pressure below 10^{-2} Pa for 24 h, the tubes were sealed. ^{27}Al and ^{11}B

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measurements were generally carried out on rehydrated samples which had been kept in a desiccator for 48 h over aqueous NH_4Cl. IR measurements in the range 1800–2400 nm were recorded on the sealed glass ampoules (prepared for ^1H MAS NMR) in diffuse reflectance on a modified IR Beckman DK-2A spectrometer.

3. Results and discussion

The ^{11}B MAS NMR spectra of the fully hydrated samples show a narrow line (0.6–1.2 ppm wide) with a chemical shift in the range -3.3 to -3.7 ppm from BF_3OEt_2 (see figs. 1b and 1c). This line is assigned to tetrahedrally coordinated framework boron atoms [4,7]. Table 1 gives the concentration of boron in the framework determined from the intensities of this line. For all samples, boron concentration decreases by a factor of 2–3 during preparation of the hydrogen form from the synthesized sample. On the zeolite SABO 1.7 we demonstrate this removal step by step. Calcination causes a loss of about 1/4 of framework boron, whereas no loss can be observed after ammonium exchange. After deammoniation about one half of the boron concentration in the synthesized sample remains. The pelletization process (using 30% Al_2O_3 binder) and the following calcination at 600°C cause a further loss of boron in the framework (see table 1). After 10 h on stream in a MTG process no boron could be detected in framework positions. Boron must either have been removed in

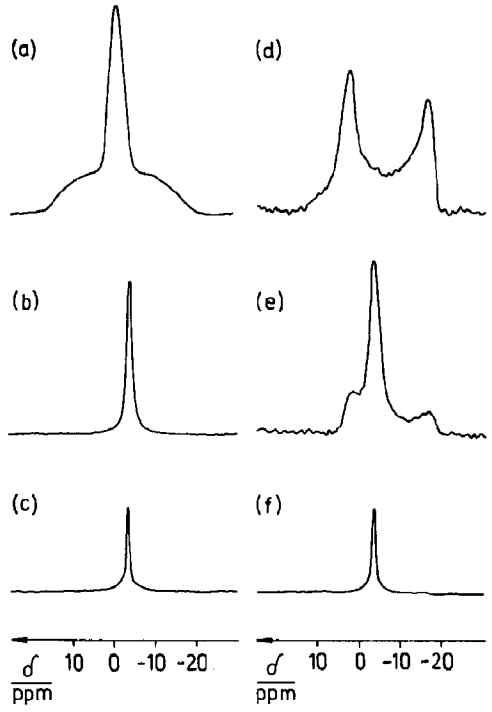


Fig. 1. ^{11}B MAS NMR spectra of (a) boron glass, (b) SABO 2.0 fully hydrated, (c) H-SABO 2.0 fully hydrated, (d) H-SABO 2.0 dehydrated at 500°C, (e) H-SABO 2.0 5 h rehydrated in the desiccator, (f) H-SABO 2.0 48 h rehydrated in the desiccator.

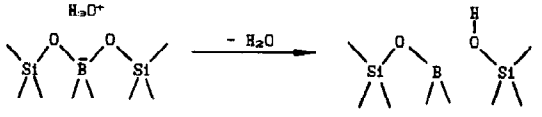
Table 1
Characterization of samples

Sample	Characteristics	Boron atoms per unit cell	Si/B	Si/Al
H-ZSM-5	boron-free sample in hydrogen form	0.00		30
SABO 0.6	as-synthesized	0.62	148	26
H-SABO 0.6	hydrogen form of SABO 0.6	0.20	464	30
SABO 2.0	as-synthesized	2.00	45	29
H-SABO 2.0	hydrogen form of SABO 2.0	0.72	128	32
SABO 2.6	as-synthesized	2.59	35	26
H-SABO 2.6	hydrogen form of SABO 2.6	1.05	88	35
SABO 1.7	as-synthesized	1.71	54	44
C-SABO 1.7	after calcination 6 h at 600°C	1.32	70	
E-SABO 1.7	after exchange with 0.5 N NH_4NO_3	1.32	70	
H-SABO 1.7	after deammoniation 3 h at 500°C	0.95	98	
P-SABO 1.7	after pelletization and calcination	0.65	143	
Q-SABO 1.7	after time on stream in MTG process	<0.06	>1500	
R-SABO 1.7	after regeneration	<0.06	>1500	

the form of volatile boron hydrocarbons or is present in an extremely asymmetric environment on non-framework positions, which make this quadrupolar nucleus "NMR invisible". The regeneration of the SABO catalysts does not lead to any reinsertion of boron into the framework.

If SABO is dehydrated at 500°C in vacuum, the spectrum shows the typical quadrupolar pattern due to the trigonal coordination of boron (see fig. 1d). From the line shape a quadrupole frequency $\nu_Q = 1.23 \pm 0.06$ MHz is calculated. Partially rehydrated samples give spectra (see fig. 1e) with the superposition of a quadrupolar pattern and a single line due to tetrahedrally coordinated boron, as reported by Scholle and Veeman [7]. After complete rehydration no signal due to the trigonal coordination of boron could be observed (see fig. 1f), in contrast to the results of Kessler et al. [3].

Consider two coordinations of boron: the ideal BO_4 tetrahedron in the framework of the hydrated sample and the trigonal BO_3 unit in the dehydrated sample.



For the hydrated zeolite the BO_4 tetrahedra are negatively charged and balanced by H_3O^+. Fig. 2 shows the dependence of ν_Q on the O–B–O angle calculated by means of an ionic model ($\theta = 109°$ corresponds to the tetrahedral coordination). In this model we assume a rigid oxygen tetrahedron. The B–O distances change with θ. For $\theta = 90°$ (trigonal coordination) we assume the B–O distance to be equal to 0.136 nm in the BO_3 unit and the O–H distance equal to 0.096 nm [8]. If boron is in tetrahedral coordination the quadrupole frequency is at a minimum. A simple estimation using Pauling's ionic radii [8] shows that a planar arrangement is possible. This is not so for aluminium, the ionic radius of which is more than twice that of boron. The experimental value $\nu_Q = 1.23$ MHz proves that in the dehydrated sample boron is in a planar configuration.

The acid strength of hydroxyl groups is reflected in the ^{1}H MAS NMR spectrum [9]. Non-acidic SiOH groups give rise to a line at 1.8–2.3 ppm and acidic bridging OH groups give rise to a line at 4.3 ppm in

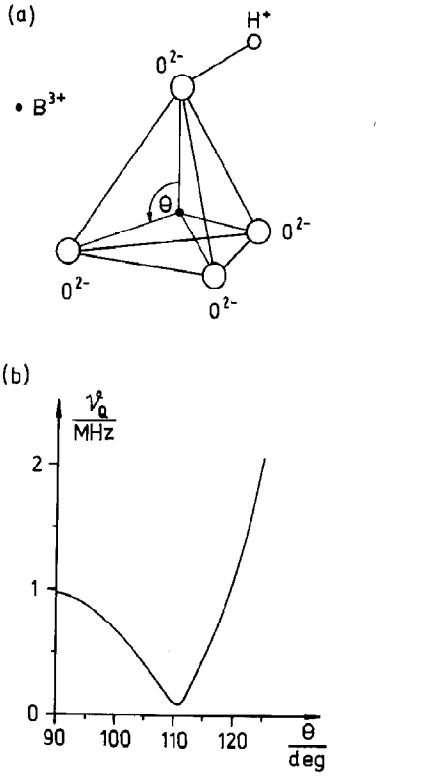


Fig. 2. Boron coordination, (a) ionic coordination model for framework boron atoms, (b) quadrupole frequency calculated for different values of the angle θ.

silicon-rich zeolites [9]. Figs. 3a and 3b show the ^{1}H MAS NMR spectrum of boron-free H-ZSM-5 and the spectrum of sample H-SABO 2.6. Both spectra contain a line at 4.3 ppm due to the bridging OH groups in the SiOHAl arrangement. The number of bridging OH groups is equal to the number of framework aluminium atoms in these samples (see table 2). It follows that there is no increase in intensity of the line at 4.3 ppm due to OH groups on boron sites. Instead, boron incorporation causes an increase in the intensity of the line of non-acidic OH groups at about 2 ppm (see table 2) and a slight shift of this line from 2.1 ± 0.1 to 2.4 ± 0.2 ppm. This increase agrees well with the number of boron atoms in the zeolitic framework detected by ^{11}B MAS NMR (see table 2). Therefore it is probable that these additionally observed OH groups correspond to the abovementioned OH groups in the neighborhood of boron atoms. The result that OH groups in the SiOHB arrangement are non-acidic is confirmed by IR spec-

Table 2
Concentrations of framework aluminium and boron atoms and hydroxyl groups [a]

Sample	Number of species per unit cell (96 framework tetrahedra)				
	(1) framew. Al	(2) framew. B	(3) total OH	(4) SiOH	(5) bridging OH
H-ZSM-5	3.10	0.00	3.82	0.94	2.88
H-SABO 0.6	3.10	0.20	4.40	1.32	3.08
H-SABO 2.0	2.88	0.72	4.50	1.61	2.89
H-SABO 2.6	2.64	1.05	4.40	2.39	2.01

[a] (1) The concentration of framework aluminium atoms determined by ^{27}Al MAS NMR; (2) the concentration of framework boron atoms determined by ^{11}B MAS NMR; (3) the total concentration of OH groups obtained from the maximum amplitude of the free induction decay; (4) the concentration of SiOH groups obtained from the intensity of the 2 ppm line in the ^{1}H MAS NMR spectrum; (5) the concentration of bridging SiOHAl groups obtained from the intensity of the 4.3 ppm line in the ^{1}H MAS NMR spectrum.

troscopy. Figs. 3c and 3d show the spectra of H-ZSM-5 and H-SABO 2.6 in the region of the OH combination vibration. Generally three bands can be identified [10]:

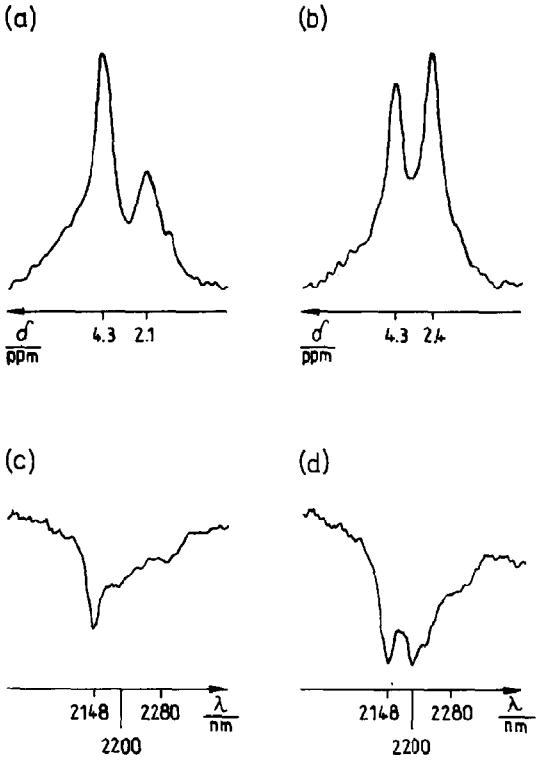


Fig. 3. Spectra describing the acid strength of OH groups: (a) ^{1}H MAS NMR spectrum of H-ZSM-5; (b) ^{1}H MAS NMR spectrum of H-SABO 2.6; (c) IR spectrum of H-ZSM-5; (d) IR spectrum of H-SABO 2.6.

(i) the band due to bridging OH at 2148 ± 5 nm;

(ii) the band due to non-acidic SiOH at 2200 ± 5 nm;

(iii) the band due to non-acidic AlOH at 2280 ± 25 nm.

Boron incorporation causes an increase of the band of non-acidic SiOH groups at 2200 nm.

We conclude that on the ^{1}H MAS NMR scale the OH groups in the SiOHB arrangement are much less acidic than the bridging hydroxyl groups in the neighborhood of framework aluminium and only slightly more acidic than SiOH groups on framework defects. The framework boron is not very stable and can easily be removed by hydrothermal treatment.

Acknowledgement

We thank Dr. J. Klinowski (Cambridge) for helpful comments.

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