CHEMICAL AND CATALYTIC PROPERTIES
OF ZSM-5 TYPE BOROALUMINOSILICATES

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ABSTRACT
Isomorphous incorporation of boron into ZSM-5 and the influence on the properties of the products were investigated. Acidity and catalytic activity in paraffin cracking reactions strongly depend on the concentration of framework aluminium atoms. Incorporated boron perfectly detectable by \textsuperscript{11}B MAS NMR influences shape selectivity only.

INTRODUCTION
Isomorphous substitution of aluminium or silicon by boron in pentasil-type zeolites and the consequences of this for the properties of these so-called SABO zeolites have been recently investigated to some extent (ref. 1). However, mainly samples, which either show only a small boron concentration (ref. 2) or aluminium in the ppm range (ref. 3) were studied. Little information is available about the properties of SABO zeolites with comparatively large amounts of both elements in the framework (ref. 4). Published studies disagree about the acidic and catalytic properties of boron-containing pentasil-type zeolites.

We describe zeolites of H-ZSM-5 type containing 0.8 - 2.8 Al/u.c. and 0.0 - 3.1 B/u.c.
EXPERIMENTAL

Materials
SABO zeolites were prepared by hydrothermal crystallization in conformity with the conditions of ZSM-5 synthesis (ref. 5). Boric acid was added to the reaction mixture. The pentasil structure and crystallinity were checked by XRD and transmission IR. The highly crystalline material consists of uniform crystallites of a size of about 3 μm. Chemical composition was determined using EPMA and PIXE/PIGE.

After calcination at 600 °C (to remove organic material) and ion exchange with aqueous NH₄NO₃, the H-SABO was produced by deamination at 500 °C.

Methods
Acidic properties were investigated by thermal desorption of ammonia: i) adsorption at 100 °C followed by stepwise static desorption in the temperature range of 150 °C - 600 °C in 50 K steps, ii) after adsorption at 150 °C by TPAD in the range up to 650 °C with a linear heating rate of 11 K/min.

Catalytic activity was determined for the cracking reaction of n-hexane at 300 °C in an integral flow reactor with a feed rate of 0.014 mole per gram catalyst and hour. Thus, the first order reaction rate constant (kₒ) is given as a measure for catalytic activity.

Shape selectivity is expressed as the "constraint index", defined as the ratio kₒ/k₃-MP (kₒ, k₃-MP = reaction rate constants), in the cracking reaction of an equimolar n-hexane/3-methylpentane mixture at 450 °C in a microcatalytic pulse system. 

¹¹B magic-angle-spinning (MAS) NMR measurements were conducted using a single pulse excitation, a Larmor frequency of 96 MHz and spinning rate of c. 4 kHz. The chemical shift is given in ppm from BF₃.OEt₂.

RESULTS AND DISCUSSION

MAS NMR

The spectrum of RASOTHERM glass, given in Fig. 1 (a), shows the superposition of the typical quadrupolar pattern due to the trigonal coordination and of a single line (at about -3 ppm) due to the tetrahedrally coordinated boron atoms for RASOTHERM glass. Spectrum (b) is similar to spectrum (a), but shows a superposition of two lines due to the trigonal and tetrahedral coordination of boron in the zeolite at a lower signal to noise ratio. We measured this type of spectra for partially rehydrated samples. Scholle and Veeman (ref. 6) were the first to show the superposition of a single line and a typical quadrupolar pattern for boron substituted ZSM-5.
Spectrum (c) shows a single narrow line at about -3 ppm and is typical for fully rehydrated samples. The full-width-at-half-maximum (FWHM) is 0.6 ppm, much less than for (a) and (b). The difference between the values of the chemical shift for the single lines in spectra (a) and (b) is only 0.8 ppm. FWHM seems to be a more appropriate measure of boron incorporation than the chemical shift value as proposed by Gabelica et al. (ref. 7). Tetrahedral coordination with respect to oxygen in the zeolitic framework gives relatively narrow lines for $^{11}\text{B}$ at T-positions particularly in view of the relatively small electric quadrupole moment of $^{11}\text{B}$.

Measurements of the intensity of the narrow line at -3.1 ppm for the as-synthesized SABO and for the zeolite after calcination, ammonium exchange, and deammoniation gave the following important result: Only for samples with a content of more than 2 boron atoms per u.c. can the loss of boron in the framework during the treatment be neglected. On the samples with a lower concentration (after synthesis) the majority of the boron is washed out during the treatment.

Thus, samples with a comparable content of boron and aluminium atoms show a relatively stable boron incorporation.

Fig. 1. $^{11}\text{B}$ MAS NMR spectra of the RASOTHERM glass (a), partially rehydrated H-SABO with 0.9 B/u.c. (b), and fully rehydrated H-SABO with 3.1 B/u.c. (c).
Ammonia desorption

i) Effects of stepwise static thermal desorption of NH₃ on the protonic forms of a dealuminated mordenite (ref. 8), a ZSM-5 and a SABO all having nearly the same Si/Al ratio of about 35 are shown in Fig. 2 (a). The concentration of the ammonia remaining on zeolite surface as a measure of the concentration of acidic centres with its temperature dependence as a measure of acid strength show that H-SABO possesses acidic sites of a lower average strength than other zeolites in the H-form: Nearly all of the ammonia is desorbed at 400 °C in the case of H-SABO and at 500 °C in the case of H-ZSM-5, whereas on H-mordenite desorption of ammonia is still incomplete at 600 °C.

ii) Fig. 2b illustrates the TPAD spectra of H-SABO zeolites having various compositions. The results show that the amount of desorbed ammonia does not differ significantly between samples with the same Si/Al ratio but different boron contents, including boron-free H-ZSM-5. A slight shift of desorption maxima in H-SABO to lower desorption temperatures in comparison with H-ZSM-5 indicates, in accordance with the results discussed in i), that boron incorporation leads to a decrease in acid strength.

Fig. 2. Thermal desorption of ammonia measured under stepwise static (a) and temperature programmed (b) conditions.
A change in the amount of desorbed ammonia was only detected when the Si/Al ratio changed. The areas of both, the low temperature and the high temperature peaks, became smaller with increasing Si/Al ratio. It follows that the concentration of acidic sites in (Al, B)-ZSM-5 is determined only by the amount of framework aluminium. The increase of both peaks in the TPAD spectra with increasing aluminium content suggests that this aluminium is responsible for both, a coordinative interaction with NH$_3$ molecules (low temperature peak) and with Bronsted acidic sites (high temperature peak) (ref. 9).

A decrease of the acidity of H-ZSM-5 in dependence on impregnation with boron has been reported by Auroux et al. (ref. 10). However, it is difficult to compare samples prepared by boron impregnation with samples prepared by direct synthesis.

**Catalytic behaviour**

The number of catalytically active Bronsted acidic sites is determined by the amount of framework aluminium. As can be seen from Fig. 3, there is a correlation between $k_0$ in the n-hexane cracking reaction and the aluminium content.

![Fig. 3. Catalytic activity for n-hexane cracking at 300 °C versus aluminium content in H-SABO.](image)
Fig. 4. Reaction rate constant (related to one Al/u.c.) as a function of boron content in H-SABO.

Fig. 5. Effect of boron incorporation on shape selectivity of H-SABO.
The TPAD data demonstrate that the concentration of the active acidic sites increases with Al concentration, and so does the cracking activity.

Fig. 4 describes catalytic activity of SABO zeolites, \( k_{o,rel.} \) on the number of boron atoms per unit cell. The variation of the boron content in the range up to 3.1 B/u.c. does not affect the cracking activity, as is to be expected from the acidity measurements.

However, it should be possible to control shape selective properties of pentasil-type zeolites by controlled isomorphous incorporation of boron (ref. 11). Indeed, the "constraint index" (see Fig. 5) shows that H-SABO with a boron content of more than 2 B/u.c. exhibit increasing shape selectivity. This is in a good agreement with the NMR data: In samples with higher shape selectivity boron occupies stable tetrahedral framework positions.

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REFERENCES