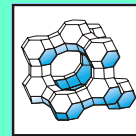


Coordination Transformation of Framework Boron Atoms in Zeolite H-[B]ZSM-5 upon the Adsorption of Probe Molecules Studied by Solid-State NMR Spectroscopy

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Introduction

In general, boron in boron-substituted zeolites exists as trigonally ($B^{[3]}$) or tetrahedrally ($B^{[4]}$) coordinated species. However, their existence depends on the state (hydrated/as-synthesized or dehydrated) of the zeolite, the presence of counter ions, and the size and amount of extra framework cations [1]. Interestingly, the coordination of these species can be converted into each other upon hydration, dehydration, adsorption and desorption of organic molecules [2]. Nevertheless, reports concerning the effect of probe molecules on the framework boron in boron-substituted zeolites are very scarce. Moreover, the detailed investigation on the structural transformation of $B^{[3]}$ species into $B^{[4]}$ species has not been reported. In the current work, an attempt has been made to investigate the structural transformation of $B^{[3]}$ into $B^{[4]}$ species in dehydrated zeolite H-[B]ZSM-5 upon the adsorption of probe molecules with different proton affinities (PA).

Experimental Section

Probe molecules such as pyridine, ammonia and acetone were loaded by using *in situ* technique with the utilization of the injection equipment as described in ref. [3]. Probe molecules such as dimethylsulfoxide, pyrrole, acetamide, and tetrahydrothiophene were loaded by *ex situ* technique under dry nitrogen flow in a glove box. The 1H and ^{11}B MAS NMR spectra were acquired on a Bruker MSL 400 spectrometer using a 4 mm probe with a sample spinning rate of 8.0 to 9.0 kHz at resonance frequencies of 400.1 and 128.3 MHz, respectively. The MAS NMR measurements were recorded by applying a single pulse excitation with pulse lengths of 2.25 and 1 μs , repetition times of 10 and 2 s, and 48 and 800 accumulations for 1H and ^{11}B nuclei, respectively.

Results and Discussion

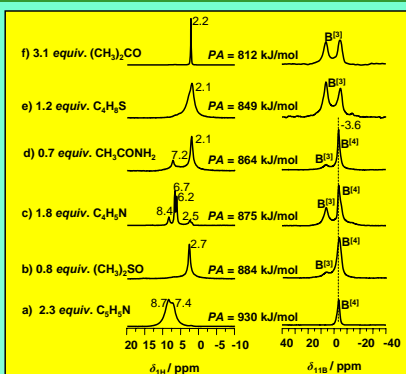


Fig. 1. 1H (left) and ^{11}B (right) MAS NMR spectra of zeolite H-[B]ZSM-5 recorded in the magnetic field of $B_0 = 9.4$ T, upon adsorption of a) pyridine, b) dimethylsulfoxide, c) pyrrole, d) acetamide, e) tetrahydrothiophene, and f) acetone.

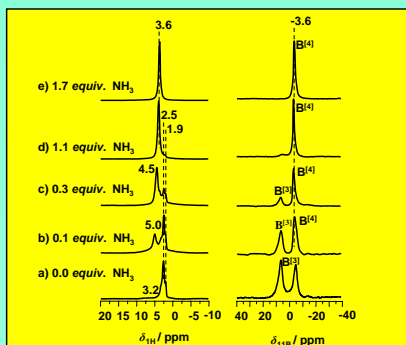
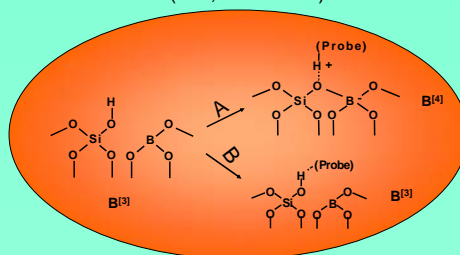


Fig. 2. 1H (left) and ^{11}B (right) MAS NMR spectra of zeolite H-[B]ZSM-5 recorded upon adsorption of ammonia ($PA = 854$ kJ/mol) by *in situ* technique in the magnetic field of $B_0 = 9.4$ T.

• Probe molecules with PA values higher than 850 kJ/mol could induce the coordination transformation of $B^{[3]}$ species into $B^{[4]}$ species in zeolite H-[B]ZSM-5, upon adsorption (see, Figs. 1a to 1d, right). In contrast, probe molecules with PA values lower than 850 kJ/mol could not (see, Figs. 1e and 1f, right).

• For the probe molecules with $PA > 850$ kJ/mol, protonation occurs, and leads to the transformation of $B^{[3]}$ into $B^{[4]}$ species. Whereas in case of probe molecules with $PA < 850$ kJ/mol, only hydrogen bonds are formed (see, Scheme 1).



Scheme 1. Paths of zeolite H-[B]ZSM-5 load with probe A) $PA > 850$ and B) $PA < 850$ kJ/mol

• Fig. 2, left, shows 1H MAS NMR spectra of zeolite H-[B]ZSM-5 upon adsorption of ammonia ($PA = 854$ kJ/mol) in different stages by *in situ* technique. Upon adsorption of ammonia, a signal at ca. 5 ppm is observed at lower loadings (Fig. 2b, left), which is then shifted to ca. 3.6 ppm at higher loadings of ammonia (Fig. 2e, left). Due to the rapid exchange of protons between ammonia and ammonium ions, these 1H MAS NMR signals are attributed to (NH_3/NH_4^+) [4].

Table 1. Quadrupole coupling constants (C_{QCC}) and asymmetry parameters (η) of $B^{[3]}$ and $B^{[4]}$ species of framework boron in zeolite H-[B]ZSM-5 upon adsorption of probe molecules with different proton affinities determined with the use of Bruker WINFIT software.

Probe molecule	Proton affinity (kJ/mol)	$B^{[3]}$		$B^{[4]}$	
		C_{QCC} (MHz)	η	C_{QCC} (MHz)	η
Pyridine	930	2.65	0.10	0.80	0.01
Dimethylsulfoxide	884	2.76	0.10	0.98	0.01
Pyrrole	875	2.68	0.10	0.84	0.01
Acetamide	864	2.66	0.10	0.76	0.01
Ammonia	854	2.68	0.10	0.75	0.01
Tetrahydrothiophene	849	2.69	0.10	-	-
Acetone	812	2.65	0.10	-	-

• Table 1, shows the C_{QCC} and η values of $B^{[3]}$ and $B^{[4]}$ species. It was observed that, upon adsorption of probe molecules with $PA > 850$ kJ/mol, the C_{QCC} value of $B^{[3]}$ species remains the same, but the amount of $B^{[3]}$ species gradually reduces and transforms into $B^{[4]}$ species (see, Fig. 2, right). The local electric field gradient of ^{11}B nuclei in its tetrahedral coordination is much smaller than in its trigonal coordination [1]. Therefore, the C_{QCC} values of $B^{[4]}$ species are much lower than those of $B^{[3]}$ species as shown in Table 1.

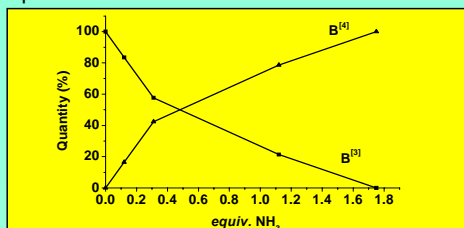


Fig. 3. Sequential transformation of $B^{[3]}$ into $B^{[4]}$ species in zeolite H-[B]ZSM-5 against loading of ammonia, obtained by the simulation and integration with the use of Bruker WINFIT software.

• The gradual transformation of $B^{[3]}$ into $B^{[4]}$ species (ca. -3.6 ppm) upon adsorption of ammonia is shown in ^{11}B MAS NMR spectra (Fig. 2, right). With the help of simulation and integration, quantitative evaluation of $B^{[3]}$ and $B^{[4]}$ species at different stages was accomplished and plotted as a function of ammonia loading (Fig. 3). It indicates that ca. 1.7 equiv. ammonia loading is required for the complete structural transformation of $B^{[3]}$ into $B^{[4]}$ species.

Conclusions

^{11}B MAS NMR spectra of dehydrated zeolite H-[B]ZSM-5 upon adsorption of probe molecules with different proton affinities reveal that a proton affinity of 850 kJ/mol is necessary to induce the structural transformation of $B^{[3]}$ species into $B^{[4]}$ species. The quadrupole coupling constants of $B^{[3]}$ and $B^{[4]}$ species obtained from the simulation are ca. 2.6 and 0.8 MHz, respectively. Complete structural transformation of $B^{[3]}$ into $B^{[4]}$ species, and the quantity of $B^{[3]}$ and $B^{[4]}$ species depend upon the loading of probe molecules.

Acknowledgements

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