Nitrogen-15 and Boron-11 NMR Spectroscopy of the System Acetonitrile / H-ZSM-5

F. C. Feyen, P. K. Burkert*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching

Dedicated to Professor H. P. Fritz on the occasion of his retirement

Z. Naturforsch. 50b, 1753–1758 (1995); received May 4, 1995

15N NMR Spectra, 11B NMR Spectra, ZSM-5, Acetonitrile, Acid Sites

The interaction of adsorbed acetonitrile with microporous [Si,Al]-ZSM-5 and [Si,B]-ZSM-5 was investigated by solid state NMR. 15N-CP MAS NMR of the system H-[Si,Al]-ZSM-5 / acetonitrile clearly shows the Bronsted and Lewis acid site interactions. Different coordination types of the complex ZSM-5/MeCN are considered. The accessibility of the acid sites of [Si,B]-ZSM-5, a material structurally analogous to zeolite ZSM-5, was studied by 11B-MAS NMR. The complexation of acetonitrile at the BO₃ sites gives a narrow line at -4 ppm. In contrast to hydration phenomena of ZSM-5, the experiments show that acetonitrile is not capable of interacting with all of the BO₃ sites of the borosilicate, presumably due to steric effects.

Introduction

Zeolites and zeolite-analogous materials are microporous crystals that have great significance in catalysis as size- and shape-selective molecular sieves [1-3]. A fundamental characteristic of these materials is their Bronsted and Lewis acidity. Highly acidic Bronsted behavior of these materials, which is due to the isomorphous substitution of a tetrahedrally coordinated tetravalent atom of the lattice (T-atom) by a trivalent element, is well known to be responsible for many catalytic processes [4]. The proton-donating Bronsted sites are characterized by spectroscopic methods, like infrared spectroscopy (IR) or solid state nuclear magnetic resonance spectroscopy (solid state NMR). The vibrational frequencies of the OH group and the 1H chemical shifts are common measures of the acid strength of the Bronsted sites. Unfortunately, the nature of the Lewis sites of the zeolite framework is not accessible by these spectroscopic methods. Several investigators have reported on a study of the interaction between the acid sites of the zeolite materials and adsorbed probe molecules [5-8]. The primary goal of this work was the characterization of the acid sites (Bronsted and Lewis sites) of a zeolite by using the weak Lewis base acetonitrile.

The present contribution addresses two objectives. We first report the solid-state CP MAS NMR study of the system acetonitrile/H-[Si,Al]-ZSM-5. The formation of various absorption complexes due to different loading ratios of the probe molecule was proven by 15N-CP MAS NMR spectroscopy. The loaded zeolite was sealed in MAS glass inserts to prevent coadsorption of other molecules during the NMR experiment.

The second objective was to study the accessibility of the acid sites of the lattice. We used the structurally analogous borosilicate H-[Si,B]-ZSM-5 to determine the interaction between the probe molecule acetonitrile and the acid sites of the lattice. The borosilicate [Si,B]-ZSM-5 was synthesized using a conventional hydrothermal method [9,10]. The structure was verified by X-ray diffraction (XRD) and 11B-MAS NMR. In contrast to its aluminum analogues, the dehydrated borosilicate possesses a planar trigonally coordinated BO₃-unit [11,12]. In dehydrated [Si,Al]-ZSM-5 no trigonally coordinated aluminum could be detected. However, the intracrystalline volumes of the microporous materials remain almost constant. Results estimated from the system acetonitrile/borosilicate contribute in addition valuable information on the system acetonitrile/alumosilicate.

* Reprint requests to Prof. Dr. P. K. Burkert.
$^{11}\text{B}$ has spin 1=3/2 and thus an electric quadrupole moment. Under the influence of magic-angle-spinning at high magnetic field strength, tetrahedral $^{11}\text{B}$ sites give relatively narrow lines, while trigonal boron produces a quadrupolar doublet pattern [13]. The dipolar $^{11}\text{B} - ^1\text{H}$-interaction is removed by proton decoupling during the NMR experiment, and the $^{11}\text{B}-^{11}\text{B}$ and the $^{11}\text{B}-^{10}\text{B}$ interactions are small because of the long distance between the boron atoms within the framework. However, the $^{11}\text{B}$ chemical shift range is small and the peaks corresponding to the two boron sites often cannot be clearly separated. A deconvolution routine was used to calculate the areas of the signals. Axon et al. studied the effect of dehydration and rehydration on the coordination of boron in the borosilicate H-[Si,B]-ZSM-5 [12]. The $^{11}\text{B}$-MAS NMR spectra of the fully hydrated samples consist of a single sharp line at the chemical shift of -4 ppm from BF$_3$·Et$_2$O, indicating a highly symmetric arrangement of the four oxygens in the BO$_4$ tetrahedron in the framework. Upon dehydration the intensity of the peak decreases and a second resonance with a characteristic quadrupolar shape appears, showing the lowering of the symmetry (BO$_3$ site). Complete dehydration of the borosilicate results in a spectrum showing only the quadrupolar broadened signal of the BO$_3$ sites. Rehydration restores the single $^{11}\text{B}$-NMR signal. We present here the study of the interaction between the weak base molecule acetonitrile and the acid sites of the borosilicate H-[Si,B]-ZSM-5.

**Experimental**

High purity samples of the aluminosilicate and the borosilicate were prepared hydrothermally using a mixture of Ludox AS-40 silica sol, tetrapropylammonium bromide (TPABr), H$_2$O and Al(OH)$_3$ or H$_3$BO$_3$, respectively. The molar compositions of the mixtures were as follows: 4TPA$_2$O 30SiO$_2$ Al$_2$O$_3$ Na$_2$O 750 H$_2$O ([Si,Al]-ZSM-5) and 4TPA$_2$O 30SiO$_2$ Na$_2$O B$_2$O$_3$ 750 H$_2$O ([Si,Al]-ZSM-5). Crystallizations were carried out at 190 °C for 5–6 days in 25 ml teflon-coated stainless steel autoclaves. The ratios of the microcrystalline solid products were: Si/Al=26 and Si/B=34 (determined by AAS). Fig. 1 ([Si,Al]-ZSM-5) and Fig. 2 ([Si,B]-ZSM-5) show the X-ray powder diffraction spectra of the materials. The crystallite size of the samples prepared in this way was in the range of 50 μm (maximum dimension). Fig. 3 and
Fig. 4. REM-picture of [Si,B]-ZSM-5 (as-synthesized form). Magnification: 1500. The crystallite size of the bo-
rosilicate was in the range of 50 μm. The molar composi-
tion of the synthesis mixture were as follows: 4TPA2O
30SiO2 B2O3 Na2O 750H2O. Obviously the crystals are
strongly twinned.

procedure was completed the samples were loaded
with defined amounts of the probe molecule ace-
tonitrile. The acetonitrile was allowed to adsorb
into the microporous sample by breaking the seal
of the ampoule (Fig. 5; Valve A). Co-adsorption of
inert gas molecules was excluded. After adsorp-
tion was completed (>24 h) the MAS glass insert
was sealed off. Spinning speeds of 4 kHz could be
achieved by using the sealed glass insert and a 7
mm Bruker MAS rotor.

Nitrogen is present in natural abundance as 99.6
% 14N and 0.4 % 15N. There were only few 15N
MAS NMR studies in the past, because of this low
natural abundance of 15N-nuclei (I=1/2) which
makes isotropic enrichment necessary. To over-
come these problems of low signal intensity and / 
or time-consuming NMR experiments, the aceto-
nitrile used in our studies was 99 % enriched in
15N. However, low loading ratios of acetonitrile
and the long spin-lattice relaxation times still
causen experiment times greater than 24 h.

The 15N-MAS NMR experiments were carried
out by straightforward 90°-puls excitation on a
Bruker AMX 400 spectrometer at 40.55 MHz. The
repitition times of 4 s gave full relaxation (CP). A
spinning frequency of 4 kHz proved to be suffi-
cient. Nitrogen-15 chemical shifts are reported rel-
tive to the nitrate resonance of solid NH4NO3
(NO3 = 0.0 ppm, external). The 11B-MAS NMR
and 27Al-MAS NMR experiments were carried
out on a Bruker MSL 300 spectrometer at 96.305
MHz for 11B and at 78.2 MHz for 27Al. The chemi-
cal shifts are reported relative to the BF3·Et2O
resonance and to Al(H2O)63+, respectively.

Results and Discussion

Table I shows the loading ratios of the acetoni-
trile and the number of acid sites of the zeolite.
The number of the acid sites was calculated from
the Si/Al-ratio of the H-ZSM-5 sample. The 15N-
CP MAS NMR spectra as a function of the aceto-
nitrile content are shown in Fig. 6. The two signals
at the chemical shifts -269.2 ppm and -253.9 ppm
indicate the protonated acetonitrile [MeCN-H]+
and the acetonitrile interacting with the acid sites
of the zeolite, respectively. The signal at -253.9
ppm may be due to a Lewis complex of acetoni-
trile with lattice and / or extralattice acid sites of
ZSM-5 (four- and six-coordinated aluminum).

For the more highly loaded samples, however,
the situation is different. Fig. 6 (sample 2, 3) shows
the spectra of zeolite ZSM-5 loaded with increas-
ing amounts of the probe molecule (ratio 3.7 and
11.0, respectively). The spectra clearly show lines
at -143.5 ppm attributed to acetonitrile which is
not adsorbed and thus not interacting with the
framework of the zeolite, and at -243.4 ppm [8].
This line may be due to acetonitrile which is physi-
cally absorbed in the ZSM-5 lattice without in-
teracting with the acid sites. GC-MS analysis of
the samples did not reveal any impurity. For exam-
ple, no acetamide could be detected.

Following investigations by J. F. Haw [8], the
existence of the Bronsted site interaction was
proven by a proton-coupled 1:iN-MAS NMR
spectrum of sample 3. The signal to noise ratio
was low, but by comparing the line shapes one can conclude that the dipolar interaction between the protons and nitrogen is strong and that it cannot be eliminated by magic angle spinning alone. Proton decoupling strongly affects the line width of the signal at -269.2 ppm. The dipolar interaction of [MeCN-H]+ makes the 15N-line broader by a factor 7.

In order to establish whether the Lewis-interaction of the probe molecule is dominated by the tetrahedral sites of the lattice or by the largely extralattice octahedral sites (Fig. 7), the 27Al-MAS NMR spectra were recorded (Fig. 8; A-C). The spectra exhibit two different lines at 53.9 ppm and 0.0 ppm. The aluminum coordination can be determined on the basis of these chemical shift data. The line at 53.9 ppm is attributed to four-coordinated Al. The line at 0.0 ppm originates from the six-coordinated aluminum [14], which we assign to the extralattice Lewis sites (Fig. 7), presumably Al(H2O)6+. Fig. 8 B shows the 27Al-MAS NMR spectra of the sample containing MeCN without isotropic enrichment of 15N. While the line at 53.9 ppm (four-coordinated Al) is nearly unchanged, the line at 0.0 ppm (six-coordinated Al) is broader, because of the strong quadrupolar 14N-27Al-interaction.

The lower spectrum (Fig. 8 C) shows the situation of the system ZSM-5/acetonitrile-15N. As expected, the line shape of spectrum C, which turned
Table I. Ratios of the probe molecule acetonitrile and the acid sites of the zeolite H-ZSM-5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetonitrile / Acid site of ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>3.7</td>
</tr>
<tr>
<td>3</td>
<td>11.0</td>
</tr>
</tbody>
</table>

The Bronsted and Lewis interaction between the probe molecule acetonitrile and ZSM-5, as estimated by $^{15}$N-NMR, could thus be proven by $^{27}$Al-MAS NMR spectroscopy. While the linewidth of the signal at 0.0 ppm was affected by quadrupolar broadening, the interaction between the tetrahedrally coordinated aluminum and the probe molecules could not be verified by $^{27}$Al-NMR.

Kentgens and Axon investigated the influence of water on the line shape of the $^{27}$Al-NMR spectra of the alumosilicate ZSM-5, respectively [12,14]. We recorded $^{11}$B-NMR spectra to prove the accessibility of the Lewis acid sites of the [Si,B]-ZSM-5 framework by water and the probe molecule acetonitrile. Dehydrated borosilicate possesses planar trigonally coordinated BO$_3$-units, while the framework of hydrated [Si,B]-ZSM-5 shows only tetrahedral BO$_4$-units. Under the influence of magic-angle-spinning at high magnetic field strength, tetrahedral $^{11}$B sites give relatively narrow lines. Trigonally coordinated boron produces a quadrupole doublet pattern. Fig. 9 shows the $^{11}$B-MAS NMR spectra of the system [Si,B]-ZSM-5/acetonitrile as a function of the loading ratio (A-H, Table II). The spectra show that the loading of the dehydrated [Si,B]-ZSM-5 sample generates a narrow line at 4 ppm, apparently due to the formation of a [MeCN-BO$_3$]-complex. In contrast to the system [Si,B]-ZSM-5/water, the intensity of the quadrupole pattern of the BO$_4$-units is also decreasing but still detectable even at the loading ratio of 50 (H). We suggest that the acetonitrile does not have
access to all boron acid sites of [Si,B]-ZSM-5, because of the different molecular dimensions. Fig. 10 shows that the water interacts with virtually all acid sites of the borosilicate even at a low or moderate loading rate, while the BO₄/BO₃-ratio as a measure of the accessibility of the acid sites remains constant in the case of the more highly loaded [Si,B]-ZSM-5/acetonitrile system.

**Acknowledgements**

We thank Mr. M. Zähres (Universität Duisburg) for his skilful technical assistance. Furthermore, we are grateful to Professor H. P. Fritz (TU München) and Professor W. S. Veeman (Universität Duisburg) for supporting this work and for helpful discussions.