Charge-Induced Partial Ordering of Boron around Structure Directing Agents in Zeolites Observed by ^{13}C{^{11}B} Rotational Echo Double Resonance NMR

Christian Fild, Hellmut Eckert, and Hubert Koller*

Institut für Physikalische Chemie
Westfälische Wilhelms-Universität Münster
Schlossplatz 4/7, D-48149 Münster, Germany

Received September 14, 2000

Zeolites are microporous solids which are formed by a three-dimensional network of tetrahedrally oxygen-coordinated framework atoms (e.g., Si, Ti, Al, B, Ga, ...), and they are important catalysts for commercial applications.[1] However, the location of the active sites is unknown in most zeolites, preventing a mechanistic understanding of catalytic function. To study a possible influence of the structure directing agent (SDA) on the genesis of the charge center distribution (e.g. $BO_{4/2}^{-}$), we have investigated the relative orientation of the SDA in the zeolite channels toward the heteroatoms in two borosilicate zeolites.

To this end, the ^{13}C{^{11}B} rotational echo double resonance (REDOR) NMR method was employed which has been developed to measure the spatial proximity between two different NMR nuclei.[2] The technique is used to study the boron distribution around *N*,*N*,*N*-trimethyl-(−)-*cis*-myrtanylammonium ions, TMMA, in B-CIT-1,[3] and around *N*-methyl-(−)-sparteinium ions, MSP, in B-SSZ-24.[4] The REDOR method already has been applied successfully to other problems in zeolite science.[5]

In the REDOR experiment, the decay of transverse magnetization due to heteronuclear dipolar coupling is measured in an element- and site-selective manner: First, a spectrum is acquired using a rotor-synchronized spin−echo pulse sequence where the NMR intensity (S_0) of the nucleus of interest is observed as for example ^{13}C nuclei of TMMA (Figure 1a). A second spectrum (REDOR spectrum) is then acquired with the spin−echo pulse sequence applied to the observed nuclei while additional rotor-synchronized 180° pulses are applied to the coupled nuclei (e.g. ^{11}B in the zeolite framework, Figure 1b) during the rotor period. These π-pulses serve to reintroduce the dipolar coupling that is otherwise eliminated by magic-angle spinning (MAS). The resulting difference signal, $\Delta S = S_0 - S$ (Figure 1c), depends on the strength of the dipolar coupling as well as the dipolar evolution time, NT_r (N is the number of rotor cycles and T_r the rotor period). The normalized REDOR difference, $\Delta S/S_0$, is shown in Figure 1d as a function of evolution time for C1, C2, C7, C8/C9, and C11 of the TMMA cation in B-CIT-1. The other ^{13}C resonances are not resolved well enough, and some intensities are too small for detailed analyses.

To estimate the expected minimum dipole coupling from the boron content of the framework[6] a virtual C atom was placed in the center of the channel, and a lattice summation of the second moment of the ^{13}C−^{11}B heteronuclear dipole interaction was calculated assuming a statistical distribution of boron over the framework. The corresponding REDOR curve was calculated using an approximation valid for short dipolar evolution times,[7] assuming selective irradiation of the central $|+^1/_2\rangle \leftrightarrow |-^1/_2\rangle$ coherences of ^{11}B (solid line in Figure 1d, ^{11}B rf nutation frequency was 62.5 kHz). This curve represents the minimum background for a virtual C atom in the center of the zeolite channel for a statistical boron distribution. If boron would be randomly oriented relative to the SDA, then all ^{13}C lines would yield the same initial REDOR effect close to or above the solid line. However, the experimental data show that C11 yields an overall stronger effect than the other C atoms of TMMA. Accordingly, at least partial ordering of boron near the fragment of the SDA (i.e., C11) with the highest positive charge density exists for zeolite B-CIT-1.

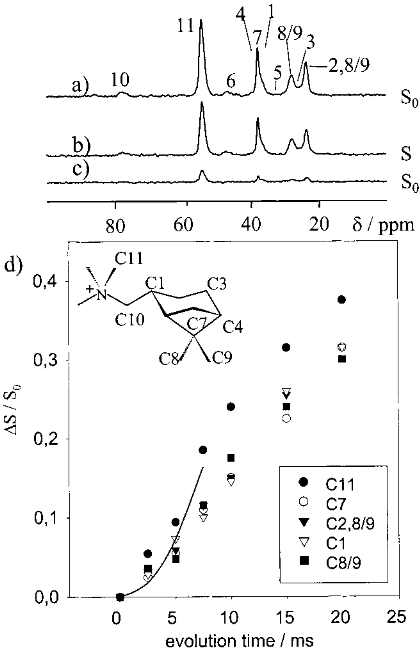

Figure 1. (a) ^{13}C{^{1}H} CPMAS spin−echo NMR, (b) ^{13}C{^{1}H}−^{11}B REDOR spectrum, (c) difference spectrum, (d) evolution of $\Delta S/S_0$ values for zeolite B-CIT-1 with TMMA. The solid line represents the initial REDOR curve attributed to the lattice background (see text).

A rigorous quantitative analysis of the evolution of $\Delta S/S_0$ values in Figure 1d in terms of B−C distances was not possible due to several factors. First, the contributions of the different ^{11}B Zeeman levels to the REDOR dephasing are difficult to quantify, because the quadrupole coupling constant is only 210 kHz. Second, ^{2}H NMR of TMMA partially deuterated at C11 revealed a two-axes motion about the N−C11 and N−C10 bonds. The effect of this motion on the REDOR curve cannot be calculated, because it is unknown how the B−C distance vector is oriented relative to these rotation axes. Finally, based on the lattice background it is doubtful whether the two-spin approximation is valid here.

Nevertheless, the motion of the SDA does not interfere with the main conclusion that C11 is on the average in closer proximity to boron than the other carbons. The difference in ^{13}C−^{11}B dipolar coupling strength would be even larger if the aforementioned two-axes rotations were frozen out at low temperatures.[8]

Figure 2 shows the results on zeolite B-SSZ-24. The ^{13}C{^{1}H} CPMAS spin−echo NMR spectrum of the MSP guest molecule (Figure 2a) can be divided into two main regions which differ in

---

[1] (a) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982. (b) Treacy, M. M. J.; Marcus, B. K.; Bisher, M. E.; Higgins, J. B. *Proceedings of the 12th International Zeolite Conference*; Materials Research Society: Warrendale, 1998.

[2] Gullion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196.

[3] Lobo, R. F.; Davis, M. E. *J. Am. Chem. Soc.* **1995**, *117*, 3766.

[4] Zones, S. I.; Nakagawa, Y. *Microporous Mater.* **1994**, *2*, 543.

[5] (a) Fyfe, C. A.; Lewis, A. R.; Chézeau, J. M.; Grondey H. *J. Am. Chem. Soc.* **1997**, *119*, 12210. (b) Grey, C. P.; Kumar, B. S. A. *J. Am. Chem. Soc.* **1995**, *117*, 9071. (c) Blumenfeld, A. L.; Fripiat, J. J. *J. Phys. Chem. B* **1997**, *101*, 6670.

[6] Chemical analysis yields 2.8 TMMA and 2.24 B per unit cell (Si/B = 24).

[7] Bertmer, M.; Züchner, L.; Chan, J. C. C.; Eckert, H. *J. Phys. Chem. B* **2000**, *104*, 6541.

[8] Such low-temperature measurements were not possible because of the long acquisition times (several days) and rotation instability at low temperatures.

10.1021/ja005609e CCC: $19.00

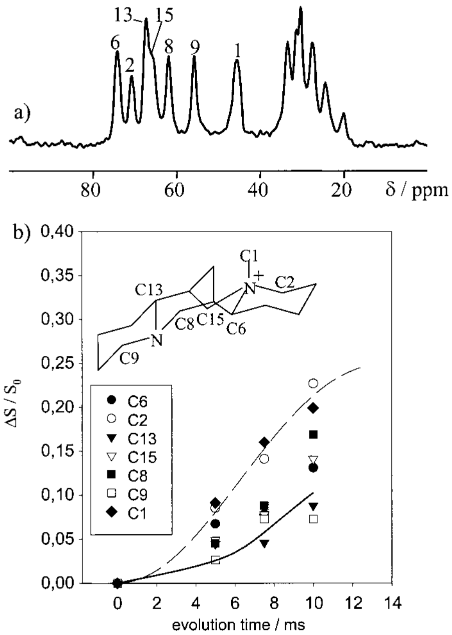

Figure 2. (a) ^{13}C{^{1}H} CPMAS spin−echo NMR and (b) evolution of $\Delta S/S_0$ values for zeolite B-SSZ-24 with MSP cations as SDA. The solid line represents the initial REDOR curve from the lattice background, and the broken line corresponds to a theoretical REDOR curve (see text).

the resolution of the lines. While the signals between 15 and 40 ppm overlap heavily, the lines between 40 and 80 ppm are clearly resolved which makes possible an unambiguous peak assignment by comparison with liquid NMR spectra. Only the REDOR effect of the lines in this latter range are quantitatively analyzed. The evolution of $\Delta S/S_0$ values is shown in Figure 2b. The resolved carbon nuclei can be divided into those with a relatively strong ^{13}C−^{11}B heteronuclear dipole interaction (C1, C2), those having an interaction of intermediate strength (C6, C8, C15), and weakly interacting species (C9, C13). Static and MAS ^{2}H NMR spectra of the methyl-deuterated compound indicate only a motion of the methyl group about the C−N axis which leaves the ^{13}C−^{11}B dipole interaction unaffected.

The corresponding minimum background dipole interaction under selective irradiation of central spin states of ^{11}B is again illustrated by the solid line in Figure 2b,[9] and the experimental data points for C9 and C13 can be well explained by this lattice background.[10] On the other hand, the data clearly show that C1 and C2 which are next to the quaternized nitrogen atom of the SDA are closest to the boron atoms in the zeolite framework. Interestingly, C9 and C13 show the smallest ^{13}C−^{11}B dipole coupling constant although they are also near a nitrogen atom in the SDA which is, however, not quaternized. Additionally, the REDOR effects of C6, C8, and C15 show that these C atoms also have ^{13}C−^{11}B dipolar couplings that are above the lattice background. These results clearly indicate partial ordering of boron around the SDA.

We have simulated the REDOR evolution of C1 and C2 with an analytical two-spin model that is a reasonable approximation based on the comparatively small background interaction. If only the central spin states, $|\pm{}^{1}/_{2}\rangle$, contribute to the effect (selective case), then a dipole coupling constant of 120 ± 10 Hz (C−B distance 4.3 ± 0.1 Å) results (broken line in Figure 2b). This analysis takes into account the stoichiometric factor of 0.6 for the number density of boron atoms per SDA. Under nonselective conditions the dipole coupling constant has to be scaled by a factor of 3 for ^{11}B nuclei that are in spin states $|\pm{}^{3}/_{2}\rangle$ instead of $|\pm{}^{1}/_{2}\rangle$.[11] Data analysis in terms of this model would yield a C−B distance of 6.4 Å. The aforementioned estimations of the lattice background for B-CIT-1 and B-SSZ-24 suggest selective rather than nonselective conditions. Interestingly, the shortest distance between C atoms of tetrapropylammonium cations and tetrahedral framework atoms in zeolite ZSM-5 is 4.2 Å,[12] which is in excellent agreement with our result for selective conditions.

For both zeolites, B-CIT-1 and B-SSZ-24, a preferential dipole interaction between ^{11}B and those ^{13}C nuclei is observed, which are near the fragment of the SDA with the largest positive charge density. These results are in good agreement with a study of Shantz et al., who investigated the aluminum distribution in zeolite ZSM-12, which was made in the presence of benzyltrimethylammonium ions with various versions with selective deuteration.[13] In the latter work especially ^{29}Si{^{1}H} REDOR experiments provided the most significant indication of charge ordering. However, those experiments have a lower spatial resolution than the ^{13}C{^{11}B} REDOR method suggested here because of the larger volume of an Al(OSi)$_4$ site compared to a corresponding boron center. Another charge ordering effect was found for anionic defect sites and the SDA in zeolite nonasil.[14]

In summary, ^{13}C−^{11}B rotational echo double resonance is a suitable and direct method to investigate the spatial ordering between boron in the zeolite framework and the structure directing agents. These results are the first proof of a local charge ordering of boron atoms in zeolite frameworks, and they have large implications on the synthesis design of these catalysts. The positive charge of the SDA induces the boron atoms to be preferentially implanted nearby for zeolites B-CIT-1 and B-SSZ-24. Future experiments will show how charge ordering and implanting of catalytic centers can be tailored by the choice of structure directing agents.

Acknowledgment. We thank Prof. R. F. Lobo, University of Delaware, for permission to use the synthesis laboratory and for helpful discussions. Elemental analyses by Dr. U. Müller at BASF AG are acknowledged. H.K. highly appreciates support by the Deutsche Forschungsgemeinschaft (grant Ko 1817/1-2).

JA005609E

---

(9) Chemical analysis yields 0.7 SDA and 0.42 B per unit cell (Si/B = 56).

(10) Assuming nonselective irradiation of ^{11}B would result in an unreasonably high lattice background which would be higher than all experimental data points. Therefore, selective conditions seem to apply irrespective of the moderate quadrupole coupling constant of 130 kHz.

(11) Hudalla, C.; Eckert, H.; Dupree, R. *J. Phys. Chem.* **1996**, *100*, 15986.

(12) Van Koningsveld, H.; Van Bekkum, H.; Jansen, J. C. *Acta Crystallogr.* **1987**, *B43*, 127.

(13) Shantz, D. F.; Fild, C.; Koller, H.; Lobo, R. F. *J. Phys. Chem. B* **1999**, *103*, 10858.

(14) Shantz, D. F.; Lobo, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 2482.