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Chemically Nonequivalent Sites in Mesoporous BCN Revealed by Solid-state NMR at 21.8 T

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Solid-state ^{11}B magic-angle spinning (MAS) NMR studies on novel mesoporous BCN material are described. While the ^{11}B MAS spectrum at 11.7 T shows severe signal overlap as a result of the second-order quadrupolar broadening, the resolution improves significantly at 21.8 T and three distinct peaks are observed, indicating the presence of three sites in the material. Possible microstructures of the three sites are discussed in terms of their isotropic chemical shifts, quadrupolar coupling constants, and asymmetric parameters determined from spectral simulation.

Mesoporous boron carbon nitride (MBCN) and mesoporous boron nitride (MBN) have been prepared for the first time using mesoporous carbon as a template.[1] Application of these novel materials for fabrication of gas-storage devices, molecular adsorbents, and catalysts is envisaged, because the materials are resistant to oxidation and can be used at high temperatures. So far, high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), and nitrogen adsorption measurement have been applied to examine the structure and compositions of the materials.[1] However, detailed local structures of these materials have not yet been fully examined. In this work, we applied solid-state NMR, which is of particularly useful in analysis of amorphous inorganic solids having no long-range order. As the natural abundance of ^{13}C and ^{15}N is low, ^{11}B is the most accessible nucleus in these materials. By applying the magic-angle spinning (MAS), one can remove the chemical-shift anisotropy as well as homonuclear ^{11}B–^{11}B and heteronuclear ^{11}B–^{10}B dipolar broadening. In fact, ^{11}B solid-state NMR has been applied to similar B–N systems.[2] However, the resolution of ^{11}B NMR in solid is not always good enough to distinguish chemically different ^{11}B sites owing to line broadening brought about by the second-order quadrupolar interaction.[3] Since the second-order quadrupolar interaction is inversely proportional to the strength of the applied magnetic field, we apply in this work the 21.8 T static magnetic field recently established in our institute[4] to reduce effects of the second-order quadrupolar interaction.

MBCN prepared at 1450 °C (MBCN (1450) in ref 1) and MBN prepared at 1750 °C (MBN in ref 1) were examined in this work. Cubic boron nitride (cBN) was purchased from Showa-Denko Co., Ltd., Japan. Hexagonal boron nitride (hBN) was obtained from Shin-etu Kagaku Co., Ltd., Japan. ^{11}B MAS NMR spectra were recorded at 21.8 T on a JEOL ECA 930 spectrometer with a JEOL 4 mm MAS probe and at 11.7 T on a JEOL ECA 500 spectrometer with a Chemagnetics 4 mm MAS probe. The ^{11}B resonant frequency at 21.8 and 11.7 T were 298.4 and 160.5 MHz, respectively. The MAS frequency was 16 kHz at 21.8 T and 15 kHz at 11.7 T. The ^{11}B chemical shift is referenced to saturated H_3BO_3 solution at 19.49 ppm. All spectra were observed by using a single 26° pulse. The rf strength at 21.8 T was ca. 147 kHz and at 11.7 T ca. 179 kHz.

Figure 1a shows the ^{11}B MAS spectrum of MBCN observed at 11.7 T. The signal overlap as a result of the second-order quadrupolar broadening makes determination of the number of chemically different boron sites difficult. On the other hand, the ^{11}B MAS spectrum observed at 21.8 T (Figure 1b) exhibits three distinct peaks at 0.94, 16.6 and 27.2 ppm. The better resolution at 21.8 T indicates that the magnetic field of 21.8 T is high enough to reduce the broadening due to the second-order quadrupolar interaction.

To assign the three peaks, we observed ^{11}B MAS spectra of two ^{11}B compounds, for which structures were reported;[5] one is cBN and the other is hBN. Figures 1c and 1d show the ^{11}B MAS

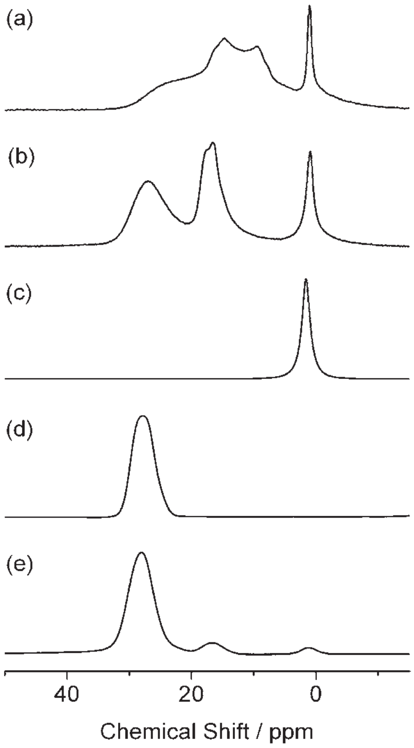

Figure 1. ^{11}B MAS NMR spectra in powdered MBCN (a) and (b), cBN (c), hBN (d), and MBN (e); (a) observed at 11.7 T, while (b)–(e) at 21.8 T.

spectra of cBN and hBN, respectively. cBN gave a sharp signal at 1.6 ppm, while hBN gave a broad one at 27.8 ppm. From these spectra, the observed sharp peak at 0.94 ppm is assigned to ^{11}B in a four-coordinated boron site, whose local structure is similar to ^{11}B in cBN, and the broad peak at 27.2 ppm is to a three-coordinated boron similar to ^{11}B in hBN. To examine the origin of the peak at 16.6 ppm, we observed the ^{11}B MAS spectrum of MBN (Figure 1e), whose elemental composition estimated from its XPS survey spectrum (the Supporting Information of ref 1) is $B_{42.3}C_{4.1}N_{45.2}O_{8.5}$. The elemental composition of MBCN reported in ref 1 is $B_{21.1}C_{37.7}N_{23.0}O_{18.2}$. Note that the signal for O mainly comes from the moisture, ethanol, or atmospheric O_2 adsorbed on the surface. In fact, the EELS spectra of those materials do not exhibit O K-shell excitation edges expected at 530–540 eV.[1]

The ^{11}B MAS spectrum of MBN shows three peaks at 1.1, 16.6, and 28.0 ppm. Differences between the corresponding peak positions for MBCN and MBN are small, and we consider they are the same borons. Notably, however, their relative intensities are different; the intensity ratio for the the three peaks from the right to the left is 0.5:1:1 for MBCN and 0.05:0.1:1 for MBN. It is worthy to point out here that we adopted a 26° pulse for the quantitative observation of peak intensities[6] with a pulse-repetition time of 40 s being much longer than the apparent longitudinal relaxation time (ca. 8 s). Hence, the intensity ratio represents the compositional ratio of the three boron sites. By comparing the NMR-intensity ratios with the elemental compositions determined by XPS, we tentatively assign the 16.6 ppm peak to a boron in a boron carbon nitride (B/C/N) structure, such as $Si_3B_3N_7$ (ref 7) whose Si being replaced with C. The small intensity of the peak at 1.1 ppm in MBN can be ascribed to the structural transformation of cBN to hBN at temperatures higher than 1400–1600 °C.[8]

To determine isotropic chemical shifts (δ_{iso}), quadrupolar coupling constants (e^2qQh^{-1}), and asymmetric parameters (η) for the three boron sites, the observed ^{11}B spectra of MBCN (Figures 1a and 1b) are fitted to a sum of three ^{11}B MAS signals. A ^{11}B MAS lineshape governed by the second-order quadrupolar interaction is calculated employing a theory given in ref 3. With exponential or Gaussian broadening functions for expressing the experimental linewidth, a sum of three calculated ^{11}B signals (Figures 2c and 2d) can successfully reproduce the corresponding observed ^{11}B MAS spectra of MBCN at 21.8 T (Figure 2a) and 11.7 T (Figure 2b) with the parameters collected in Table 1. We also list the parameters for hBN and cBN in Table 1 for comparison. The isotropic chemical shifts thus obtained are deviated from the apparent peak positions observed at 21.8 T as a result of the isotropic second-order quadrupolar shift.[3]

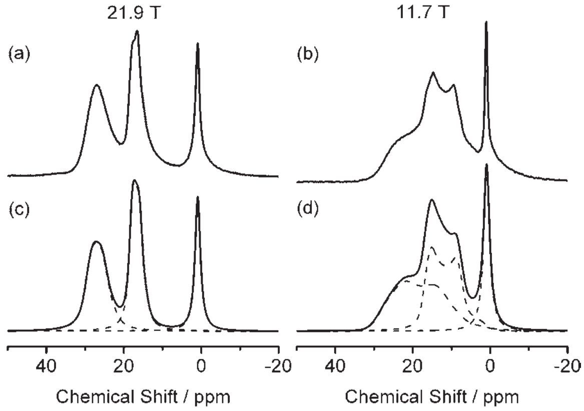

Figure 2. Comparison of experimental ^{11}B MAS NMR spectra of MBCN ((a) at 21.8 T and (b) at 11.7 T) and simulated ones ((c) at 21.8 T and (d) at 11.7 T). Dotted lines are three lineshapes calculated by using three sets of parameters for MBCN given in Table 1.

Table 1. NMR lineshape parameters used for simulation

	δ_{iso}/ppm	e^2qQh^{-1}/MHz	η	Coordination number
MBCN	30.4	3.5	0.4	3
	18.8	2.7	0.2	—
	0.94	<0.1	0	4
hBN[a]	30.4 ± 0.5	2.936 ± 0.020	0	3
cBN[a]	1.6 ± 0.2	<0.05	0	4

[a] Ref. 2b.

It is noted that the quadrupolar coupling constant and the asymmetric parameter for the peak at around 27.2 ppm (the isotropic chemical shift is 30.4 ppm (Table 1)) in MBCN are appreciably different from those of hBN. The large asymmetric parameter indicates that the local symmetry in MBCN is reduced as compared to that in the highly symmetric hexagonal structure in hBN. Further studies of local structures in these mesoporous materials including a decisive assignment of the peak at 16.6 ppm are currently undergoing by using NMR measurements of various related compounds, the multiple-quantum MAS NMR (MQMAS),[9] and other methods.

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