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Surface Modification of Boron Nitride Nanoparticles by Decylphosphonic Acid Characterized by Solid-state NMR

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We have attempted to modify the surface of boron nitride (BN) nanoparticles by decylphosphonic acid and have characterized the surface layer of BN nanoparticles by means of high-resolution solid-state ^{31}P NMR. The surface of BN nanoparticles was successfully modified, and the ^{31}P NMR spectra showed two types of bonding states for the organic modifier. They are tentatively assigned to P–B and P–N bonding states from consideration of the residual line broadening due to interaction with quadrupole nuclei.

Surface modification of inorganic nanoparticles with organic substances is useful to disperse nanoparticles into an organic medium homogeneously.[1] Aggregation of nanoparticles can be suppressed by surface modification. Boron nitride (BN) is an electric insulator with high thermal conductivity. A flexible insulator sheet with high thermal conductivity is obtainable, if BN nanoparticles are dispersed in an organic medium at high concentrations. The surface of BN nanoparticles should be modified by organic groups to enable homogeneous dispersion. However, few studies have been carried out on surface modification of BN, which is in contrast to metals and metal oxides.[2] Organophosphorus compounds such as alkylphosphonates and phosphonic acids are attracting increasing attention as a surface modifier, because they bind strongly on various metal oxides.[3–5]

In the present work, we have attempted to modify the surface of BN nanoparticles by alkylphosphonic acid. We have characterized the surface-modified BN nanoparticles by means of high-resolution solid-state ^{31}P NMR as well as thermogravimetric analysis. Solid-state NMR is a powerful method to characterize the surface layers at atomic and molecular levels. ^{31}P NMR is suitable to characterize the surface binding of alkylphosphonic acid, because ^{31}P is a sensitive nucleus.

Boron nitride nanopowder was obtained from Alfa Aesar, whose average particle size was nominally 5 to 20 nm. Decylphosphonic acid (DPA, CH_3–$(CH_2)_9$–P(O)$(OH)_2$, 97%) was obtained from Strem Chemicals.

A surface-modified BN sample (DPA/BN) was prepared in a similar manner to surface modification of TiO_2 by Gao et al.[4] We used BN nanoparticles instead of TiO_2. 0.323 g of DPA was dissolved in 110 mL of an 8:3 mixed methanol–water solvent. To the above solution, a suspension of 0.5 g of BN nanopowder in 30 mL of deionized water was added dropwise. The resulting suspension was stirred at 373 K for 3 days. The solid part was separated by centrifugation and washed with methanol to remove unreacted DPA as well as physisorbed species. The process of centrifugation and washing was recycled seven times. The product was dried under vacuum at room temperature for 1 day.

Thermogravimetric and differential thermal analyses (TG-DTA) were performed with a Rigaku Thermo Plus TG 8120 under an air flow. The samples were heated up to 1273 K with a heating rate of 5 K min^{-1}.

^{31}P magic-angle-spinning (MAS) NMR spectra were measured at room temperature with Bruker ASX400 and ASX200 spectrometers at Larmor frequencies of 161.98 and 81.01 MHz, respectively. Bruker MAS probe heads were used with a zirconia rotor of a 4.0-mm outer diameter. The pulse sequence used for ^{31}P measurements was a cross-polarization pulse sequence with high-power ^{1}H decoupling during signal acquisition (CP). The frequency scale was expressed with respect to 85% aqueous H_3PO_4 solution by adjusting the signal of $(NH_4)_2HPO_4$ to 1.33 ppm.[6] Samples were packed into the 4-mm MAS rotor under an N_2 atmosphere in a glove bag.

The amount of the attached alkylphosphonic group was evaluated by thermogravimetric analysis. Figure 1 shows TG and DTA curves of DPA/BN. The TG curve shows gradual mass loss up to 550 K and then steep decrease up to 720 K. The mass starts to increase at 720 K. The gradual mass loss below 550 K is ascribed to desorption of water. The desorbed water is either physisorbed water or water produced by condensation reaction of OH groups. The steep mass loss between 550 and 720 K is accompanied by an exothermic peak. The organic part burns in an air flow. The mass increase above 720 K is caused by oxidation of BN. The mass loss due to burning of the organic part is 6.19 mass %. If the organic part is lost leaving P atoms as an oxide, the attached alkylphosphonic group amounts to 0.57 mmol per 1 g of BN. If one alkylphosphonate molecule is assumed to occupy 0.24 nm^2,[4] the covered surface is estimated to be 85 m^2/g-BN.

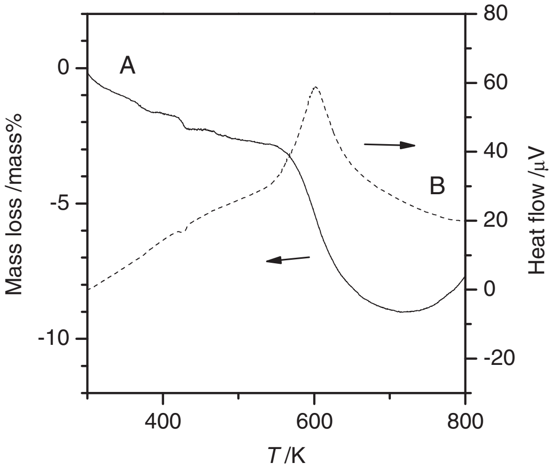

Figure 1. (A) TG and (B) DTA curves of DPA/BN in an air flow.

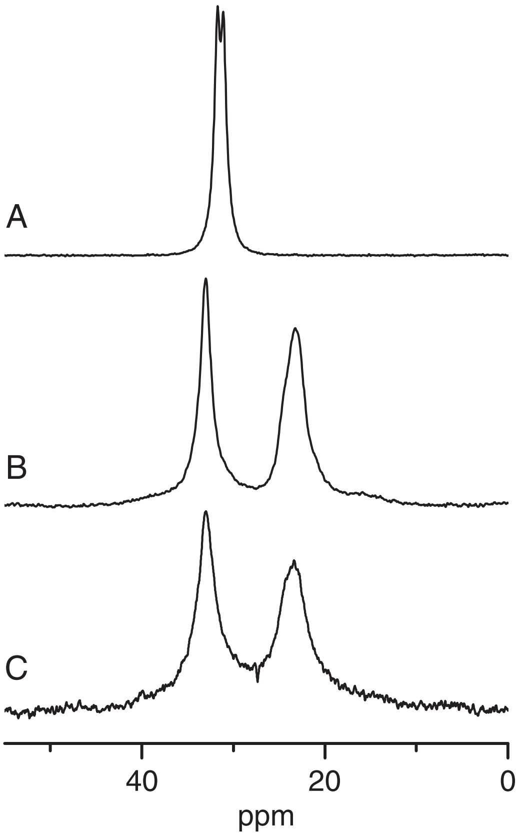

Figure 2. ^{31}P CP/MAS NMR spectra of (A) DPA and DPA/BN at (B) 161.98 and (C) 81.01 MHz. The spinning rates were (A) 8.00 and (B, C) 6.00 kHz. The broadening factors were (A, C) 10 and (B) 20 Hz.

The bonding state of the attached molecule is probed by ^{31}P NMR. Figure 2 shows ^{31}P CP/MAS NMR spectra of crystalline DPA and DPA/BN. Crystalline DPA has two signals at 31.7 and 31.1 ppm, as shown in Figure 2A, being ascribed to crystallographically inequivalent sites.

DPA/BN has two signals at 33.0 and 23.2 ppm of comparable intensities, as shown in Figure 2B. This means that there are two phosphonic group bonding states. The 33.0-ppm signal is not crystalline DPA, although the shift value is close to those of crystalline DPA. Unreacted and physisorbed DPA were excluded by repeated washing. Furthermore, DPA/BN shows relaxation behavior much different from crystalline DPA as follows.

Figure 3 shows contact time dependence of the signal intensity in ^{31}P CP/MAS NMR spectra. The signal intensity increases with a cross relaxation time between ^{1}H and ^{31}P, T_{HP} and decays with a ^{1}H spin–lattice relaxation time in the rotating frame, $T_{1\rho}$(H).[7] DPA shows a negligible decay during the contact time range studied, indicating a long $T_{1\rho}$(H) value. On the other hand, the two signals in DPA/BN have $T_{1\rho}$(H) values of about 10 ms. The $T_{1\rho}$(H) value is sensitive to a motion of the order of several ten kilohertz. The obtained results suggest that the attached molecules undergo some kind of motion, and the molecules are in different states from those in the crystalline state. The methylene chain is tightly packed in crystalline DPA, while the packing is loose in DPA/BN.

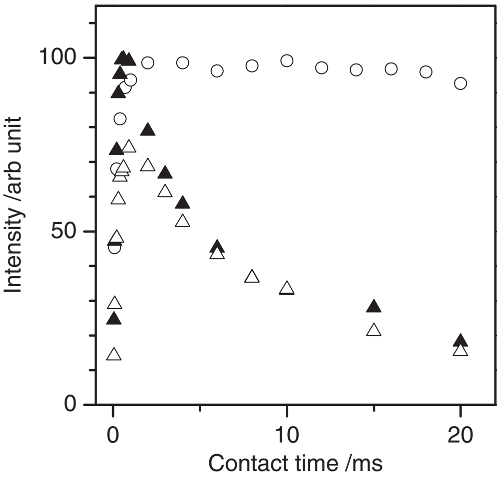

Figure 3. Contact time dependence of the signal intensity in ^{31}P CP/MAS NMR spectra of DPA (31.7 ppm: open circle) and DPA/BN (33.0 ppm: solid triangle, 23.2 ppm: open triangle), measured at 161.98 MHz.

The assignments of the two signals in DPA/BN are in question. The surface of BN is not clearly understood. Functional groups such as B–OH, B–H, N–OH, and N–H might be present on the plane edge in addition to bare B and N atoms. When alkylphosphonic acid attaches to the surface, possible bonding states are P–B, P–N, P–O–B, and P–O–N. We wish to narrow down the possible bonding states by using frequency dependence of interactions between nuclear spins.

MAS cannot completely average out the dipole–dipole interaction when the observed spin interacts with a quadrupole nucleus.[8–11] Two NMR active quadrupole nuclei are present in boron; ^{11}B and ^{10}B with natural abundances of 80.1 and 19.9%. ^{11}B has a magnetic moment about three times larger than ^{10}B. Thus, the effect of ^{10}B is negligible compared to ^{11}B. The spin quantum number (S) of ^{11}B is 3/2. On the other hand, ^{14}N, which is a quadrupole nucleus with a spin quantum number of 1, has a natural abundance of 99.6%. ^{17}O is the only active nucleus in oxygen with a natural abundance of 0.038%. The effect of oxygen can be neglected because of the low natural abundance of ^{17}O. Consequently, interaction of ^{31}P with ^{11}B and ^{14}N might help us to assign the ^{31}P signals. In addition, the indirect spin coupling through the chemical bond is not affected by MAS at all.

Figure 2C shows a ^{31}P CP/MAS NMR spectrum of DPA/BN measured at 81.01 MHz. The peak positions are 33.1 and 23.2 ppm, which agree to those at 161.98 MHz. We want to discuss the frequency dependence of the line width. The full width at half-maximum (FWHM) of the 33.0- and 23.2-ppm signals are 1.5 and 2.8 ppm, respectively, at 161.98 MHz. They are 2.5 and 3.8 ppm, respectively, at 81.01 MHz. The line broadening in the data processing is set at 0.12 ppm for both measuring frequencies (20 and 10 Hz at 161.98 and 81.01 MHz, respectively). The line widths of both signals increase by 1.0 ppm when the measuring frequency changes from 161.98 to 81.01 MHz.

In the same measuring conditions, the reference compound $(NH_4)_2HPO_4$ shows FWHM values of 0.70 and 0.50 ppm at measuring frequencies of 161.98 and 81.01 MHz, respectively.

The line width is broader at 161.98 MHz than at 81.01 MHz. In conclusion, the broader line width at the lower frequency in DPA/BN is not produced by instrumental artifacts such as field inhomogeneity and incomplete ^{1}H decoupling.

The indirect spin coupling or the residual dipolar interaction with quadrupole nuclei is the most probable mechanism of the broader line width at the lower measuring frequency.[12]

The indirect spin couplings of ^{31}P–^{31}P in P–P and P–O–P are about 110 and 15–20 Hz, respectively.[13] The coupling constant is independent of the applied magnetic field and is proportional to the magnetic moment of the nuclear spin. Thus, the couplings of ^{31}P–^{11}B and ^{31}P–^{14}N in P–B in P–N are less than 110 Hz, even if present. They are less than 20 Hz in P–O–B and P–O–N. Conclusively, the indirect spin coupling cannot explain the line width increase without the effect of residual dipolar interaction with quadrupole nuclei.

The line width caused by the residual dipolar interaction with quadrupole nuclei is roughly $D\chi/Z_S$,[12] where D expresses the magnitude of the dipole–dipole interaction ($\gamma_I\gamma_S h/(4\pi^2 r_{IS}{}^3)$), χ is a quadrupole coupling constant ($\chi = e^2Qq/h$), and Z_S is a Zeeman frequency of the quadrupolar S spin ($Z_S = \gamma_S H_0/2\pi$). Strictly speaking, the line width for ^{11}B ($S = 3/2$) is 2/3 of that for ^{14}N ($S = 1$), if other conditions are the same. We have attempted to calculate the $D\chi/Z_S$ value assuming the internuclear distance (r_{IS}) and the quadrupole coupling constant.

The $D\chi/Z_S$ values for P–O–N and P–O–B are too small because the internuclear distances are too large. P–B can explain the line width increase of 1.0 ppm. The χ value of ^{11}B in hexagonal BN is 2.936 MHz,[14] where boron is threefold-coordinated by N atoms. The χ value of ^{14}N in hexagonal BN is only 140 kHz.[14] To explain the 1.0-ppm increase, ^{14}N should have a quadrupole coupling constant of about 2 MHz. The coupling constants of 1–4 MHz are ordinary in N-containing organic compounds.[15]

Consequently, P–B and P–N are the most probable bonding states. $(C_6H_5)_3PO$, $(C_6H_5)_3PBH_3$, and $(C_6H_5)_3PN(C_6H_5)$ have ^{31}P chemical shifts of 29, 21, and −1 ppm, respectively.[16] Changes of the bonding state from P–O to P–B and P–N cause shifts of −8 and −30 ppm, respectively. By analogy to these changes, the most probable assignments at the present stage are as follows: The 33.0-ppm signal is P–B, and the 23.2-ppm signal is P–N.

In summary, we have successfully modified the surface of BN nanoparticles by decylphosphonic acid (DPA) and have characterized the surface layer of BN nanoparticles by means of high-resolution solid-state ^{31}P NMR. The ^{31}P NMR spectra showed two types of bonding states. They are probably P–B and P–N bonding states from the residual dipolar broadening due to interaction with quadrupole nuclei. Further study is in progress in order to specify the surface bonding state of the modifier.

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