Structural Characterization of Carbonaceous Solids by High-Field NMR Spectroscopy

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In high-field NMR experiments of carbonaceous solids such as coal and pitch, the high-speed magic-angle spinning (MAS) method is a powerful technique for reducing the intensity of the spinning sidebands that disturbs the precise interpretation of the spectrum. However, the high-speed MAS produces two unfavorable problems. One is the decline in the rate of polarization transfer from ^1H to ^{13}C during the cross-polarization (CP), and another is the NMR signal intensity fluctuation in the dipolar-dephasing (DD) experiments. Therefore, the availability of high-speed MAS, variable amplitude (VA)-CP pulse sequence, and DD experiments with the delay times synchronized with sample spinning were examined in the high-field NMR of a carbonaceous sample. Consequently, it was confirmed that the high-field NMR spectroscopy is a useful technique for the structural characterization of carbonaceous solids as well as the low-field NMR.

Key Words

VA-CP NMR, High-Speed MAS, Dipolar-Dephasing

1. INTRODUCTION

The structural characterizations of carbonaceous solids such as coal¹⁻⁵⁾ and pitch⁶⁾ were carried out using cross-polarization magic-angle spinning (CP-MAS) NMR experiments combined with dipolar-dephasing (DD), although CP method has a problem concerned with a quantitative reliability of a signal intensity⁷⁾. Almost all experiments were performed using a low-field, generally 2.35 T, magnet^{1,6)} because a high-field, greater than 4.7 T, measurement produces a lot of spinning sidebands (SSB) and the precise interpretation of the spectrum is difficult because the SSB overlap with other bands. Recently, high-speed magic-angle spinning equipment has become commonplace. High-speed spinning is a powerful technique for reducing the intensities of SSB.

However, two problems are associated with high-speed CP-MAS spectroscopy. One problem is the decline in the rate of polarization transfer from ^1H to ^{13}C during the CP^{8,9)}. Peersen et al.¹⁰⁾ proposed the variable amplitude (VA)-CP pulse sequence for improving the efficiency of polarization transfer during the CP. Therefore, we confirmed the availability of the VA-CP pulse sequence for carbonaceous solids with the high-speed MAS at high-field NMR. Another problem arises with the DD experiments using the high-speed MAS. Newman¹¹⁾ pointed out that the NMR signal intensities destructively fluctuated in the DD experiments with the high-speed MAS through the interference of different orientations of the C-H vectors within a powder. Therefore, we attempted to use the delay times synchronized with the spinning rates to avoid the influence of

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intensity fluctuations in the DD experiments^{12/13}.

2. Experimental

MP-N pitch (materials for pitch-based carbon fiber) was prepared by the Maruzen Petroleum Chemical Co., Japan. The ultimate analysis results of the MP-N pitch are 93.5%C, 3.9%H, 1.5%N, and 1.1%diff. L-alanine was obtained from Nacalai Tesque, Inc. and 1-methylfluorene was obtained from Aldrich. They were studied at room temperature as polycrystalline powders.

The solid-state ^{13}C NMR spectra were obtained using a Bruker DSX-300 NMR spectrometer operating at 75.48 MHz and 300.13 MHz for ^{13}C and ^1H , respectively, with a double air-bearing CP-MAS probe and ^1H and ^{13}C high-power amplifiers. The spectra were obtained using VA-CP pulse sequence and high-speed magic-angle spinning (MAS). The 90° pulse length of ^{13}C and ^1H was $3.8\ \mu\text{s}$ for the Hartman-Hahn matching conditions of CP with 2 kHz MAS. In the VA-CP experiments, the preamplifier power of the ^1H channel was modulated from 70% to 100% during the CP spin-lock pulses. A sample was packed in a 4-mm ceramic capsule, and the capsule was spun at rates up to 13 kHz using an air drive. 4096 free induction decays (FID) with 2048 data points were accumulated with a 4-s repetition time, and were Fourier-transformed to a 35.21-kHz spectral width using 50-Hz line broadening after extending the size of the FID to 16K by zero filling. The contact time and spinning rate varied from 0.25 to 5 ms, and from 5 to 13 kHz, respectively. A 2 ms contact time and a 12.5 kHz spinning rate were chosen for the DD experiments. A 180° refocusing pulse of ^{13}C was used during the delay period in the DD experiments¹⁴. The delay time varied from 20 to 1600 μs . Chemical shifts were calibrated with respect to tetramethylsilane using glycine as a secondary standard. The curve-fitting of the NMR spectrum was performed using a Bruker line-fitting program with 70 % Gaussian and 30 % Lorentzian mixture functions for minimizing the error.

3. RESULTS AND DISCUSSION

3.1 VA-CP with high-speed spinning

Fig. 1 shows the ^{13}C NMR spectra of the MP-N pitch at high-field (7.05T) NMR. Spectrum (a) was obtained using 5 kHz spinning and a conventional CP pulse sequence. The spectrum is composed of aromatic (100–150 ppm) and aliphatic (10–50 ppm) bands^{15/16}. Several spinning sidebands (SSB) of the aromatic bands appeared in spectrum (a). Spectrum (b) was obtained using 11 kHz spinning and a conventional CP pulse sequence. SSB moved to both outside of the main bands in spectrum (b), and their intensities were significantly weakened. The intensities of the aromatic and aliphatic bands also significantly decreased in spectrum (b) compared with spectrum (a). Spectrum (c) was obtained using 11 kHz spinning and a VA-CP pulse sequence. The SSB intensities were also very weak in this spectrum.

Fig. 1 Solid-state ^{13}C -NMR spectra of the MP-N pitch with different spinning rates (contact time; 2 ms)

The intensities of the aromatic and aliphatic bands in spectrum (c) were almost same as those in spectrum (a). Fig. 2 shows the intensity variations for the aromatic main bands with several spinning rates. The intensity rapidly decreased with increasing spinning rate in the conventional CP pulse sequence. On the other hand, the intensity was almost constant in the range of a 9–12.5 kHz spinning rate using the VA-CP pulse sequence. Table 1 shows the aromaticities of the MP-N pitch obtained by using several spinning rates and the conventional CP or VA-CP pulse sequence. The aromaticity obtained by the VA-CP pulse sequence with high-speed spinning did not sig-

Fig. 2 Intensity variations for the aromatic main bands in the conventional CP and VA-CP NMR of the MP-N pitch with magic-angle spinning rates (contact time; 2 ms)

Table 1 Aromaticities for the MP-N pitch obtained from the solid-state ^{13}C -NMR spectra using several magic-angle spinning rates (contact time; 2 ms)

Spinning rate (kHz)	Conventional CP	VACP
5	0.960	0.952
7	—	—
9	0.933	0.955
11	0.938	0.950
13	0.945	0.951

—; The values of 7 kHz spinning cannot be obtained because the spinning sidebands overlapped with the aliphatic bands.

nificantly differ from the aromaticity obtained by the conventional CP with low-speed spinning, and it was confirmed that the aromaticity obtained using high-speed spinning and the VA-CP pulse sequence was sufficiently reliable.

The ^{13}C magnetization during the CP experiment increases with contact time (t_{CP}) by polarization transfer from the ^1H to ^{13}C . On the other hand, the ^1H magnetization decreases during CP spin-lock pulses by the spin-lattice relaxation processes in a rotating frame. The signal intensity is a result of a complicated interplay by the CP and the spin-lattice relaxation processes using the following equation^{(1)6/7/17}:

$$M(t_{\text{CP}}) = M_0 b^{-1} (1 - \exp(-bt_{\text{CP}}/T_{\text{CH}})) \exp(-t_{\text{CP}}/T_{1\rho}^{\text{H}}); \quad (1)$$

where M_0 is the equilibrium magnetization of the ensemble of carbon spins, $b = 1 - T_{\text{CH}}/T_{1\rho}^{\text{H}}$, and T_{CH} and $T_{1\rho}^{\text{H}}$ are the time constants of the cross-polarization and ^1H spin-lattice relaxation, respectively.

The intensity variations are different between the aromatic and aliphatic carbons, and the selection of contact time for the CP is important for a precise determination of aromaticity⁷. Fig. 3 shows the intensity variations in carbon signals of the MP-N pitch with contact times. The intensity of the aliphatic carbons increased fast, while that of the aromatic carbons slowly increased with increasing contact time. The maximum intensities of the aliphatic and

Fig. 3 Intensity variations for the aromatic and aliphatic carbons in the VA-CP NMR of the MP-N pitch with contact times (spinning rate; 12.5 kHz)

aromatic carbons were at 0.5 ms and 1.75 ms, respectively. These intensity variations of the aliphatic and aromatic carbons obtained by VA-CP were similar to those of previous studies^{6,17)} obtained using a low-field NMR with a conventional CP pulse sequence. Both intensities of the aliphatic and aromatic carbons slowly decreased with contact times after their maximum, and the aromaticities of the MP-N pitch did not significantly vary among the range of contact times from 1.75 to 5 ms. About 0.95 of these values were slightly greater than about 0.90 obtained by Pruski et al.⁶⁾ with a low-field NMR as the 94% carbon content of the MP-N pitch used in this work was greater than about 88% of their samples. It can be considered that the aromaticity obtained by the high-field NMR with high-speed spinning and a VA-CP pulse sequence was reliable enough by considering the difference in the carbon contents compared with the low-field NMR with low-speed spinning and a conventional CP pulse sequence. Some papers^{18,19)} reported that a single pulse excitation (SPE) pulse sequence had a high quantitative reliability of aromaticity. But a sensitivity of SPE pulse sequence is lower than that of CP, and repetition times of SPE need to be lengthened greatly, because ^{13}C thermal relaxation times are so longer than those of ^1H . Moreover, a little amount of sample is limited in high-speed MAS experiments. We thought that a VA-CP pulse sequence was a useful technique in the following DD NMR experiments because of the more time-consuming of SPE.

3. 2 Dipolar-dephasing with high-speed spinning.

To differentiate the protonated carbons with directly bonded protons from the non-protonated carbons without protons in the ^{13}C CP-MAS spectra of carbonaceous solids, DD experiments with a low-field NMR using low-speed spinning were used^{11,6)}. For the high-field NMR, it was reported that high-speed spinning produces destructive intensity fluctuations in the delay period¹¹⁾. Therefore, the intensity variations in the DD NMR spectra of L-alanine as a model compound were examined because L-alanine has a non-protonated carbon (carbonyl carbon), a pro-

tonated carbon (methyne carbon), and a methyl carbon. The intensity variations of these carbons with delay times in the VA-CP DD experiments of 8 or 12.5 kHz MAS are shown in Fig. 4. Fig. 4-a shows the intensity variations of the carbonyl carbon for 8 kHz and 12.5 kHz spinning rates, respectively. These figures show that both of these intensities oscillated with the different cycles. The first minimum position in the upper spectra was at about a $120\ \mu\text{s}$ delay time, and that in the lower spectra was at $80\ \mu\text{s}$, and the first maximum position in the upper was at about $250\ \mu\text{s}$, and that in the lower was at $160\ \mu\text{s}$. The period of sample rotation with 8 kHz spinning was $125\ \mu\text{s}$, and that with 12.5 kHz spinning was $80\ \mu\text{s}$. In both cases, the cycle of the intensity oscillation

Fig. 4 Intensity variations for the carbonyl and methyne carbons in the VA-CP DD NMR of L-alanine with delay times using 8 kHz and 12.5 kHz spinning rates, respectively (contact time; 2 ms)

matched twice the period of the sample rotation. Fig. 4-b shows the intensity variations of the methyne carbon with 8 kHz and 12.5 kHz spinning. Remarkably, the peak disappeared at a $60\ \mu\text{s}$ delay time and the echo appeared around twice the rotational period for both spinning rates. The intensity variations of the methyl carbon are not shown, but the behaviors were almost the same as those of the carbonyl carbon. Similar phenomena based on the chemical shift anisotropy have been observed in the low-speed MAS and are called a rotational echo^{20,21}. The rotational echo is caused by an alternation in the ^{13}C - ^1H dipolar interaction that is averaged out after each full rotational period. The direct ^{13}C - ^1H dipolar interaction is averaged out during a rotational period. Therefore, the decay of the refocusing peak intensities with the delay times chosen as twice the multiple of the rotational period is responsible for the ^1H - ^1H dipolar fluctuations during a sample rotational period, as more or fewer ^1H nuclei in the vicinity of the ^{13}C have spin up or spin down.

In several previous applications of DD experiments¹⁻⁶, a two-component Gaussian-Lorentzian decay has been applied to fit the results as in

$$M(t_d) = M_{\text{PC}}^{\text{exp}}(-0.5(t_d/T_{\text{PC}})^2) + M_{\text{NC}}^{\text{exp}}(-t_d/T_{\text{NC}}); \quad (2)$$

where M_{PC} and M_{NC} are the initial intensities of the

Fig. 5 Intensity variations for the carbonyl, methyne, and methyl carbons in the VA-CP DD NMR of L-alanine with delay times chosen as twice the multiple of the rotational period (contact time; 2 ms, spinning rate; 12.5 kHz)

protonated carbons and non-protonated carbons, and T_{PC} and T_{NC} are the decay constants of the protonated and non-protonated carbons, respectively. The ^{13}C intensity decays in the DD experiments are caused by the strong ^{13}C - ^1H dipolar interaction as the ^1H high-power decoupling rf fields are turned off during the delay period. The intensity decay of the protonated carbons is faster than that of the non-protonated carbons as the ^{13}C - ^1H dipolar interaction of the protonated carbons is greater than that of the non-protonated carbons. Methyl carbons behave like non-protonated carbons because the ^{13}C - ^1H dipolar interaction is weakened by the internal rotation of the methyl group. Fig. 5 shows the intensity variation of each carbon of L-alanine with delay times. The delay times in this figure were chosen as twice the multiple of the rotational period. In these experiments with high-speed spinning and high-field NMR, the protonated (methyne) carbon intensity decayed faster than the non-protonated (carbonyl) and methyl carbons intensities, which was enough to differentiate the protonated carbons from the non-protonated carbons. In addition, it was understandable in this figure that the non-protonated (carbonyl) and methyl carbons intensities decay as an exponential of the delay time as well as the experiments with low-spinning speed and low-field NMR¹⁻⁶.

Furthermore, the intensity variations in the DD experiments using 1-methylfluorene as a model compound were examined. Fig. 6 shows the DD spectra of 1-methylfluorene. The delay times were chosen as twice the multiple of the rotational period. In the lowest spectrum of the conventional CP, the peak around 20 ppm was assigned to the methyl carbon, the peak around 35 ppm was assigned to the methylene carbon, three peaks from 110 to 130 ppm were assigned to the protonated aromatic carbons, and two peaks from 135 to 145 ppm were assigned to the non-protonated aromatic carbons. The intensities of the methylene and protonated aromatic carbons rapidly decreased with increasing delay time. The peak of the methylene carbon disappeared at a $320\ \mu\text{s}$ delay time, and the peaks of the protonated aromatic carbons disappeared at a $960\ \mu\text{s}$ delay time. On the other hand, the intensities of the methyl and non-pro-

Fig. 6 VA-CP dipolar-dephasing spectra of 1-methylfluorene. The different delay times are noted on the figure (contact time; 2 ms, spinning rate; 12.5 kHz)

tonated aromatic carbons slowly decreased, and these peaks were still observed in the spectrum with a $1600\ \mu\text{s}$ delay time. Fig. 7 shows the intensity variation for aromatic carbons of 1-methylfluorene with the delay times synchronized with sample spinning. The ratio of the non-protonated aromatic carbons to all aromatic carbons can be obtained by the extrapolation of the later portion of the decay curve. The 36.7 % ratio obtained by this DD experiments showed a good agreement with the 38.4 % ratio for the non-protonated aromatic carbon intensity to all aromatic carbon intensity in the conventional CP spectrum (The theoretical ratio is 41.7%). It was confirmed that the DD experiments with the high-speed spinning were useful for differentiation of the protonated carbons from the non-protonated carbons by choosing the delay times synchronized with sample spinning.

Fig. 8 shows the VA-CP dipolar-dephasing spectra of the MP-N pitch with the delay times synchronized with sample spinning. In the aliphatic region, the

Fig. 7 Intensity variation for the aromatic carbons in the VA-CP DD NMR of 1-methylfluorene with delay times chosen as twice the multiple of the rotational period (contact time; 2 ms, spinning rate; 12.5 kHz)

intensity of the methyl carbons around 20 ppm decreased more slowly than that of other aliphatic carbons around 35 ppm with increasing delay time as well as in the case of 1-methylfluorene. The aromatic

Fig. 8 VA-CP dipolar-dephasing spectra of the MP-N pitch. The different delay times are noted on the figure (contact time; 2 ms, spinning rate; 12.5 kHz)

bands of the MP-N pitch have the shoulder bands around 138 ppm. The shoulder bands were assigned to the alkyl-substituted (non-protonated) aromatic carbons and the aromatic bands around 127 ppm were assigned to the protonated and bridgehead (non-protonated) aromatic carbons²²⁾. The intensity of alkyl-substituted aromatic carbons decreased more slowly than that of the protonated and bridgehead aromatic carbons as is evident in this figure. Fig. 9 shows the intensity variation for the aromatic carbons of the MP-N pitch with delay times chosen as twice the multiple of the rotational period. The ratio of non-protonated aromatic carbons to all aromatic carbons was estimated to be 52.8 % by the extrapolation of the later portion of the decay curve. This value is slightly greater than the value from 37 to 47 % obtained by Pruski et al.⁶⁾, and this reason was explained such that the aromaticities of the MP-N pitch were greater than those of their samples. The 1932 μ s delay constant obtained in this figure is quite greater than the 500 μ s in a previous work⁶⁾. The dipolar-dephasing relaxation in a low-speed spinning experience¹⁾⁻⁶⁾ is caused by the direct ^{13}C - ^1H dipolar interaction, but in a high-speed spinning experience, the relaxed peaks appear again as a rotational echo shown in Fig. 4. The intensity decay of the echo peaks in this study is a result of a complicat-

Fig. 9 Intensity variation for the aromatic carbons in the VA-CP DD NMR of the MP-N pitch with delay times chosen as twice the multiple of the rotational period (contact time; 2 ms, spinning rate; 12.5 kHz)

ed interplay between the ^{13}C - ^1H dipolar interaction and the ^1H - ^1H dipolar interaction. That is to say, the relaxation mechanism in this study is different from that in the previous work⁶⁾.

3.3 Structural Parameters of MP-N pitch

The procedure for the structural parameters of the MP-N pitch conformed to the lozenge model proposed by Ollivier et al.²³⁾. This method requires two parameters, one is the ratio of the quaternary (non-protonated) aromatic carbons to the tertiary (protonated) aromatic carbons, and the other is the ratio of the substituted aromatic carbons to all aromatic carbons. The ratio of the quaternary carbons to the tertiary carbons was obtained from the previously described DD experiments. We obtained the ratio of the substituted aromatic carbons to all aromatic carbons using the curve-fitting of the aromatic bands in the conventional VA-CP NMR spectrum of the MP-N pitch. Fig. 10 shows the curve-fitting of the aromatic bands in the MP-N pitch. The ratio of the substituted aromatic carbons to the aromatic carbons was 0.082.

Table 2 shows the parameters of the MP-N pitch obtained from the lozenge model of Ollivier et al.²³⁾. The number of aromatic rings for the MP-N pitch is about 6. The number of substitutions is about 2. It

Fig. 10 Curve-fitting of the ^{13}C NMR spectrum of the aromatic carbons for the MP-N pitch using 70% Gaussian add 30% Lorentian mixture function $\text{C}_\text{S}^\text{ar}$, $\text{C}_\text{P}^\text{ar}$, $\text{C}_\text{B}^\text{ar}$; substituted, protonated, and bridgehead aromatic carbons, respectively)

Table 2 Structural parameters of the MP-N pitch

C_S^{ar}	C_P^{ar}	C_B^{ar}	N_R	n
0.082	0.472	0.446	5.6	1.7

C_S^{ar} , C_P^{ar} , C_B^{ar} ; substituted, protonated and bridgehead aromatic carbons, respectively.

N_R ; The number of aromatic rings.

n; The number of substitutions.

can therefore be presumed that the MP-N pitch consists of approximately six aromatic rings with about two alkyl substituents. The linkages such as biaryl bonding are not considered in this model, because the differentiation between the non-protonated perimeter aromatic carbons and the inner aromatic carbons is unavailable in the ^{13}C NMR spectra of carbonaceous solids. But we think that the ^{13}C solid-state NMR with DD experiments is a unique and powerful instrument to characterize the chemical structure of carbonaceous solids such as coal and pitch.

4. CONCLUSION

The following conclusions were obtained by using high-speed MAS, variable amplitude (VA)-CP pulse sequence, and DD experiments with the delay times

synchronized with sample spinning in the high-field NMR of a carbonaceous sample.

(1)VA-CP pulse sequence provides sufficient efficiency of CP in high-speed spinning to obtain the structural parameters as aromaticity.

(2)Intensity fluctuation based on the rotational echo during the DD experiments can be overcome by choosing delay times of twice the multiple of the rotational period.

(3)It was presumed from VA-CP and DD experiments with high-speed MAS that the MP-N pitch consists of approximately six aromatic rings with approximately two alkyl substituents.

(4)By using VA-CP and DD experiments with high-speed MAS, high-field NMR spectroscopy is a useful technique for the structural characterization of carbonaceous solids as well as the low-field NMR.

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