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Letter to the Editor

Through-bond and through-space connectivities of amorphous aluminophosphate by two-dimensional ^{27}Al–^{31}P heteronuclear NMR

Koji Kanehashi [a,*], Takahiro Nemoto [b], Koji Saito [a]

[a] *Advanced Technology Research Laboratories, Nippon Steel Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan*
[b] *JEOL Ltd., 3-1-2 Musashino, Akishima, Tokyo 196-8558, Japan*

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Abstract

The connectivities between Al and P through chemical bond and internuclear distance have been studied for an amorphous aluminophosphate (a-AlPO$_4$) using two-dimensional (2D) solid-state ^{27}Al–^{31}P correlation NMR (MAS *J*-HMQC and CP HETCOR). Whereas the conventional ^{31}P MAS spectrum provides less informative results because of poor resolution caused by large distributions of the nucleus surroundings, the 2D HETCOR shows much better resolution and at least four non-equivalent P sites in the a-AlPO$_4$. These P sites are found to be correlated with one $^{[4]}$Al, two $^{[5]}$Al and one $^{[6]}$Al species, and have different chemical shifts. This result might indicate that the mean P–O–$^{[n]}$Al ($n = 4, 5, 6$) bond angles are different each other, and they are estimated using the relationship with the ^{31}P chemical shifts in crystalline AlPO$_4$ previously reported.

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1. Introduction

The alminophosphate (AlPO$_4$) system is one of the useful molecular sieves, and is widely utilized as catalysts and molecular sieves in industrial processes. AlPO$_4$s are usually synthesized by the hydrothermal reaction, and become either crystalline or amorphous depending on pH in a solution and on calcined temperature [1]. It is important to elucidate the connectivities between PO$_4$ tetrahedrons and AlO$_n$ ($n = 4, 5, 6$) polyhedrons, because they greatly affect the molecular designs. Double resonance NMR is a very useful technique to obtain information about the connectivities between heteronuclei. The connectivities between Al and P via bridging oxygen have been well investigated by solid-state HETCOR (HETeronuclear CORrelation) NMR for various crystalline AlPO$_4$s (c-AlPO$_4$s) such as hydrated VPI-5 [2–6], AlPO$_4$-5 [7], AlPO$_4$-8 [4], AlPO$_4$-14 [8–10], AlPO$_4$-31 [11], AlPO$_4$-34 [11], AlPO$_4$-40 [5] and AlPO$_4$-41 [12]. These HETCOR NMR techniques are of two distinct types: the through-bond connectivities via *J* couplings ($^2J_{\mathrm{Al-P}}$) [6,8,10,13,14] and the through-space connectivities via ^{27}Al–^{31}P dipolar couplings [2–5,7–9,11,12].

On the other hand, the Al–P connectivities in amorphous AlPO$_4$s (a-AlPO$_4$s) have been less examined compared with those in c-AlPO$_4$s. The ^{27}Al–^{31}P REDOR and the TRAPDOR experiments have been performed to estimate interactions between Al and P species for the a-AlPO$_4$ [15]. The through-space Al–P connectivities in the intermediate gel phases of the AlPO$_4$ have been studied by one- (1D) and two-dimensional (2D) CP/MAS [16]. We have investigated not only the O–P connectivities by 1D ^{31}P → ^{17}O and ^{17}O → ^{31}P CP/MAS [17], but also the Al–P correlations by 2D ^{31}P{^{27}Al} HETCOR combined

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[*] Corresponding author.
E-mail address: kojikane@stanford.edu (K. Kanehashi).

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with 3QMAS (triple quantum magic angle spinning) for the purpose of averaging out the second-order quadrupolar interaction in the ^{27}Al dimension [18]. Because the powder X-ray diffraction pattern of a-$AlPO_4$s provide no informative results because of lacking the long-range structural order, *J* coupling- and dipolar-driven HETCOR NMR should be quite powerful techniques to estimate the connectivities in a-$AlPO_4$s. In this study, we examine the through-bond and through-space connectivities in an a-$AlPO_4$ using 2D ^{27}Al–^{31}P MAS *J*-HMQC and CP HETCOR NMR, respectively. From the observed correlation spectrum, the mean P–O–Al bond angles of each P–O–$^{[n]}$Al ($n = 4,5,6$) species in the a-$AlPO_4$ are estimated using the relationship between the angle and the ^{31}P chemical shift for c-$AlPO_4$s (i.e. VPI-5 and $AlPO_4$-14).

2. Experimental

The a-$AlPO_4$ studied here was prepared from $Al(NO_3)_3 \cdot 9H_2O$ and H_3PO_4 under controlled pH according to the previous reports [1,17]. All NMR spectra were acquired on a JEOL JNM-ECA700 spectrometer with a 16.4 T (^{1}H = 700 MHz) narrow-bore magnet. The home-built 4-mm XY double resonance probe was resistant to high rf fields, and produced quite a short π/2 pulse for both channels: 1.8 μs at 1000 W (probe-in) for the ^{27}Al channel for solid $AlK(SO_4)_2 \cdot 12H_2O$ (the quadrupolar coupling constant $C_Q \approx 0$) and 2.2 μs at 560 W (probe-in) for the ^{31}P channel for solid $(NH_4)_2HPO_4$. The resonant frequencies of ^{27}Al and ^{31}P were 182.4 and 283.4 MHz, respectively. The sample spinning rate was 18 kHz ± 10 Hz. The ^{27}Al and ^{31}P chemical shifts were referenced to 1.0 mol/l $AlCl_3$ aqueous solution at −0.1 ppm and solid $(NH_4)_2HPO_4$ at 1.33 ppm, respectively. A small (solids 15–20°) tip angle was applied for single pulse ^{27}Al and ^{31}P MAS experiments, and pulse recycle delays were long enough to allow full relaxation. The *z*-filter sequence was applied for ^{27}Al MQ (M = 3, 5) MAS [19]. The MAS *J*-HMQC [6] and the CP HETCOR pulse scheme were used for analysis of the connectivities through chemical bond and internuclear distance, respectively (Fig. 1). In the CP process from the quadrupolar spin (e.g. ^{27}Al) to the spin-1/2 (e.g. ^{31}P), its efficiency strongly depends on the adiabaticity parameter α [20]:

$$\alpha = \nu^2_{\mathrm{rf(Al)}} / \nu_{\mathrm{Q}} \nu_{\mathrm{MAS}},$$

where $\nu_{\mathrm{rf(Al)}}$ is the rf field of ^{27}Al under the spin-locking, ν_{Q} is the quadrupolar parameter ($= 3C_Q/[2I(2I-1)]$), ν_{MAS} is the MAS frequency. We chose the sudden passage condition ($\alpha \gg 1$) to preserve the transverse magnetization under the spin-locking: $\nu_{\mathrm{rf(Al)}} = 6$ kHz, $\nu_{\mathrm{MAS}} = 18$ kHz. Centers of gravity for cross sections in a 2D spectrum were determined by integration.

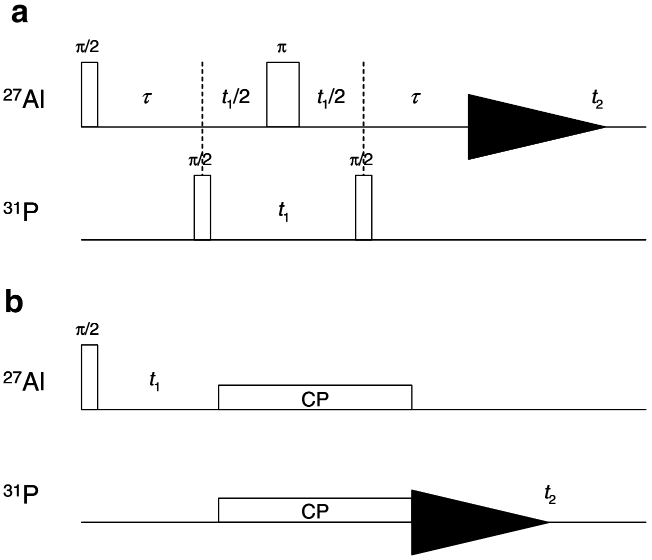

Fig. 1. Pulse sequences of two-dimensional ^{27}Al–^{31}P NMR: (a) MAS *J*-HMQC (through-bond connectivities) and (b) CP HETCOR (through-space connectivities).

3. Results and discussion

First, ^{27}Al MAS and MQMAS spectra and a ^{31}P MAS spectrum were measured (not shown). For ^{27}Al, three distinct Al species assigned to tetrahedral ($^{[6]}$Al), pentacoordinated ($^{[5]}$Al) and octahedral ($^{[6]}$Al) Al environments were observed at 42, 20 and −5 ppm, respectively, in the MAS spectrum. The higher coordinated Al sites ($^{[5]}$Al and $^{[6]}$Al) were attributed to the coordination of extra water molecules or hydroxyl groups to AlO_4 tetrahedrons by the fact that a $^1H \rightarrow {}^{27}Al$ CP/MAS spectrum enhanced the relative intensities of these Al species. Compared with the MAS spectrum, spectral resolution of MQMAS was slightly better due to the line narrowing caused by the cancellation of the second-order quadrupolar interaction. However, the overall line shapes of the MAS and MQMAS spectra were quite similar because of the relatively small quadrupolar coupling constants ($C_Q = 2.0$–2.7 MHz) of each Al site. All cross peaks in the MQMAS spectrum were dispersive along the chemical shift line (a slope of 1) rather than the quadrupolar induced shift line (a slope of −10/17), indicating that the line broadening of the ^{27}Al spectrum results mainly from chemical shift distributions, and quadrupolar distributions less affects the broadening. This result means that there is a variety of combinations of AlO_n polyhedrons with adjacent PO_4 tetrahedrons such as the P–O–Al bond angles and the Al–O bond lengths, whereas distributions of the distortion of AlO_n ($n = 4,5,6$) polyhedrons are relatively small.

A ^{31}P MAS spectrum showed one broad, featureless peak at −23.1 ppm (peak top) which is assigned to Q^4 tetrahedral units (all four O ions in PO_4 are shared with the adjacent PO_4 or AlO_n units), because no non-bridging oxygen have been found to present in this sample from the previous ^{17}O NMR result [17]. This broad peak is probably due to distributions of the nucleus surroundings mainly. Remaining ^{31}P–^{27}Al and ^{31}P–^{1}H dipole interactions might also broaden the ^{31}P MAS spectrum [9].