Structural Study on Amorphous AlPO$_4$ by ^{17}O MQMAS and Mutual (^{31}P $\leftrightarrow$ ^{17}O) CP/MAS NMR

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The ^{17}O multiple quantum magic angle spinning (MQMAS) and the mutual (^{31}P $\leftrightarrow$ ^{17}O) CP/MAS (MCP) NMR was applied to clarify the detailed chemical structure in amorphous AlPO$_4$. An application of the mutual CP/MAS method being capable of mapping out the connectivity with the ^{17}O MQMAS for characterization of oxygen sites provided precious structural information in amorphous AlPO$_4$.

Extensive researches on aluminophosphate (AlPO$_4$) have been done because of its industrial needs. While crystalline AlPO$_4$-based molecular sieves such as zeolites were much investigated by ^{27}Al and ^{31}P NMR,[1] there are few structural analysis of amorphous AlPO$_4$. Kraus *et al.* studied the aluminum environment in amorphous AlPO$_4$ by ^{27}Al MQMAS NMR and obtained the useful information of aluminum sites and distributions of its structure.[2]

The connectivity information is also necessary to make the structure clear. The Al/P CP method is a very powerful tool for the connectivity in the crystalline AlPO$_4$-based molecular sieves[3–5] and the intermediate gel phases of AlPO$_4$ synthesis.[6]

However, the oxygen structure including the linkage in amorphous AlPO$_4$ has never spotlighted so far. The difficulty in ^{17}O measurement arises from two reasons mainly; one is a much lower sensitivity compared with ^{27}Al and ^{31}P, and the other is a larger quadrupolar coupling constant than ^{27}Al. Since the oxygen atoms form the core of framework of amorphous AlPO$_4$, it is very important to obtain the structural information of oxygen sites and the connectivity between oxygen and phosphorus/aluminum.

In this paper, we aim to elucidate not only the oxygen structure by ^{17}O MQMAS NMR being capable of averaging the second-order quadrupolar interaction in half integer nuclear spins[7] but also the connectivity of P–O bond through the distance dependence of the mutual CP process in ^{17}O-enriched amorphous AlPO$_4$.

^{17}O-enriched amorphous AlPO$_4$ was prepared by neutralizing an aqueous solution of Al(NO$_3$)$_3$·9H$_2$O and ^{17}O-enriched H$_3$PO$_4$ (min. 20 atom% ^{17}O) at a controlled pH of 8 using ammonium hydroxide.[8] The precipitate was dried at 393 K for a time of 20 h and calcined at 773 K for a time of 6.5 h. XRD measurement confirmed that the sample was completely amorphous (not shown).

The ^{17}O MQMAS spectrum was carried out using a Varian/Chemagnetics CMX Infinity 500 NMR spectrometer with 5 mm HX probe at 67.8 MHz. The ^{17}O MAS, ^{31}P MAS and ^{31}P $\leftrightarrow$ ^{17}O CP/MAS spectra were performed on a Varian Unity plus 500 NMR spectrometer with 5 mm HXY MAS probe at 67.8 (^{17}O) and 202.5 (^{31}P) MHz. The ^{17}O and ^{31}P chemical shift were referenced to distilled water at 0 ppm and (NH$_4$)$_2$HPO$_4$ at 1.33 ppm, respectively. The three-pulse sequence that includes z-filter pulse that is selective at low rf-power was applied[9] and the triple quantum coherence was selected in the MQMAS experiment.

Hypercomplex method was used for pure absorption mode line shapes. The final 2D MQMAS spectrum was obtained after the sharing transformation. The CP process of quadrupolar spins (^{17}O) was carried out in the rapid passage condition to preserve the spin locking efficiency.[10–12]

First, a very broad peak was observed in the ^{17}O MAS spectrum of ^{17}O-enriched amorphous AlPO$_4$ (Figure 1(a)). The shape of the resonance is asymmetric and contains a shoulder on the up-field side. Although there seem to be some oxygen sites in the compound, it is difficult to clarify the precise chemical structure of oxygen atoms from the ^{17}O MAS spectrum because of the influence on the second-order quadrupolar interaction that cause a spectral broadening and splitting, and a shift of the resonance from essential value. We have already verified the existence of two different oxygen environments by ^{17}O triple quantum MAS (3QMAS) spectrum (Figure 2) averaging the second-order quadrupolar interaction. Moreover, careful inspection of Figure 2 also reveals that the cross section is distributed along chemical shift axis, which is caused by the amorphous structure. Thus, MQMAS can also provide valuable information regarding the dispersion of chemical shift in disordered materials,[2] whereas such distribution is difficult to analyze by the conventional MAS technique.
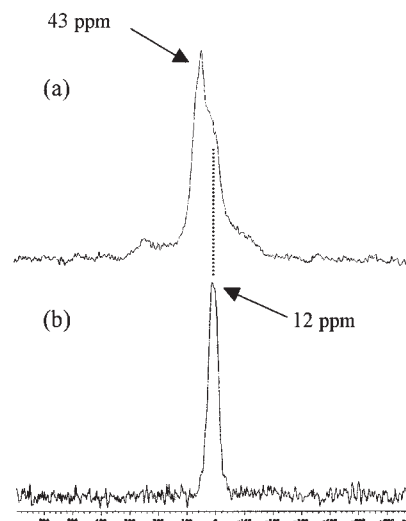
Figure 1. Observation of ^{17}O in ^{17}O-enriched amorphous AlPO$_4$. (a) ^{17}O MAS spectrum; spinning rate: 14 kHz, pulse delay: 0.4 s 4000 scans. (b) ^{31}P $\rightarrow$ ^{17}O CP/MAS spectrum: ν_O: 5 kHz, contact time: 1 ms, spinning rate: 14 kHz, pulse delay: 60 s, 1660 scans.

Next, in order to determine which kind of atoms the two oxygen sites bond to, the ^{31}P $\rightarrow$ ^{17}O CP/MAS experiment was implemented. The ^{31}P $\rightarrow$ ^{17}O CP/MAS spectrum of ^{17}O-
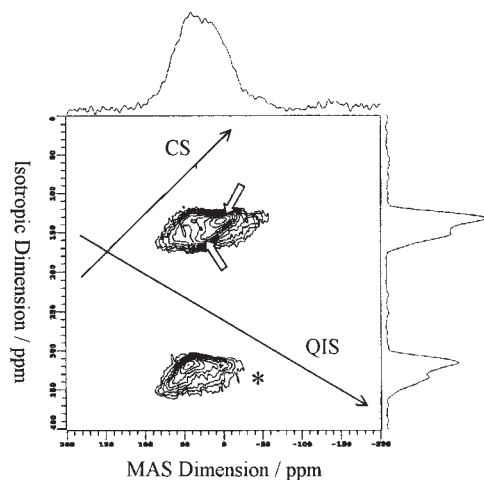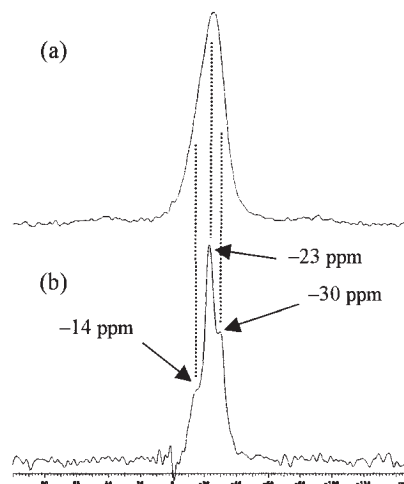
Figure 2. ^{17}O-3QMAS spectrum of ^{17}O-enriched amorphous $AlPO_4$ after sharing: excitation pulse width: $4.2\,\mu s$, conversion pulse width: $1.4\,\mu s$, z-filter pulse width: $14\,\mu s$, t1 increment: $13.3\,\mu s$, spinning rate: $12.5\,kHz$, pulse delay: $0.3\,s$, 4800 scans. * is spinning sideband.

Figure 3. Observation of ^{31}P in ^{17}O-enriched amorphous $AlPO_4$: (a) ^{31}P MAS spectrum: spinning rate: $10\,kHz$, pulse delay: $20\,s$, 40 scans. (b) $^{17}O \rightarrow {}^{31}P$ CP/MAS spectrum; ν_P: $8\,kHz$, contact time: $1\,ms$, spinning rate: $10\,kHz$, pulse delay: $0.4\,s$, 1000000 scans.

enriched amorphous $AlPO_4$, displayed in Figure 1(b), shows an interesting feature. The resonance at 12 ppm corresponding to the up-field shoulder peak on the ^{17}O MAS spectrum was only observed. It means that the peak at 12 ppm is attributed to the oxygen atoms of direct linkage with the phosphorus, P–O–Al, P–O–P and terminal P–O considered from the structure of $AlPO_4$. On the other hand, the peak at 43 ppm in the ^{17}O MAS spectrum which does not show up in the $^{31}P \rightarrow {}^{17}O$ CP/MAS spectrum is considered to be the oxygen sites in Al–O–Al and terminal Al–O that is not dipolar coupled to phosphorus atoms in the compound.

The research aimed at phosphorus sites was also carried out. In the ^{31}P MAS spectrum (Figure 3(a)), a very broad peak caused by its amorphous structure was seen at -25 ppm. It is not easy to characterize exact chemical structure of phosphorus from this spectrum. However, the $^{17}O \rightarrow {}^{31}P$ CP/MAS spectrum clearly shows that there are at least three different phosphorus environments in the sample (Figure 3(b)). Since phosphorus atoms exist in PO_4 tetrahedral units, phosphorus atoms should have direct P–O bond. There are P–O bonds that are long distance and cause inefficient CP process, however, because of its amorphous structure; as a result, the phosphorus species which are not shown in the ^{31}P MAS spectrum seem to exist. From the fact that ^{31}P chemical shifts is sensitive to the condensation degree of PO_4 units denoted Q^n (n is the number of oxygen atoms shared with the next PO_4 unit), it is possible to evaluate the network of PO_4 units. The peak at -14, -23 and -30 ppm is assumed to correspond to Q^2, Q^3 and Q^4 unit, respectively so far.

Thus, mutual ($^{31}P \leftrightarrow {}^{17}O$) CP/MAS method is effective measures for estimation of connectivity in ^{17}O-enriched amorphous $AlPO_4$ as well as the ^{17}O MQMAS measurement that is capable of determining the oxygen structure. Further experiments regarding the linkage between oxygen and aluminum sites are necessary to get more detailed structural information of the compound. The MCP is considered to provide precious structural

information for a variety of inorganic materials, catalyst, glasses, and so on. Moreover, the combination of this technique and REDOR for decision of the distance between nuclei may provide precious structural information of three-dimensional network of various materials.

References and Notes
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