**CHARACTERIZATION OF POLYMORPHIC CERIUM
PHOSPHATES AS STUDIED BY SOLID-STATE
HIGH-RESOLUTION ^{31}P NMR**

HIROKAZU NAKAYAMA, AKI HAYASHI, MITSUTOMO
TSUHAKE, TARO EGUCHI* AND NOBUO NAKAMURA*
*Kobe Pharmaceutical University and *Department of Chemistry,
Graduate School of Science, Osaka University*

Abstract In order to characterize various forms of layered cerium phosphates, ^{31}P MAS and CP/MAS NMR spectra were measured in the solid state. Two peaks around -10 and -30 ppm suggest them to be γ -type structure with the non-stoichiometric amount of hydration waters.

Introduction

Since layered zirconium phosphates were first synthesized by A. Clearfield *et al.* in 1964,^{1,2)} extensive studies concerning the ion-exchange capability of these compounds were performed in 1970's. Recently, inorganic-organic hybrid materials with new functions have been tried to be synthesized using the layered phosphates. There are two types of layered phosphates, α - and γ -types. The difference of the physicochemical properties, such as ion-exchange capability, thermal stability and intercalation of organic compounds, in these two types of compounds (α - and γ -types) is closely related to their structural differences. Single crystal structure analyses were only performed for α -Zr(HPO₄)₂·H₂O and α -Zr(HPO₄)(NaPO₄)·H₂O, because of the difficulty in synthesizing single crystals of layered phosphates.^{3,4)} And the crystal structure of γ -

$\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ was resolved by Rietveld analysis of powder sample in 1995,⁵⁾ and ^{31}P MAS (Magic Angle Spinning) NMR in 1987.⁶⁾ It was clear that $\gamma\text{-Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ has two different phosphate groups, H_2PO_4^- and PO_4^{3-} , in the crystal. Thus, γ -zirconium phosphate should not be expressed in chemical formula as $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, but as $\text{Zr}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$. As it is sometimes difficult to elucidate the structure from powder X-ray diffraction, it is important to distinguish these two types by the other method.

Layered cerium phosphates are reported to have many polymorphic forms, $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$ and 2), depending on the number of hydration water.⁶⁾ These forms exchange reversibly under the different humidity. In the case of layered zirconium and titanium phosphates, two polymorphic forms, $\text{M}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -form) and $\text{M}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (γ -form), have completely different structure as mentioned above and can be obviously distinguished by the number of hydration water. However, layered $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ has non-stoichiometric number of hydration water and can not be classified in the α - or γ -type by only the number of it. Recently, we showed that ^{31}P MAS NMR is a useful technique to know the local structure of layered phosphates.⁷⁾ Thereupon, we applied this method to $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n=0.33, 1.33$ and 2).

FIGURE 1. ^{31}P MAS NMR spectra of $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ with ^1H high-power decoupling where $n =$ (a) 2, (b) 1.33, (c) 0.33.

Results and Discussion

Figure 1 shows ^{31}P MAS NMR spectra of layered $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$ and 2) with ^1H high-power decoupling. Two main peaks around -10 and -30 ppm are observed as listed in Table 1.

Alpha-form of layered phosphate has one kind of phosphate group,

TABLE 1. Chemical Shifts in $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$

n	δ / ppm	
	$(\text{H}_2\text{PO}_4)^-$	$(\text{PO}_4)^{3-}$
0.33	-11.7	-29.0
1.33	-10.6	-28.3
2.00	-11.2	-28.6

HPO_4^{2-} , whereas γ -form of layered phosphate has two chemically different kinds of phosphate groups, PO_4^{3-} and H_2PO_4^- .^{3,5)} These three types of phosphate groups in layered zirconium and titanium phosphates have characteristic chemical shift values as shown in Fig. 2.⁷⁾ The chemical shift

FIGURE 2. ^{31}P chemical shift values of various layered phosphates.

values of H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} groups are about -10, -20, and -30 ppm, respectively. And the peaks in γ -form appear at around -10 and -30 ppm, with equal intensity. Using Fig. 2, the structural type and the site of phosphate can be estimated for layered phosphate with unknown structure. $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$, and 2) are estimated to be γ -form. As the number of hydration water in layered cerium phosphate is non-stoichiometric, it must be careful to conclude $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$, and 2) to be γ form.

^{31}P MAS without ^1H high-power decoupling and ^{31}P - ^1H CP/MAS measurements were performed to confirm this conclusion. For $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ the peak at -10.6 ppm, which will be due to H_2PO_4^- group, broadens without ^1H high-power decoupling, suggesting stronger ^{31}P - ^1H dipolar interaction compared with the case of PO_4^{3-} group. Contact time, t_m , dependence of CP/MAS spectra elucidates the strength of ^{31}P - ^1H dipolar interaction semi-

quantitatively through cross-polarization time, T_{PH} .⁹⁾ Figure 3 shows CP/MAS

FIGURE 3. Contact time, t_m , dependence of ^{31}P CP/MAS spectra of $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ with $t_m =$ (a) 100 μs , (b) 1 ms, (c) 3 ms. * shows spinning side bands.

spectra of $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ at different t_m . On increasing t_m , the intensity of the signal at -10.6 ppm (H_2PO_4^- site) increases within 100 μs , then that of the signal at -28.3 ppm (PO_4^{3-} site) increases. T_{PH} at -10.6 and -28.3 ppm are estimated to be <100 μs and $\sim 2\text{ms}$, respectively. T_{PH}^{-1} is proportional to the r^{-6} where r is the distance between P and H. Therefore, the peaks at -10.6 and -28.3 ppm can be assigned to H_2PO_4^- and PO_4^{3-} groups, respectively. And T_{PH} values are similar to the values in $\gamma\text{-Zr}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$. The similar experiment was performed for $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33$ and 2). And all the forms are confirmed to be γ -form, irrespective of the number of hydration water.

The interlayer distances of cerium phosphates ($n = 0.33, 1.33$, and 2) are 14.4, 16.1, and 18.0 $\text{\AA}$,⁶⁾ which are considerably long compared with 11.6 $\text{\AA}$ in $\gamma\text{-M}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Zr}, \text{Ti}$). These differences are beyond the difference of ionic radius (Zr^{4+} 0.86 $\text{\AA}$, Ti^{4+} 0.75 $\text{\AA}$, Ce^{4+} 1.09 $\text{\AA}$). Although $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$, and 2) are γ -form, having two chemically different phosphates, PO_4^{3-} and H_2PO_4^- , the arrangements of phosphate groups of cerium phosphates are considered to be different from those of the other layered phosphates with γ -form. The local structures of phosphate groups within three polymorphic forms are similar, that is, the existence of both H_2PO_4^- and PO_4^{3-} groups. The only difference is the interlayer structure, especially, the hydrogen bond scheme of water molecules, which connect the sheets of phosphates. This reflects the increase of interlayer distance by 3.6 $\text{\AA}$ on increasing the amount of hydration water.

In conclusion, layered cerium phosphates, $\text{Ce}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$, and 2), were confirmed to be γ -form by ^{31}P solid-state NMR spectra. $\text{Ce}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33$, and 2) has two different phosphate groups, H_2PO_4^- and PO_4^{3-} , and non-stoichiometric water of

hydration. The interlayer distances of cerium phosphates is longer than those of the other layered phosphates of γ -form.

Experimental

Hydrated cerium bis(hydrogenphosphates), $\text{Ce}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0.33, 1.33, \text{ and } 2$) were synthesized according to the previous method.^{6,8)} Their compositions were determined by elemental analyses of cerium and phosphorus. X-ray diffraction patterns of the above compounds were consistent with the reported values of the interlayer spacing, d .

A Bruker MSL-200 and DSX-200 spectrometers operating at 81.0 MHz for ^{31}P were used to measure solid-state NMR spectra. A single pulse sequence with a $\pi/2$ pulse of 2 μs with ^1H high-power decoupling was used for ^{31}P MAS spectra. Cross-polarization (CP) pulse sequence with ^1H high power decoupling was used to get ^{31}P CP/MAS spectra. Contact time, t_m , dependence of ^{31}P CP/MAS spectra was measured in order to distinguish between H_2PO_4^- and PO_4^{3-} sites in the γ -form. For the MAS and CP/MAS spectra, it was enough to accumulate 8 FID's with a recycle time of 10 s to get the spectra with reasonable signal to noise ratio, S/N. The MAS rate was 3-4 kHz. Chemical shift is referenced from 85% H_3PO_4 aqueous solution.

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