

Solid NMR Study of the Ion-Exchange Properties on γ-Titanium Phosphate with Alkali Metal Ions

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Abstract
Layered γ-titanium phosphate (γ-TiP), Ti(HPO₄)₂·2H₂O, is well known as the host material of intercalation compounds and the inorganic ion-exchanger of H⁺/metal ion system. It was found to have high ion-exchange selectivity for Rb⁺ and Cs⁺ among alkali metal ions. The ion-exchange reactions for these ions progressed in two steps according to pH. Part of water molecules in the interlayer of γ-TiP was taken away during ion-exchange reaction and an amorphous γ-TiP resulted. This phenomenon was first studied by thermal analysis and further investigation was carried out using solid NMR of ¹H and ¹³³Cs in detail. Moreover, the interaction between Fe²⁺ and Cs⁺ for the ion-exchange reaction was investigated. Despite Fe²⁺ was hard to adsorb to γ-TiP, the amount of sorbed Fe²⁺ increased when Cs⁺ coexisted and the amount of sorbed Cs⁺ decreased.

1 Introduction
Inorganic ion-exchangers usually have thermal stability and resistance for radiation compared with the organic ion-exchange resins. The phosphates of multi-valent metals are well known as inorganic ion-exchangers. It has also been used as a host material for intercalation compounds such as supports of immobilized enzymes.[1] The acid salts of tetravalent metals are classified in α-type, γ-type, three-dimensional structure, fibrous structure according to their crystalline structures.[2] Among crystalline titanium phosphates, γ-titanium phosphate (γ-TiP), Ti(HPO₄)₂·2H₂O, is the only type of the crystal which can adsorb cesium ion.[3] Since γ-TiP has the high selectivity for cesium ion, it must be the promising material for the recovery of cesium from the radioactive waste water. Ion-exchange property of γ-TiP was studied by thermal analysis and powder X-ray diffraction.[3] However, few studies were carried out using solid NMR.

It has been confirmed that NMR is one of the effective tools to study the ion-exchanged metal ions as well as the accommodated water molecules.[4-6] The information obtained from solid NMR data is line sharpness, chemical shift, signal splitting and relaxation time. NMR is the only method by which the mobility of ions or molecules of interest can be analyzed. This paper deals with the basic ion-exchange property of γ-TiP and its NMR consideration. In addition, the interference of the coexisting ion with the ion-exchange selectivity for Cs⁺
and Rb\(^+\) is reported. Fe\(^{2+}\) was selected for this study.

## 2 Experimental

### 2.1 Materials

Amorphous titanium phosphate was prepared as reported.[3] 800 cm\(^3\) of 2 mol dm\(^{-3}\) HCl and 50 g of TiCl\(_4\) were mixed in a glass vessel. 800 cm\(^3\) of 1.45 mol dm\(^{-3}\) H\(_3\)PO\(_4\) was slowly added to the beaker and stirred vigorously. Amorphous titanium phosphate was precipitated and the precipitant was separated by centrifugation. It was washed with ultra purified water and centrifuged again. The product was air-dried. Crystalline dihydrated Ti(IV) phosphate was obtained by hydrothermal synthesis as follows.[4] 1 g of amorphous titanium phosphate and 20 cm\(^3\) of 10 mol dm\(^{-3}\) H\(_3\)PO\(_4\) were placed in a glass tube and sealed. The tube was then put in an autoclave. Hydrothermal synthesis was carried out at 270 °C and 7 x 10\(^6\) Pa for 36 h. The product was characterized by a powder X-ray diffractometer (MO3X-HF, MAC Science Co., Ltd., Japan) equipped with monochromized Cu-K\(_{\alpha}\).

### 2.2 Ion-Exchange Reaction

Ion-exchange reaction of \(\gamma\)-TiP with alkali metal ions was carried out as follows. 1.0 x 10\(^{-4}\) mol dm\(^{-3}\) LiCl, NaCl, KCl, RbCl and CsCl solutions were prepared, and HCl solution was added to vary the solution pH. 20 cm\(^3\) of each solution and 0.2 g of \(\gamma\)-TiP were immersed in a glass ampoule except NaCl solution. A polyethylene vessel was used in the case of NaCl solution to avoid the contamination of Na\(^+\) from the glass ampoule. The mixture of 5 x 10\(^{-5}\) mol•dm\(^{-3}\) FeCl\(_2\) and alkali metal chloride solution was used to examine the interfering of Fe\(^{2+}\). The amounts of the alkali metal ions and Fe\(^{2+}\) in the supernatant solution were measured to analyze the sorbed amounts by an atomic absorption spectrophotometer (HITACHI 170-30) and a sequential plasma spectrophotometer (SHIMADZU ICPS-5000), respectively.

### 2.3 pH Titration Curve

0.1 g of \(\gamma\)-TiP was placed in a glass ampoule with 10 cm\(^3\) of the metal ion solution. The various pH solutions were prepared with the various ratios of 0.1 mol dm\(^{-3}\) HCl and 0.1 mol dm\(^{-3}\) MOH (M = Rb, Cs) to adjust ionic strength constant. After equilibrium, pH of each solution was measured. pH titration curve was made by the relation between pH and the uptake of metal ions, which was estimated from the difference between initial and final pH of the solution.

### 2.4 NMR Study

\(^1\)H and \(^{133}\)Cs spectra were measured using a 270 MHz FT-NMR Spectrometer (JNM-GX270, JEOL, Japan) and a 300 MHz FT-NMR Spectrometer (JNM-AL300, JEOL, Japan), respectively.

## 3 Results and Discussion

### 3.1 Ion-Exchange Property

Figure 1 shows \(K_d\) values of alkali metal ions as a function of pH. The ion-exchange reaction with sodium ion and lithium ion hardly occurred. Although the ion-exchange selectivity was low, the ion-exchange reaction occurred with potassium ion at pH values larger than 1.5. \(\gamma\)-TiP showed high ion-exchange selectivity for cesium ion and rubidium ion among alkali metal ions.

### 3.2 Effect of Fe\(^{2+}\)

Table 1 shows the ratio of the amount of sorbed ions relative to the added amount of ions after ion-exchange reaction in the presence of Fe\(^{2+}\). Ion-exchange reaction was hardly observed for Fe\(^{3+}\) in the reactant of Fe\(^{2+}\) and Fe\(^{2+}\)-Rb\(^+\). K\(^+\) in both reactants did not ion-exchange. The amount of ion-exchanged Fe\(^{2+}\) was
increased when Cs⁺ coexisted, but the amount of ion-exchanged Cs⁺ was slightly decreased at the same time.

### 3.3 pH Titration Curve

Figures 2 and 3 show the pH titration curves of Cs⁺ and Rb⁺, respectively. Ion-exchange reaction of both ions progressed in two steps. In the case of Cs⁺, the first exchange occurred at pH 2.6 and the second exchange was at around pH 8.0. Different ion-exchange character was observed in powder X-ray diffraction and thermal analysis (figures are not shown). Although the gallery height of γ-TIP, which was 1.16 nm, did not change after the first exchange, it increased to 1.44 nm after the second ion-exchange reaction. Moreover, the diffraction pattern of the ion-exchanged sample at pH 8.3 was ambiguous, which must be assigned to the collapse of γ-TIP. Despite the gallery height was kept constant, part of the hydrated water was taken out during the ion-exchange reaction because the number of water molecules decreased from 2.0 to 0.3 mol/γ-TIP that were estimated from TG data. This fact indicated that the gallery height was not supported by water layer such as the case of sodium difluorotetrasilicate (Na-TSM). After the second ion-exchange reaction, however, the gallery height extended by 0.28 nm that was equivalent to the diameter of a water molecule. Water molecules must be incorporated into the interlayer of γ-TIP after the second exchange reaction. The change in the gallery height was also confirmed by thermal analysis. A similar property was observed in case of the ion-exchange reaction with Rb⁺. The first ion-exchange reaction occurred at pH 2.2 and the gallery height was 1.17 nm. The second reaction continuously occurred at pH 6.9. The X-ray diffraction peak was broad and indicated amorphous of γ-TIP, which meant the collapse of the crystal like Cs⁺ in pH 8.3.
3.4 NMR Study

Figure 4 shows the $^1$H NMR spectrum of $\gamma$-TiP after the ion-exchange with Cs$^+$ at pH 2.6. The chemical formula of ion-exchanged $\gamma$-TiP at pH 2.6 was Ti(HPO$_4$)$_2$CsPO$_4$·0.3H$_2$O as discussed above. The ratio of proton number in water molecule to that in phosphoric acid should be 0.6 : 1.0. The observed curve in Fig. 4 was composed of two Lorentz type spectra with half line widths of 3.8 kHz and 30 kHz. The ratio of the area, i.e. proton numbers, was calculated to be about 0.1 : 1.0. Because the curve fitting was performed under the assumption of the two-spin system, the result was inconsistent with the thermal analysis. In other words, the inconsistency suggested more than two kinds of protons. In addition, if water molecules were adhesive ones, the drying condition, such as humidity, widely affects thermal analysis. Moreover, the first endothermic peak at 70 °C in DTA was decreased to 45 °C after ion-exchange reaction, which indicated that the water molecules must be in less restricted state. Accordingly, these spectra with the half line width of 30.0 kHz and 3.8 kHz were assigned to the protons of Ti(HPO$_4$) and H$_2$O, respectively. In general, the shorter correlation time resulted in the narrow spectrum and indicated high mobility. The spectra with the half line width of 3.8 kHz indicated the considerably rapid motion of water molecules in $\gamma$-TiP. The mobility suggested that water molecules in $\gamma$-TiP after ion-exchanged at pH 2.6 should be adhesive ones rather than accommodated in interlayer gallery.

Figure 5 shows the $^{133}$Cs NMR spectrum of $\gamma$-TiP after the ion-exchanged with Cs$^+$ at pH 2.6. A sharp signal at 0 kHz indicated the internal standard of aqueous CsCl solution. The single signal with the half line width of 2.0 kHz indicated the simple ion-exchange reaction in H$^+$ / Cs$^+$ system. The adsorbed state was suggested to be homogenous and rather restricted.

References