

Intercalation of 2-Aminoethanethiol into Layered Titanium Phosphate and Its Adsorption of Heavy Metal Ions

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In order to develop a new type of adsorbent of toxic heavy metal ions, 2-aminoethanethiol-intercalated layered phosphates were synthesized. 2-Aminoethanethiol was intercalated into titanium(IV) dihydrogenphosphate phosphate dihydrate (γ-titanium phosphate), $Ti(H_2PO_4)(PO_4)\cdot 2H_2O$, with a monolayer structure. The intercalation compound could adsorb heavy metal ions, such as Ag^+, Hg^{2+}, Cd^{2+}, Pb^{2+} and Cr^{3+}, by interacting with a mercapto group (–SH). Also, it could completely adsorb Ag^+ and Hg^{2+}, even from any concentration of aqueous solutions. The adsorption amounts increased with an increase of the 2-aminoethanethiol content in the intercalation compound. The adsorption mechanism was investigated by using powder X-ray diffraction and solid-state NMR. For a comparison, propylamine-intercalated γ-titanium phosphate was also examined.

Crystalline-layered phosphates of tetravalent metals (M), such as Zr(IV) and Ti(IV), are known as inorganic ion exchangers and the host compounds for intercalation reactions.[1,2] There are two types of layered phosphates, that is, α-$M(HPO_4)_2\cdot H_2O$ (α-MP) and γ-$M(H_2PO_4)(PO_4)\cdot 2H_2O$ (γ-MP). These layered phosphates are solid acids with a phosphate group (P-OH) in the interlayer region. Therefore, they can easily intercalate various organic bases, such as aliphatic and aromatic amines, by an acid–base reaction.[2–4] Also, the proton of α-$Zr(HPO_4)_2\cdot H_2O$ (α-ZrP) is able to exchange with alkali metal ions.[5] Extensive studies on the intercalation of alkylamines,[2,6] alkanediamines,[7] and organic metal compounds[8] have been reported since the discovery of α-ZrP in 1964.[9]

Recently, various intercalation compounds have been synthesized while aiming to obtain inorganic–organic hybrid materials with new functions. For example, polyamine-intercalated α-ZrP can adsorb carboxylic acid and aldehyde gases through an interaction with an amino and/or imino group in the interlayer region.[10,11] Enzymes can also be intercalated into the expanded interlayer space of propylamine-intercalated layered phosphate.[12]

The pollution of the environment by toxic heavy metal ions and pesticides has been noted all over the world, and many researchers have devoted themselves to green chemistry. We have reported the recovery of some amino acids from industrial and household sewage by using layered phosphates.[13] The mercapto group (–SH) is known to react with heavy metal ions to form mercaptide. By using this reaction, the selective adsorption of heavy metal ions can be expected by thiol (R–SH)-intercalated layered phosphate. Although the ion-exchange of alkali metal ions by layered phosphates was extensively investigated,[5] the adsorption property of heavy metal ions has not been well understood. The purpose of the present work is the recovery and the concentration of a slight amount of toxic heavy metal ions in rivers and soils by 2-aminoethanethiol (cysteamine)-intercalated layered phosphate. Also, the adsorption mechanisms were investigated using powder X-ray diffraction and solid-state NMR. For a comparison, the adsorption of heavy metal ions by alkylamine-intercalated layered phosphate was also examined to definitely determine the interaction site.

Experimental

Chemicals. γ-Titanium phosphate was prepared according to a procedure described in a previous paper.[14] 2-Aminoethanethiol hydrochloride (abbreviated as NC_2SH) was purchased from Aldrich Chemical Ind. Co., Ltd. Propylamine (C_3N) and heavy metal ions were purchased from Wako Chemical Ind. Co., Ltd.

Intercalation Procedure. In order to obtain a good crystalline NC_2SH-intercalated γ-TiP (abbreviated as NC_2SH/γ-TiP), the intercalation reaction was performed under various reaction conditions. That is, one gram of γ-TiP was added to 0.1 dm^3 of 0.02–0.2 mol dm^{-3} NC_2SH aqueous solution; the suspension was stirred at room temperature −50 °C for 5–48 h. The recommended condition for preparing NC_2SH/γ-TiP was as follows: the concentration of NC_2SH was 0.1 mol dm^{-3} and the reaction time was 24 h at room temperature. The propylamine-intercalated γ-TiP (C_3N/γ-TiP) was prepared for a comparison. One gram of γ-TiP was added to a mixture of 0.1 dm^3 of 0.1 mol dm^{-3} C_3N aqueous solution and 0.01 mol of HCl, and the suspension was stirred at room temperature for 24 h.

Their resultant products were filtrated, washed with distilled water, and dried in air.

Adsorption of Heavy Metal Ions. Half a gram of the intercalation compound (NC_2SH/γ-TiP or C_3N/γ-TiP) or γ-TiP was added to 1–1000 ppm aqueous solution of heavy metal ions (Ag^+, Hg^{2+}, Cd^{2+}, Pb^{2+} and Cr^{3+}). The suspension was stirred for 0.5–5 h at room temperature. The adsorption amount of heavy metal ions was calculated from the residual metal ions in the filtrate.

Analysis. The X-ray diffraction (XRD) patterns were measured with a Rigaku Denki Rint 2000 diffractometer using Ni-filtered Cu-$K\alpha$ radiation to monitor all new phases and to determine their interlayer distances. The amounts of guest compounds in the

intercalation compounds were determined by elemental analysis using a Sumigraph NC-90A. The concentrations of residual heavy metal ions in the filtrate were measured with ICP (inductively coupled plasma) using a Seiko Electron Industry model SRS1200VR.

The ^{31}P and ^{13}C solid-state NMR spectra of the intercalation compounds were obtained by a JEOL GX-270W spectrometer operating at 81.0 MHz for the ^{31}P nucleus and 50.2 MHz for the ^{13}C nucleus, respectively. A single-pulse sequence with a $\pi/2$ pulse of 7.5 μs was used to obtain ^{31}P magic angle spinning (MAS) NMR spectra with ^{1}H high-power decoupling. For the ^{13}C CP/MAS NMR spectra, a recycle time of 6 s and accumulation between 600 and 10,200 scans were used. The MAS rate was 4 kHz. The chemical shifts were referenced from an 85% H_3PO_4 aqueous solution and tetramethylsilane (TMS) for ^{31}P and ^{13}C nuclei, respectively.

Results and Discussion

When 0.1 dm^3 of 0.1 mol dm^{-3} 2-aminoethanethiol (NC_2SH) aqueous solution was stirred with 1.0 g of γ-TiP at room temperature for 24 h, the (001) reflection at $2\theta = 7.6°$ ($d = 11.6$ Å) shifted to a lower degree ($2\theta = 5.9°$), as shown in Figs. 1-(a) and (b). This expansion of the interlayer distance from 11.6 to 14.9 Å indicates that NC_2SH was intercalated into γ-TiP. The diffraction peak of γ-TiP observed at $2\theta = 16°$ is assigned to the (011) reflection.[15] For the other layered phosphates (α-titanium phosphate, α- and γ-zirconium phosphates), the intercalation reaction of NC_2SH was not successful due to its low basicity. Upon increasing the concentration of NC_2SH, the diffraction peaks of the intercalation compound (NC_2SH/γ-TiP) grew together along with a decrease of the host γ-TiP. However, the unreacted γ-TiP remained even after the prolonged reaction. Therefore, the intercalation compound (Fig. 1-(b)), in which the content of NC_2SH per gram of γ-TiP determined from elemental analysis was less than 0.87 mmol, was used for the adsorption of heavy metal ions. In order to clarify the role of the –SH group in the NC_2SH molecule for the adsorption of heavy metal ions, C_3N/γ-TiP was examined as well. The C_3N molecule has almost the same size as the NC_2SH molecule, but no –SH group. It is known that the different arrangements of C_3N depend on the amounts of C_3N taken up into the layered phosphate.[16,17] The degree of intercalation into the host γ-TiP would be different for NC_2SH and C_3N in the direct intercalation reaction, because NC_2SH is the hydrochloride form and a weak base. In this work, it was preferred that the degree of intercalation into γ-TiP is the same for NC_2SH and C_3N to elucidate the effect of the –SH group. Therefore, 0.01 mol of HCl was added into 0.1 dm^3 of a 0.1 mol dm^{-3} C_3N aqueous solution, and the suspension with γ-TiP was stirred at room temperature for 24 h. The result of XRD for the product, C_3N/γ-TiP, is shown in Fig. 1-(c).

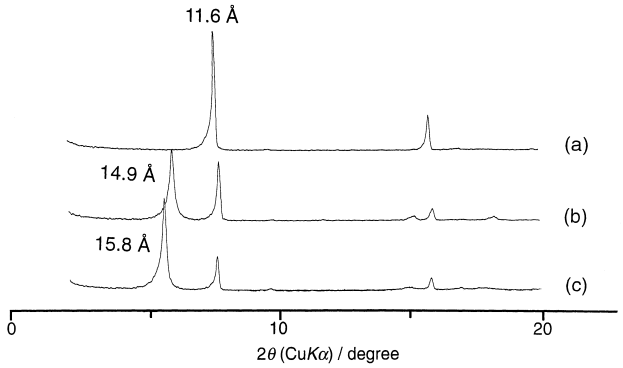

Fig. 1. X-ray diffraction patterns of (a) γ-TiP, (b) NC_2SH/γ-TiP and (c) C_3N/γ-TiP.

The characterizations of the intercalation compounds were carried out by XRD, solid-state NMR and elemental analysis. The interlayer distances, chemical shifts of the ^{31}P solid-state NMR spectra, and the amount of NC_2SH or C_3N in the intercalation compounds are summarized in Table 1. The interlayer distance of γ-TiP expanded from 11.6 to 14.9 and 15.8 Å by the intercalation of NC_2SH and C_3N molecules together with the remaining host γ-TiP (11.6 Å), respectively, as shown in Fig. 1. Taking into account the expansion of interlayer space

Table 1. Characteristics of Three Compounds

	NC_2SH/γ-TiP	C_3N/γ-TiP	γ-TiP
Chemical shifts of ^{31}P solid-state NMR (ppm)	−10.4	−10.5	−10.4
	−13.5	−13.2	
	−27.1	−26.7	
	−32.3	−32.4	−32.3
Interlayer distance (Å)	11.6	11.6	11.6
	14.9	15.8	
Arrangement	50° monolayer	51° monolayer	—
Uptake of guest compounds (mmol/g of γ-TiP)	0.87	1.1	—
Amount of guest compounds after adsorption of 100 ppm Ag^+ solution (mmol/g of γ-TiP)	0.87	0.3	—

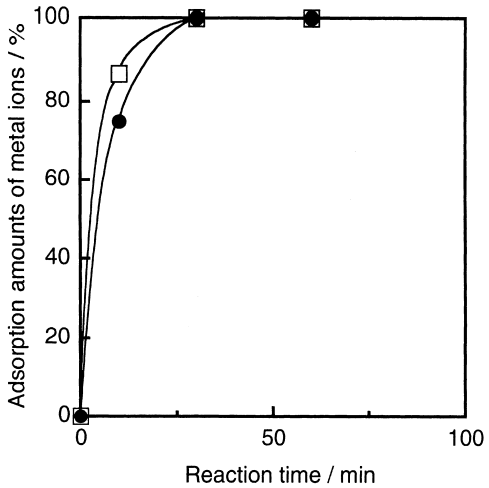

Fig. 2. Time dependence of the adsorption amounts of Ag^+ (□) and Hg^{2+} (●) ions by NC_2SH/γ-TiP.
Initial concentrations of Ag^+ and Hg^{2+}: 100 ppm, NC_2SH/γ-TiP: 0.5 g.

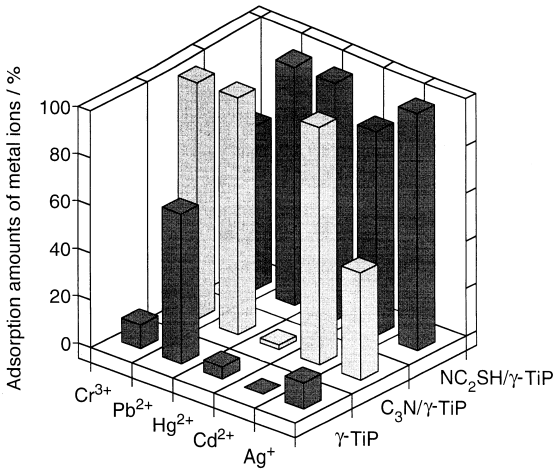

Fig. 3. Adsorption amounts of heavy metal ions by γ-TiP, C_3N/γ-TiP, and NC_2SH/γ-TiP.
Initial concentrations of heavy metal ions: 100 ppm, γ-TiP, C_3N/γ-TiP and NC_2SH/γ-TiP: 0.5 g, reaction time: 5 h.

and the size of the guest molecules, NC_2SH and C_3N molecules were arranged as a mono-molecular layer in the interlayer region, and their axial axes were inclined at about 50° to the plane of the phosphate layer.[2] On the other hand, the amounts of guest compounds taken up into γ-TiP were about one third of the theoretical exchangeable capacity (3.3 mmol g^{-1} of γ-TiP).

In order to explore the microscopic interaction between the amino group of the guest molecules and the P–OH group of the host γ-TiP, the ^{31}P MAS NMR spectra were measured (Table 1).[11,16,18,19] Two main peaks observed at −10.4 and −32.3 ppm in the NMR spectrum of γ-TiP are attributable to the $H_2PO_4^-$ and PO_4^{3-} groups in γ-TiP, respectively.[19] When NC_2SH and C_3N molecules were intercalated into γ-TiP, a peak at −10.4 ppm shifted to about −13 ppm and a peak at −32.3 ppm shifted to −27 ppm in both compounds. The high-field shift of a peak at −10.4 ppm indicates that the interaction between the amino group and the P–OH group is weak ($–NH_2 \cdots$ H–O–P) due to the low basicity,[16] and that there is no difference in the interaction between the amino group and the P–OH group for both NC_2SH/γ-TiP and C_3N/γ-TiP. Therefore, the arrangements of the NC_2SH and C_3N molecules and the extent of the interaction between the amino group and the P–OH group in the interlayer region were almost the same for both compounds.

Figure 2 shows the reaction-time dependence of the amounts of Ag^+ and Hg^{2+} ions adsorbed by NC_2SH/γ-TiP. The rate of adsorption was very fast, and heavy metal ions in aqueous solution were completely adsorbed within 30 minutes at room temperature.

Figure 3 shows the adsorption amounts of heavy metal ions by the reaction of γ-TiP, C_3N/γ-TiP and NC_2SH/γ-TiP with 100 ppm aqueous solutions of them for 5 h. γ-TiP adsorbed only Pb^{2+} with considerable amount, whereas C_3N/γ-TiP adsorbed Cr^{3+}, Pb^{2+}, Cd^{2+} and Ag^+, but showed no adsorption of Hg^{2+}. On the other hand, NC_2SH/γ-TiP could almost completely adsorb all heavy metal ions examined in the present work. It has been revealed that these three compounds have different adsorption abilities for heavy metal ions. The adsorption amounts of heavy metal ions by these compounds are plotted against the initial concentration of heavy metal ions in Fig. 4. Pb^{2+} (▽) was adsorbed significantly for any compounds. In the case of γ-TiP (Fig. 4-(A)), the heavy metal ions, except for Hg^{2+} (●), were adsorbed to some extent (about 40%) at lower initial concentration, and the adsorption amounts decreased with increasing the concentration of heavy metal ions. C_3N/γ-TiP could adsorb Cd^{2+} (▲), Pb^{2+} (▽) and Cr^{3+} (◇) completely between 10 and 100 ppm (Fig. 4-(B)). However, the adsorption amounts of Ag^+ (□) decreased with an increase of its concentration. In the case of Hg^{2+} (●), no adsorption was observed above 30 ppm. On the other hand, NC_2SH/γ-TiP could adsorb more than 70% for any heavy metal ions (Fig. 4-(C)). Upon comparing these three compounds, the adsorption ability of γ-TiP for heavy metal ions was low, because of no adsorption of heavy metal ions, except for Pb^{2+}. For C_3N/γ-TiP and NC_2SH/γ-TiP, the adsorption abilities of Cd^{2+} (▲), Pb^{2+} (▽) and Cr^{3+} (◇) were comparable, and there was no decrease in the adsorption amount, even above 100 ppm. NC_2SH/γ-TiP could completely adsorb Ag^+ (□) and Hg^{2+} (●). This fact suggests that Ag^+ and Hg^{2+} are adsorbed by strongly interacting with the –SH group. Therefore, NC_2SH/γ-TiP is efficiently applicable to remove all heavy metal ions. The ion-exchange of transition metal ions, such as Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+} and Zn^{2+}, was previously reported for the sodium form of zirconium phosphate with a reaction of 4 d at room temperature.[20] In the case of Cu^{2+}, direct ion exchange was completed at ca. 100 °C.[21] However, there are no reports on the adsorption of heavy metal ions. Compared with these previous work, the adsorption ability of NC_2SH/γ-TiP is remarkably satisfactory, even under mild conditions, namely, 30 minutes at room temperature.

Figure 5 shows the relationship between the adsorption amount of heavy metal ions and the amounts of NC_2SH taken up into γ-TiP. The adsorption amounts of heavy metal ions increased with increasing the amounts of NC_2SH taken up into γ-TiP, suggesting that the heavy metal ions interact with the

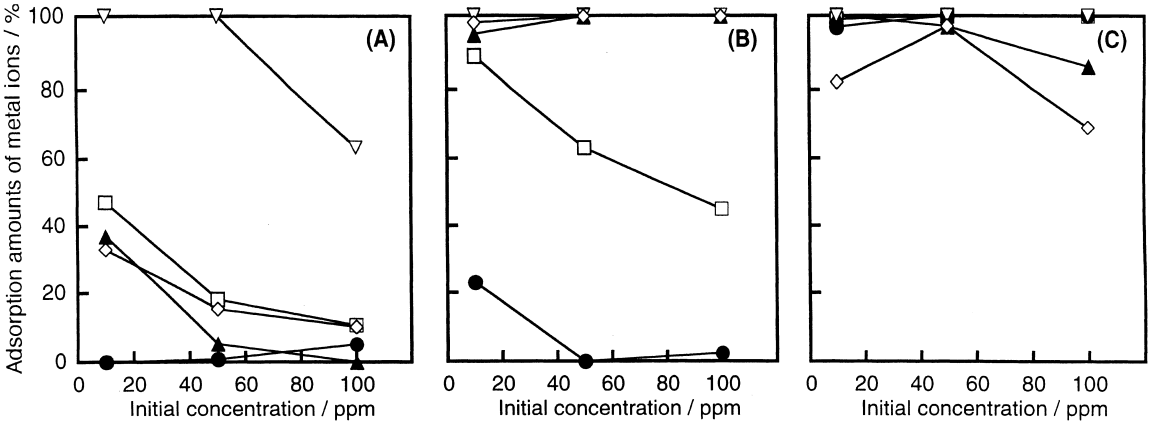

Fig. 4. Adsorption amounts of heavy metal ions by (A) γ-TiP, (B) C_3N/γ-TiP and (C) NC_2SH/γ-TiP. γ-TiP, C_3N/γ-TiP and NC_2SH/γ-TiP: 0.5 g, reaction time: 5 h. □: Ag^+, ●: Hg^{2+}, ▲: Cd^{2+}, ▽: Pb^{2+}, ◇: Cr^{3+}.

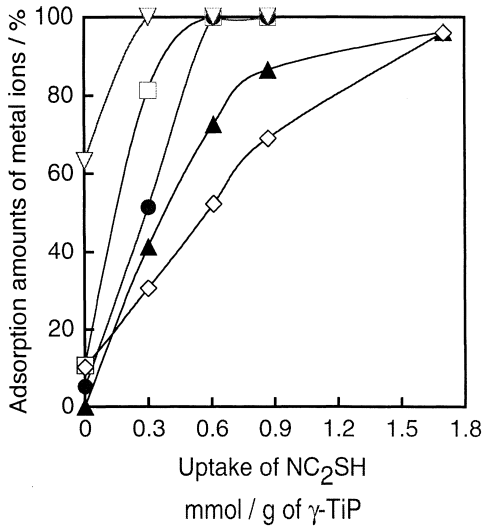

Fig. 5. Relationship between uptake of NC_2SH in NC_2SH/γ-TiP and the adsorption amount of heavy metal ions. Initial concentration: 100 ppm, NC_2SH/γ-TiP: 0.5 g, reaction time: 5 h.
□: Ag^+, ●: Hg^{2+}, ▲: Cd^{2+}, ▽: Pb^{2+}, ◇: Cr^{3+}

NC_2SH molecule in the interlayer region. The amounts of NC_2SH needed to completely remove the ions in 0.1 dm^3 of 100 ppm aqueous solution were 0.3 mmol g^{-1} of γ-TiP for Pb^{2+}, 0.6 mmol g^{-1} of γ-TiP for Ag^+ and Hg^{2+}, and 1.8 mmol g^{-1} of γ-TiP for Cd^{2+} and Cr^{3+}.

In order to clarify the adsorption mechanism of heavy metal ions, NC_2SH/γ-TiP and C_3N/γ-TiP after the adsorption of heavy metal ions were characterized by XRD and ^{13}C CP/MAS NMR. Figure 6-(A) shows XRD patterns of NC_2SH/γ-TiP after reactions with various initial concentrations of Ag^+. The diffraction peak (14.9 Å) of the intercalation compound became broad without any change of the interlayer distance upon increasing the adsorption amounts of Ag^+. This suggests that the crystallinity of the intercalation compound becomes worse through the adsorption of Ag^+ ions, although the arrangement of NC_2SH is retained in the interlayer region. This fact is also supported by the fact that NC_2SH is not released after the adsorption of Ag^+ (Table 1). On the other hand, the XRD pattern of C_3N/γ-TiP became broader and the interlayer distance decreased with increasing the adsorption amounts of Ag^+ (Fig. 6-(B)). Also, a considerable amount of C_3N was released from C_3N/γ-TiP by the adsorption of Ag^+ (Table 1). Previously, A. Menéndez et. al. have reported that C_3N/γ-TiP forms phases with two different interlayer distances (16 and 18.4 Å), depending on the amount of C_3N taken up into γ-TiP.[17] Below 2.5 mmol of C_3N taken up into γ-TiP, C_3N/γ-TiP shows a phase with an interlayer distance of 16 Å. Therefore, the decrease in the interlayer distance to 14.6 Å of C_3N/γ-TiP after the adsorption of Ag^+ suggests that C_3N molecules arrange irregularly together with Ag^+ in the interlayer region.

^{13}C CP/MAS NMR is a very effective tool to investigate the interaction between heavy metal ions and guest molecules microscopically.[22,23] Figure 7 shows the ^{13}C CP/MAS NMR spectra of intercalation compounds (NC_2SH/γ-TiP and C_3N/γ-TiP) before and after the adsorption of Ag^+, respectively. Two peaks at 37.5 and 21.9 ppm in NC_2SH/γ-TiP (Fig. 7-(A)-(a)) are assigned to carbon bonded to a nitrogen atom (C_α) and a sulfur atom (C_β), respectively. The peak at 21.9 ppm disappeared after the adsorption of Ag^+. It is known that NMR signals broaden or shift because of the existence of neighboring metal ions, especially paramagnetic ions.[24] Therefore, this disappearance is probably due to the coordination of Ag^+ ions with the –SH group of the NC_2SH molecule in the interlayer region. For the ^{13}C CP/MAS NMR spectra of C_3N/γ-TiP (Fig. 7-(B)-(a)), three peaks at 42.0, 21.3 and 11.9 ppm are assigned to the C_α, C_β and C_γ of C_3N molecules, respectively. These peaks do not shift, although the peak intensity decreases owing to a decrease in the amounts of C_3N taken up into γ-TiP, showing that Ag^+ does not interact with the C_3N molecule directly. That is, it has been found that the heavy metal ions are taken up either by exchanges with C_3N molecules or by rearrangements of the C_3N molecules in the interlayer region. These results were the same for the adsorption of other heavy metal ions. Consequently, the adsorption mechanisms of heavy metal ions were different for NC_2SH/γ-TiP and C_3N/γ-TiP.

In conclusion, 2-aminoethanethiol-intercalated γ-TiP could remove toxic heavy metal ions in an aqueous solution by interactions with the –SH group in the interlayer region. The ad-

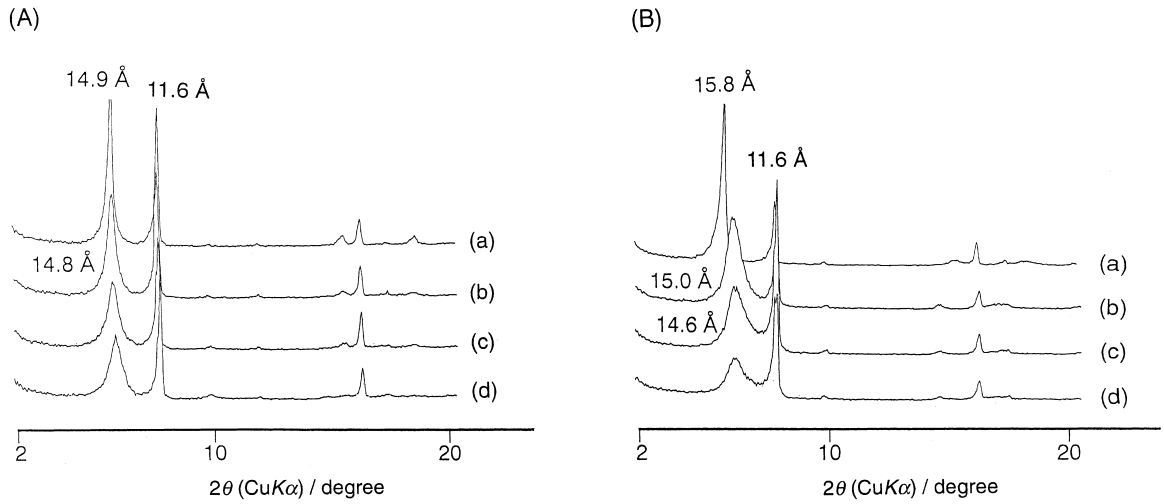

Fig. 6. X-ray diffraction patterns of (A) NC_2SH/γ-TiP and (B) C_3N/γ-TiP after the reaction with various initial concentration of Ag^+. Initial concentration: (a) 0 ppm, (b) 10 ppm, (c) 50 ppm, (d) 100 ppm
NC_2SH/γ-TiP and C_3N/γ-TiP: 0.5 g, reaction time: 5 h.

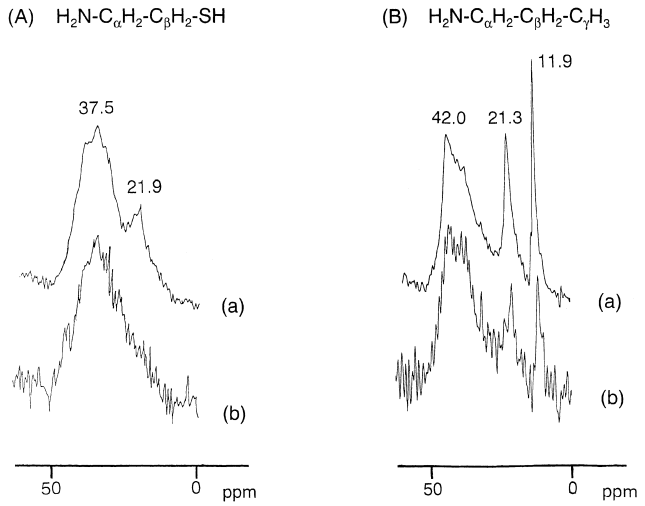

Fig. 7. ^{13}C CP/MAS NMR spectra of (A) NC_2SH/γ-TiP and (B) C_3N/γ-TiP before and after the adsorption of Ag^+. (a) before the adsorption, (b) after the adsorption.
Initial concentration: 100 ppm, NC_2SH/γ-TiP and C_3N/γ-TiP: 0.5 g, reaction time: 5 h.

sorption amounts of Ag^+ and Hg^{2+} reached to 100%, even for any concentration of the aqueous solution. The other heavy metal ions could also adsorb more than 70% from the aqueous solution. Furthermore, the adsorption could be performed under mild conditions, that is, within 30 minutes and at room temperature.

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