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Preparation and Chemical Properties of a Novel Layered Cerium(IV) Phosphate

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A synthetic method of a novel cerium(IV) bis(hydrogenphosphate) dihydrate, $Ce(HPO_4)_2\cdot 2H_2O$, hereafter referred to as $CeP\cdot 2H_2O$, has been established by the hydrothermal reaction of cerium(IV) oxide with phosphoric acid in an autoclave. The preparation of $CeP\cdot 2H_2O$ was significantly affected by the reaction conditions: the mixing ratio (P_2O_5/CeO_2) of CeO_2 and phosphoric acid, heating temperature and time, and water vapor pressure. The optimum condition for the preparation of $CeP\cdot 2H_2O$ was the mixing ratio of 1.5—2.0, heating temperature 175—200 °C, heating time 5 h, and water vapor pressure 5.0—7.0 atm.

The results of X-ray powder diffraction, fluorescent X-ray analysis, differential thermal analysis and thermogravimetry (DTA-TG), IR spectrum, and phase transition showed that $CeP\cdot 2H_2O$ is a novel crystalline layered cerium(IV) phosphate having a interlayer distance $d = 18.0$ Å, longer than any layered phosphates (zirconium(IV), titanium(IV), and tin(IV) phosphates) so far reported.

The reversible phase transition of $CeP\cdot 2H_2O$ occurred as follows, when exposed to various relative humidities:

$$\begin{tikzcd} Ce(HPO_4)_2\cdot 2H_2O \arrow[r, shift left, "33\%"] \arrow[d, shift left, "P_2O_5"] & Ce(HPO_4)_2\cdot 1.33H_2O \arrow[l, shift left, "97\%"] \arrow[r, shift left, "33\%"] & Ce(HPO_4)_2\cdot 0.33H_2O \arrow[l, shift left, "75\%"] \\ Ce(HPO_4)_2\cdot 0.33H_2O \arrow[u, shift left, "97\%"] & & \end{tikzcd}$$

$CeP\cdot 2H_2O$ dissolved slightly in distilled water and hydrochloric acid, and much more in aqueous sodium hydroxide and aqueous ammonia. $CeP\cdot 2H_2O$ effectively adsorbed ammonia in an aqueous solution and ammonia gas.

Crystalline acid phosphates of tetravalent metals having a layered structure, $M^{IV}(HPO_4)_2\cdot nH_2O$ (M^{IV}=Zr and Ti; n=1 and 2), are known as a typical inorganic ion exchanger.[1,2] Layered zirconium and titanium phosphates can readily intercalate polar organic compounds such as amines,[3—6] amino acids,[7] and alcohols.[3,8—10] Thus, they are attracting interest for potential applications as a heat-resistant ion exchanger, catalyst, new functional material, and the intercalating agent for significant organic compounds.[11—13]

Clearfield and Smith,[14] based on the X-ray crystal structure analysis, described the structure of α-zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$ (α-ZrP), as a layered one; each layer consists of zirconium atoms lying nearly in a plane and bridged through phosphate groups which alternate above and below zirconium atom planes. Three oxygens of each phosphate are bound to three different zirconium atoms. The fourth oxygen bears a hydrogen atom and points toward an adjacent plane. Also, Clayden[15] demonstrated in 1987 that γ-zirconium phosphates (γ-ZrP) has two different phosphate groups ($H_2PO_4^-$ and PO_4^{3-}) in the molecule, on the basis of ^{31}P MAS NMR. Thus γ-zirconium phosphate as a compound should not be expressed in chemical formula as $Zr(HPO_4)\cdot 2H_2O$, but as $Zr(H_2PO_4)(PO_4)\cdot 2H_2O$ (γ-ZrP).

On the other hand, many publications[16—25] have reported about cerium phosphates which varied widely in accordance with the preparation methods and the reaction conditions. Cerium orthophosphates $CePO_4$ and $CePO_4\cdot 0.5H_2O$, metaphosphate $Ce(PO_3)_3$ and ultraphosphate CeP_5O_{14}, are known as trivalent cerium phosphates,[16—19] and cerium diphoshate CeP_2O_7, metaphosphate $Ce(PO_3)_4$, and hydrogenphosphates $Ce(HPO_4)_2\cdot nH_2O$ (n=0, 0.33, 1, 1.33, and 3) as tetravalent cerium phosphates.[20—25] Many kinds of crystalline acid cerium(IV) phosphates, $Ce(HPO_4)_2\cdot nH_2O$, have been formed by the reaction of $Ce(SO_4)_2$ and H_3PO_4, and their structures varied according to the reaction conditions: PO_4/Ce ratio, phosphoric acid concentration, reaction temperature, digestion time, and humidity.[21—23,25]

We have developed a simple technique for the preparation of crystalline layered zirconium(IV) and titanium(IV) phosphates by the direct reaction of metal oxide or hydroxide with phosphoric acid in an autoclave.[26)] By employing this simple hydrothermal reaction method for the synthesis of cerium phosphate, we could obtain a novel layered cerium(IV) phosphate having a layer distance $d=18.0$ Å, longer than any other layered phosphate.[1,3)] This paper will describe the preparation method for a novel layered cerium phosphate and chemical properties (thermal stability, phase transition in various relative humidity environments, solubility, and adsorption of ammonia).

Experimental

Preparation of Crystalline Layered Cerium(IV) Phosphate. Crystalline layered cerium(IV) bis(hydrogenphosphate) dihydrate, $Ce(HPO)_4)_2\cdot 2H_2O$ ($CeP\cdot 2H_2O$), was prepared by the following method. Cerium(IV) oxide CeO_2 and 85% phosphoric acid were mixed uniformly at molar ratios (P_2O_5/CeO_2) of 0.5—2.0. Then a prescribed amount of the mixture was placed in a test tube (25 cm^3) and heated in an autoclave (300 cm^3) at 100—250 °C for 1—5 h. The water vapor pressure in the autoclave was controlled to the dictated levels either with the amount (5—50 g) of the mixture or by adding water in the autoclave before heating. The cerium phosphate obtained was completely washed with distilled water and stored in a vacuum desiccator over saturated potassium dihydrogenphosphate solution (relative humidity ca. 97%).

Analytical Procedures. X-ray diffraction patterns were measured with a Rigaku Geigerflex 2011 using Ni-filtered Cu $K\alpha$ radiation to monitor cerium phosphates and to determine the interlayer spacings. A Rigaku Denki Differential Thermogravimetric Analyzer, TG8110, was used for the DTA and TG measurements with a platinum–rhodium pan in an air flow. Analyses of Ce and P in cerium phosphate were performed on a Rigaku X-ray fluorescence spectrometer RIX 2000.

Phase Transition of $CeP\cdot 2H_2O$ in Various Relative Humidity Environments. The phase transition of $CeP\cdot 2H_2O$ at various relative humidities was investigated by leaving the sample of cerium phosphate in vacuum desiccators over the saturated KH_2PO_4 (relative humidity ca. 97%), NaCl (75%) and $MgCl_2$ solutions (33%), and over P_2O_5 (0%) at room temperature. The phase transition was monitored by X-ray diffraction until equilibrium at intervals of one day.

Measurement of Solubility. A part of $CeP\cdot 2H_2O$ was dissolved into the distilled water, 0.1 mol dm^{-3} hydrochloric acid or sodium hydroxide solution by stirring in a water bath controlled at 30±0.1 °C. A suspension was taken at intervals and centrifuged. Phosphorus concentration in supernatant liquid was determined by spectrophotometry of phosphorus–molybdenium blue complex, and the amounts (g dm^{-3}) of $CeP\cdot 2H_2O$ dissolved in the corresponding solutions were determined.

Adsorption of Ammonia in an Aqueous Solution. $CeP\cdot 2H_2O$ (1.00 g) was added to 200 cm^3 of 0.1 mol dm^{-3} aqueous ammonia and well shaken in an incubator of 30 °C. A suspension was taken at intervals and centrifuged, and 10 cm^3 of the supernatant was evaluated for ammonia adsorbed into $CeP\cdot 2H_2O$ by the titration with 0.05 mol dm^{-3} hydrochloric acid. Solubility of $CeP\cdot 2H_2O$ in 0.1 mol dm^{-3} aqueous ammonia was also determined by the method described above.

Adsorption of Ammonia Gas. $CeP\cdot 2H_2O$ (0.05 g) was placed in a gas bag (3000 cm^3) of polyethylene, which was then filled with ammonia gas (1040 ppm). The concentration of ammonia gas was determined with a Kitagawa gas detector. A similar experiment was carried out with an activated characoal-based commercial deodorants (0.5 g) for comparison.

Results and Discussion

Structure of a Novel Layered Cerium Phosphate. Unknown cerium phosphate and cerium(IV) pyrophosphate, CeP_2O_7, were obtained by the hydrothermal reaction of CeO_2 and phosphoric acid. Figure 1 shows the X-ray diffraction pattern of the unknown cerium phosphate formed by the reaction of CeO_2 and phosphoric acid at a molar ratio of 1.5, 200 °C for 5 h, and water vapor pressure 7 atm.

Ce and P contents in the unknown cerium phosphate were

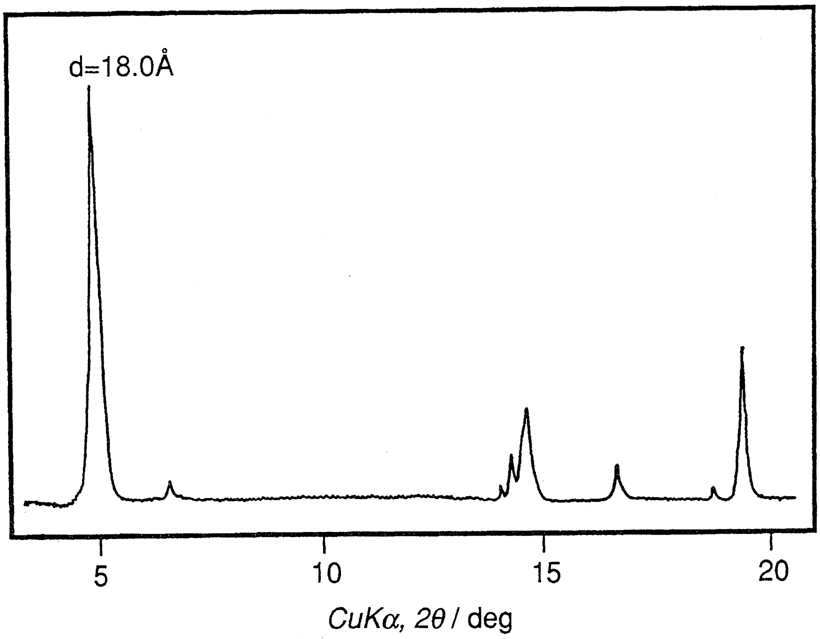

Fig. 1. X-Ray diffraction pattern of the unknown cerium phosphate.

determined by fluorescent X-ray analysis, and resulted in a P to Ce ratio of 2.0.

Figure 2 shows the DTA-TG curves of the unknown compound, showing three remarkable endothermic peaks with 9.6% weight loss due to the dehydration of water of crystallization between 60 and 100 °C. There is another endothermic peak at 385 °C, with 4.9% loss in weight. The weight loss is attributed to the dehydration of structural water. Thus, the unknown cerium phosphate was found to contain about 14.5% water in total.

From the results of fluorescent X-ray analysis and DTA-TG, the unknown cerium phosphate can be formulated as $CeO_2 \cdot P_2O_5 \cdot 3H_2O$ in the chemical composition. Two water molecules dehydrated up to 150 °C are considered to be waters of crystallization. The remaining one water molecule should be a structural water, since the unknown cerium phosphate was condensed to cerium(IV) diphosphate, CeP_2O_7, at 385 °C. The total observed and calculated weight losses, 14.5 and 14.4%, are in good agreement.

IR Spectrum of Unknown Cerium Phosphate. The IR spectrum of unknown cerium phosphate is shown in Fig. 3. As can be seen, characteristic absorptions of hydrogenphosphate group[27,28] appeared at about 2360, 1240, and 1050—850 cm^{-1}, and remarkable absorption of the PO_4^{3-} group[28] between 1100 and 1000 cm^{-1}. On the other hand, there are no absorptions at 950—930 and 750—720 cm^{-1}, indicating the absence of any P–O–P groups[28] in the unknown compound. Therefore, the unknown cerium phosphate is cerium hydrogenphosphate with the P–OH group in the structure. This compound contains water of hydration, as shown by the strong absorption bands at the vicinity of 3300 and 1600 cm^{-1}.

The IR spectrum of the unknown cerium phosphate was consistent with that of layered cerium(IV) bis(hydrogenphosphate) $Ce(HPO_4)_2 \cdot 1.33H_2O$ ($CeP \cdot 1.33H_2O$) formed by the hydrothermal synthesis, except for the absorption band at 3000—3500 cm^{-1} by hydration water of $CeP \cdot 1.33H_2O$. This result indicates that the unknown cerium phosphate in a layered phosphate such as $CeP \cdot 1.33H_2O$.

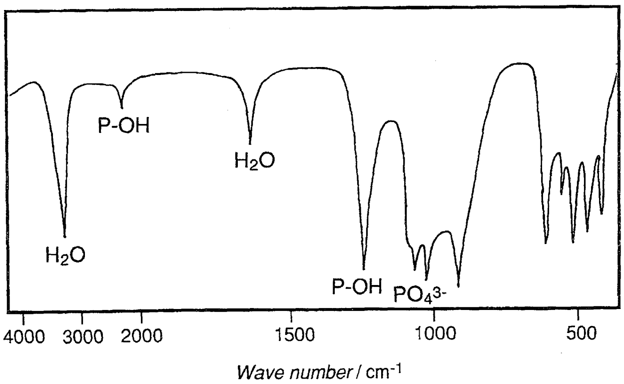

Fig. 3. IR spectrum of the unknown cerium phosphate.

Phase Transition of Unknown Cerium Phosphate in Various Relative Humidity Environments. Figure 4 summarizes the phase transition of the unknown phosphate, $CeO_2 \cdot P_2O_5 \cdot 3H_2O$, in various relative humidity environments. When kept in a relative humidity of 33% (in a desiccator with saturated $MgCl_2$ solution), it gradually lost a part of the water of hydration and transformed to the layered cerium(IV) bis(hydrogenphosphate), $Ce(HPO_4)_2 \cdot 1.33H_2O$ (interlayer distance $d=$ 16.1 Å, $CeP \cdot 1.33H_2O$), and dehydrated further to $Ce(HPO_4)_2 \cdot 0.33H_2O$ ($d=14.5$ Å, $CeP \cdot 0.33H_2O$) already reported by Alberti et al.[23] In a relative humidity of 75% (saturated NaCl solution), on the other hand, the unknown compound did not change. When left in the desiccator with P_2O_5, this unknown compound changed completely to Ce-

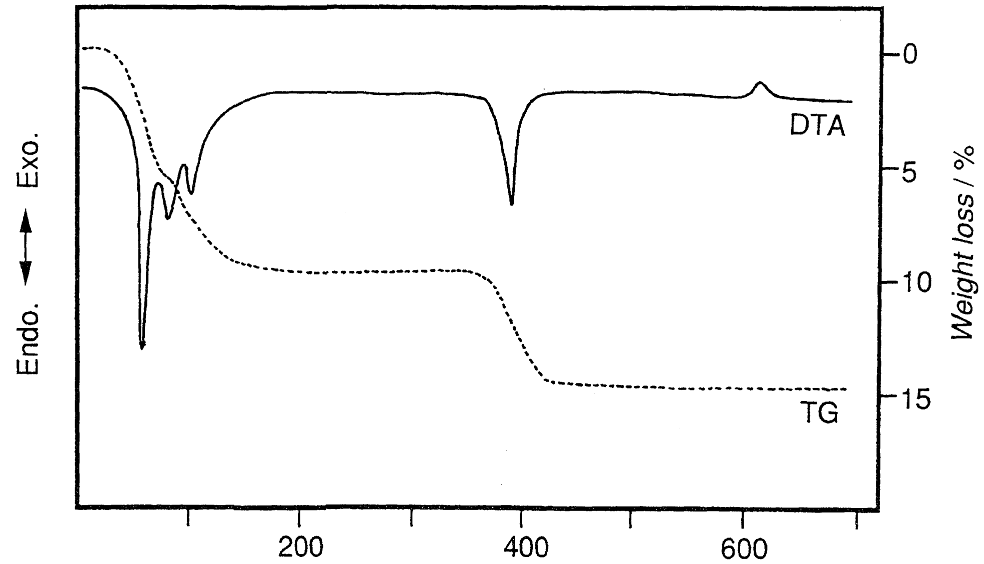

Fig. 2. DTA and TG curves of the unknown cerium phosphate.

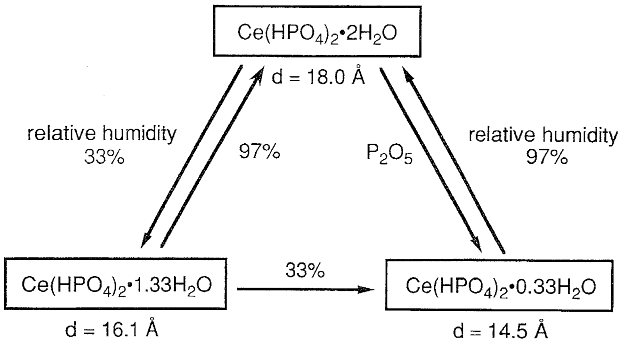

Fig. 4. Phase transition of the unknown cerium phosphate under various relative humidities.

$(HPO_4)_2$·$0.33H_2O$ which, when kept in an relative humidity of 97% (saturated KH_2PO_4 solution), turned back to the initial unknown compound.

From the results of fluorescent X-ray analysis, DTA-TG, IR spectrum, and phase transition in different relative humidity environments, the chemical formula for the unknown cerium phosphate can be proposed to be $Ce(HPO_4)_2$·$2H_2O$, which is a novel layered phosphate having a much longer layer distance (d=18.0 Å).

While Alberti et al.$^{21—24)}$ reported some layered cerium(IV) bis(hydrogen phosphate), $Ce(HPO_4)_2$·nH_2O (n=0, 0.33, 1, 1.33, and 3) in the reaction of $Ce(SO_4)_2$ and phosphoric acid, these phosphates are not the same as the $Ce(HPO_4)_2$·$2H_2O$ obtained in the present study.

Relation between the Formation of CeP·2H$_2$O and Heating Temperature. Figure 5 shows the relation between the yields of CeP·$2H_2O$ and heating temperature in the hydrothermal reaction of CeO_2 and H_3PO_4. The preparation conditions were the mixing ratio (P_2O_5/CeO_2) of 1.5 and the heating time 5 h. CeP·$2H_2O$ was readily obtained at 175—200 °C, and not at all over 225 °C, where CeP_2O_7 prevailed. Although CeP·$2H_2O$ was also formed below 150 °C, considerable amounts of the starting material (CeO_2) remained. Thus, the preparation of CeP·$2H_2O$ was carried out at the temperatures between 175 and 200 °C in the following synthetic experiments.

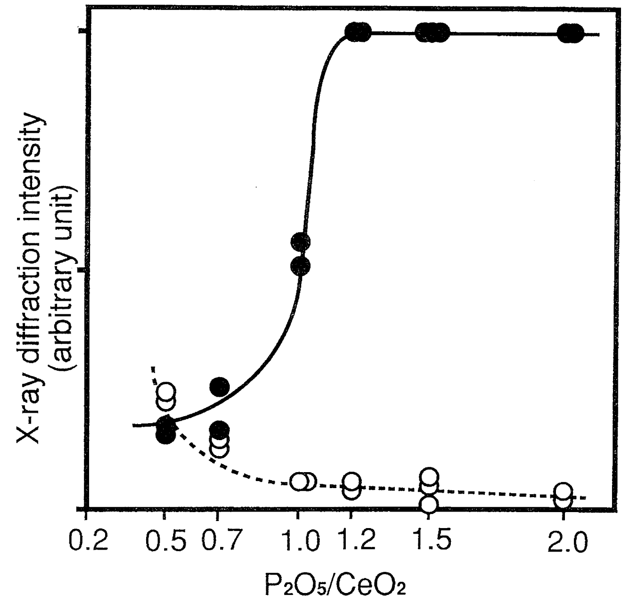

Fig. 6. Relation between the yields of $Ce(HPO_4)_2$·$2H_2O$ and the mixing ratio (P_2O_5/CeO_2). Heating temperature: 175 °C, heating time: 5 h, ●: $Ce(HPO_4)_2$·$2H_2O$, ○: CeO_2.

At 175—200 °C, CeP·$2H_2O$ was formed in the heating time of an hour, but 3 h or more heating were necessary for the high degree of crystallinity of the product and for reproducibility in yield.

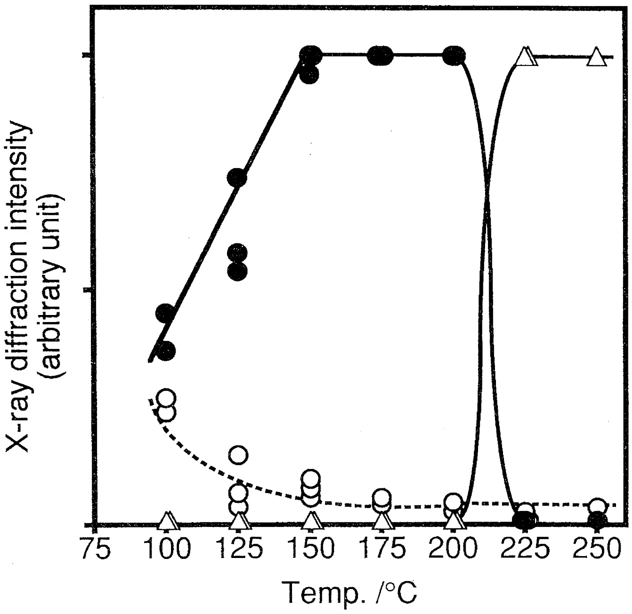

Fig. 5. Relation between the yields of $Ce(HPO_4)_2$·$2H_2O$ and heating temperature. P_2O_5/CeO_2: 1.5, heating time: 5 h, ●: $Ce(HPO_4)_2$·$2H_2O$, △: CeP_2O_7, ○: CeO_2.

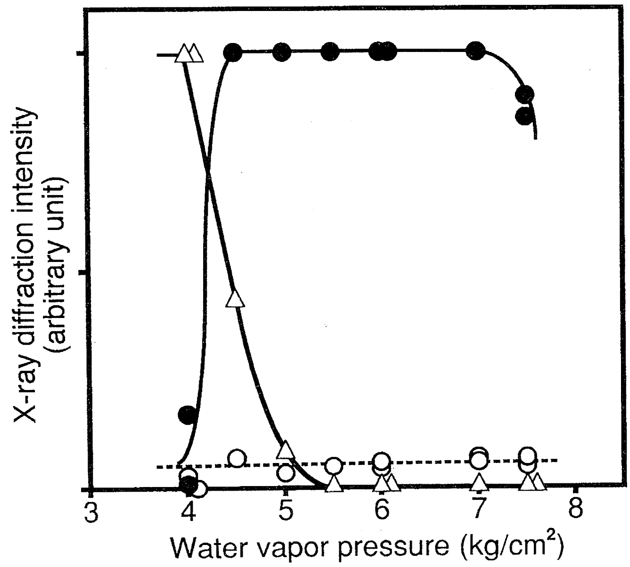

Fig. 7. Relation between the yields of $Ce(HPO_4)_2$·$2H_2O$ and water vapor pressure. P_2O_5/CeO_2: 1.5, heating temp: 175 °C, heating time: 5 h, ●: $Ce(HPO_4)_2$·$2H_2O$, △: CeP_2O_7, ○: CeO_2.

Relation between the Yield of CeP·2H$_2$O and Mixing

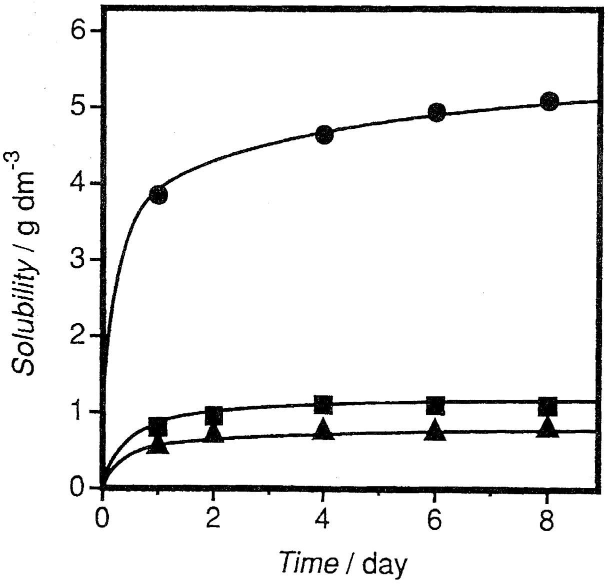

Fig. 8. Solubility of $Ce(HPO_4)_2\cdot 2H_2O$ in H_2O, HCl, and NaOH. ■: H_2O, ▲: 0.1 mol dm^{-3} HCl, ●: 0.1 mol dm^{-3} NaOH.

Ratio. Figure 6 shows the relationship between the yields of $CeP\cdot 2H_2O$ and the mixing ratio (P_2O_5/CeO_2) at 175 °C for 5 h. The yield of $CeP\cdot 2H_2O$ gradually increased with the molar ratio (P_2O_5/CeO_2), and was constant at a P_2O_5/CeO_2 of over 1.5. However, at a mixing ratio of 1.2 and more the product was hydroscopic due to the excess phosphoric acid.

Relation between the Yield of $CeP\cdot 2H_2O$ and Water Vapor Pressure. Figure 7 shows the relation between the yields of $CeP\cdot 2H_2O$ and water vapor pressure at a mixing ratio of 1.5 and 175 °C. The water vapor pressure was controlled by the amount (5—50 g) of the mixture of CeO_2 and H_3PO_4, and by adding water in advance in the autoclave. As can be seen, the yields of $CeP\cdot 2H_2O$ increased remarkably at the water vapor pressures of around 4.5 atm and more, and attained at a maximum between 5.0 and 7.0 atm. However, it decreased gradually at more than 7.5 atm. Below 4.0 atm, $CeP\cdot 2H_2O$ was not formed but CeP_2O_7 alone. Thus, it can be pointed out that the preparation of $CeP\cdot 2H_2O$ was significantly affected by the water vapor pressure in the autoclave, and $CeP\cdot 2H_2O$ was predominantly formed at water vapor pressures of 5.0—7.0 atm.

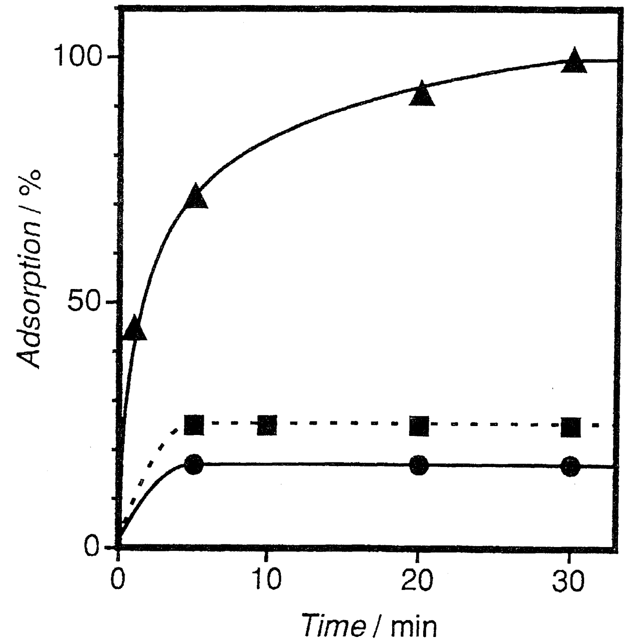

Fig. 10. Adsorption of ammonia gas by $Ce(HPO_4)_2\cdot 2H_2O$ and commercial adsorbents. NH_3: 1040 ppm, gas bag: 3000 cm^3, ▲: $Ce(HPO_4)_2\cdot 2H_2O$ (0.05 g), ■: commercial adsorbent A (0.5 g), ●: commercial adsorbent B (0.5 g).

Solubility of $CeP\cdot 2H_2O$. Figure 8 shows the solubility of $CeP\cdot 2H_2O$ in distilled water, and 0.1 mol dm^{-3} hydrochloric

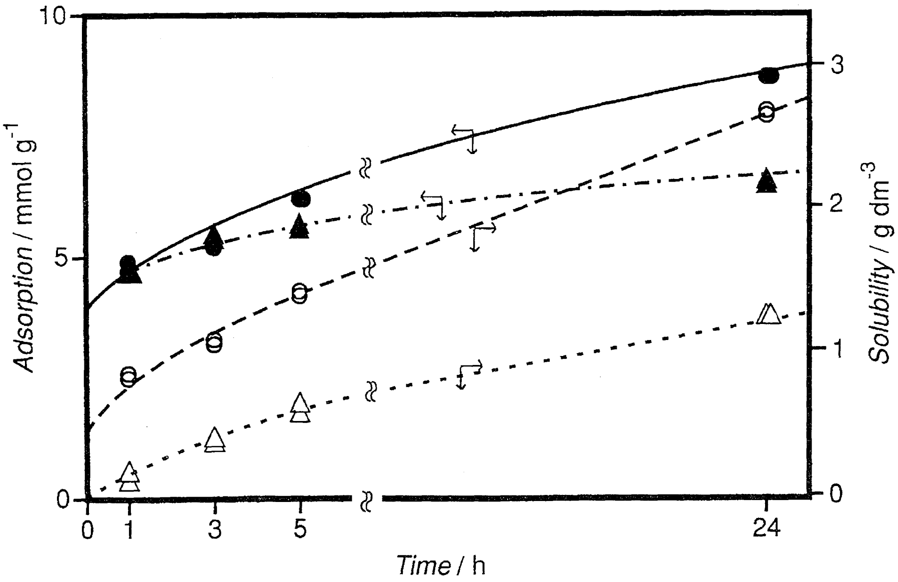

Fig. 9. Adsorption of ammonia in an aqueous solution by $Ce(HPO_4)_2\cdot 2H_2O$ and $Ce(HPO_4)_2\cdot 1.33H_2O$ and their solubilities. ●, ○: $Ce(HPO_4)_2\cdot 2H_2O$, ▲, △: $Ce(HPO_4)_2\cdot 1.33H_2O$.

acid and sodium hydroxide solution. CeP·2H_2O dissolved slightly in water and hydrochloric acid, and much more in sodium hydroxide solution. It is also known that the layered zirconium and titanium phosphates tend to undergo hydrolysis in alkaline solutions[26] and increase in solubility as a result of destruction of the crystal structure. CeP·2H_2O was observed to be rather unstable in alkaline solutions.

Adsorption of Ammonia in an Aqueous Solution. Figure 9 shows the adsorption of ammonia in an aqueous solution by CeP·2H_2O. The adsorption into CeP·1.33H_2O is also shown for comparison. CeP·2H_2O adsorbed ammonia as much as about 4.9 mmol g^{-1} by an hour of contact with an aqueous solution of ammonia. The amount of ammonia adsorbed into CeP·2H_2O increased gradually with the stirring time, and attained to about 8.8 mmol g^{-1} at 24 h. This exceeded by far the theoretical adsorption value (amounts of proton, 5.43 mmol g^{-1}) of CeP·2H_2O because of the dissolution of CeP·2H_2O in aqueous ammonia. On the other hand, CeP·2H_2O dissolved more in aqueous ammonia than CeP·1.33H_2O.

Adsorption of Ammonia Gas Due to CeP·2H_2O. The adsorption of ammonia gas due to CeP·2H_2O is shown in Fig. 10. CeP·2H_2O completely adsorbed about 1000 ppm ammonia gas within 30 min. The maximal acid strength of CeP·2H_2O, measured by Benesi's method,[29] was $pK_a = -3.3$. Thus, it is noted that the adsorption of ammonia to CeP·2H_2O is the chemisorption based on the acid–base reaction. Although CeP·2H_2O adsorbed ammonia gas somewhat less quickly than the layered zirconium and titanium phosphates formed by the same method, CeP·2H_2O exhibited a far better deodorant effect than activated characoal-based commercial adsorbents.

Conclusion

Unknown crystalline cerium(IV) phosphate was obtained by the hydrothermal reaction of CeO_2 and phosphoric acid. The unknown phosphate was recognized as a novel cerium(IV) bis(hydrogenphosphate) dihydrate, $Ce(HPO_4)_2 \cdot 2H_2O$, by fluorescent X-ray analysis, DTA-TG, IR spectroscopy, and phase transition study in various relative humidity environments. CeP·2H_2O has a layered structure with a interlayer distance d=18.0 Å, longest of any known layered phosphates.

CeP·2H_2O was readily formed by the hydrothermal reaction of CeO_2 and H_3PO_4 in an autoclave at the mixing ratio (P_2O_5/CeO_2) of 1.5—2.0, heating temperature 175—200 °C for 5 h, and water vapor pressure 5.0—7.0 atm. When CeP·2H_2O was kept in a lower relative humidity environment, a part of the water of hydration was dehydrated to give $Ce(HPO_4)_2 \cdot 1.33H_2O$ (d=16.1 Å) and $Ce(HPO_4)_2 \cdot 0.33H_2O$ (d=14.5 Å). CeP·1.33H_2O and CeP·0.33H_2O rehydrated in higher humidity environments and turned back to the starting CeP·2H_2O.

CeP·2H_2O exhibited a small solubility (0.08—0.11 g/100 cm^3) in water and hydrochloric acid, while it dissolved somewhat in sodium hydroxide and aqueous ammonia. Ammonia in an aqueous solution and ammonia gas were quickly adsorbed into CeP·2H_2O.

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