Additional effects of urea on formation of various cerium phosphates

HIROAKI ONODA*, ATSUSHI TAKENAKA** and HIROYUKI NARIAI***

Abstract : Urea ($CO(NH_2)_2$) was added in the system of phosphoric acid (H_3PO_4) and cerium carbonate ($Ce_2(CO_3)_3 \cdot 8H_2O$), and the system of phosphoric acid and cerium oxide (CeO_2). The thermal behaviors of these dried mixtures were estimated by differential thermal analyses, X-ray diffraction, and Fourier - transform infrared spectroscopy. Furthermore, specific surface area of phosphates was calculated by BET method using nitrogen adsorption. In P/Ce = 1/1, the addition of urea made specific surface area of cerium orthophosphate larger. The formation of tetra-valent cerium phosphates was suppressed by the addition of urea.

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Key words : Cerium phosphate, Thermal synthesis, Urea addition

Introduction

A large part of phosphates has some characteristics; hydrophilic property, volatility at high temperature, corrosiveness, low melting point, relationship to organism, and so on. Phosphates have been used for ceramic materials, catalyst, fluorescent materials, dielectric substance, metal surface treatment, fertilizer, detergent, food additives, fuel cells, etc.[1-4]. Because rare earth phosphates have different properties of a large part of phosphates, for example, be stable for dehydration, have high melting point, etc., rare earth phosphates are interesting materials for many use[5,6].

Phosphates transform to various other phosphates with hydrolysis and dehydration reactions by heating[7-11]. The formation and structure of phosphates depend on heating temperature, rate, and time, the cooling rate of melts, the atmosphere, kinds of cations in phosphate, and the ratio of phosphorus / cation. Thermal products were severely depended on the ratio of phosphorus / cation. The ratio of phosphorus / cation varied in orthophosphate and various condensed phosphates. There are orthophosphate (RPO_4), polyphosphate ($R(PO_3)_3$), ultraphosphate (RP_5O_{14}), and so on in the group of rare earth phosphates.

Monazite and Xenotime-type rare earth orthophosphates anhydrous (RPO_4) are the main component of rare earth elements ores. Rhabdophane-type orthophosphate hydrate ($RPO_4 \cdot nH_2O$) has the specific structure with vacancy in which water can move[12]. Polyphosphate ($R(PO_3)_3$) has chain structure in which tetrahedral PO_4 groups are linked together by oxygen bridges[13]. Ultraphosphate has the network structure that consists the anion represented by $P_5O_{14}^{3-}$ [14,15]. A large part of ultraphosphate is not stable for hydrolysis reaction. However, rare earth ultraphosphate is stable. In cerium phosphates, there are tetravalent cerium salts, CeP_2O_7, $Ce(PO_3)_4$, etc.

The formation of phosphates is much influenced from various thermal conditions. By changing raw materials, new functional substances have been synthesized, and higher yields of products and sintering effect at lower temperature can be expected. The additional effects of organic nitrogen compounds on synthesis of various phosphates were reported. Urea, biuret, cyanuric acid, and melamine were added on synthesis of sodium *cyclo*-

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triphosphate from sodium dihydrogenphosphate[16]. The addition of urea and biuret brought the high yield of sodium *cyclo*-triphosphate. The addition of urea into lithium phosphate made to change the thermal product from *cyclo*-hexaphosphate to *cyclo*-triphosphate[17]. A novel *cyclo*-octaphosphate was formed in the mixture of copper (+II) oxide - ammonium dihydrogenphosphate - urea[18]. The addition of urea supported the formation of *cyclo*-octaphosphate in the mixture of lead (+II) oxide - ammonium dihydrogenphosphate - urea[19]. On synthesis of Rhabdophane-type neodymium and cerium orthophosphates, the influences by the addition of urea or biuret were also investigated[20]. The addition of urea or biuret greatly had the influence on synthesis and specific surface area of Rhabdophane-type neodymium and cerium phosphates. Furthermore, the addition of urea, biuret, and cyanuric acid was roughly studied on formation of Monazite-type neodymium orthophosphate, polyphosphate, and ultraphosphate[21,22]. The addition of urea promoted the dehydration - condensation reaction of phosphates.

The addition of urea has worthwhile for syntheses of target phosphates. For example, neodymium ultraphosphate used as optical material is synthesized in the condition under a smaller amount of phosphorus than usual method, and phosphates with large specific surface area are obtained. In this work, the changes of thermal products and their specific surface areas were discussed in the formation systems of various cerium phosphates, systematically.

Experimental

Urea ($CO(NH_2)_2$) was mixed with cerium carbonate ($Ce_2(CO_3)_3 \cdot 8H_2O$), and then phosphoric acid (H_3PO_4) was added to the mixture, in the molecular ratio of P/Ce= 1-5 and that of P/urea = 1/0 and 1/1. All chemicals were of guaranteed reagent from Wako Chemicals Industries Ltd. (Osaka, Japan) without further purification. These mixtures were dried at 100 °C. These mixtures were analyzed by differential thermal analyses (DTA), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR), and then their thermal products heated at several temperatures for 1 hour were also analyzed by XRD and FT-IR. DTA curves were measured at 10 °C/min with a Shimadzu DTA50. X-ray diffraction patterns were recorded on a Rigaku Denki RINT2000M X-Ray diffractometer using monochromated Cu - K alpha radiation. The IR spectra were recorded on a Shimadzu FT-IR spectrometer FT-IR8600 with a KBr disk method. Furthermore, specific surface area of phosphates was estimated by BET method using adsorbed nitrogen gas with Belsorp mini from BEL JAPAN, INC.

For comparison about the influence of starting materials, thermal products prepared from phosphoric acid, cerium oxide (CeO_2), and urea heated at 700 °C for 1 hour were also estimated.

Results and discussion

P/Ce = 1

Figure 1 shows DTA curves of samples prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$, H_3PO_4, and $CO(NH_2)_2$ in P/Ce/urea = 1/1/0 and 1/1/1. Sample prepared in P/Ce/urea = 1/1/0 had two endothermic peaks at 70 and 260 °C in DTA curve (Figure 1 (a)). On the other hand, DTA curve of sample prepared in P/Ce/urea = 1/1/1 had two endothermic peaks at 90 and 185 °C and an exothermic peak at 315 °C (Figure 1 (b)).

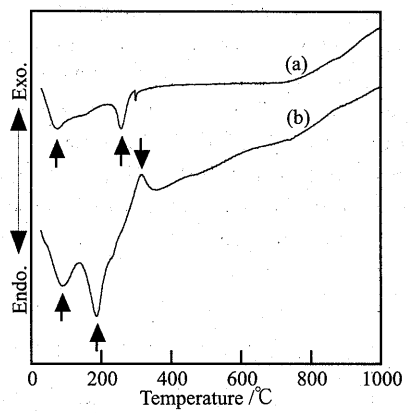

Fig. 1 DTA curves of samples prepared in several P/Ce/urea ratios, (a) 1/1/0 and (b) 1/1/1.

Figure 2 shows XRD patterns of samples prepared in P/Ce/urea = 1/1/0 and 1/1/1 heated at several temperatures. Rhabdophane-type $CePO_4$ (JCPDS card No. 35-0614) was formed in samples prepared with and without urea at 100 °C (Figure 2 (a) and (b)), and transformed to Monazite-type $CePO_4$ at 700 °C (Figure 2 (c) and (d)). Cerium carbonate easily reacted with phosphoric acid to Rhabdophane-type and Monazite-type $CePO_4$ (JCPDS card No. 32-0199) in P/Ce = 1/1. XRD patterns of samples prepared from CeO_2 and H_3PO_4 were shown at Figure 2 (e) and (f). The strong peaks of CeO_2 and weak peaks of CeP_2O_7 (JCPDS card No. 30-0164) were observed in XRD patterns of the both samples prepared with and without urea.

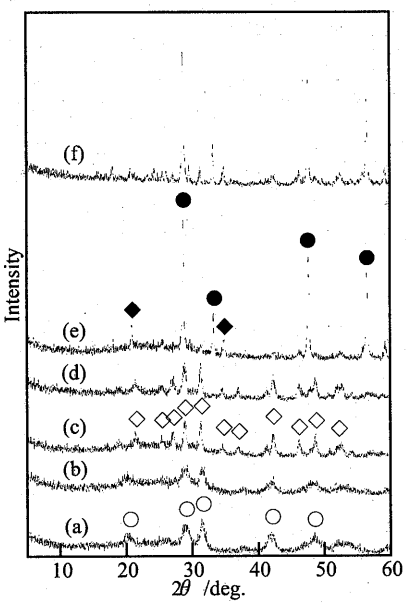

Fig. 2 XRD patterns of samples prepared in various conditions, (a) P/Ce/urea = 1/1/0, carbonate, 450 °C, (b) 1/1/1, carbonate, 450 °C, (c) 1/1/0, carbonate, 700 °C, (d) 1/1/1, carbonate, 700 °C, (e) 1/1/0, oxide, 700 °C, and (f) 1/1/1, oxide, 700 °C, ○ ; Rhabdophane-type $CePO_4$, ◇ ; Monazite-type $CePO_4$, ● ; CeO_2, and ◆ ; CeP_2O_7.

Figure 3 shows IR spectra of samples prepared in P/Ce/urea = 1/1/0 and 1/1/1 heated at several temperatures. Samples prepared in P/Ce/urea = 1/1/0 heated below 550 °C had absorption peaks due to Rhabdophane-type $CePO_4$ (Fig.3 (a)). Samples prepared in P/Ce/urea = 1/1/1 heated below 300 °C had absorption peaks due to urea with those of Rhabdophane-type $CePO_4$ (Figure 3 (b)). The peaks of Monazite-type $CePO_4$ were observed in IR spectra of samples prepared with and without urea heated at 700 °C (Figure 3 (c) and (d)). Samples prepared from CeO_2 and H_3PO_4 heated at 700 °C had IR absorption peaks of CeP_2O_7 (Figure 3 (e)). On the other hand, sample prepared from CeO_2, H_3PO_4, and $CO(NH_2)_2$ heated at 700 °C had IR absorption peaks of condensed phosphate and CeP_2O_7 (Fig.3 (f))[23]. As cerium condensed phosphates, for example, $Ce(PO_3)_3$, $Ce(PO_3)_4$, and so on were considered.

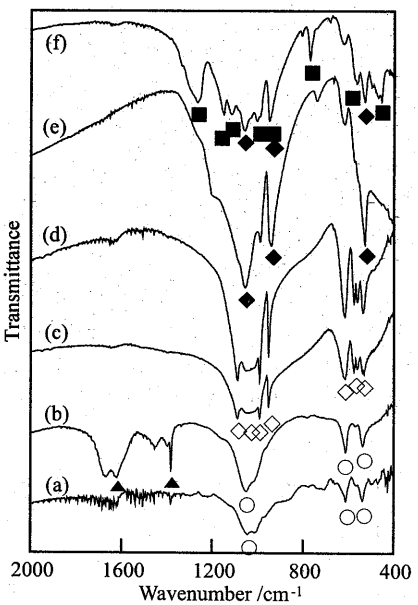

Fig. 3 IR spectra of samples prepared in various conditions, (a) P/Ce/urea = 1/1/0, carbonate, 100 °C, (b) 1/1/1, carbonate, 100 °C, (c) 1/1/0, carbonate, 700 °C, (d) 1/1/1, carbonate, 700 °C, (e) 1/1/0, oxide, 700 °C, and (f) 1/1/1, oxide, 700 °C, ○; Rhabdophane-type $CePO_4$, ▲; $CO(NH_2)_2$, ◇; Monazite-type $CePO_4$, ◆; CeP_2O_7, and ■; cerium condensed phosphate.

The endothermic peaks at 70 and 90 °C in DTA curves of samples prepared with and without urea (Figure 1 (a) and (b)) were considered to be due to volatilization of adsorbed water. The endothermic peak at 260 °C in DTA curve of sample prepared without urea (Figure 1 (a)) was considered to be due to that Rhabdophane-type $CePO_4$ lost crystalline water. After the volatilization of this water, Rhabdophane-type $CePO_4$ remained up to 550 °C and transformed to Monazite-type $CePO_4$ at 700 °C. Sample prepared with urea didn't have this endothermic peak due to volatilization of crystalline water in DTA curve (Figure 1 (b)). The exothermic peak at 315 °C was thought to put the endothermic peak out of sight. This exothermic peak at 315 °C was considered to be due to decomposition of urea in cerium phosphates from previous report[22]. A part of urea was considered to transform to biuret and/or cyanuric acid in endothermic peak at 185 °C as following equations.

$$2CO(NH_2)_2 \rightarrow NH(CONH_2)_2 + NH_3 \quad (1)$$

$$3CO(NH_2)_2 \rightarrow (CONH)_3 + 3NH_3 \quad (2)$$

Thermal products in the systems of P/Ce/urea = 1/1/0 and 1/1/1 were summarized in Table 1. The addition of urea had influence on thermal products prepared from CeO_2 and H_3PO_4. However, thermal products prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$ and H_3PO_4 changed a little by the addition of urea. This difference of the additional effects of urea was considered to be from the valence of cerium cation and the existence of carbonate anion.

Table 1 Thermal products in P/Ce = 1/1

Ce compound	Temperature/℃	P/urea = 1/0	1/1
carbonate	100	R-type $CePO_4$	R-type $CePO_4 + CO(NH_2)_2$
	300	R-type $CePO_4$	R-type $CePO_4 + CO(NH_2)_2$
	450	R-type $CePO_4$	R-type $CePO_4$
	550	R-type $CePO_4$	R-type $CePO_4$
	700	M-type $CePO_4$	M-type $CePO_4$
oxide	700	$CeO_2 + CeP_2O_7$	$CeO_2 + CeP_2O_7$ + comp. A

R-type $CePO_4$; Rhabdophane-type $CePO_4$, M-type $CePO_4$; Monazite-type $CePO_4$, and comp. A; cerium condensed phosphates.

Table 2 shows specific surface area of thermal products prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$ and H_3PO_4 in the systems of P/Ce/urea = 1/1/0 and 1/1/1. Samples prepared with urea had larger specific surface area than sample prepared without urea. Because urea decomposed to CO_2 and NH_3, and then volatilized, as a result, cerium phosphate was considered to be porous materials. Because of the remained urea in samples at 150 °C, the difference of specific surface area between samples with and without urea was considered to be small. The large part of urea decomposed and volatilized up to 300 °C, therefore the difference became large. At high temperature, this difference became small by sintering.

Table 2 Specific surface area of thermal products in P/Ce = 1/1 /$m^2 \cdot g^{-1}$

Temperature/℃	P/urea = 1/0	P/urea = 1/1
150	88.86	93.21
300	65.69	102.89
450	110.55	117.94
550	90.75	96.04
700	19.22	24.36

P/Ce = 2

Figure 4 shows DTA curves of samples prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$, H_3PO_4, $CO(NH_2)_2$ in P/Ce/urea = 2/1/0 and 2/1/2. Sample prepared in P/Ce/urea = 2/1/0 had endothermic peaks at 105 and 485 °C on DTA curve (Figure 4 (a)). On the other hand, DTA curve of sample prepared in P/Ce/urea = 2/1/2 had endothermic peaks at 105 and 190 °C and exothermic peaks at 440 and 520 °C (Figure 4 (b)).

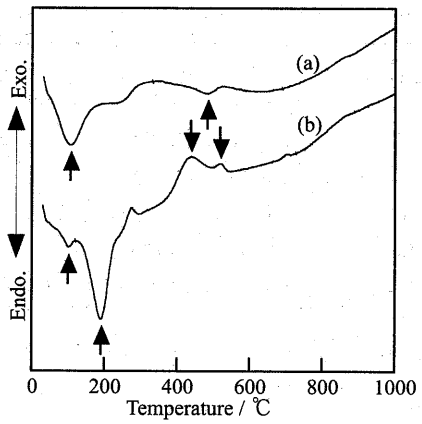

Fig. 4 DTA curves of samples prepared in several P/Ce/urea ratios, (a) 2/1/0 and (b) 2/1/2.

Figure 5 shows XRD patterns of samples prepared in P/Ce/urea = 2/1/0 and 2/1/2 heated at several temperatures. Samples prepared with and without urea at 100 °C were amorphous phase in XRD analyses. The peaks of Monazite-type $CePO_4$ appeared in XRD patterns of samples heated at 300 °C in spite of the addition of urea. The peak intensity of Monazite-type $CePO_4$ and $Ce(PO_3)_3$ (JCPDS card No. 33-0336) became weak by the addition of urea in XRD patterns of samples heated at 450 and 550 °C (Figure 5 (a) and (b)). This change was the same with the additional effect on formation of neodymium phosphates[22]. Sample prepared in P/Ce/urea = 2/1/0 heated at 700 °C had XRD peaks of $Ce(PO_3)_3$, Monazite-type $CePO_4$, and CeP_2O_7 (Figure 5 (c)). On the other hand, sample prepared in P/Ce/urea = 2/1/2 heated at 700 °C had weak XRD peaks of Monazite-type $CePO_4$ and $Ce(PO_3)_3$ (Figure 5 (d)). The peaks of CeP_2O_7 and CeO_2 were observed in XRD patterns of samples prepared from CeO_2 and H_3PO_4 in P/Ce/urea = 2/1/0 heated at 700 °C (Fig.5 (e))[21]. The peaks of CeO_2 and $Ce(PO_3)_3$ were observed in XRD pattern by the addition of urea (Figure 5 (f)). The addition of urea prevented the formation of CeP_2O_7. The additional effect of urea was larger in samples prepared from CeO_2 and H_3PO_4 than that in samples prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$ and H_3PO_4. The changes by the addition of urea became small in the system of cerium carbonate because cerium carbonate caused the volatilization of CO_2.

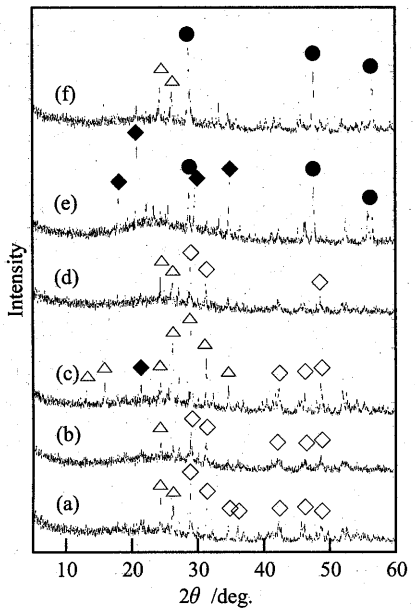

Fig. 5 XRD patterns of samples prepared in various conditions, (a) P/Ce/urea = 2/1/0, carbonate, 450 °C, (b) 2/1/2, carbonate, 450 °C, (c) 2/1/0, carbonate, 700 °C, (d) 2/1/2, carbonate, 700 °C, (e) 2/1/0, oxide, 700 °C, and (f) 2/1/2, oxide, 700 °C, ◇ ; Monazite-type $CePO_4$, △ ; $Ce(PO_3)_3$, ◆ ; CeP_2O_7, and ● ; CeO_2.

Figure 6 shows IR spectra of samples prepared in P/Ce/urea = 2/1/0 and 2/1/2 heated at several temperatures. Sample prepared in P/Ce/urea = 2/1/0 at 100 °C had broad IR absorption peaks due to Rhabdophane-type $CePO_4$ (Figure 6 (a)). The peaks due to urea were observed by the addition of urea in IR spectra of samples heated below 300 °C (Figure 6 (b)). By heating above 450 °C, samples prepared with and without urea had the same IR spectra due to cerium condensed phosphate (Figure 6 (c) and (d)), which was thought to be $Ce(PO_3)_3$ from XRD analyses (Figure 5 (c) and (d)). On the other hand, sample prepared from CeO_2 and H_3PO_4 in P/Ce/urea = 2/1/0 had IR absorption peaks of CeP_2O_7 (Figure 6 (e)). Sample prepared from CeO_2, H_3PO_4, and $CO(NH_2)_2$ in P/Ce/urea = 2/1/2 had IR absorption peaks of cerium condensed phosphates (Figure 6 (f)). From IR spectra, the additional effect of urea also appeared much in samples prepared from cerium oxide and phosphoric acid, less in samples prepared from cerium carbonate and phosphoric acid.

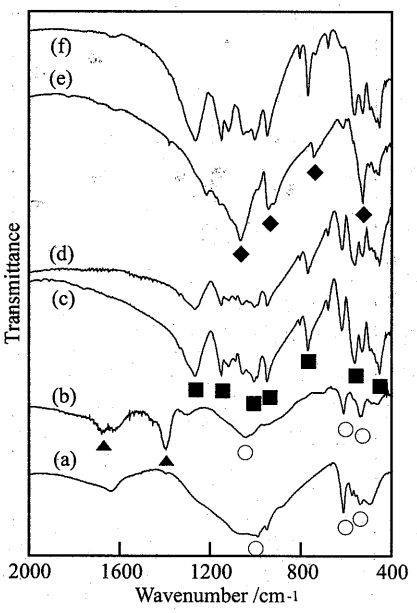

Fig. 6 IR spectra of samples prepared in various conditions, (a) P/Ce/urea = 2/1/0, carbonate, 100 °C, (b) 2/1/2, carbonate, 100 °C, (c) 2/1/0, carbonate, 700 °C, (d) 2/1/2, carbonate, 700 °C, (e) 2/1/0, oxide, 700 °C, and (f) 2/1/2, oxide, 700 °C, ○ ; Rhabdophane-type $CePO_4$, ▲ ; $CO(NH_2)_2$, ◇ ; Monazite-type $CePO_4$, ■ ; cerium condensed phosphate, and ◆ ; CeP_2O_7.

From XRD and IR analyses, the endothermic peaks at 105 and 485 °C in DTA curve (Figure 4 (a)) of sample prepared in P/Ce/urea = 2/1/0 were considered to be due to volatilization of adsorbed water and dehydration condensation of phosphates to $Ce(PO_3)_3$, respectively. The endothermic peaks at 105 and 190 °C in DTA curve of sample prepared in P/Ce/urea = 2/1/2 (Figure 4 (b)) were considered to be due to volatilization of adsorbed water and condensation of a part of urea to biuret and/or cyanuric acid in equations (1) and (2), respectively. The exothermic peaks at 440 and 520 °C were thought to be due to decomposition of urea. It was difficult to clear the reason that the decomposition of urea caused two exothermic peaks on DTA curve.

Thermal products in the systems of P/Ce/urea = 2/1/0 and 2/1/2 were summarized in Table 3. The addition of urea prevented the formation of CeP_2O_7 at 700 °C. It was considered that ammonia produced from the decomposition of urea made up a reducing atmosphere and that in this atmosphere Ce(+IV) cation was reduced to Ce(+III) cation. CeP_2O_7 was a little formed in the system of $Ce_2(CO_3)_3 \cdot 8H_2O$ without urea, the formation of CeP_2O_7 was inhibited by the addition of urea. On the other hand, the formation of CeP_2O_7 was much inhibited in sample prepared from CeO_2 and H_3PO_4. Because cerium oxide had tetra-valent cerium cation, CeP_2O_7 was relatively easy to form in the system of CeO_2. Furthermore, in the system of cerium carbonate, the volatilization of CO_2 was considered to dilute a reducing atmosphere. The change of thermal products was thought to be as following equation in a reducing atmosphere[6].

$$2CeP_2O_7 \rightarrow CePO_4 + Ce(PO_3)_3 + 1/2O_2 \quad (3)$$

Table 3 Thermal products in P/Ce = 2/1

Ce compound	Temperature/℃	P/urea = 1/0	1/1
carbonate	100	amo.	amo. + $CO(NH_2)_2$
	300	M-type $CePO_4$	M-type $CePO_4$ + $CO(NH_2)_2$
	450	M-type $CePO_4$ + $Ce(PO_3)_3$	M-type $CePO_4$ + $Ce(PO_3)_3$
	550	M-type $CePO_4$ + $Ce(PO_3)_3$	M-type $CePO_4$ + $Ce(PO_3)_3$
	700	$Ce(PO_3)_3$+ M-type $CePO_4$ + CeP_2O_7	M-type $CePO_4$ + $Ce(PO_3)_3$
oxide	700	CeP_2O_7 + CeO_2	CeO_2 + $Ce(PO_3)_3$

amo.; amorphous phase and M-type $CePO_4$; Monazite-type $CePO_4$.

In neodymium salts, much condensed phosphates were formed by the addition of urea[21, 22]. However, this change was not observed in cerium salts, which was considered to be from the existence of tetravalent cerium phosphate.

Specific surface area of thermal products in the systems of P/Ce/urea = 2/1/0 and 2/1/2 was also estimated by BET method to investigate the additional effect of urea. However, these samples had smaller specific surface area than 2 $m^2 \cdot g^{-1}$, therefore it was difficult to discuss the additional effect of urea.

P/Ce = 3~5

Figure 7 shows DTA curves of samples prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$, H_3PO_4, and $CO(NH_2)_2$ in various P/Ce/urea ratios. DTA curve of sample prepared in P/Ce/urea = 3/1/0 had two endothermic peaks at 150 and 430 °C (Figure 7 (a)). These peaks were considered to be due to volatilization of adsorbed water and dehydration - condensation of phosphate to $Ce(PO_3)_3$ from XRD and IR analyses. On the other hand, sample prepared in P/Ce/urea = 3/1/3 had an endothermic peak at 200 °C and an exothermic peak at 480 °C in DTA curve (Figure 7 (b)). This endothermic peak at 200 °C was considered to be due to transformation of a part of urea to biuret and cyanuric acid in equations (1) and (2). The exothermic peak at 480 °C was considered to be due to decomposition of urea. The blurring was observed in DTA curves of samples prepared in P/Ce/urea = 4/1/0, 5/1/0, and 5/1/5 (Figure 7 (c), (e), and (f)). The blurring of DTA curve like them was occasionally occurred in phosphorus abundant materials. Sample prepared in P/Ce/urea = 4/1/4 didn't have the blurring in DTA curve (Figure 7 (d)). It was thought to have a relationship that the addition of urea made sample lower viscous state. DTA curve of sample prepared in P/Ce/urea = 4/1/4 had an endothermic peak at 190 °C and a broad exothermic peak at 435 °C. These peaks were considered to be due to transformation of a part of urea to biuret and cyanuric acid, and decomposition of urea, respectively.

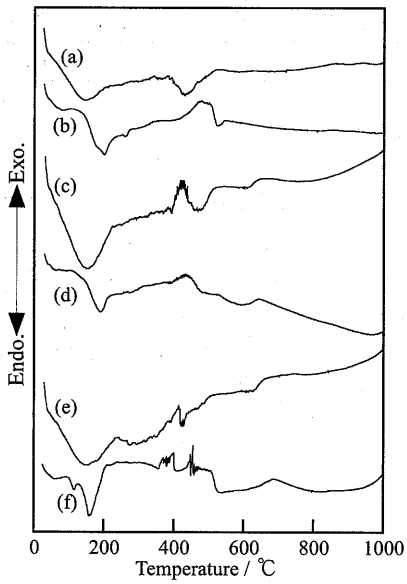

Fig. 7 DTA curves of samples prepared in several P/Ce/urea ratios, (a) 3/1/0, (b) 3/1/3, (c) 4/1/0, (d) 4/1/4, (e) 5/1/0, and (f) 5/1/5.

Figure 8 shows XRD patterns of samples prepared in P/Ce/urea = 4/1/0 and 4/1/4 heated at 700 °C. Sample prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$ and H_3PO_4 in P/Ce/urea = 4/1/0 had XRD peaks of $Ce(PO_3)_4$ (JCPDS card No. 25-0188) and $Ce(PO_3)_3$ (Figure 8 (a)). The peaks of $Ce(PO_3)_3$ and $Ce(PO_3)_4$ were observed in XRD pattern of sample prepared in P/Ce/urea = 4/1/4 (Figure 8 (b)). The addition of urea made the XRD peak intensity weak, in particular that of $Ce(PO_3)_4$. The change of thermal products was clearly observed in samples prepared from cerium oxide. Sample prepared from CeO_2 and H_3PO_4 in P/Ce/urea = 4/1/0 had XRD peaks of $Ce(PO_3)_4$ (Figure 8 (c)), on the other hand sample prepared in P/Ce/urea = 4/1/4 had XRD peaks of $Ce(PO_3)_3$ (Figure 8 (d)) [21].

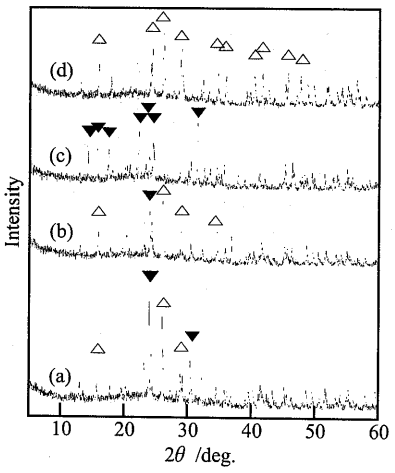

Fig. 8 XRD patterns of samples prepared in P/Ce/urea = 4/1/0 and 4/1/4 heated at 700 °C, (a) 4/1/0, carbonate, (b) 4/1/4, carbonate, (c) 4/1/0, oxide, and (d) 4/1/4, oxide, △ ; $Ce(PO_3)_3$, and ▼ ; $Ce(PO_3)_4$,

Thermal products in the systems of various P/Ce/urea ratios were summarized in Table 4. CeP_5O_{14} was estimated from JCPDS card No. 34-0021 in the XRD analyses. By the addition of urea, the changes of the thermal products were observed in samples prepared from cerium carbonate in P/Ce = 3 heated at 550 and 700 °C, samples in P/Ce = 4 heated at 700 °C, samples prepared in P/Ce = 5 heated at 550 and 700 °C, samples prepared from cerium oxide in P/Ce = 3, 4, and 5 heated at 700 °C. From these thermal products, the addition of urea was considered to have tendency to prevent the formation of $Ce(PO_3)_4$. It was considered that ammonia produced from the decomposition of urea made up a reducing atmosphere and that in this atmosphere Ce(+IV) cation was reduced to Ce(+III) cation. The change of thermal products was thought to be as following equation in a reducing atmosphere[6].

$$2Ce(PO_3)_4 \rightarrow Ce(PO_3)_3 + CeP_5O_{14} + 1/2O_2 \quad (4)$$

Table 4 Thermal products in P/Ce = 3/1, 4/1, and 5/1

Ce compound	Temperature /℃	P/Ce = 3/1 P/urea = 1/0	1/1	4/1 1/0	1/1	5/1 1/0	1/1
carbonate	100	M-type CePO4	R-type CePO4 + CO(NH2)2	M-type CePO4	R-type CePO4 + unk. + CO(NH2)2	amo.	R-type CePO4 + unk. + CO(NH2)2
	300	amo.	amo. + CO(NH2)2	M-type CePO4	amo. + CO(NH2)2	amo.	amo. + CO(NH2)2
	450	Ce(PO3)3	Ce(PO3)3	Ce(PO3)3	Ce(PO3)3	Ce(PO3)3	amo. + CO(NH2)2
	550	Ce(PO3)3 + Ce(PO3)4	Ce(PO3)3	Ce(PO3)3 + Ce(PO3)4	Ce(PO3)3 + Ce(PO3)4	Ce(PO3)4 + Ce(PO3)3	Ce(PO3)3 + Ce(PO3)4
	700	Ce(PO3)3 + Ce(PO3)4	Ce(PO3)3	Ce(PO3)4 + Ce(PO3)3	Ce(PO3)3 + Ce(PO3)4	Ce(PO3)3 + Ce(PO3)4	Ce(PO3)3 + Ce(PO3)4
oxide	700	Ce(PO3)4 + CeP2O7	Ce(PO3)3	Ce(PO3)4	Ce(PO3)3	Ce(PO3)4	Ce(PO3)3 + CeP5O14

amo.; amorphous phase, unk.; unknown compound, M-type $CePO_4$; Monazite-type $CePO_4$, and R-type $CePO_4$; Rhabdophane-type $CePO_4$.

Samples prepared in P/Ce =3, 4, and 5 had small specific surface area, therefore it was difficult to discuss about additional effect of urea on specific surface area.

Conclusion

The additional effects of urea were investigated in formation systems of cerium phosphates. Urea decomposed at 400-450 °C in cerium phosphates, which was the same with that in neodymium phosphates. The additional effects of urea on thermal products were much observed over 450 °C. The addition of urea prevented the formation of tetra-valent cerium phosphates, CeP_2O_7 and $Ce(PO_3)_4$. These changes of thermal products were observed much in samples prepared from CeO_2 and H_3PO_4, less in samples prepared from $Ce_2(CO_3)_3 \cdot 8H_2O$ and H_3PO_4. These changes of the additional effects of urea between samples prepared from cerium carbonate and samples prepared from cerium oxide were considered to be from the valence of cerium cation and the existence of carbonate anion. It was considered that ammonia produced from the decomposition of urea made up a reducing atmosphere and that in this atmosphere Ce(+IV) cation was reduced to Ce(+III) cation. In the system of cerium carbonate, the volatilization of CO_2 was considered to dilute a reducing atmosphere.

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