

A study of thermal behavior of cesium phosphate

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Abstract Cesium phosphates with different Cs/P molar ratios were prepared by a solution evaporation method. X-ray powder diffraction, thermogravimetric, and differential thermal analyses were performed in order to reveal the chemical transformation and phase compositions which take place during the heating of the mixtures Cs₂CO₃/ (NH₄)₂HPO₄ and CsNO₃/(NH₄)₂HPO₄ as well as individual compound. The effects of the Cs/P molar ratio, Cs source and treatment temperature on thermal behavior of the cesium phosphates were investigated. The results showed that different reactions take place with molar ratio from 1/2 to 3/1. Meanwhile, the thermostability of Cs_2CO_3 and CsNO₃ intimately affects the phase composition and phase transition during heating process. However, for all the Cs-P oxides samples, the crystallinity was decreased differently after higher temperature treatment.

Keywords Phosphate · Thermal behavior · Phase transition · Thermostability · Dehydration

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Introduction

Metal phosphates play an important role in chemical engineering as protonic conductors, ion exchangers, catalysts, intercalation carriers, catalyst support, and novel functionalized materials [1–5]. As such, synthesis and applications of metal phosphates have received considerable attention [6]. Blanco et al. [7] prepared a series of metal orthophosphates $[Ca_3(PO_4)_2, Sr_3(PO_4)_2, and Ba_3(PO_4)_2]$ and metal pyrophosphates $(Ca_2P_2O_7, Sr_2P_2O_7, and Ba_2P_2O_7)$ for gas-phase dehydration of lactic acid. Matsuura et al. [8] also prepared $Ca_{10}(PO_4)_6(OH)_2$, $Sr_{10}(PO_4)_6(OH)_2$, $Ba_{10}(PO_4)_6(OH)_2$, and other hydroxyapatite catalysts to synthesize acrylic acid from lactic acid. Tang et al. [9] further studied the catalytic dehydration of lactic acid to acrylic acid over $Ba_2P_2O_7$.

Phosphates exhibit a complex phase transition when prepared with different molar ratios and at different heating treatment temperatures [10, 11]. Ai et al. [10] reported that the structure of iron phosphates prepared with a P/Fe atomic ratio close to 1 varied from the amorphous phase to the quartz-type phase (FePO₄) via an unidentified phase with increasing calcination temperature. The quartz-type phase was formed, accompanied with the formation of polycondensed phosphates at P/Fe atomic ratio = 1.3-1.5. Muneyama et al. [11] further investigated the reduction and oxidation of iron phosphates and found that FePO₄ was reduced to $Fe_2P_2O_7$ through $Fe_3(P_2O_7)_2$ at Fe/P > 1.2. However, the sample did not pass through $Fe_3(P_2O_7)_2$ at Fe/P = 1. Masui [12] studied the thermal behavior of amorphous cerium phosphate and found that crystallization from the amorphous phase occurred at 500 °C to form CeP₂O₇. CePO₄ was then formed at 650 °C in the presence of a small amount of Ce(PO₃)₃. Sun et al. [13] prepared zeolites modified with the cesium phosphate catalyst through wet impregnation and then calcined at 800 °C to

improve dehydration activity. They discussed the effect of cesium phosphate modification and cesium content on the catalytic performance. Previous studies on cesium phosphate focused on cesium dihydrogen phosphate (CsH₂PO₄) because of its anhydrous proton conductors [14–16] and the thermodynamics and kinetics of its dehydration reaction at temperatures lower than 300 °C [17–22]. However, systematic studies on the thermal behavior of cesium phosphate and phase translation at high temperatures have been rarely reported.

As we all know that the thermoanalytical tools such as thermogravimetry (TG) and differential thermal analysis (DTA) and X-ray powder diffraction (XRD) analysis play an important role in the thermal behavior research and phase identification of a crystalline material, respectively [23–28]. Therefore, in this study, the TG/DTA and XRD analyses were used to obtain information on the thermal behavior and phase composition of cesium phosphate at different Cs/P molar ratios. Different Cs sources were used to prepare cesium phosphates with Cs/P molar ratios of 1/2, 1/1, 2/1, and 3/1 through evaporation.

Experimental

Product preparation

Cesium phosphate was synthesized through reaction of diammonium hydrogen phosphate [(NH₄)₂HPO₄, 99.0 %] with cesium carbonate (Cs₂CO₃, 98.0 %) and cesium nitrate (CsNO₃, 99.0 %), respectively.

Cesium phosphate was prepared using Cs_2CO_3 (signed as CCP). Briefly, 0.025 mol Cs_2CO_3 (8.3117 g) was dissolved in 50 mL deionized water and added with 0.05 mol (NH₄)₂ HPO₄ (6.6695 g) solution under constant stirring for 1 h. The mixture was vaporized at 150 °C, and the precipitated precursor with Cs/P molar ratios of 1/1 was obtained. Samples with Cs/P molar ratios of 1/2 [0.025 mol Cs₂CO₃ and 0.1 mol (NH₄)₂HPO₄], 2/1 [0.025 mol Cs₂CO₃ and 0.025 mol (NH₄)₂HPO₄], and 3/1 [0.03 mol Cs₂CO₃ and 0.02 mol (NH₄)₂HPO₄] were prepared using the same procedure.

Another group of cesium phosphate was prepared using cesium nitrate (signed as CNP) at different Cs/P molar ratios of 1/2, 1/1, 2/1, and 3/1. Generally, 0.05 mol CsNO₃ (9.8439 g) was dissolved in 50 mL deionized water and added with 0.05 mol (NH₄)₂HPO₄ (6.6695 g) solution under constant stirring for 1 h. The mixture was vaporized at 150 °C, and the precipitated precursor with Cs/P molar ratios of 1/1 was obtained. Samples with Cs/P molar ratios of 1/2 [0.05 mol CsNO₃ and 0.1 mol (NH₄)₂HPO₄], 2/1 [0.05 mol CsNO₃ and 0.025 mol (NH₄)₂HPO₄], and 3/1 [0.06 mol CsNO₃ and 0.02 mol (NH₄)₂HPO₄] were prepared using the same procedure.

All precursors were calcined at 450, 650, and 800 °C for 6 h. The obtained samples were sealed in a dry place after calcination.

Product characterization

XRD patterns were obtained with an X'Pert PRO MPD diffractometer at 40 kV and 40 mA with Cu K α radiation. Angle (2 θ) was measured in steps of 10° min⁻¹ between 5° and 90°. Mass loss and temperature associated with phase transformation were determined through TG/DTA on a Shimadzu DTG-60H analyzer. The samples were heated from room temperature to 850 °C at rate of 10 °C min⁻¹ in air flow (30 mL min⁻¹).

Results and discussion

Thermal behavior of cesium phosphates with Cs/P = 1/2 and 1/1

The TG/DTA data of CCP samples with Cs/P molar ratios of 1/2 and 1/1 were shown in Fig. 1. During heating at a constant heating rate of 10 °C min⁻¹ up to 850 °C, five transformations accompanied by mass loss occurred at Cs/P = 1/1: (1) up to 68 °C, endothermic peak at 35 °C, mass loss of 1.3 %; (2) between 80 and 174 °C, endothermic peak at 131 °C, mass loss of 4.0 %; (3) between 174 and



Fig. 1 TG and DTA curves of samples with Cs/P molar ratios of 1/2 (a) and 1/1 (b) at a heating rate of 10 °C min⁻¹



Fig. 2 TG and DTA curves of Cs₂CO₃ at a heating rate of 10 °C \min^{-1}

224 °C, endothermic peak at 209 °C, mass loss of 0.7 %; (4) between 224 and 300 °C, endothermic peak between 235 and 280 °C, mass loss of 4.4 %; and (5) between 300 and 442 °C, endothermic peak at 335 °C, mass loss of 3.4 %. Two endothermic peaks were further observed at 473 and 735 °C, but without mass loss as the temperature increased to 850 °C. For Cs/P = 1/2, four evident endothermic peaks were observed at 35, 131, 169, and 204 °C, with a mass loss of 0.7 % up to 51 °C and continuous drop of mass to 74 %. An unobvious endothermic peak was further observed at 630 °C with a mass loss of 1.6 %.

In order to identify process that causes mass loss and verify reaction during heating, the thermoanalytical curves of the pure Cs₂CO₃ and (NH₄)₂HPO₄ were invested and shown in Figs. 2 and 3, respectively. TG and DTA curves of Cs₂CO₃ showed that Cs₂CO₃ was stable with only two small endothermic peaks at 124 and 174 °C, which could be due to desorption of water and decomposition of impurities [29]. After that, it started to melt and meanwhile decompose (Eq. 1).

$$Cs_2CO_3 \to Cs_2O + CO_2 \tag{1}$$

Based on TG/DTA curves of $(NH_4)_2$ HPO₄ (Fig. 3), the thermoanalytical analysis revealed three main endothermic peaks at 208, 285, and 382 °C. Intensive mass loss started at temperatures higher than 120 °C and continued throughout the whole heating range. The first endothermic peak at 200 °C is mainly correlated with the melting of $(NH_4)_2$ HPO₄ and partial elimination of ammonia (Eq. 2) [30]. The theoretical mass loss of the elimination of one ammonia molecule is 12.9 %, which was reached on the recorded TG curve at 210 °C. However, according to the literature, a small amounts of H_3PO_4 (Eq. 3), $(NH_4)_2$ $H_2P_2O_7$ (Eq. 4), and $H_4P_2O_7$ (Eq. 5) were also formed at temperature lower than 210 °C [31, 32]. When the $(NH_4)_2$ HPO₄ sample was continuously heated at higher



Fig. 3 TG and DTA curves of (NH₄)₂HPO₄ at a heating rate of 10 °C min⁻

temperatures, a second endothermic peak appeared at 285 °C; this peak is related to the elimination of the second ammonium molecule (Eq. 3) and further dehydration of the corresponding phosphates (Eqs. 4, 5). This process started at temperatures higher than 200 °C [27, 33, 34] and accompanied by gradual mass loss on the TG curve (Fig. 3) immediately after the formation of NH₄H₂PO₄. The theoretical mass loss of this process is 26.5 %, which was reached on the recorded TG curve at 376 °C. A third endothermic peak appeared at 382 °C is mainly associated with the condensation of H_3PO_4 (Eq. 5) and dehydration of H₄P₂O₇-HPO₃ (Eq. 6) [30]. NH₄PO₃ (Eq. 7) was simultaneously formed at temperature higher than 400 °C [31]. As these processes are complex, accurate interpretation of the TG/DTA results is difficult. Moreover, the sample started to decompose (Eqs. 8, 9) and evaporate at 550 °C.

$$(\mathbf{NH}_4)_2 \mathbf{HPO}_4 \to \mathbf{NH}_4 \mathbf{H}_2 \mathbf{PO}_4 + \mathbf{NH}_3 \tag{2}$$

$$\mathrm{NH}_4\mathrm{H}_2\mathrm{PO}_4 \to \mathrm{H}_3\mathrm{PO}_4 + \mathrm{NH}_3 \tag{3}$$

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O \tag{4}$$

DC

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O \tag{5}$$

$$H_4 P_2 O_7 \rightarrow 2 H P O_3 + H_2 O \tag{6}$$

$$(\mathrm{NH}_4)_2\mathrm{H}_2\mathrm{P}_2\mathrm{O}_7 \to 2\mathrm{NH}_4\mathrm{PO}_3 + \mathrm{H}_2\mathrm{O} \tag{7}$$

$$2\text{HPO}_3 \rightarrow \text{P}_2\text{O}_5 + \text{H}_2\text{O} \tag{8}$$

$$2\mathrm{NH}_4\mathrm{PO}_3 \to \mathrm{P}_2\mathrm{O}_5 + 2\mathrm{NH}_3 + \mathrm{H}_2\mathrm{O} \tag{9}$$

The XRD patterns of CCP sample with Cs/P = 1/2 and 1/1 (Fig. 4) showed that the crystal phase was mainly composed of CsH₂PO₄ phase (PDF NO. 35-0746). As such, the reaction (Eq. 10) occurred when Cs_2CO_3 and $(NH_4)_2$ HPO₄ were mixed. According to previous studies, phase transition and dehydration occur upon heating of CsH₂PO₄ [17, 18, 20, 21]. The phase transition from the low temperature phase (paraelectric phase) to the high temperature



Fig. 4 XRD patterns of CCP precursor samples with Cs/P = 1/2 and 1/1

phase (super-protonic phase) was observed at 230 °C [22, 27, 28]. Pyrophosphate ($Cs_2H_2P_2O_7$) was formed (Eq. 11) at 235 °C [28] and then converted to cesium polyphosphate (Eq. 12) temperatures higher than 260 °C [17, 18, 20, 28]. At higher temperatures, phosphate such as (CsPO₃)_n (n » 1) polymerized at about 330 °C [28] (Eq. 13). The (CsPO₃)_n phase underwent crystallographic transition at 480 °C and melting at 735 °C with increasing temperature [22, 28].

$$\begin{aligned} \mathrm{Cs_2CO_3} + 2\mathrm{(NH_4)_2HPO_4} &\rightarrow \mathrm{2CsH_2PO_4} + \mathrm{4NH_3} + \mathrm{CO_2} \\ &+ \mathrm{H_2O} \end{aligned} \tag{10}$$

$$2CsH_2PO_4 \rightarrow Cs_2H_2P_2O_7 + H_2O \tag{11}$$

$$n\mathrm{Cs}_{2}\mathrm{H}_{2}\mathrm{P}_{2}\mathrm{O}_{7} \to 2\mathrm{Cs}_{n}\mathrm{H}_{2}\mathrm{P}_{n}\mathrm{O}_{3n+1} + (n-2)\mathrm{H}_{2}\mathrm{O}$$
(12)

$$nCsH_2PO_4 \rightarrow (CsPO_3)_n + nH_2O \tag{13}$$

$$Cs_3PO_4 + CsH_2PO_4 \rightarrow Cs_4P_2O_7 + H_2O$$
(14)

Aside from the CsH₂PO₄ phase, $(NH_4)_2HPO_4$ (PDF NO. 29-0111) was also observed at in Cs/P = 1/2. The decomposition and dehydration of $(NH_4)_2HPO_4$ led to continuous mass loss without separation step, similar to that of pure $(NH_4)_2HPO_4$. In this regard, the endothermic peak of DTA at 630 °C is due to the formation and evaporation of P₂O₅.

Samples were calcined at 450, 650, and 800 °C to analyze the crystal phase structure through XRD analysis (Fig. 5a, b) and information on processes that occur during heating at high temperatures. The CsH₂PO₄ phase disappeared because of dehydration and polymerization. At Cs/P = 1/1, the sample was mainly composed of the metaphosphate phase (CsPO₃, PDF NO. 38-0135 and Eqs. 12, 13) and pyrophosphate (Cs₄P₂O₇, PDF NO. 38-0001, and possible reaction as Eq. 14) after calcination at 450 and 650 °C. However, the sample was mainly composed of non-crystalline compound, in addition to metaphosphate and pyrophosphate phases at



Fig. 5 XRD patterns of CCP samples with Cs/P molar ratios of 1/2 (a) and 1/1 (b) and calcination temperatures of 450, 650, and 800 °C, respectively

Cs/P = 1/2. The crystallinity slightly increased when the calcination temperature was increased to 650 °C. The differences between the two CCP samples may be attributed to polycondensation and decomposition of phosphoric acid derived from the decomposition of excess $(NH_4)_2HPO_4$ (Eq. 3) during heating. When the calcination temperature was increased to 800 °C, the crystal phase of all the samples disappeared and only the amorphous phase was observed because of the melting of $(CsPO_3)_n$ leading to formation of the glassy state [20].

The TG/DTA data indicated that the endothermic peak at 131 °C is related to water desorption. The two endothermic peaks at 169 and 209 °C are related to the melting of $(NH_4)_2HPO_4$ companied with the elimination of ammonia (Eqs. 2, 3) and dehydration reaction, respectively. The endothermic peak at 235 °C, with a corresponding mass loss, is related to the superionic phase transition and dehydration of CsH₂PO₄-Cs₂H₂P₂O₇ (Eq. 11); Moreover, the endothermic peaks at 280 and 335 °C are attributed to the



Fig. 6 TG and DTA curves of samples with Cs/P molar ratios of 2/1 (a) and 3/1(b)

dehydration reaction forming a liquid phase (Eq. 12) and conversion of $Cs_2H_2P_2O_7$ into cesium polyphosphate with the melting of CsH_2PO_4 , respectively. The endothermic peaks at 473 and 735 °C without mass loss are attributed to the crystallographic transition from polyphosphate to metaphosphate and melting of CsPO₃, respectively. In sample with a Cs/P molar ratio of 1/2, an endothermic peak at 630 °C is present, which may be attributed to the evaporation of P₂O₅, as calculated Eq. 8 and 9.

Thermal behavior of CCP samples with Cs/P molar ratios of 2/1 and 3/1

Cesium phosphates with Cs/P molar ratios of 2/1 and 3/1 were also prepared, and the thermal behavior of these samples was investigated using TG/DTA (Fig. 6). The TG and DTA curves show that the two samples exhibited similar behavior during continuous heating. Four endothermic peaks accompanied by mass loss were observed at 71, 140, 204, and 341 °C, accompanied with certain mass loss. The XRD patterns of the CCP precursor (Fig. 7) showed the presence of the cesium hydrogen phosphate hydrate phase (Cs₂) HPO₄·1.5H₂O, PDF NO. 37-0106), in addition to the CsH₂PO₄ phase and reactant Cs₂CO₃ (PDF NO. 35-0962). The two samples were treated at 450, 650, and 800 °C. The XRD patterns of the corresponding samples (Figs. 8a, b) showed that all the samples exhibited poor crystallinity, and the Cs₃PO₄ phase (PDF NO. 26-1097) was observed because of sufficient Cs source in the reaction. However, Cs₃PO₄ phase can still be observed as the heating temperature was



Fig. 7 XRD patterns of CCP precursors with Cs/P molar ratios of 2/1 and 3/1



Fig. 8 XRD patterns of CCP samples with Cs/P molar ratios of 2/1 (a) and 3/1 (b) at different calcination temperature

increased from 650 to 800 °C. This finding suggested that the structure of CCP samples with Cs/P molar ratios of 2/1 and 3/1 is stable after calcination at 450 °C.

The first endothermic peak at 71 °C during heating is correlated with the desorption of the adsorbed water, whereas the peak at 140 °C is related to the decomposition of Cs_2HPO_4 ·1.5H₂O [11]. The third endothermic peak at 204 °C is possibly associated with the dehydration of Cs_2HPO_4 ; moreover, the peak at 341 °C is attributed to the dehydration reaction and conversion of CsH_2PO_4 to cesium polyphosphate accompanied by melting of CsH_2PO_4 [22–26, 28, 30]. The TG curves are stable without mass loss from 450 to 850 °C because of the formation of the Cs_3PO_4 phase. Mass losses were observed at 800 °C because of the decomposition of excess Cs_2CO_3 .

Thermal behavior of the CNP samples with different Cs/P molar ratios

Cesium phosphates with Cs/P molar ratios of 1/2, 1/1, 2/1, and 3/1 were prepared using CsNO₃ to compare and analyze the influence of using different Cs sources. Figure 9 shows the TG/DTA cures of the four CNP samples. The thermal behavior is similar below 400 °C. At high temperatures, CNP samples with Cs/P molar ratios of 1/2 and 1/1 are stable and exhibit no mass loss. However, one broad endothermic peak at 600 °C accompanied with mass loss and another one at 400 °C without mass loss can be observed at Cs/P = 2/1 and 3/1, respectively. The XRD patterns of the CNP precursors are shown in Fig. 10. Aside from the characteristic peaks of the reactants CsNO₃ (PDF NO. 09-0403) and (NH₄)₂HPO₄ (PDF NO. 29-0111), only the NH₄H₂PO₄ phase (PDF NO. 37-1479) is observed



Fig. 9 TG and DTA curves of CNP samples with different Cs/P molar ratios $% \left({{{\rm{CS}}} \right)_{\rm{T}}} \right)$

because of the decomposition of partial $(NH_4)_2HPO_4$. The CsH₂PO₄ phase cannot be observed in all CNP precursors. This finding suggested that the reaction of CsNO₃ with NH₄H₂PO₄ did not occur at low temperatures.

The TG and DTA curves of $CsNO_3$ are also shown in Fig. 11 to identify transformation that occurred during heating. Two apparent endothermic peaks at 160 and 406 °C without mass loss were observed due to melting impurities in $CsNO_3$ [26, 31] and the melting point of $CsNO_3$, which was reported at 414 °C in the literatures. Most of the mass loss, accompanied with two broad endothermic DTA peaks from 500 to 800 °C, is attributed to decomposition and volatilization of $CsNO_3$.

Therefore, the thermal behavior of CNP samples (Fig. 9) with endothermic peak at 152 °C without mass loss is correlated with melting impurities from CsNO₃. The second peak at 188 °C with starting mass loss attributed to the decomposition of $(NH_4)_2HPO_4$ and dehydration of phosphate (Eq. 11). The third peak at 266 °C is possibly



Fig. 10 XRD patterns of the CNP precursor with different Cs/P molar ratios $\$



Fig. 11 TG and DTA curves of CsNO₃



Fig. 12 XRD patterns of CNP samples calcined at 450 $^\circ$ C with different Cs/P molar ratios



Fig. 13 XRD patterns of the CNP samples calcined at 650 °C with different Cs/P molar ratios

attributed to conversion into polyphosphate [17, 18, 20, 28]. Finally, the peaks at 400 and 600 °C are associated with the melting and decomposition of $CsNO_3$, respectively.

Base on the XRD patterns of CNP samples calcined at 450 °C (Fig. 12), the $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ phases disappeared, whereas the metaphosphate (CsPO₃) and pyrophosphate (Cs₄P₂O₇) phases appeared. Moreover, the corresponding characteristic peaks decreased, and the CsNO₃ phase still can be observed as the Cs/P molar ratio was increased from 1/2 to 3/1. However, based on the XRD patterns of CNP samples calcined at 650 °C (Fig. 13), the crystallinity of the CNP samples obviously decreased and the CsPO₃ and Cs₄P₂O₇ phases disappeared at Cs/P molar ratio of 1/2 and 1/1 (Fig. 14). The CsNO₃ phase disappeared, and some cesium oxides were further observed at Cs/P molar ratio of 2/1 and 3/1 because of the decomposition of CsNO₃. Besides, weak Cs₃PO₄ crystal phase was



Fig. 14 XRD patterns of CNP samples calcined at 800 $^\circ \rm C$ with different Cs/P molar ratios

also formed during heating process from 450 to 650 °C. The XRD patterns of CNP samples calcined at 800 °C showed that the $Cs_4P_2O_7$ crystal phase was observed at Cs/P molar ratios of 1/2 and 1/1. These changes are different from those of the CCP samples, which could be due to the melting of $(CsPO_3)_n$ that destroys the polycondensation structure, resulting in formation of the $Cs_4P_2O_7$ crystal phase.

Conclusions

The thermal behavior of cesium phosphate is significantly influenced by Cs/P molar ratio and Cs source. The CsH₂ PO₄ phase was formed at low temperatures, with Cs₂CO₃ as the Cs source at Cs/P molar ratios of 1/2 and 1/1. Moreover, CsPO₃ and Cs₄P₂O₇ were formed during heating process due to the decomposition and dehydration reactions. Crystal phases disappeared, and only the amorphous phase was observed when the temperature was increased to 800 °C. At Cs/P molar ratios of 2/1 and 3/1, only the Cs₃PO₄ phase was formed, in addition to non-crystalline compounds, during continuous heating from 450 to 800 °C.

The CsH₂PO₄ phase was not formed, and only the decomposition of partial $(NH_4)_2HPO_4$ was observed when CaNO₃ was used as the Cs source. Similarly, the CsPO₃ and Cs₄P₂O₇ phases were presented at 450 °C, but disappeared with further increase in temperature. Only non-crystalline compounds were observed at temperatures up to 650 °C, in addition to cesium oxides, because of decomposition of CsNO₃. The Cs₄P₂O₇ phase was observed again when the temperature was increased to 800 °C at Cs/P molar ratios 1/2 and 1/1. The melting of (CsPO₃)_n and the decomposition and volatilization of CsNO₃ possibly led to the reconstruction of these compounds.

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