NEW DEVELOPMENT IN THE STUDY OF CONDENSED PHOSPHATES

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Abstract: New development in the recent study of condensed phosphates was described in the fields of synthetic process of newly prepared short-chain oligophosphates of tetra-, hexa- and octaphosphates, industrial preparation process of ammonium polyphosphates of phases II, V and VI as well as their flame retardation effect, and preparation of proton-conductive phosphate glasses as solid electrolytes.

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INTRODUCTION

Phosphates and condensed phosphates have been used widely in industrial fields such as detergents, chemical fertilizers, food additives, biomaterials, electric and electronic materials, glass ceramics, flame retardants, etc. The wide application fields are due to the special properties of phosphorus-oxide compounds.\(^1\)\(^-\)\(^4\) In this paper, recent development of condensed phosphates will be described according to experimental results obtained by the present author and coworkers. First subject is development in the preparation of condensed phosphates. Among condensed phosphates, short-chain oligophosphates of di- and triphosphates as well as small-ring phosphates of cyclo-tri-, cyclo-tetra-, cyclo-hexa-, cyclo-octa- and cyclo-decaphosphates have been prepared. According to our recent study, short-chain oligophosphates of tetra-, hexa- and octaphosphates have been prepared by the hydrolytic process. Second subject is the preparation of ammonium polyphosphate (APP) and its use as flame retardants. APP has six crystal phases of I to VI. Phase I can most easily be prepared, while other APP phases are difficult to prepare, especially in factory scale. In this paper, our new preparation process which can be applicable in a large scale will be described. The flame-retardation effect of APP to organic polymer materials will also be shown in the same section. Third subject is new development of phosphate-glass compounds on the characteristic property as proton-conductive materials. The compounds can be applicable to solid electrolytes of a fuel cell working at a moderately high temperature (150 to 400 °C).

PREPARATION OF SHORT-CHAIN OLIGO-PHOSPHATES

According to usual heating process, it is
difficult to prepare individual short-chain oligophosphates in a high quality and only di- and triphosphates can be prepared by the process. In our research group, tetra-, hexa- and octaphosphates have been prepared according to the hydrolytic process of ring oligophosphates with the same polymerization degree as the chain oligophosphates. The process is due to the characteristic hydrolysis-property of short-chain and small-ring oligophosphates. The hydrolysis of short-chain oligophosphates is acid catalyzed reaction and that of small-ring oligophosphates is acid and base catalyzed reaction. When small-ring oligophosphate is hydrolyzed in a basic solution, selective ring-opening process will be occurred and the produced chain oligophosphate having the same polymerization degree as the ring phosphate can be expected to prepare in the basic solution and the produced chain oligophosphate will be stable in the basic solution. According to the original idea, preparation of short-chain oligophosphates of tetra-, hexa- and octaphosphates was examined and was successfully achieved.

(1) PREPARATION OF TETRAPHOSPHATE

Tetraphosphate was very difficult to prepare according to usual heating process. Cyclo-tetraphosphates can easily be prepared by dissolving $\alpha \text{P}_2\text{O}_5$ in water under 15 °C and by salting out with addition of sodium chloride in the solution, and sodium cyclo-tetraphosphate tetrahydrate was prepared. The cyclo-tetraphosphate was hydrolyzed in a strongly basic solution of 5M-NaOH solution at 20 °C. The result is listed in Table 1. According to the result, tetraphosphate was produced in a high yield by hydrolyzing cyclo-tetraphosphate in the basic solution at reaction time of 3 to 4 days. Highly selective ring-opening hydrolysis of cyclo-tetraphosphate was observed and the produced tetraphosphate was fairly stable in the solution.

<table>
<thead>
<tr>
<th>Reaction Time (day)</th>
<th>Cyclo-tetra</th>
<th>Tetra</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>67.0</td>
<td>33.0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>32.8</td>
<td>63.7</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>94.5</td>
<td>5.5</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>91.8</td>
<td>8.2</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>87.0</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Next step was isolation of the produced tetraphosphate from the resulting solution. Enough guanidine hydrochloride was added to the solution and the solution was kept in a freezer at -15 °C for one week. Guanidine tetraphosphate dihydrate was obtained by the preparation process. The tetraphosphate was stable and did not decompose at room temperature (10 to 30 °C). Metal tetraphosphates were obtained by adding metal chlorides to the tetraphosphate solution mentioned above. The metal (calcium, strontium and barium) tetraphosphates were amorphous and not stable at room temperature. They decomposed to phosphates with shorter chain lengths at a temperature higher than room temperature.

(2) PREPARATION OF HEXAPHOSPHATE

Preparation of hexaphosphate was examined by hydrolysis of lithium cyclo-hexaphosphate dihydrate in strongly basic solutions and the most preferable result was obtained by the hydrolysis in 10M-NaOH solution...
at -7 °C and the result is shown in Table 2. The highest hexaphosphate content of about 70 P% was obtained under the reaction condition. Amorphous sodium hexaphosphate was prepared from the resulting hydrolysis solution by cooling the solution with ice, neutralizing with hydrochloric acid and then adding methanol. The sodium hexaphosphate was not stable and decomposed to phosphates with shorter chain lengths at room temperature.

**TABLE II Hydrolysis of cyclo-hexaphosphate in 10M-NaOH solution at -7 °C.**

<table>
<thead>
<tr>
<th>Reaction Time (h)</th>
<th>Phosphates (P%)</th>
<th>Cyclo-hexa</th>
<th>Hexa</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.5</td>
<td>73.5</td>
<td>23.2</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>6.5</td>
<td>59.0</td>
<td>37.2</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>13.5</td>
<td>36.2</td>
<td>58.0</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td>22.2</td>
<td>66.7</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>28.0</td>
<td>10.7</td>
<td>69.7</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td>32.0</td>
<td>8.1</td>
<td>67.4</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>42.0</td>
<td>4.6</td>
<td>63.4</td>
<td>32.0</td>
<td></td>
</tr>
</tbody>
</table>

Stable and crystalline hexaphosphate, (NH₄)₆P₆O₁₉ - 2H₂O, was prepared by dissolving the sodium hexaphosphate in water, removing sodium ion by passing the solution through a column filled with cation-exchange resin, putting the resulting solution into concentrated ammonia water and then adding enough ethanol to the solution to produce precipitate.

(3) PREPARATION OF OCTAPHOSPHATE

Preparation of octaphosphate was tried by hydrolyzing cyclo-octaphosphate in 10M-KOH solution. Phosphate composition in the hydrolysis solution is shown in Table 3. According to the result, the highest octaphosphate content of almost 60 P% was obtained under the reaction condition. Isolation of octaphosphate from the hydrolysais solution has been examined by the present author’s group, but stable and crystalline octaphosphate is not isolated yet.

**TABLE III Hydrolysis of cyclo-octaphosphate in 10M-KOH solution at 0 °C.**

<table>
<thead>
<tr>
<th>Reaction Time (h)</th>
<th>Phosphates (P%)</th>
<th>Cyclo-octa</th>
<th>Octa</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>66.9</td>
<td>25.2</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>55.6</td>
<td>29.6</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>43.4</td>
<td>38.7</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>30.2</td>
<td>50.3</td>
<td>19.5</td>
<td></td>
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<td>24</td>
<td>20.3</td>
<td>59.5</td>
<td>20.2</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>17.3</td>
<td>57.3</td>
<td>27.0</td>
<td></td>
</tr>
</tbody>
</table>

PREPARATION OF AMMONIUM POLY-PHOSPHATE AND ITS USE AS FLAME RETARDANTS

Ammonium polyphosphate (APP) has six crystal phases of I to VI. XRD diagrams of the crystal phases are shown in Fig. 1. Phase I can most easily be prepared and other phases need sophisticated process to prepare, especially under...
large scale production in a factory. Modification of heating process of APP for the preparation in a large scale would be useful in commercial treatment for the production, and present author and coworkers modified the heating process for preparation of APP phases II, V and VI by using soft and easy reaction system.

(1) PREPARATION OF APP PHASE II

According to description about the transition of APP phase I to II, the following transition mechanism was proposed.\textsuperscript{14,15}

\[
\text{APP phase I } \rightarrow \text{Amorphous APP} \\
\text{Step I } \rightarrow \text{APP phase II} \\
\text{Step II}
\]

The phase transition process of I to II requires sophisticated process and direct preparation of APP phase II needed a lot amounts of diphosphorus pentaoxide. Diphosphorus pentaoxide is expensive and chemically active materials. Much easier direct preparation process of phase II APP without diphosphorus pentaoxide was successfully achieved by heating a mixture of ammonium orthophosphate and urea under wet ammonia. Desirable reaction conditions are as follows:

a. Preferable ammonium orthophosphate, diammonium hydrogen orthophosphate;

b. Mixing molar ratio of diammonium hydrogen orthophosphate to urea, 1/3 to 1/4;

c. Mixing weight ratio of APP phase II to raw material as an additive, larger than 1/15;

d. Heating temperature, 280 to 305 °C;

e. Heating time for total raw-materials amount of about 1 g, longer than 0.5 h;

f. Concentration of aqueous ammonia, 1 to 8%. Average particle size of the phase II APP prepared according to the process was about 7 to 10 µm.

(2) PREPARATION OF APP PHASE V

Preparation process of phase V APP written in a previous paper is not useful to a large scale production in a factory.\textsuperscript{12} Present author tried to develop a new, easy and useful process for production of phase V APP by using an usual heating process from the ammonium orthophosphate–urea system. The reaction system is advantageous in commercial base. The following reaction conditions were obtained for the preparation of phase V APP in a high quality:

a. Preferable ammonium orthophosphate, diammonium hydrogen orthophosphate;

b. Mixing molar ratio of diammonium hydrogen orthophosphate to urea, 1/4 to 1/5;

c. Heating temperature, 340 to 350 °C;

d. Heating time for total raw-materials amount of about 1 g, longer than 1 h;

e. Atmospheric condition, wet ammonia gas which was prepared by passing ammonia gas through concentrated aqueous ammnia.

Average particle size of the phase V APP obtained by the process was about 4 µm.

(3) PREPARATION OF APP PHASE VI

According to a previous paper,\textsuperscript{13} phase VI APP was obtained by heating phase V APP at 340 to 350 °C at 1 atm of ammonia pressure. Present author tried to develop a direct production of phase VI APP from the system of phosphorus pentaoxide–urea. New production process was successfully developed. The following reaction conditions were obtained to have a good result:
a. Molar mixing ratio, phosphorus pentaoxide to urea=1/2 to 1/3;
b. Heating temperature, 250 to 290 °C;
c. Heating time for total raw-materials amount of about 1 g, around 1h;
d. Atmospheric condition, under air or wet ammonia gas which was prepared by passing air through ammonia water with concentration less than 10%.

Average particle size of the phase VI APP prepared by the process was about 2 µm and the particle had very small size.

(4) FLAME RETARDATION EFFECT OF APP

APP phases I and VI have relatively high solubility to water, and phases II and V are hardly soluble in water. Water soluble additives in organic polymer materials usually show unfavorable bleeding property. Accordingly, APP phases II and V are better flame retardation additives than I and VI to organic materials. Flame retardation effect of APP phases II and V was examined and the result is shown in Table 3. Average particle size of APP phases II and V tested in this experiment was 12.6 and 30 µm, respectively. APP phases II and V showed flame retardation effect to PE and PP. The effect was higher to PP than to PE, and phase V showed a larger oxygen index than phase II.

PROTON CONDUCTIVE PHOSPHATE GLASS

From environmental view point, energy resource should be transferred to clean substances from fossil fuel in the near future, because fossil fuel is producing air pollution and the problem is considered now to be very serious. Hydrogen is a very clean energy resource because the substance produces only water when it is used as fuel. Accordingly, hydrogen would be one of the most important substances as fuel in the world to build up sustainable society.

Recently, it is very much interested to develop a fuel cell because the cell can produce electric power from chemical reaction energy of the following reaction:

\[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \]

The cell device needs proton-conductive substances to produce electric power from the cell according to the above chemical reaction. There are several types of fuel cell shown in Table 4. Among these fuel cells, polymer electrolyte and solid-oxide electrolyte types would be in the most developed step and in the very near future, they would be in commercial treatment.

<table>
<thead>
<tr>
<th>Type</th>
<th>PAFC</th>
<th>AFC</th>
<th>MCFC</th>
<th>SOFC</th>
<th>PEFC</th>
<th>PGFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Phosphoric</td>
<td>Acid</td>
<td>Aqueous</td>
<td>Molten</td>
<td>ZrO₂-</td>
<td>Polymer</td>
</tr>
<tr>
<td>Carrier</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>Co³⁺</td>
<td>O²⁻</td>
<td>H⁺</td>
<td>H⁺</td>
</tr>
<tr>
<td>Temp.(°C)</td>
<td>180~220</td>
<td>5~240</td>
<td>600~700</td>
<td>800~1000</td>
<td>60~80</td>
<td>150~400</td>
</tr>
<tr>
<td>Step</td>
<td>Comm.</td>
<td>Proof</td>
<td>Proof</td>
<td>Comm.</td>
<td>Basic</td>
<td></td>
</tr>
</tbody>
</table>

PAFC, AFC, MCFC, SOFC, PEFC and PGFC stand for phosphoric acid fuel cell, alkaline fuel cell, molten carbonate fuel cell, solid oxide fuel cell, polymer electrolyte fuel cell and phosphate glass fuel cell, respectively. Working temperature of polymer electrolyte and solid-oxide electrolyte type fuel cells is lower than 100 and higher than 800 °C, respectively. In the sense of a facility of home usage, co-generation system is desired to

Review

maintain high-level energy efficiency. According to the idea, the most desirable working temperature of a fuel cell in home usage would be 200–400°C. Recently, studies on solid electrolytes which can act as a proton-conductive electrolyte at a moderately high temperature are developing on some substances.  

By the way, it has been believed for a long time that proton conduction in glass is impossible. Abe and his coworkers published their first paper on proton conduction in glass in 1982 and after that, they published several important papers on proton conduction in phosphate glasses.  

They found phosphate glass having 10^{-2} S/cm order of proton conductivity, but the glass was very unstable under usual atmospheric condition and changed to liquid phase with adsorption of water vapor in air. If it is possible to prepare stable phosphate glass, it is very useful to use the glass as a solid electrolyte, because the glass can easily be prepared with a low cost and also glass is easy to form any shapes of large plates, thin films, etc. In this paper, some stable phosphate glasses having proton-conductive property will be written.

Glasses were prepared by mixing a mixture of \( \text{La}_2\text{O}_3 \), \( \text{SrO} \) and phosphoric acid with molar ratios of 70\( \text{P}_2\text{O}_5 \)-20\( \text{SrO} \)-3\( \text{La}_2\text{O}_3 \), 70\( \text{P}_2\text{O}_5 \)-20\( \text{SrO} \)-5\( \text{La}_2\text{O}_3 \) and 70\( \text{P}_2\text{O}_5 \)-20\( \text{SrO} \)-7\( \text{La}_2\text{O}_3 \) for 60 min by automatic mill, heating the mixture in a platinum crucible at 900°C for 10 min, pouring the melt into a glass-tube cast with diameter of 17 mm, annealing it in a furnace with 250°C, and then cooling to room temperature by putting off a power source of the furnace. A phosphate-glass sample was taken out by breaking the glass-tube cast. A specimen of the glass disc (17 mm of diameter and 1mm of thickness) was cut from the phosphate-glass block and the surface of the specimen was polished. Thin gold film was sputtered onto the surface of the sample to avoid surface conduction due to water in ambient atmosphere. Conductivity of the phosphate-glass sample was measured by alternative-current (ac) method with an LCR meter in frequency range from 42 Hz to 5 MHz, over a temperature range from 200 to 470°C. Direct-current (dc) conductivity was evaluated from the Cole-Cole plot assuming an RC parallel circuit for the specimen. Conductivity of the phosphate glasses is shown in Fig. 2. According to the result, conductivity of the glasses increased with increasing temperature and the highest conductivity.
conductivity was obtained for the glass of 70P_2O_5-20SrO-3La_2O_3 system and was order of 10^{-4} S/cm at about 450 °C. All the glass systems exhibited similar activation energy of about 91 to 94 kJ/mol. The glass having the system of 70P_2O_5-20SrO-3La_2O_3 was not stable and broken in a few days under an usual atmospheric condition.

REFERENCES