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Carbothermic Reduction of Phosphoric Acid Extracted from Dephosphorization Slags to Produce Yellow Phosphorus

Ryoko Yoshida, Jyunpei Yoshida, Hua Fang Yu, Yasushi Sasaki, Tetsuya Nagasaka

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Abstract—Phosphorous is an important element for agriculture and industry and is a non-renewable resource. Especially, yellow phosphorus is an essential material in advanced industrial technology, but phosphorus resources were not produced in Japan at all, and all depend on imports. It has been suggested, however, that the remaining accessible reserves of phosphate ore will be depleted within 50 years. Therefore, alternative resources for phosphate ore must be found. In this research, we have developed a process that enables the production of high-purity yellow phosphorus from domestic unused phosphorus resources such as steelmaking slags. The process consists of two parts: (1) the production of crude phosphoric acid from wastes such as steelmaking slag; (2) producing high-purity yellow phosphorus by low-temperature carbothermic reduction of phosphoric acid (H_3PO_4). The details of the carbothermic reduction of phosphoric acid are presented in this paper. Yellow phosphorus is commercially produced by carbothermic reduction of phosphate ore in an electric arc furnace at more than 1673K. In the newly developed system, gaseous P_4O_{10} evaporated from H_3PO_4 is successfully reduced to yellow phosphorus by using carbon packed bed at less than 1273K. To meet the depletion of phosphate ore, the proposed process in this study to produce yellow phosphorus by carbothermic reduction of H_3PO_4 that are extracted from dephosphorization slags will be one of the effective and economical solutions.

Keywords—Carbothermic reduction, dephosphorization slags, phosphoric acid, yellow phosphorus.

I. INTRODUCTION

PHOSPHORUS is an essential element in food production [1], [2]. Phosphorus is also used as an important material in a wide range of industrial fields such as an electronic component (semiconductor GaP, secondary battery cathode material, etc.), automobiles (steel plate surface treatment liquid and secondary battery electrolyte), pharmaceuticals (osteoporosis treatment), and plastics. After World War II, humans have rapidly consumed phosphorus ore resources for fertilizer to produce food, so the depletion of phosphate ore with high quality and easy to mine is rapidly progressing [2].

As already mentioned, yellow phosphorus is critically important to produce sophisticated industrial products such as semiconductor electronic parts and pharmaceuticals. With existing technology, about 300 million kWh of electricity is required to produce about 20,000 tons of yellow phosphorus that Japan consumes annually. The huge electrical demand is simply due to the high-temperature reduction of phosphate ore at about more than 1673K. Due to this huge energy consumption, current yellow phosphorus producing countries are limited to China, the United States, Kazakhstan, and Vietnam. After the United State banned the export yellow phosphorus as a strategic commodity from 1996, other yellow phosphorus producing countries also limited their export. Thus, Japan's imports of phosphorus ore, as well as yellow phosphorus, are becoming increasingly severe year by year. Fig. 1 shows the material flow of phosphorus in Japan (2014).

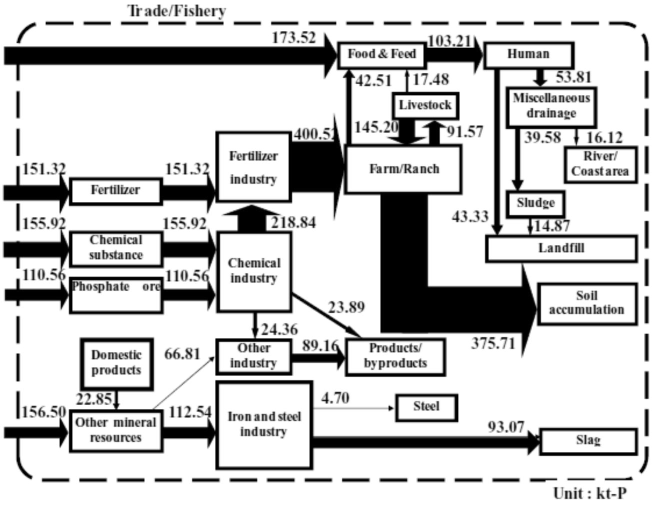

Fig. 1 Material flow of phosphorus in Japan (2014)

As shown in Fig. 1, the phosphorus of 110.5 kt as phosphorus ore is imported, and the comparable amount of phosphorus (93.07 kt) is accumulated in steel slag. Namely, the amount of phosphorus in phosphate ore is almost comparable to that in the imported iron ore. Thus, the exploitation of steel slags [3]-[11] and sewage sludge [12], [13] as a phosphorus secondary resource and are an emerging research project and many studies have been carried out now. Phosphorus extraction from slags as crude H_3PO_4 has been extensively studied and the details of the results are found elsewhere [3]-[11]. As already mentioned, all of the yellow phosphorus is imported in Japan. Thus, if yellow phosphorus is also possibly produced from steelmaking slags, it is a great benefit. Thus, the investigation to develop a new

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R. Yoshida, H. Yu, and T. Nagasaka are with the School of Engineering, Tohoku University, Sendai, 980-8579 Japan (e-mail: ryoko.yoshida.r2@dc.tohoku.ac.jp, yuhuafang1012@gmail.com, tetsuya.nagasaka.d3@tohoku.ac.jp).

J. Yoshida is with Honda Motors (e-mail: junmoomin@gmail.com).

Sasaki is with the School of Engineering, Tohoku University, Sendai, 980-8579 Japan (corresponding author, phone: +81-22-795-7305; fax: +81-22-795-7305; e-mail: yaz@tohoku.ac.jp).

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economical process to produce yellow phosphorus by the reduction of crude H_3PO_4 extracted from slags has been carried out to replace the current production one. However, yellow phosphorus production form H_3PO_4 has not yet been studied. The aim of this study is to confirm the feasibility of the yellow phosphorus production by low-temperature carbothermic reduction of phosphoric acid (H_3PO_4) with reasonable reaction rates.

II. EXPERIMENTAL

A. Apparatus

The experimental system for the reduction is schematically shown in Fig. 2. It is composed of a reactor, a yellow phosphorus water bath trap, a silica gel tube for dehydration of exhaust gas, and a gas flow meter.

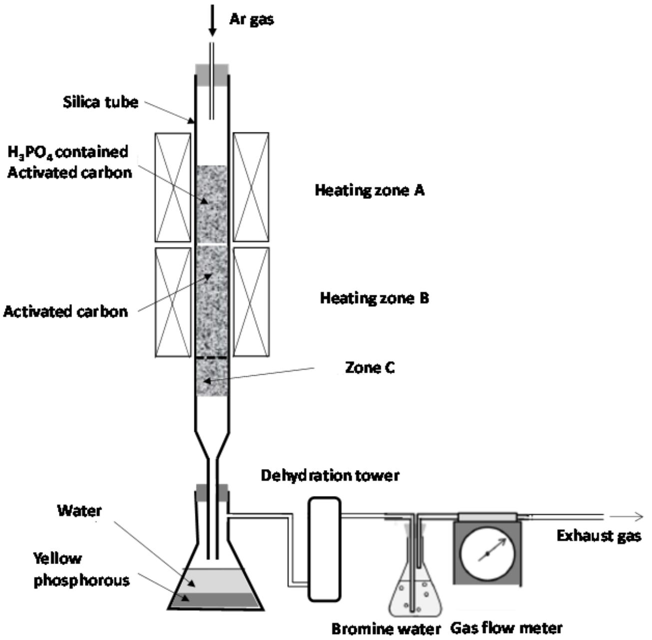

Fig. 2 Schematic of the reacting system

The vertical electric furnace is composed of two heating parts with a length of 30 cm that can control the temperatures independently. Each heating unit corresponds to (1) a heating unit for vaporizing phosphoric acid, and (2) a heating unit for the reduction of vaporized phosphorus compounds. As a reactor, a quartz reaction tube (inner diameter: 32 mm, length: 1200 mm) was used. The lower end of the tube was connected to a thin quartz tube.

In the reactor quartz tube, activated carbon as a reducing agent was filled to a length of about 40 cm. The activated carbon was almost spherical and the diameter is about 2-5 mm. The upper 30 cm of the packed bed was placed in the heating region B, and the lower 10 cm of the packed bed (zone C) was placed outside the heated part B. The role of zone C is to enhance the collisions among P_4 gas molecules to produce liquid yellow phosphorus. The region A above the packed bed in region B was filled with phosphoric acid-containing activated carbon with a height of about 15 cm. Phosphoric acid (H_3PO_4) is a chemical agent grade and it contains about 15% water. Phosphoric acid-containing activated carbon was prepared by immersing phosphoric acid in activated carbon.

For the purpose of recovering the produced gaseous yellow phosphorus as a liquid, a thin quartz tube at the lower end of the quartz tube was placed in a flask filled with hot water (343K) and the gas mixture was bubbled into the flask to collect the gaseous yellow phosphorus as a liquid yellow phosphorous. The melting point of yellow phosphorus is 317.3K. To avoid the escape of gaseous yellow phosphorus from the flask, the discharged gas was further bubbled into another flask filled with bromine water to trap and completely remove yellow phosphorus. The exhaust gas discharged from the second flask was passed through a dehydration tube filled with silica gel, and then the total flow rate of exhaust gas was measured every minute using a gas flow meter.

B. Procedure

Initially, the air in the system is replaced by introducing Ar with a flow rate of 20 cm^3/min, and then the temperature of the reduction reaction zone B filled with activated carbon was raised to 1273K. When the temperature reached 1273K, the temperature of region A in which the phosphoric acid-containing activated carbon was found to increase to about 573K, even without power input at that zone. In the temperature raising process, the outlet gas flow rate was continuously measured with the flow meter.

Through the preliminary experiments, it was found that unreacted phosphorous compounds adhered to the reactor wall when the total flow rate exceeded more than 200 cm^3/min. Therefore, to avoid the unreacted phosphorous compounds, the temperature of zone A was carefully raised manually by keeping the exhaust gas flow rate below 200 cm^3/min up to 973K. After that temperature, the unreacted phosphorous compounds were not observed, even though the outlet gas flow rates exceeded more than 200 cm^3/min.

When the temperature of region A reaches about 773K, it was observed that droplets started to adhere to the wall surface of the lower part of the quartz tube and, they coalesced and trickled down along the wall surface of the quartz tube and captured in the flask.

After 5 hours, the power was turned off in region A and region B, and the experiment was terminated. After the furnace temperature reached room temperature, the samples collected in the flask were analyzed by Raman spectroscopy. In this study, gaseous phosphorus oxide existed in the packed bed and yellow phosphorus is presented by P_4 and P_4O_{10}, respectively.

III. RESULTS AND DISCUSSION

A. Vaporization Behavior of H_3PO_4

The details of H_3PO_4 vaporization behavior was not well known. The vaporization behavior of H_3PO_4 with temperature was studied by using thermogravimetric analysis (TGA). The TGA result is shown in Fig.3. In the figure, four inflection points indicated from (1) to (4) were observed.

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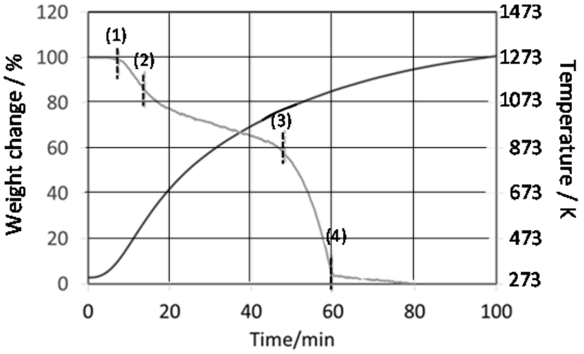

Fig. 3 Change in weight of phosphoric acid by heating

The thermodynamic study of H_3PO_4 vaporization behavior was studied by [14]. The modified temperature-composition diagram for the system P_4O_{10}-H_2O based on their result [14] was presented as Fig. 4. The relationship indicates that the system is azeotropic and that a composition containing about 92% P_4O_{10} has the highest boiling point (1139K) in the P_4O_{10}-H_2O system. Namely, all of the polyphosphoric acids can be vaporized at more than 1139K. In the figure, the point A, point B, and point C correspond to H_3PO_4 (P_4O_{10}: 72.4 %), $H_4P_2O_7$ (P_4O_{10}: 79.7 %), HPO_3 (P_4O_{10}: 88.8 %), respectively.

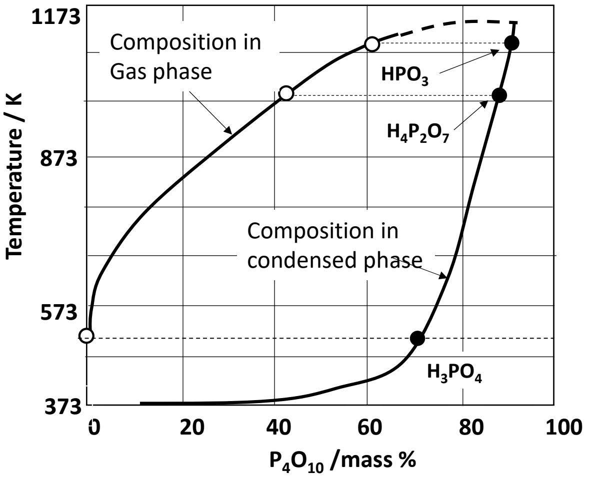

Fig. 4 Temperature-composition diagram for the system P_4O_{10}-H_2O

From the weight decrease and results shown in Fig. 3, the inflection points of (2) and (3) can correspond to the formation of H_3PO_4 and HPO_3, respectively. Based on these, the TGA result can be interpreted as follows: after reaching the boiling point of water, the weight rapidly decreased due to the water boiling (point 1). Water evaporation continued to form pure H_3PO_4 at about 573K (point 2). At point 2, the water in the solution was all evaporated. After this, water removal was driven by the condensation or polymerization of phosphoric acid. Namely, the polyphosphoric acid formation will start. The dehydration continues with temperature and HPO_3 (point 3) was formed at about 1023K via the formation of $H_4P_2O_7$. At more than 1139K, the condensed phase composition is close to P_4O_{10} and P_4O_{10} will vaporize rapidly, almost all of them were vaporized at point 4.

B. Carbothermic Reduction of H_3PO_4

Typical results of the temperature changes of heating zone A and the exhaust gas flow rate with time during the reduction of H_3PO_4 are shown in Fig. 5. The total weight of H_3PO_4 (15% H_2O) in the activated carbon (20 g) was about 40 g. The total amount of carbon packed in the reduction zone is about 70 g. The reduction temperature (heating zone B) was 1273K. Ar with a flow rate of 20 cm^3/min was always supplied during the experiment to transport the evaporated P_4O_{10} (g) and H_2O (g) from zone A to the reduction zone B.

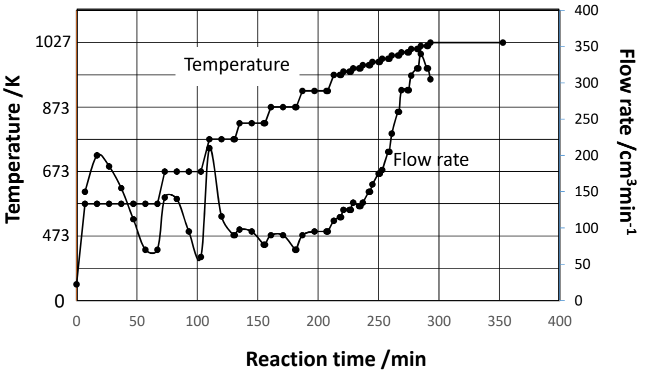

Fig. 5 The variation of temperature at zone A, and the total exhaust gas flow rate as a function of time

The exhaust gas flow rate is supposed to practically reflect the overall reaction rates. The exhaust gas flow rate fluctuated at less than 673K. This is simply due to the difficulty of temperature control at this temperature range. As already mentioned, the unreacted phosphorous compounds adhered to the reactor wall when the total flow rate exceeded more than 200 cm^3/min. Therefore, the exhaust gas flow rate was carefully controlled by manually adjusting the temperature of zone A up to 973K. This manually adjusting is the reason for the fluctuation at a lower temperature range. After reaching 973K, the unreacted phosphorous compounds were not observed even the outlet gas flow rates excessed over more than 200 cm^3/min.

From Fig. 5, the exhaust gas flow rate started to increase rapidly after the zone A temperature reached around 1100K. This increase is simply due to the increase of the P_4O_{10} supply rate since P_4O_{10} vaporizes rapidly at more than 1139K as shown in Fig. 4. The gas flow rate gradually decreased since the P_4O_{10} supply rate decreased after reaching to 973K.

The collected sample in the flask was analyzed by Raman spectroscopy. The measured spectra and standard spectra of yellow phosphorus [15] were shown in Fig. 6. All the peaks well correspond to these standard yellow phosphorus. Thus, the sample produced in the present study was confirmed to be yellow phosphorus.

Generally, the recovery rate of yellow phosphorus is around 50% evaluated from the weigh difference between supplied H_3PO_4 and formed P_4. The produced yellow phosphorus was shown in Fig. 7. The spherical parts and those accumulated at the bottom are yellow phosphorus.

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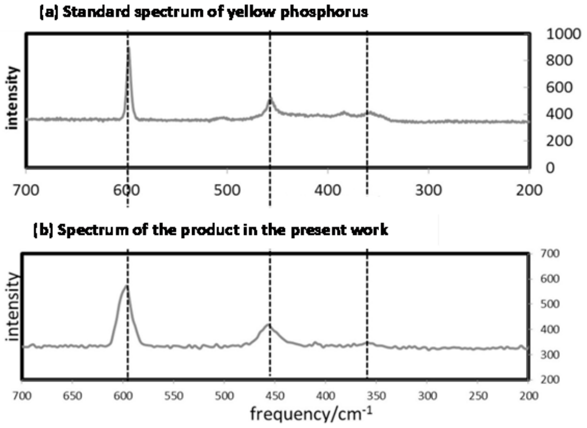

Fig. 6 Comparison of Raman spectra of (a) the yellow phosphorus standard sample, (b) obtained sample in the present study

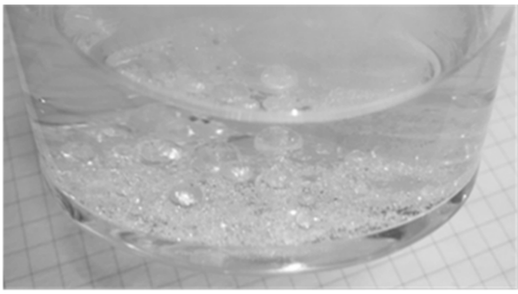

Fig. 7 Overview photo of the generated yellow phosphorus

In the present work, the feasibility of the production of yellow phosphorus by carbothermic reduction of H_3PO_4 was confirmed. For the implementation of this process, however, further investigations, especially the quantitative kinetics approach, are certainly required.

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