Synthesis of tetrakis (hydroxymethyl) phosphonium chloride by high-concentration phosphine in industrial off-gas

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ABSTRACT

With increasing consumption of phosphate rock and acceleration of global phosphate production, the shortage of phosphate resources is increasing with the development and utilization of phosphate. China’s Ministry of Land and Resources has classified phosphate as a mineral that cannot meet China’s growing demand for phosphate rock in 2010. The phosphorus chemical industry is one of the important economic pillars for Yunnan province. Yellow phosphorus production in enterprises has led to a significant increase in the amount of phosphorus sludge. This paper focuses on phosphine generation in the process of phosphoric sludge utilization, where the flame retardant tetrakis (hydroxymethyl) phosphonium chloride (THPC) is synthesized by high concentrations of phosphine. The optimum conditions are determined at a space velocity of 150 h⁻¹, a reaction temperature of 60°C, 0.75 g of catalyst, and a ratio of raw materials of 4:1. Because of the catalytic oxidation of copper chloride (CuCl₂), the synthesis of THPC was accelerated significantly. In conclusion, THPC can be efficiently synthesized under optimal conditions and with CuCl₂ as a catalyst.

Key words | liquid-phase catalysis, phosphine, phosphoric sludge, tetrakis (hydroxymethyl) phosphonium chloride

INTRODUCTION

Yunnan province is one of the world’s major yellow phosphorus production areas, where the reserves of phosphate rock are the greatest in China (Chen 2006; Shi et al. 2009). Although the yellow phosphorus industry contributes significantly to the economic development in China, the economic efficiency is still lower than in other countries (Zhang et al. 2008). Reserves of phosphate rock in Yunnan reached 3.826 billion tonnes by the end of 2005, when the basic reserves reached 849 million tonnes, and the amount of resources reached 2.977 billion tonnes (Bai 2009). Yellow phosphorus production in Yunnan occupies an eminent position in the world phosphorus industry (Huang et al. 2009). Phosphoric sludge produced in the phosphorus industry is a hazardous phosphorus mix (Gao et al. 2008); however, owing to the high content of yellow phosphorus in phosphoric sludge (Anazia et al. 1992), efficient recovery of the yellow phosphorus from the phosphoric sludge is a crucial issue.

Phosphoric sludge exposed to air produces combustion phenomenon and the highly toxic gas phosphine, which leads to serious environmental and public health impacts (Wei et al. 2011). Reasonable treatment of phosphoric sludge is a major issue facing the yellow phosphorus industry (Bessarabov et al. 2010). The main disposal of phosphoric sludge consists of production of dibasic lead phosphate (I) (Aganina et al. 1998), preparing phosphoric acid by incineration (Ma 2009), ceramsite production (Shchepochkina 2008), stockpiling (Huang et al. 2009), etc. Because of the shortcomings of control technology, a method of changing phosphoric sludge to sodium hypophosphite has been found (Bessarabov et al. 2009); however, higher levels of phosphine are produced from the process.

Tetrakis (hydroxymethyl) phosphonium chloride (THPC) has been widely used as a precursor to fire-retardant materials. In this work, we used a copper chloride (CuCl₂) catalyst to catalyse and oxidize phosphine generated in the
phosphoric sludge to prepare THPC. Because the catalyst is not used in traditional THPC industries, the conversion rate of phosphine is low. The catalyst helps efficient preparation of flame retardants, so a CuCl₂ catalyst was used, and optimum conditions were obtained to dispose of the phosphine emissions harmlessly. In addition, the utilization of high-efficiency exhaust gas also improved the comprehensive utilization rate of phosphorus resources.

**METHODS**

**THPC preparation**

The process for the production of sodium hypophosphite from phosphoric sludge has been developed effectively and economically (Bessarabov et al. 2010; Tovazhnyansky et al. 2010). Our previous studies (Huang et al. 2009; Wei et al. 2011) showed that the highest conversion rate of sodium hypophosphite was obtained under the conditions of 100% nitrogen (N₂), 20 mL min⁻¹ flow rate, 110:1 water/phosphorus ratio, 3.6:1 alkaline/phosphorus ratio, and a reaction temperature of 85°C. Phosphine generation under these conditions was used to produce a reaction of phosphine. In this study, N₂ carrier gas was passed through the reactor and well mixed with phosphine in the buffer bottle to transport phosphine. A flowmeter was used to adjust and measure the flow of N₂. Solid particles and other impurities were removed in a gas washing bottle using concentrated phosphoric acid. THPC was generated by the reaction of phosphine with hydrochloric acid (HCl) and formaldehyde (HCHO) in a bubble absorption bottle. Exhaust gas was absorbed in concentrated sulphuric acid, and ultimately discharged into the air. The concentration of phosphine was analysed by phosphine detection tubes at A and B sampling points. The phosphine concentration before THPC reaction ranged from 5,000 to 150,000 ppm, and synthesis of flame-retardant THPC in the bubble absorption bottle was conducted as shown in Figure 1. The equation for the reaction is given in Equation (1):

\[
4\text{HCHO} + \text{HCl} + \text{PH}_3 \xrightarrow{\text{CuCl}_2} \text{(HOCH}_2)_4\text{PCl}
\]  

(1)

THPC was obtained through the reaction of HCl and HCHO in the presence of phosphine gas by delivery of N₂. A THPC synthesis experiment investigated the effects of the amount of catalyst and space velocity (SV), the reaction temperature, the amount of catalyst, and the ratio of raw materials on the synthesis reaction.

**Analytical methods**

Composition and content of the catalyst after the synthetic experiments were determined by X-ray diffraction (XRD) analysis, which was completed in the Analytic and Testing Research Institute of Yunnan. XRD was carried out on a diffractometer (Rigaku D/MAX-2200 Ultima). The XRD patterns were obtained with CuKα radiation (\(\lambda = 0.154056 \text{ nm}\)) operating at an X-ray tube voltage and a tube current of 40 kV and 20 mA, respectively. Diffraction patterns were recorded in the range from 10 to 80° (2θ) at a scanning rate of 4°/min. The catalyst samples were analysed under the same experimental conditions.

**RESULTS AND DISCUSSION**

**Effect of preparation conditions on synthesis of THPC**

This study analysed factors that influence the conversion tests. Temperature has a definite impact on the rate of a chemical reaction, and can accelerate or reduce the conversion rate of phosphine. The synthesis of THPC is an endothermic reaction, so this reaction can be controlled by a constant temperature water bath to determine the optimal conditions. Temperature, SV, the ratio of raw materials, and the amount of catalyst influence the catalytic reactions. By controlling the conditions of SV, reaction temperature, amount of catalyst, and ratio of raw materials, optimal synthesis conditions of liquid-phase catalytic oxidation of phosphine for preparation of THPC were achieved.

**Effects of amount of catalyst**

The amount of catalyst has a significant effect on the catalyst performance, and the optimal amount of catalyst can
obviously enhance the catalytic activity. The optimal amounts of catalyst were selected by the conversion rate of phosphine. In this study we investigated the effects of the amount of catalyst at 0.01, 0.25, 0.5, 0.75, and 1 g, corresponding to selecting the optimum amount of catalyst. The effects of catalyst amount are shown in Figure 2.

Figure 2 shows that when the optimum amount of catalyst is 0.75 g, the highest conversion rate of phosphine (95.3%) can be obtained; the conversion rate of phosphine decreases dramatically when the catalyst amount is less than 0.75 g. With 1 g of catalyst, the conversion rate of phosphine decreased to a minimum of 84%. Consequently, when the amount of catalyst is 0.75 g, it is most favourable for the liquid-phase catalytic oxidation of phosphine. In fact, excess CuCl₂ reduces the effective concentration of Cu (I) in the reaction, and late-stage study indicates that Cu (I) would act as a catalyst in the reaction. This is the main reason for reducing the conversion rate of phosphine.

**Effects of ratio of raw materials**

The ratio of raw materials has a direct influence on the preparation of THPC. It is commonly adopted in industrial production of THPC at a ratio of 4–5:1 (HCHO/HCl), which is of great significance to the conversion rate of phosphine.

As shown in Figure 3, the conversion rate of the phosphine was considerably improved at an \( n(\text{HCHO})/n(\text{HCl}) \) ratio of 4:1, which is higher than other levels. When the ratios are 4.25:1, 4.5:1, and 5:1, the conversion efficiency of phosphine is also similar to a conversion rate of phosphine of 83–87%. Hence, the excess of HCHO is not conducive to THPC synthesis. Greater amounts of HCHO hinder the synthesis of flame retardants. Therefore, the optimum ratio of HCHO/HCl is 4:1.

**Effects of airspeed**

Product output of the reaction was affected directly by the SV. Production capacity reduces at low SV, and increased air speed reduces the residence time of the gas in the catalysis reaction system, resulting in a low product synthesis rate and consumption of high energy. It is therefore important to select the appropriate SV.

In this study, the flowmeter was used to precisely control SV. The result is shown in Figure 4. From this figure,
it can be seen that the conversion rate of phosphine was only 80.0–82.0% at an SV of 50 h\(^{-1}\). The conversion rate of phosphine is increased dramatically when the SV increases. The conversion rates of the phosphine were 89.5–91.3% and 92–93.5% at SVs of 100 and 150 h\(^{-1}\), respectively. The conversion rate of phosphine decreased when the SV continued to increase. The lowest conversion rate of phosphine was obtained at an SV of 250 h\(^{-1}\). This is because the amounts of phosphine gas per unit time improved with a gradual increase of SV, so the conversion rate of the phosphine was rising. At the same time, owing to the production of more energy to meet the increasing demand for the SV, the heat in the system taken away by the phosphine gas increased correspondingly. When the heat taken away from the phosphine gas was higher than the heat of reaction, the temperature of the catalyst reduced the effect on the preparation process of THPC. Therefore, a suitable SV should be 150 h\(^{-1}\).

Effects of reaction temperature

Temperature is an important factor that affects the rate of chemical reactions (Hu et al. 2012). The conversion rate of phosphine was investigated at 45, 50, 55, 60, and 65 °C under the conditions of a ratio of raw materials 4:1, an SV of 150 h\(^{-1}\), an amount of catalyst of 0.75 g, and a reaction time of 2 h. The result is shown in Figure 5.

It can be seen from Figure 5 that the conversion rate of phosphine gradually increased with increasing reaction temperature; the highest conversion rate of phosphine was 91–93.7% at 60 °C. This shows that heating-up is conducive to the preparation of THPC. The highest conversion rate of phosphine was obtained when the temperature reached the optimal value at 60 °C.

XRD analysis

According to the results of catalyst-phase analysis by XRD, it was found that the catalyst comprised CuCl, copper (I) oxide (Cu\(_2\)O), copper (II) oxide (CuO), and C\(_x\)H\(_y\)O\(_z\). The quantitative analysis of XRD was conducted by analysing and calculating the height of the strongest peak in the diffraction pattern (Wei et al. 2012). Accurate amounts of the respective substances in the catalyst samples were determined and are shown in Table 1.

The results show that the catalyst sample was dominated mainly by CuCl and C\(_x\)H\(_y\)O\(_z\), and a small amount of Cu\(_2\)O and CuO. As shown in Figure 6, the strongest diffraction peaks of CuCl, Cu\(_2\)O, and CuO appear at 28.5°, 34.32°, and 35.78°, respectively.

Catalyst composition was almost the same, but owing to the different operating conditions of the reaction, the catalyst content in the reaction system fluctuates slightly. Cu\(^+\) was produced under catalytic conditions, it generated Cu\(_2\)O, and the specified content of Cu\(_2\)O in the catalyst was obtained. The study shows that Cu (I) comes from Cu (II), and that Cu (II) plays a significant role in the catalytic oxidation of phosphine.

CONCLUSIONS

This study examined the effect of parameters on the process of THPC preparation on the conversion rate of phosphine under various operating conditions. The optimum conditions for synthesis of THPC were found at an SV of 150 h\(^{-1}\), a reaction temperature of 60 °C, an amount of catalyst of 0.75 g, and a ratio of raw materials of 4:1. The XRD result showed that the catalyst samples under different conditions contained large amounts of CuCl\(_2\). Owing to the catalytic oxidation of CuCl\(_2\) to accelerate the synthesis of THPC, the conversion rate of

<table>
<thead>
<tr>
<th>Sample</th>
<th>CuCl (%)</th>
<th>Cu(_2)O (%)</th>
<th>CuO (%)</th>
<th>C(_x)H(_y)O(_z) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30.9</td>
<td>6.7</td>
<td>0.8</td>
<td>61.6</td>
</tr>
<tr>
<td>B</td>
<td>19.8</td>
<td>9.8</td>
<td>–</td>
<td>70.4</td>
</tr>
<tr>
<td>C</td>
<td>43.8</td>
<td>–</td>
<td>1.3</td>
<td>54.9</td>
</tr>
</tbody>
</table>
phosphine was significantly improved. Further studies should be directed towards a purification and pilot study of THPC. This research has significant theoretical and practical values in comprehensive utilization of phosphoric sludge and high concentrations of phosphine treatment in industrial emissions.

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REFERENCES


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