Preparation of Li$_2$PtO$_3$ and its dissolution properties in hydrochloric acid

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A double oxide containing Pt and Li, Li$_2$PtO$_3$, was prepared to search for an environment-friendly route to dissolve Pt in hydrochloric acid (HCl). Li$_2$PtO$_3$ powder was obtained by calcination of a mixture of Pt black and Li$_2$CO$_3$ powder at 600, 700 and 800°C. The resulting Li$_2$PtO$_3$ powder was soluble in HCl which has no oxidizing power at ambient temperatures. The Pt solubility of Li$_2$PtO$_3$ obtained at 600°C increased from 39.2 to 99.9% as the temperature of 12 M HCl increased from 40 to 80°C. From ultraviolet–visible absorption spectra, it was found that, a complex ion [PtCl$_6$]$^{2-}$ formed as a result of a reaction of Li$_2$PtO$_3$ with HCl. The dissolution process by way of this compound is expected to benefit the establishment of environment-friendly recovery process of Pt.

1. Introduction

The recovery of platinum group metals (PGMs) is an important issue in view of their economic importance and supply risks. In recovery processes for PGMs, dissolution is one of the key steps, because subsequent extraction and separation are performed in solution. To dissolve PGMs in the metallic state, a significant oxidizing agent, e.g. aqua regia is used frequently. In spite of its indispensable oxidizing power, aqua regia evolves toxic gases as follows: nitrosyl chloride (NOCl), chlorine (Cl$_2$), and nitrogen oxides (NOx). Therefore, it is desired to develop a recovery process using a cleaner alternative such as hydrochloric acid (HCl).

In recent years, the following complex oxides containing PGMs have been reported to be soluble in HCl: Ca$_4$PtO$_6$ and Ca$_2$Pt$_3$O$_7$-type multiple oxides. These complex oxides contain PGMs in the oxidation state, and this could be the reason why PGMs in these compounds can be dissolved in non-oxidative HCl. However, the fabrications of these PGM-containing complex oxides are complicated or need treatment at a high temperature. For example, Ca–Pt alloys were produced through a reaction between Pt and Ca vapor at 800–900°C for 3 h and they were further oxidized at 900°C for 24 h to obtain Ca$_5$Pt$_2$O$_9$. A heat treatment at 1525°C for 10 h was needed to adsorb Pt vapor in the perovskite-type multiple oxide, La$_4$Si$_2$Ba$_4$ScO$_{13-δ}$. Thus, it is desired to prepare complex oxides using simple procedures and/or under mild conditions.

In this letter, we report the preparation of Li$_2$PtO$_3$ and its dissolution properties in HCl. It was found that the compound could be prepared through a simple process and was soluble in HCl even at ambient temperatures. The dissolution process by way of this compound is expected to benefit the establishment of environment-friendly recovery process of PGMs.

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2 Experimental

Pt black (Wako chemical, 250.0 mg) and lithium carbonate (Li$_2$CO$_3$, Wako chemical, 94.7 or 189.4 mg) were mixed in an agate mortar. The feed ratio of Li$_2$CO$_3$ to Pt black, Li/Pt, was 2.0 or 4.0 (atomic ratio). A mixture of Pt black and Li$_2$CO$_3$ powder mounted on gold foil was placed in an electric tube furnace and then calcined at different temperatures from 500 to 800°C for 1 h in air. To determine the crystalline phase and crystallite size, the calcined sample powders were characterized using X-ray diffractometer (XRD, Rigaku RINT 2000) equipped with a Cu Kα radiation source.

To characterize the dissolution properties of Li$_2$PtO$_3$ in HCl, a 1/10 of the sample powders calcined at 600–800°C in weight, containing 25.0 mg of Pt, was added in 20 mL of HCl (Wako chemical; HCl concentration: 1–12 M) in a flask and the mixture was stirred for 9 h in a water bath using a magnetic stirrer. Even in the dissolution experiment using 1 M HCl, the solution was stirred for 9 h in a water bath using a magnetic stirrer. The Pt concentration in HCl solution was measured using an ultraviolet–visible absorption spectrophotometer (UV–vis, JASCO V-530). The solutions obtained after dissolution treatment were filtered through a PTFE filter (pore size, 0.1 μm) under reduced pressure to separate the solution from the solid residue.

The XRD patterns of the sample powders calcined at different temperatures from 500 to 800°C in weight and the Li/Pt ratio of 2.0 are
of the diffraction peaks were assigned to Li$_2$PtO$_3$ for the samples calcined at 500, 600, 700, and 800°C. The atomic ratio of Li to Pt was 2.0. Plus signs and asterisks indicate the diffraction peaks due to Li$_2$CO$_3$ and Pt, respectively.

Reaction temperatures are lower than the melting point of Li$_2$CO$_3$ and asterisks indicate the diffraction peaks due to Li$_2$CO$_3$ and Pt, (c) 700, and (d) 800°C. The atomic ratio of Li to Pt was 4.0. Plus signs and asterisks indicate the diffraction peaks due to Li$_2$CO$_3$ and Pt, respectively.

The crystallite sizes of Li$_2$PtO$_3$ in excess Li$_2$CO$_3$ overlapped the diffraction patterns of Li$_2$PtO$_3$. This result clearly indicates that the yield of Li$_2$PtO$_3$ could be increased by way of high reaction temperatures. The solubility of Li$_2$PtO$_3$ in 12 M HCl is displayed in Fig. 3. The Pt solubility of the sample calcined at 600°C reached 76.5%, whereas that in the case of Pt black was only 3.1%. These results indicate that the Pt solubility in 12 M HCl can be significantly increased by way of Li$_2$PtO$_3$. However, the Pt solubilities in HCl solutions were 1.2 and 3.7% for the samples calcined at 700 and 800°C, respectively. The Pt solubility in 12 M HCl decreased with increasing calcination temperature. This result is probably because the dissolution rate of the Li$_2$PtO$_3$ particles in 12 M HCl depends on the crystallite or particle size of Li$_2$PtO$_3$.

Preparation of the compound at lower temperatures is favorable from a technological point of view. Thus, the solid-phase preparation of Li$_2$PtO$_3$ using excess Li$_2$CO$_3$ relative to Pt black was further examined. The XRD profiles of the sample powders calcined at different temperatures from 500 to 800°C with a Li/ Pt ratio of 4.0 are displayed in Fig. 2. As can be seen in Fig. 2, most of the diffraction peaks were assigned to Li$_2$PtO$_3$ for the samples calcined at 600, 700, and 800°C, while some small peaks due to excess Li$_2$CO$_3$ overlapped the diffraction patterns of Li$_2$PtO$_3$. This result clearly indicates that the yield of Li$_2$PtO$_3$ could be almost 100% with a large excess addition of Li$_2$CO$_3$ even at the reaction temperature of 600°C. The crystallite sizes of Li$_2$PtO$_3$ in the samples increased with calcination temperature: the averaged sizes evaluated using the Scherrer equation were 19, 31, and 71 nm for the samples calcined at 600, 700, and 800°C, respectively.

The formation of the double oxide is associated with the oxidation of Pt atoms. Under the assumption that CO$_2$ was released from Li$_2$PtO$_3$ during calcination, the reaction for the formation of Li$_2$PtO$_3$ can be described as Eq. (1).

Pt + Li$_2$CO$_3$ + O$_2$ → Li$_2$PtO$_3$ + CO$_2$  

Since Pt black was not oxidized with atmospheric O$_2$ upon heating at 600°C and the formation of Ca$_4$PtO$_6$ through the method in Refs. 6 and 7 requires 900°C, it is concluded that the reaction with Li$_2$CO$_3$ is very effective for the transformation of Pt to Pt$^{4+}$ at such a low temperature.

To examine the dissolution properties of Li$_2$PtO$_3$ in HCl solution, we dissolved the Li$_2$PtO$_3$ samples prepared at temperatures of 600, 700, and 800°C with a Li/ Pt ratio of 4.0. The Pt solubilities of the Li$_2$PtO$_3$ samples and Pt black were evaluated after dissolution treatment at 60°C using 12 M HCl (Fig. 3). The Pt solubility of the sample calcined at 600°C reached 76.5%, whereas that in the case of Pt black was only 3.1%. These results indicate that the Pt solubility in 12 M HCl can be significantly increased by way of Li$_2$PtO$_3$. However, the Pt solubilities in HCl solutions were 1.2 and 3.7% for the samples calcined at 700 and 800°C, respectively. The Pt solubility in 12 M HCl decreased with increasing calcination temperature. This result is probably because the dissolution rate of the Li$_2$PtO$_3$ particles in 12 M HCl depends on the crystallite or particle size of Li$_2$PtO$_3$. 

**Fig. 1.** XRD profiles of the samples calcined at (a) 500, (b) 600, (c) 700, and (d) 800°C. The atomic ratio of Li to Pt was 2.0. Plus signs and asterisks indicate the diffraction peaks due to Li$_2$CO$_3$ and Pt, respectively.

**Fig. 2.** XRD profiles of the samples calcined at (a) 500, (b) 600, (c) 700, and (d) 800°C. The atomic ratio of Li to Pt was 4.0. Plus signs and asterisks indicate the diffraction peaks due to Li$_2$CO$_3$ and Pt, respectively.

**Fig. 3.** Pt solubility of the calcined samples and Pt black in 12 M HCl upon dissolution treatment at 60°C for 9 h.
The effects of the concentration of HCl and the dissolution temperature on the Pt solubility were investigated for the sample calcined at 600°C. The Pt solubilities obtained using 1–12 M of HCl at 60°C are plotted in Fig. 4. As seen in Fig. 4, the Pt solubility increased almost linearly from 3.7 to 76.5% with the concentration of HCl from 1 to 12 M. These data show that higher HCl concentration is favorable for the dissolution of the sample despite the excess amount of H⁺ and Cl⁻ ions even at 1 M.

To investigate the effect of the dissolution temperature on the Pt solubility, the sample calcined at 600°C was dissolved in 12 M HCl at different temperatures from 40 to 80°C. The resulted Pt solubilities are plotted in Fig. 5. The enhancement of the Pt solubility with increasing dissolution temperature was confirmed: the Pt solubility increased from 39.2 to 99.9% with temperature from 40 to 80°C, as seen in Fig. 5. The high Pt solubility at moderate temperatures would be beneficial for the recovery process of Pt.

In order to characterize the coordination state of Pt in solution, we measured the UV–vis spectrum of the solution obtained by dissolving the sample calcined at 600°C in 12 M HCl at 60°C [Fig. 6(a)]. For comparison, the UV–vis spectrum of an aqueous solution of hexachloroplatinate(IV) (H₂PtCl₆; Pt concentration: 2.30 × 10⁻⁵ mol/L) is displayed in Fig. 6(b). As can be seen in Fig. 6, the UV–vis spectra of the Pt-containing solutions were quite similar in shape, exhibiting absorption maxima at 262 nm, which is characteristic of the [PtCl₆]²⁻ complex ion.¹¹ Solutions from the samples calcined at 700 and 800°C also showed a peak at 262 nm. These results indicate that Pt⁺⁺ and Cl⁻ ions formed the complex ion [PtCl₆]²⁻ during the dissolution treatment of Li₂PtO₃ in HCl. Hence, the reaction between Li₂PtO₃ and HCl can be described as Eq. (2).

\[
\text{Li}_2\text{PtO}_3 + 8\text{HCl} \rightarrow \text{H}_2\text{PtCl}_6 + 2\text{LiCl} + 3\text{H}_2\text{O} \tag{2}
\]

The present study revealed that Li₂PtO₃ can be prepared via a simple calcination procedure at relatively low temperature (600°C) from a mixture of Pt black and Li₂CO₃ and resulting Li₂PtO₃ can be dissolved in HCl at moderate temperatures. Therefore, it is hoped that the dissolution process by way of Li₂PtO₃ would lead to an environment-friendly recovery process of Pt.

4. Conclusions

A double oxide containing Pt and Li, Li₂PtO₃, was prepared from Pt black and Li₂CO₃ via a solid-phase reaction at 600°C. The obtained Li₂PtO₃ dissolved in non-oxidative HCl solution, and the Pt solubility increased with the concentration of HCl in the range of 1–12 M. The Pt solubility of Li₂PtO₃ increased with dissolution temperature, and nearly 100% of Pt solubility was recorded after dissolution treatment in 12 M HCl at 80°C.

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