

# Enhanced dissolution of alkali metal platinates in dilute hydrochloric acid by addition of calcium chloride



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## ABSTRACT

To decrease the environmental load from current Pt recovery processes that use strong acids in combination with oxidizing agents, the dissolution of Pt in hydrochloric acid (HCl) by way of alkali metal platinates was examined. The alkali metal platinates,  $\text{Li}_2\text{PtO}_3$ ,  $\text{Na}_2\text{PtO}_3$ , and a  $(\text{Na,Li})_2\text{PtO}_3$  solid solution, were prepared by calcining mixtures of Pt black and the alkali metal carbonates (Li,Na) at 600–800 °C in air. The dissolution of the resulting alkali metal platinates in HCl solutions was monitored by inductively coupled plasma–optical emission spectrometry. The results showed that Pt solubility approached 100% after choosing the appropriate calcination conditions. It was also found that by adding calcium chloride, the rate of Pt dissolution in dilute HCl significantly increased. The dissolution behavior of the alkali metal platinates was discussed based on the dissolution rates of the alkali metals and Pt ions, together with the crystal structures of the platinates.

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## 1. Introduction

Platinum group metals (PGMs) play important roles in various industrial applications, especially as environmental catalysts (Bernardis et al, 2005). In particular, their use as emission control catalysts for vehicles constitutes the largest segment of the PGMs market. The demand for PGMs is only expected to grow because of the rapid increases in motorization in developing nations and tightened exhaust emission regulations in developed countries (Johnson Matthey Plc., 2013). However, primary PGM resources are limited geographically and their production has not shown any significant increase in recent years. To stabilize the supply of PGMs, their recycling has become increasingly important.

PGMs are typically recovered after dissolution in aqueous solutions and subsequent metallurgical separation processes (Shibata and Okuda, 2002). However, PGMs in the metallic state barely dissolve in protic acids because the oxidation/reduction potentials of PGMs are more positive than that of hydrogen (Barin and Knacke, 1973). Therefore, strong acids containing oxidizing agents are used; these typically include aqua regia or a mixture of hydrochloric acid (HCl) and chlorine ( $\text{Cl}_2$ ) gas. In aqua regia, spontaneously generated compounds such as nitrosyl chloride (NOCl) and  $\text{Cl}_2$

oxidize the PGMs (Kizilaslan et al, 2009). Despite their indispensable oxidizing powers, these species are highly corrosive and extremely toxic. Therefore, an ionization process for PGMs without toxic oxidizing agents would improve the safety of hydrometallurgical recovery.

To dissolve PGMs in a non-oxidative acid such as pure HCl, this study focused on dissolution via complex oxides. In our previous study, alkali metal platinates were successfully and simply synthesized by a procedure involving calcination of a mixture of Pt black and alkali metal salts. The obtained  $\text{Li}_2\text{PtO}_3$  (Kasuya et al, 2013a,b),  $\text{Na}_2\text{PtO}_3$ , and  $(\text{Na,Li})_2\text{PtO}_3$  solid solution (Kasuya et al, 2014) have the  $\text{Na}_2\text{PtO}_3$  structure that is easily dissolved in HCl. In particular, nearly 100% Pt solubility was recorded by dissolving  $\text{Li}_2\text{PtO}_3$  obtained at 600 °C under appropriate dissolution conditions (Kasuya et al, 2013a, 2013b). This study focused on the dissolution of the alkali metal platinates using dilute HCl, which would further improve the safety profile of the recovery process. It was previously confirmed that the Pt solubility of  $\text{Li}_2\text{PtO}_3$  decreased with decreasing HCl concentration (in the range 1–12 M) (Kasuya et al, 2013a). This is probably due to the inhibition of the formation of the Pt–Cl complex ion. Thus, in this study, the effect of chloride addition on the dissolution properties of the alkali metal platinates has been investigated. Furthermore, the dissolution behavior of alkali metal platinates was characterized by monitoring the time dependence of the solubilities of the Pt and alkali metals.

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## 2. Experimental

### 2.1. Synthesis of alkali metal platinates

The details of the preparation of  $\text{Li}_2\text{PtO}_3$ ,  $\text{Na}_2\text{PtO}_3$ , and the  $(\text{Na,Li})_2\text{PtO}_3$  solid solution are provided elsewhere (Kasuya et al., 2013a, 2013b, 2014). Basically Pt black (250.0 mg) and the alkali metal salts, lithium carbonate (189.4 mg  $\text{Li}_2\text{CO}_3$ ) and/or anhydrous sodium carbonate (271.7 mg  $\text{Na}_2\text{CO}_3$ ), were mixed in an agate mortar. For  $\text{Li}_2\text{PtO}_3$  and  $\text{Na}_2\text{PtO}_3$ , the feed ratio of Na and Li to Pt,  $(\text{Na} + \text{Li})/\text{Pt}$ , was fixed at 4.0 by atomic ratio. The  $(\text{Na, Li})_2\text{PtO}_3$  solid solution was prepared with feed ratios of  $(\text{Na} + \text{Li})/\text{Pt} = 3.0$ , and  $\text{Li}/(\text{Na} + \text{Li}) = 0.20$ . The mixtures were calcined at 600 or 800 °C for 1–20 h in an electric furnace in air.

### 2.2. Dissolution of calcined samples in HCl solution

The dissolution properties of the calcined samples in HCl were characterized as follows: One-tenth (by weight) of the prepared material was added to 3 M HCl solution (dil.) or 12 M HCl (conc.) in 20 mL flask equipped with a reflux condenser. The solution was stirred at 80 °C for 5 min–9 h. Then, the flask was immediately cooled in an ice–water bath, and ice–cold ultrapure water (20 mL) was added to the suspension to disable further dissolution. For solid–liquid separation, the suspension was filtered through a PTFE filter (pore size, 0.1  $\mu\text{m}$ ) under reduced pressure. The obtained solid residue was dried at 110 °C for 3 h in an oven. For comparison purposes, Pt black (25.0 mg) and Pt dioxide ( $\text{PtO}_2$ , 29.1 mg) were also dissolved in conc. HCl at 80 °C for 9 h. To investigate the effect of chloride addition, dil. HCl containing saturated anhydrous calcium chloride ( $\text{CaCl}_2$ , 26 g) was used to dissolve the alkali metal platinates. The  $\text{Cl}^-$  concentration originating from  $\text{CaCl}_2$  was ca. 16 mol/L under saturation conditions. Thus, the total  $\text{Cl}^-$  concentration was ca. 19 mol/L in the HCl– $\text{CaCl}_2$  solution.

### 2.3. Characterization of calcined samples and solid residues

The crystalline phases of the calcined samples and residues obtained after dissolution were analyzed using an X-ray diffractometer (XRD, Rigaku RINT 2000) equipped with a  $\text{Cu K}\alpha$  radiation source (40 kV, 30 mA). The diffraction profiles were acquired over the  $2\theta$  range from 10° to 80°, with a step width of 0.02°. Detailed measurements in the  $2\theta$  range of 15–25° with a step width of 0.01° were also performed to analyze the structures of the solid residues.

The concentrations of Pt, Na, and Li in the solution samples after the dissolution tests were determined using inductively coupled plasma–optical emission spectroscopy (ICP–OES, IRIS Advantage, Thermo Jarrell Ash Co.). The total metal contents of the calcined samples and residues were measured after complete dissolution using pressure decomposition as follows (Jackwerth and Gomišček, 1984): a powder sample, either the calcined sample (1/10 of the total amount by weight) or residue, was added to conc. HCl (10 mL) in a PTFE vessel. This vessel was placed in a pressure casing made of stainless steel and heat treated. The decomposition conditions were 80 °C for 9 h for  $\text{Li}_2\text{PtO}_3$ , whereas the other calcined samples and residues were treated at 180 °C for 2 h in an oven. When unreacted Pt black was observed after this dissolution operation, conc.  $\text{HNO}_3$  (3.3 mL) was added to the vessel, and the resultant aqua regia mixture was further aged overnight at room temperature to dissolve the Pt. The Pt solubility of a sample was calculated based on its total Pt content evaluated by the above procedures.

The optical absorption spectra of the Pt-containing solution samples were measured using an ultraviolet–visible absorption

spectrophotometer (UV–vis, JASCO V-530). The solutions obtained after the dissolution tests were diluted 250-fold with ultrapure water to adjust the absorbance into a measurable range before analysis.

## 3. Results and discussion

### 3.1. Preparation of the alkali metal platinates

The alkali metal platinates were synthesized by the calcination of Pt black and alkali metal salts. The XRD profiles of the obtained samples are displayed in Fig. 1. After calcination of Pt black and  $\text{Li}_2\text{CO}_3$  at 600 °C for 1 h, nearly 100% of the Pt was converted to  $\text{Li}_2\text{PtO}_3$  (Fig. 1(a)). In contrast, the corresponding sodium salt was much less reactive. The major crystalline phase observed for the sample obtained from Pt black and  $\text{Na}_2\text{CO}_3$  was due to unreacted Pt, although small diffraction peaks for Na–Pt complex oxides were confirmed (Kasuya et al., 2013b). A higher calcination temperature (800 °C) and longer time (20 h) were needed to complete the reaction between Pt black and  $\text{Na}_2\text{CO}_3$  (Kasuya et al., 2014). The resultant compound was identified as  $\text{Na}_2\text{PtO}_3$  (Fig. 1(b)). These results indicate that  $\text{Li}_2\text{CO}_3$  is more reactive than  $\text{Na}_2\text{CO}_3$  toward alkali metal platinate formation.

In terms of reducing the cost for the Pt recovery process, the use of the inexpensive Na salt would be favored. However, the formation of the Na–Pt complex oxide requires severe preparation conditions, compared with those of  $\text{Li}_2\text{PtO}_3$ . Thus, we investigated the effect of adding a Li salt during the synthesis of Na-based platinates. By adopting the feed conditions of  $\text{Li}/(\text{Na} + \text{Li}) = 0.20$  and  $(\text{Na} + \text{Li})/\text{Pt} = 3.0$ , nearly 100% Pt reacted after calcination at 800 °C for 1 h (Fig. 1(c)). The XRD profile of the sample using  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  (Fig. 1(c)) was similar to that of pure  $\text{Na}_2\text{PtO}_3$  (Fig. 1(b)). Detailed XRD measurements revealed that the angle of the (002) diffraction peak ( $2\theta = 17.0^\circ$ ) of the sample prepared using  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  was higher than that of pure  $\text{Na}_2\text{PtO}_3$  ( $2\theta = 16.8^\circ$ ) (Kasuya et al., 2014).  $\text{Na}_2\text{PtO}_3$  and  $\text{Li}_2\text{PtO}_3$  have layered crystal structures consisting of alternating layers of  $\text{A}^+$  ( $\text{A} = \text{Na, Li}$ ) and a mixture of  $\text{PtO}_6$  octahedra and  $\text{A}^+$  that stack along the  $c$ -axis (Urland and Hoppe, 1972; O'Malley et al., 2008). The peak shift indicates a decrease in the interlayer distance in  $\text{Na}_2\text{PtO}_3$  due to the substitution of  $\text{Na}^+$  with smaller  $\text{Li}^+$ . It is noteworthy that, based on the reported preparation conditions of  $\text{Li}_2\text{PtO}_3$  with a  $\text{Li}/\text{Pt}$  ratio = 4.0, a reduction in the use of Li by 85% occurs if a

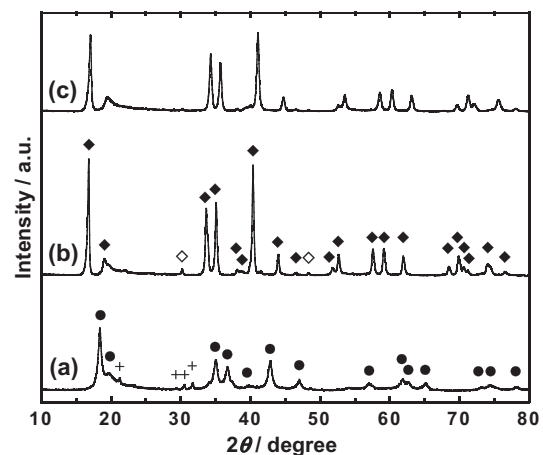


Fig. 1. XRD profiles of alkali metal platinates (a)  $\text{Li}_2\text{PtO}_3$ , (b)  $\text{Na}_2\text{PtO}_3$ , and (c)  $(\text{Na,Li})_2\text{PtO}_3$  solid solution. Calcination conditions were 600 °C, 1 h for pattern (a); 800 °C, 20 h for pattern (b); and 800 °C, 1 h for pattern (c). A/Pt ratios are 4.0 for patterns (a and b), and 3.0 for pattern (c). Solid circles, solid diamonds, plus signs, and open diamonds indicate  $\text{Li}_2\text{PtO}_3$ ,  $\text{Na}_2\text{PtO}_3$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{Na}_2\text{CO}_3$ , respectively.

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