Synthesis of sodium platinates and their dissolution behaviors in hydrochloric acid: Effects of lithium carbonate addition on platinate formation

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ABSTRACT

The Pt-containing complex oxide Li_2PtO_3 easily dissolves in HCl in the absence of an oxidizing agent. A similar dissolution behavior is expected for Na_2PtO_3 that has a crystal structure similar to Li_2PtO_3; however, the preparation of Na_2PtO_3 requires high temperature and prolonged time. In the present study, we report our investigation on the effect of Li salts on the synthesis and dissolution properties of Na_2PtO_3, a cost-effective Pt-group metal complex oxide alternative to Li_2PtO_3. The addition of a small amount of Li_2CO_3 drastically accelerates the formation of Na_2PtO_3, allowing for synthesis of the complex oxide under milder conditions. Calcination of Pt black and Na_2CO_3 at 800 °C for more than 12 h was necessary for reaction completion; however, samples calcined with Li salt with the ratio $Li/(Na + Li) = 0.20$ showed complete reaction of Pt after calcination at 800 °C after only 1 h. The obtained samples were identified as a $(Na,Li)_2PtO_3$ solid solution having the structure of Na_2PtO_3 in which Na^+ is substituted with Li^+. Investigations of the effect of Li addition on complex oxide dissolution properties in conc. HCl were performed by examining the time dependence of Pt, Na, and Li concentrations using inductively coupled plasma-optical emission spectroscopy. The results showed that $(Na,Li)_2PtO_3$ solid solutions are easily dissolved in HCl as well as Na_2PtO_3. A Pt dissolution process using $(Na,Li)_2PtO_3$ solid solutions is facile and does not require a toxic oxidizing agent; therefore, this process is promising in terms of cost-efficiency and safety.

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1. Introduction

Platinum-group metals (PGMs) play important roles in various industrial applications, most notably in the area of environmental catalysis (Bernardis et al., 2005). As motor vehicle use continues to rise in developing nations and exhaust emission regulations are tightened in developed countries, the demand for PGMs is expected to continuously increase (Johnson Matthey, 2013). Accordingly, the importance of PGM recovery from scrap metals and other materials is growing annually.

The hydrometallurgical recovery of PGMs involves the oxidation and dissolution of metallic species in acidic solution; however, PGMs in the metallic state cannot be oxidized by hydrogen ions in acidic media because the standard reduction potentials of PGMs are more positive than those of hydrogen (Lide, 2001). Thus, the generation or introduction of strong oxidizing agents such as aqua regia (Baghalha et al., 2009; Potgieter et al., 2004) and chlorine (Cl_2) (Barnes and Edwards, 1982; Okabe and Nose, 2012) is necessary for the PGM dissolution process. Despite their indispensable oxidizing powers, these agents are

highly corrosive and extremely toxic; therefore, the dissolution of PGMs in a non-oxidative acid such as pure HCl would be very effective in terms of improving the safety of the recovery process.

To improve the dissolution of PGMs in HCl, the preparation of PGM-containing complex oxides has been examined. PGM-containing complex oxides such as Ca_4PtO_6 (Okabe et al., 2008; Okabe et al., 2003) and PGM-containing perovskite-type multiple oxides (Daté et al., 2011) have been reported to be soluble in HCl. Previously, we have reported the facile and direct synthesis of Li_2PtO_3 by the calcination of Pt black and Li_2CO_3 (Kasuya et al., 2013a) and have examined its dissolution properties in HCl. Pt black was completely reacted to provide Li_2PtO_3 under the optimized preparation conditions, which were quite mild in comparison to those for Ca_4PtO_6 (Okabe et al., 2003, 2008) and PGM-containing perovskite-type multiple oxides (Daté et al., 2011). The obtained Li_2PtO_3 could easily dissolve in HCl. From the viewpoint of cost-efficiency, the use of alkali metals other than Li is favored, i.e., Na or K; however, in our previous study, potassium platinates could not be obtained under optimized synthetic conditions, whereas the preparation of Na_2PtO_3 required an elevated temperature and prolonged reaction times (Kasuya et al., 2013b). Despite these difficulties, we deemed that preparation of Na_2PtO_3 is worth further study on the basis of a previous report in which Urland and Hoppe (1972) briefly described the smooth dissolution of Na_2PtO_3 in warm diluted HCl.

In this study, we investigated the effect of Li salts on the synthesis and dissolution properties of Na_2PtO_3—a more economically feasible Na-based PGM complex oxide—by changing the feeding ratio of Li to Na, Li/(Na + Li), feeding ratio of the alkali metals to Pt, (Na + Li)/Pt, and calcination temperature. We also investigated the dissolution properties of prepared complex oxides in HCl. We also discuss the formation and dissolution mechanisms of Pt-containing complex oxides based on our experimental results.

2. Experimental

2.1. Synthesis of Pt-containing complex oxides

The preparation of Pt-containing complex oxides was as follows: Pt black (250.0 mg, Wako Pure Chemical Industries) and the requisite alkali metal carbonates were mixed in an agate mortar. The metal dispersion of Pt black was 0.36% as determined by the CO adsorption method (Komai et al., 2005), which corresponded to a mean diameter of ca. 300 nm. Anhydrous sodium carbonate (Na_2CO_3, Wako), and lithium carbonate (Li_2CO_3, Wako) were employed for the preparation of Pt-containing complex oxides. The feeding ratio of Na and Li to Pt, (Na + Li)/Pt, was 4.0 in atomic ratio unless otherwise stated. The applied (Na + Li)/Pt ratio is two times greater than the stoichiometric ratio, 2.0. The feeding ratio of Li to Na, Li/(Na + Li), was changed from 0 to 0.30. Mixtures of Pt black, Li_2CO_3, and Na_2CO_3 were mounted on gold foil to avoid the reaction between Li_2CO_3 and alumina, whereas the mixtures of Pt black and Na_2CO_3 were directly mounted on alumina boats. The mixtures were placed in an electric furnace and calcined in air within the range of 600–800 °C. The furnace temperature was raised at a rate of 10 °C/min to the desired temperature. The calcination time was fixed at 1 h for the preparation of samples containing Li and Na, whereas calcination time should be 1–20 h for the synthesis of Na_2PtO_3 without Li. A two-step reaction for the synthesis of Na_2PtO_3 from the as-prepared Li_2PtO_3 and Na_2CO_3 was also examined. In the first step, a mixture of Pt black and Li_2CO_3 was calcined at 600 °C for 1 h. In the second step, a mixture of the as-prepared Li_2PtO_3 and Na_2CO_3 was calcined at 800 °C for 1 h.

2.2. Dissolution tests of calcined samples in HCl

Characterization of the dissolution properties of calcined samples in HCl was performed as follows: conc. HCl (20 mL, Wako) was added to a sample of the obtained powder (10 wt.%) of the obtained material, containing 25.0 mg Pt) in a flask with a reflux condenser. The suspension was heated at 80 °C in a water bath with stirring over a period varying from 5 min to 9 h. After dissolution, the flask was immediately placed in an ice-water bath, followed by addition of ice cold, ultrapure water (20 mL) to the suspension to quench further dissolution. The suspension was filtered through a PTFE filter (pore size, 0.1 μm) under reduced pressure to separate the solution from the solid residue. The filtrate was retained and the residue was dried at 110 °C for 3 h in an oven.

2.3. Characterization

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 Cu Kα radiation source (40 kV, 30 mA). The diffraction profiles were acquired over the 2θ range of 10°–80°, with a step width of 0.02°. More accurate measurements in the 2θ range of 15°–25°, with a step width of 0.01°, were also performed to investigate the structural change in Na_2PtO_3 with addition of Li_2CO_3.

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 (10 wt.% of the obtained material) 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 at 180 °C for 2 h in an oven. When unreacted Pt black was observed after the dissolution operation, conc. HNO_3 (3.3 mL) was added to the vessel; the resultant aqua regia mixture was further aged overnight at room temperature to dissolve Pt. The Pt solubility of a sample was calculated based on its total Pt content evaluated by the above procedures.

3. Results and discussion

3.1. Synthesis of Na_2PtO_3

The synthesis of Na_2PtO_3 was first performed at 800 °C by varying the calcination times to determine the calcination conditions at which Pt was completely reacted. The sample preparation conditions are summarized in Table 1. The calcination temperature was fixed at 800 °C based on our previous observation that the yield of Na–Pt complex oxides was highest at 800 °C (Kasuya et al., 2013b) and to avoid the temperature at which Na_2PtO_3 decomposes in air (890 °C) (McDaniel, 1974). The XRD profiles of the samples obtained at 800 °C for 1, 6, 12, and 20 h are displayed in Fig. 1a–d, and are denoted as samples A–D, respectively. The preparation conditions and results of the XRD analysis are summarized in Table 1. The main crystalline phases were identified as $NaPt_3O_4$ (JCPDS No. 6-534) after 1 h calcination and Na_2PtO_3 (JCPDS No. 27-774) after the calcination times of 6, 12 and 20 h. Although the formation of Na–Pt complex oxides was confirmed after calcination at 800 °C, the samples calcined for 1 and 6 h also exhibited a diffraction peak attributable to unreacted Pt (JCPDS No. 4-802); in addition, samples A–D had excess Na_2CO_3 (JCPDS No. 19-1130). The calcination temperature of 800 °C is lower than the melting point of Na_2CO_3 (850 °C) (Barin and Knacke, 1973), allowing the generation of $NaPt_3O_4$ and Na_2PtO_3 via a solid-phase reaction between Pt black and Na_2CO_3. As the calcination time was increased, the reaction proceeded to yield complex oxides with higher Na content; the major crystallite phase was changed from $NaPt_3O_4$ to Na_2PtO_3.

3.2. Effect of Li_2CO_3 content on synthesis

Prolonged calcination times (over 12 h) were necessary for the complete reaction of Pt; to facilitate the preparation of Na_2PtO_3, a small amount of highly reactive Li_2CO_3 was added to the mixture of Pt black and Na_2CO_3. Different Li/(Na + Li) ratios of 0.05, 0.10, 0.15, 0.20, and 0.30 were examined and the corresponding samples were designated as E, F, G, H, and I, respectively. The calcination temperature and time were maintained at 800 °C and 1 h, respectively. After calcination, powdered samples were obtained when Li/(Na + Li) ratios in the range of 0.05–0.20 were employed, whereas a fused sample was obtained at a Li/(Na + Li) ratio of 0.30. This observed change in the appearance at the higher Li/(Na + Li) ratio (0.30) is probably due to the melting of Na_2CO_3 and Li_2CO_3.

To identify the crystalline phases, samples E–I were characterized using XRD. The obtained XRD profiles are displayed in Fig. 2. For comparison, the XRD profile of sample D is also shown in Fig. 2a. As shown in Fig. 2a–e, Na_2PtO_3 was the major phase in the Li/(Na + Li) range of 0–0.20. In contrast, unreacted Pt was the main phase of sample I prepared at a Li/(Na + Li) ratio of 0.30. This result is probably because of the lack of oxygen around the reacting sites in the molten Na_2CO_3/Li_2CO_3 reaction mixture. Only sample H did not show any significant peaks attributable to unreacted Pt; rather, diffraction peaks corresponding to Li_2PtO_3 emerged. From these results, it was revealed that the complete reaction of Pt could be achieved at the optimum Li/(Na + Li) ratio of 0.20.

To reveal the structural change of Na_2PtO_3 with addition of Li_2CO_3, the profiles of Na_2PtO_3 (002) diffraction peak were investigated in detail for samples D–H (Fig. 3). With an increase in the Li/(Na + Li) ratio from