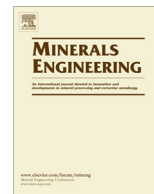




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Dissolution of platinum in catalyst materials using hydrochloric acid: A new method based on the use of complex oxides

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ABSTRACT

Platinum group metals (PGMs) are used widely in various applications, including as environmental catalysts. Since PGMs are rare and expensive, they are recycled after being recovered. Currently, PGMs are recovered, after a pyrometallurgical step that upgrades the concentration, by dissolving in strong acids containing toxic oxidizing agents like aqua regia. To avoid the use of such toxic agents, we have proposed a new route to dissolve PGMs in hydrochloric acid (HCl) using complex oxides. In the present study, we used this new process to dissolve Pt in supported metal catalysts. Complex oxides of Pt were prepared by calcining mixtures of Pt/Al₂O₃ and alkali metal salts at 600–800 °C in air. These were then dissolved in 12 M HCl. The results showed that the Pt in the calcined samples dissolved readily in HCl and that the Pt solubility was nearly 100% under the appropriate preparation and dissolution conditions. We also confirmed that the new process is suitable for leaching PGMs from spent automotive catalysts.

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1. Introduction

Platinum group metals (PGMs), which include Pt, Pd, Rh, Ir, Ru, and Os, play important roles in various industrial applications, especially as catalysts. Pt, Pd, and Rh are indispensable as catalysts for motor vehicles, because these PGMs exhibit excellent performance in the purification of exhaust gas. In fact, the primary use of PGMs is as emission-control catalysts in automobiles; in 2012, the worldwide demand of Pt, Pd, and Rh reached 40%, 67% and 81%, respectively (Johnson Matthey Plc., 2013). As the pace of automotive transportation increases rapidly in developing countries and exhaust emission regulations are tightened in developed ones, the demand for these PGMs is expected to increase continuously (Furuse, 2012). In particular, the demand for Pt and Pd will increase significantly, because the rates at which Pt and Pd are loaded are higher than that for Rh. In contrast, the supply of PGMs has not increased (Johnson Matthey Plc., 2013). This situation will eventually lead to a noticeable increase in the supply risk associated with PGMs in the near future. Thus, the recovery of PGMs from scrap materials, such as automotive catalysts, has become increasingly important.

Currently, PGMs are recovered, after a pyrometallurgical step that upgrades the concentration, by dissolving in strong acids con-

taining toxic oxidizing agents like aqua regia. The acid dissolution of PGMs is unavoidable (Okabe and Nose, 2012) because the subsequent separation and purification processes, e.g., solvent extraction, coprecipitation, and ion-exchange resin methods, are designed for use with PGM complex ions in solution. However, PGMs in the metallic state cannot be oxidized by the hydrogen ions of the acid, as the standard reduction potentials of PGMs are more positive than that of hydrogen (Lide, 2001). Therefore, the current dissolution process involves the use of a combination of acids and strong oxidizing agents such as aqua regia (Baghalha et al., 2009; Potgieter et al., 2004) and hydrochloric acid (HCl)/chlorine (Cl₂) (Okabe and Nose, 2012; Barnes and Edwards, 1982) for the ionization of the PGMs. However, these oxidizing agents are extremely corrosive and toxic.

To be able to dissolve PGM in acids without having to use toxic oxidizers, we had proposed a dissolution process that involves using the complex oxides of PGMs and alkali metals (Kasuya et al., 2013a, 2013b, 2014, 2015, in press). In this process, the oxygen in air acts as an oxidizer, resulting in the formation of complex oxides. Since the obtained complex contains oxidized PGMs, they became soluble in non-oxidative HCl. Further, in previous studies, we had synthesized alkali metal platinates and palladates using Pt and Pd powders and investigated their dissolution behaviors in HCl. The alkali metal platinates, M₂PtO₃ (M = Li, Na) (Kasuya et al., 2013a, 2013b, 2014) and Li₂PdO₂ (Kasuya et al., in press), were obtained after the calcination of PGM powders and alkali metal salts at 600–800 °C. The results of the dissolution

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experiments suggested that the obtained complex oxides dissolve readily in HCl. In this study, we investigated the applicability of the above-mentioned method in the case of catalytic materials containing Pt. The platinates were prepared using a Pt catalyst and alkali metal salts, and their dissolution properties in HCl were investigated. PGM catalysts such as Pt (Abedi and Epling, 2014) and Pd (Strobel et al., 2005) are usually loaded in the form of fine particles. As a result, they gradually aggregate and sinter during high-temperature processes. Thus, to investigate the applicability of the process with respect to sintered Pt, we also used an annealed Pt catalyst as the starting material.

2. Experimental

2.1. Synthesis of alkali metal platinates

As mentioned above, we had previously found that Li and Na salts react with Pt powder to produce platinates; however, K-Pt complex oxides are not produced during this reaction (Kasuya et al., 2013b). On the basis of these results, we prepared the platinates Li_2PtO_3 and Na_2PtO_3 . The Pt catalyst (Pt/ Al_2O_3 , Pt loading rate: 5 wt%, 1.0 g, Wako Pure Chemical Industries) and alkali metal salts were mixed in an agate mortar. The following carbonate salts were used: lithium carbonate (Li_2CO_3 , 726.3 mg, Wako) and anhydrous sodium carbonate (Na_2CO_3 , 1041.9 mg, Wako). To ensure that the Pt and the alkali metals reacted completely, we used excessive amounts of the carbonate salts. The molar ratio of the alkali metals was set as follows: (alkali metal content) = (Pt content) \times 4 + (Al content) \times 1.

The mixture of the Pt catalyst and Li_2CO_3 was placed on a gold foil spread on the inner surface of an alumina boat; this was done in order to prevent a reaction between the Li_2CO_3 and the alumina at high temperatures. The mixture containing Na_2CO_3 was placed directly in an alumina boat. The alumina boats were then placed in an electric tube furnace, and the mixtures were calcined in air at temperatures of 600–800 °C. On the basis of the previous studies on the synthesis of platinates (Kasuya et al., 2014), the calcination period was set to 1 h for the Pt/Li salt mixture and 20 h for the Pt/Na salt mixture. As mentioned previously, to confirm the applicability of the process for catalysts containing sintered Pt, we also used an aged Pt catalyst as the starting material. The aged Pt catalyst was obtained by calcination at 750 °C for 50 h in air.

2.2. Dissolution of alkali metal platinates using HCl

To characterize the dissolution behaviors of alkali metal platinates in HCl, dissolution tests were performed under various conditions. A typical dissolution treatment under atmospheric conditions was as follows: a sample of the obtained powder (50 wt% of the obtained material, containing 25 mg of Pt) was added to conc. HCl (HCl concentration: 12 M, 20 mL, Wako) in a flask with a reflux condenser. The suspension was kept at 80 °C and stirred for 5 min or 9 h. A water bath was used to maintain the temperature during the dissolution process. After the dissolution treatment, the flask was placed immediately in an ice-water bath, and ice-cold ultrapure water (20 mL) was added to the suspension to quench the dissolution process. Next, solid–liquid separation was performed using a polytetrafluoroethylene (PTFE) filter (pore size of 0.1 μm) under reduced pressure. The collected residue was dried at 110 °C for 3 h in an oven. To investigate the dissolution behaviors of aluminates, the reagent LiAlO_2 (γ - LiAlO_2 , 0.5 g, Aldrich) was dissolved in a similar manner as described above.

In order to dissolve the platinates completely, we also dissolved samples using a pressure decomposition system (Jackwerth and Gomišček, 1984), as follows. A calcined sample (1/2 of the total

weight) was added to 12 M HCl (10 mL) in a PTFE inner vessel. The vessel was placed in a pressure vessel made of stainless steel and heat treated at 180 °C for 2 h. Then, the suspension was separated into an extracted solution and a residue by filtration under reduced pressure.

2.3. Leaching of PGMs from spent automotive catalyst

The leaching of PGMs from a spent automotive catalyst was investigated using the spent automotive catalyst NIST SRM2557 (powder form <74 μm (–200 mesh), certified amounts of PGMs: Pt = 697.4 $\mu\text{g/g}$, Pd = 326.0 $\mu\text{g/g}$, Rh = 51.2 $\mu\text{g/g}$, total loading of PGMs: 0.1 wt%). A mixture of the spent automotive catalyst (1.00 g) and alkali metal salts (100 or 200 mg) was calcined in air at 800 °C. The calcination period was 1 h for the Li + catalyst combination and 20 h for the Na + catalyst combination. The automotive catalyst SRM2557 is a powdered PGM catalyst that contains promoters such as CeO_2 and the constituents of the cordierite honeycomb (Mg, Si, and Al). The certified amounts of the elements with concentrations of more than 1 wt% in SRM2577 as well as the concentrations of the alkali metals used in the batch experiments are listed in Table 2. The amounts in which the alkali metal salts were used were greater than those of the PGMs: the M (M = Li and Na)-to-PGM atomic feeding ratios were greater than 100. The entire calcined mixture (containing approximately 1 mg of PGMs) was added to 12 M HCl (10 mL) and heated at 180 °C for 2 h using a pressure decomposition system.

2.4. Characterization

The crystalline phases and crystallite sizes of the samples and residues were characterized using X-ray diffraction (XRD) analyses performed using a diffractometer (Rigaku RINT 2000) equipped with a Cu K α radiation source. The diffraction profiles were acquired over 2θ values of 10–80°, with the step width being 0.02°.

The concentrations of PGMs, the alkali metals, and Al in the solution samples after the dissolution treatment were determined using inductively coupled plasma–optical emission spectroscopy (ICP-OES, IRIS Advantage, Thermo Jarrell Ash Co.). The total metal contents of the samples were measured after complete dissolution using a pressure decomposition system. Complete dissolution was achieved as follows: either the calcined sample (1/2 of the total weight) or the solid residue, was suspended in 12 M HCl (10 mL) and heat treated at 230 °C for 24 h. When unreacted Pt was observed after the dissolution operation, concentrated HNO_3 (3.3 mL) was added to the vessel; the resultant aqua regia mixture was aged further overnight at room temperature, in order to dissolve the Pt. The Pt solubility of the samples was calculated on the basis of their total Pt content, which was evaluated using the above-mentioned procedures. Assuming that the alkali metal contents of the obtained M_2PtO_3 and MAlO_2 (M = Li and Na) samples were equal to twice that of Pt and equivalent to that of Al, the alkali metal contents of the unreacted M_2CO_3 sample were calculated using the following equation: (alkali metal content of solution sample) – (Pt content of the decomposed sample) \times 2 – (Al content of the decomposed sample) \times 1.

The spent automotive catalyst did not dissolve completely even when subjected to the dissolution process described above. Thus, the solubilities of Pt, Pd, and Rh were calculated based on the certified values determined by NIST. These values were determined using isotope dilution mass spectrometry (Pt and Pd) and inductively coupled plasma mass spectrometry (Rh).

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