Effect of Agitation on the Extraction of Palladium from Spent Industrial Catalyst with Supercritical Carbon Dioxide

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The extraction of palladium with supercritical carbon dioxide containing a ligand of tributyl phosphate was studied using a stirred batch reactor. The experiments were conducted at an extraction temperature of 60 ºC and a pressure of 30 MPa. The effects of the use of agitation and ratio of chelating ligand to metal sample on the extraction efficiency at various extraction times were investigated. The mechanism of complex formation of metal-chelating ligand was presented. The results showed that the use of stirred batch reactor could improve the extraction efficiency, especially at a short static extraction time. The chelating ligand to sample ratio and static extraction time also affect the extraction efficiency. High extraction efficiency of 90 % was obtained at the ratio of 10 mL ligand/mg-Pd and 1 h of static extraction time.

Key Words: Extraction, Palladium, Supercritical fluid extraction, Agitation, Chelating ligand.

INTRODUCTION

Noble metal, particularly palladium is in extensive use for catalysis reaction, synthesis of fine chemicals, ornaments, electronic devices and medical applications. Due to its low natural abundance and high value of the metal, there is a great interest in the development of separation and recovery processes for palladium from different containing spent materials. Significant amount of palladium can be found in petroleum refining catalysts, chemical manufacturing glass industry, electrical and electronic industries and spent automobile catalytic converter. Palladium metal is also formed as fission product and is stable during reactor operation. The metal is rejected as a waste during reprocessing of spent nuclear fuel by the PUREX process[1] and is being targeted now as valuables[2]. The concentrations of palladium in industrial catalyst may vary widely depending on the manufacturer. Spent automobile catalytic

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converter for example, contains about 200 to 800 µg/g of palladium[3]. Although the amount is quite small, but even still, the concentrations are often richer than those found in mined ores. Furthermore, the low rate production of the metal due to its low concentration in related ores and its high costs of production from naturally occurring supplies has made palladium recovery from the spent materials a viable and cost effective alternative of its preparation[4].

Extraction techniques for the separation and recovery of palladium from synthetic and industrial effluents are of critical important. Ion exchange methods using anion exchange resin[5], combining two hollow-fiber liquid membrane systems[3], supported liquid membranes (SLMs) containing a selective carrier[6], sorption by chitosan[7], selective dissolution in aqua regia[8], carbochlorination[9] and high temperature leaching[10] have attracted considerable attention of many researchers. However, these extraction methods are usually time-consuming, labour intensive and require large volumes of high purity of organic solvents. In recent years, supercritical CO_2 (sc CO_2) chelating extraction has been developed for the extraction of metal ions using coordinating ligands dissolved in supercritical CO_2[11-17]. The use of supercritical CO_2 extraction has been gaining interest to researchers because the method offers several advantages over conventional organic solvents in the separation or reaction process. Carbon dioxide is environmentally acceptable, has low toxicity and convenient critical properties (Tc = 31.1 ºC, Pc = 7.38 MPa), nonflammable and ease for recycling. Carbon dioxide is not currently regulated as a volatile organic chemical by the US environmental protection agency (EPA)[18]. The physical and chemical properties of liquid and supercritical CO_2, such as solvent power and density can be easily adjusted by varying temperature and pressure[19]. Those favorable properties of CO_2 offer the opportunities for selective extraction and fractionation.

In a previous work[20], the recovery of precious metals (platinum, palladium and rhodium) from a solid matrix sample by supercritical CO_2 containing a chelating ligand was investigated. Various extraction parameters such as pressure, temperature, static extraction time and the nature of ligand have been found to affect the extraction efficiency. The supercritical CO_2 with the ligand of tributyl phosphate showed to be effective in the extraction of palladium.

In order to optimize the extraction conditions, the process could also be improved by varying other parameters such as addition of modifier, water, acid and the use of agitation. In this paper, the effect of the use of agitation on the extraction of palladium with supercritical CO_2 and tributyl phosphate was investigated under different extraction time. The results were compared with the extraction without agitation. The mechanism of complex formation of metal-chelating ligand was also studied.

EXPERIMENTAL

Preparation of chelating ligand: The complex solution of tri-*n*-butyl phosphate/ nitric acid (TBP-HNO₃) was used as a chelating ligand. The chemical structure of tri-*n*-butyl phosphate is shown in Fig. 1. The TBP-HNO₃ was prepared by contacting

20 mL of an anhydrous TBP (Wako Pure Chemicals Co.) with the equal volume of conc. HNO₃ (70 %; Wako Pure Chemicals Co.) in a centrifuge tube. The mixture was shaken vigorously on a wrist action mechanical shaker for 5 min followed by centrifuging for 2 h. After centrifugation, the TBP phase was used for the experiments.
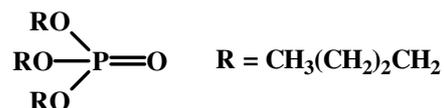
$$RO-\underset{\underset{RO}{|}}{\overset{\overset{RO}{|}}{P}}=O \qquad R = CH_3(CH_2)_2CH_2$$

Fig. 1. Chemical structure of tri-*n*-butyl phosphate

Supercritical fluid extraction procedure: The supercritical fluid extraction (SFE) apparatus was constructed in-house and is shown schematically in Fig. 2. The main part of the apparatus consisted of an extraction vessel (cylindrical stainless steel, 38 mm i.d × 46 mm length and a volume 50 mL), a high pressure pump (intelligent prep. pump, PU-2086 plus, Jasco Corp.), a cooling unit (CH-201, Scientific Instruments, Scinics Co. Ltd.), an oven (equipped with a magnetic stirrer system, SCF-Sro, Jasco Corp) and a back pressure regulator (SCF-Bpg, Jasco Corp.). Liquid carbon dioxide (more than 99.9 v/v % pure; Suzuki Shokan Co. Tokyo) was delivered from a cylinder to the high pressure pump. The pump head was cooled to -10 ℃ with a cool circulator to liquefy the gaseous CO_2. The supercritical CO_2 was flown to the extraction vessel from the top of the vessel. The extraction vessel was put in an oven, which control the temperature of the extraction vessel within ± 1.0 ℃ of the desired temper-ature. The inside pressure was controlled by the back pressure regulator to an accuracy of ± 0.1 Mpa.
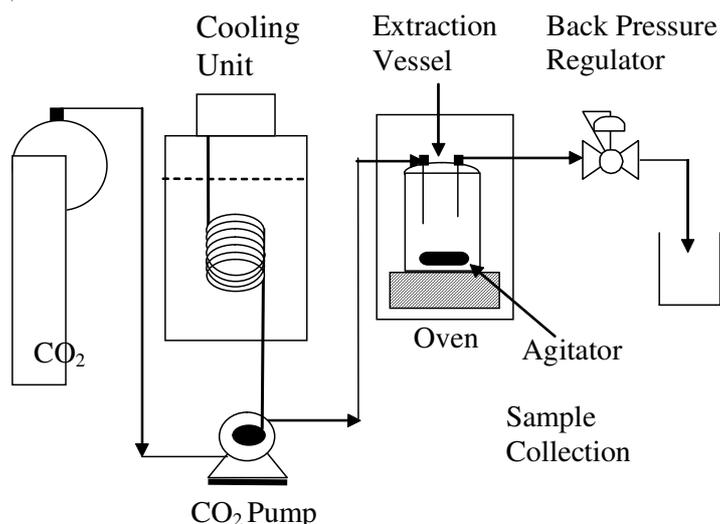

Fig. 2. Schematic diagram of supercritical fluid extraction apparatus

Sample (pure metal palladium) and the prepared chelating ligand were placed in the extraction vessel. The system was then sealed. Subsequently, the extraction vessel was pressurized with CO_2. After the temperature and pressure reached a desired value, the CO_2 pump was shut off. This moment was defined as the beginning of a static extraction. The experiments were then carried out dynamically with a desired CO_2 flow rate and extraction time. When the extraction was completed, the system was depressurized to atmospheric conditions and the extractant-metal complex was collected in a bottle sample. All experiments in this research were performed at a temperature of 60 ºC, a pressure of 30 MPa and a CO_2 flow rate of 2.4 mL/min, since they were the optimum extraction conditions obtained in previous work[20]. The concentration of metals were determined by inductively couple plasma (ICP) measurement (SPS7700R plasma spectrometer, Seiko Instrument Inc.) at a wave length of 214.423, 340.458 and 233.477 nm for Pt, Pd and Rh, respectively.

RESULTS AND DISCUSSION

Complex formation of Pd-TBP-HNO₃: Previous results[13-20] have shown that the presence of ligand and acid were necessary to extract metals sample with super-critical CO_2. The metal ions bound to organic ligands and form neutral species that could increase the solubility of the metals in supercritical CO_2[14,17]. Direct extraction of metal ions is not feasible due to the charge neutralization requirements and the week solute-solvent interactions. By adding complexing agent to the supercritical fluid phase, the charge on the metal ions can be neutralized and lipophillic groups can be introduced into the metal complex system. Solubilization of the metal complex into the supercritical fluid is then possible[14,6,17]. The TBP was chosen as a modifier in the present study taking into account its high polarity (dielectric constant = 8.91), high solubility in the supercritical CO_2 and low solubility in the aqueous solution[21,22].

The mechanism of complex formation when TBP and HNO_3 are use in the supercritical fluid extraction with CO_2 can be expressed by eqns. 1 and 2.

$$PdO + 2HNO_3 \rightarrow Pd^{2+} + 2NO_3^- + H_2O \qquad (1)$$

$$Pd^{2+} + 2NO_3^- + 2TBP \rightleftharpoons Pd(NO_3)_2(TBP)_2 \qquad (2)$$

Palladium oxides are dissolved by H^+ present in the complex. NO_3^- in the complex acts as a counter anion for neutralizing the palladium ions. The TBP which is highly soluble in supercritical CO_2 functions as a complex forming agent to be extracted. When TBP-HNO_3 is added to supercritical CO_2 and contacts palladium oxides, a chemical reaction occurs leading to formation of a hydrophobic complex of $Pd(NO_3)_2(TBP)_2$. The soluble Pd-TBP-HNO_3 complexes then dissolve into the supercritical CO_2 phase and are carried out to the bulk flow of CO_2.

Effect of static and dynamic extraction time: Static extraction was applied in order to increase the solvent penetrate into the sample matrix. Fig. 3 shows the effect of static extraction time on the extraction efficiency of palladium (with and without the use of agitation). The results show that the extraction efficiency of palladium increased with increasing the static extraction time up to 1 h. The efficiency

was then remains constant even when the static extraction time was continue to 2 h (data not shown here). The results showed that the use of agitation could improve the extraction efficiency, especially at a short static extraction time. As can be seen from the figure, the use of agitation without static extraction time (0 min) could increase the extraction efficiency at about 3 times, from 18-58 %. The use of agitator probably contributes to the mass transfer of concentrated $Pd(NO_3)_2(TBP)_2$ into the supercritical CO_2 phase. The role of agitation on the extraction efficiency was then decreased with the increasing of static extraction time. At 1 h, of static extraction time, the use of agitation could increase in only a small portion of extraction efficiency.
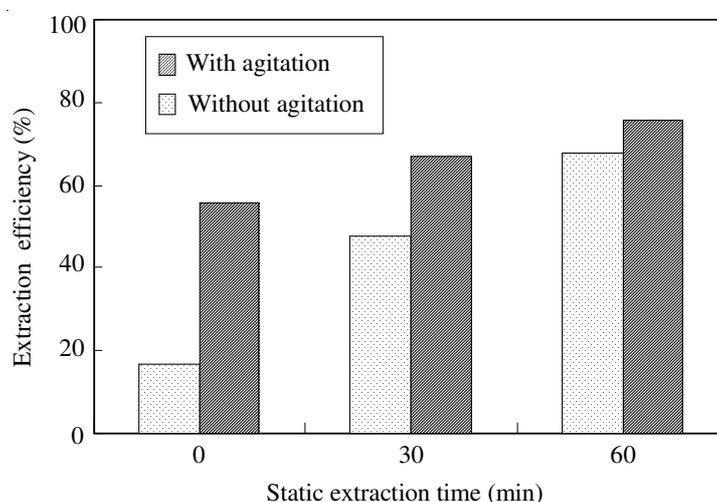

Fig. 3.   Effect of static extraction time on the extraction efficiency of palladium. (Conditions: T: 60 ºC, P: 30 MPa, CO_2 flow rate: 2.4 mL/min, dynamic extraction time: 1 h, ligand: 8 mL/mg-Pd)

Fig. 4 shows the effect of dynamic extraction time on the extraction efficiency of palladium (with the use of agitation). As expected, the extraction efficiency increased with increasing dynamic extraction time. Within 1 h of extraction time the extraction efficiency of palladium increased up to 90 %. After 1 h of extraction, there was no change of the extraction efficiency of palladium as time extended.

Effect of chelating ligand to sample ratio: Another factor, which significantly affects the extraction efficiency of palladium, is a chelating ligand to sample ratio. Fig. 5 shows the results of a series of palladium extraction with varying ratio of the chelating ligand to metal sample at 1 h of dynamic extraction time. As can be seen from the figure, the extraction efficiency increased with increasing the ratio up to 10 mL ligand/mg-Pd. The extraction efficiency of palladium was 21, 43, 60, 78 and 90 % at the ratio of 2, 4, 6, 8 and 10 mL ligand/mg-Pd, respectively. Then, the amount of extracted palladium decreased with the increased of the ratio. It seems likely that the excess chelating ligand shifted the equilibrium state in eqn. 2.
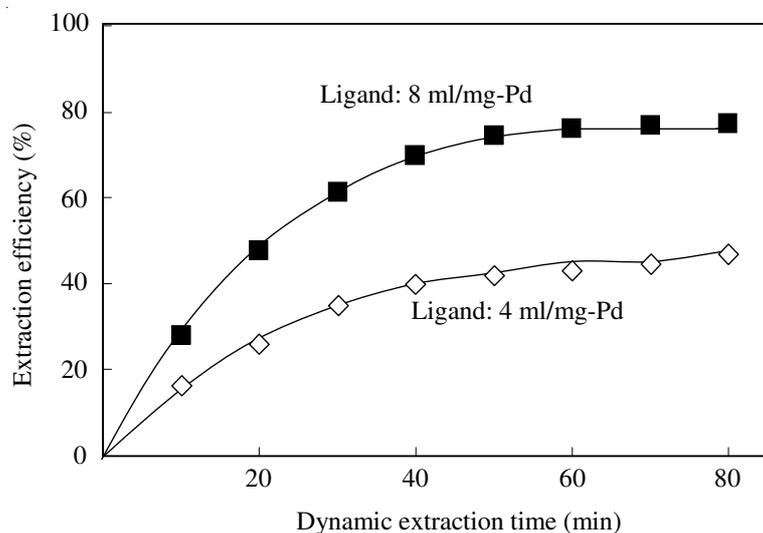
Fig. 4.   Effect of dynamic extraction time on the extraction efficiency of palladium. (Conditions: Use of agitation, T: 60 ºC, P: 30 MPa, CO_2 flow rate: 2.4 mL/min, static extraction time: 1 h)
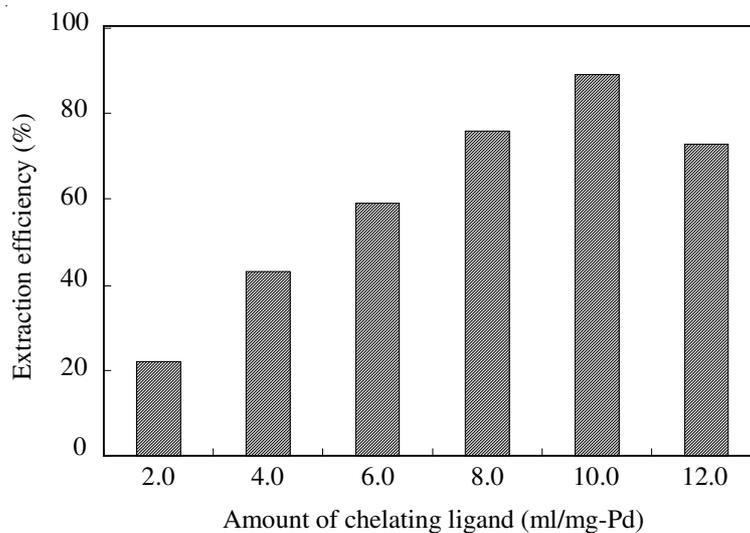

Fig. 5.   Effect of ratio chelating ligand to sample on the extraction efficiency of palladium. (Conditions: Use of agitation, T: 60 ºC, P: 30 MPa, CO_2 flow rate: 2.4 mL/min, static extraction time: 60 min, dynamic extraction time: 1 h)

Results of this study have shown that high extraction efficiency can be achieved in the extraction of palladium with supercritical CO_2. However other studies such as the kinetics and thermodynamic, ligand and phase separation behaviour and economic and feasibility of the process are equally important for utilization on an industrial scale. Future research should be conducted on such aspects of this technology.

Conclusion

The use of stirring method enhanced the extraction efficiency of palladium with supercritical CO_2, especially at a short extraction time and it is expected that the static extraction time could be shortened. The possible reaction and mechanism of complex metals-ligand in supercritical CO_2 was described. The results confirmed the presence of TBP as a chelating agent was necessary to extract palladium with supercritical CO_2. The metal ion should be bound to the organic ligand and form neutral species that could increase the solubility of the metal in supercritical CO_2. Increasing the ratio of chelating ligand to metals up to 10 mL ligand/mg-Pd could increased the extraction efficiency of palladium, however the efficiency diminished at higher chelating ligand to metal ratios.

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