Rhodium(III) Recovery from HCl Solutions Using 4-Alkylaniline-Impregnated Resins

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In this study, 4-butylaniline-impregnated resins (BuIRs) were prepared by soaking hydrophobic porous resins in aqueous solutions of 4-butylaniline hydrochloride. Rh(III) was successfully adsorbed by BuIRs from 10 ppm Rh(III) solutions (6 M HCl). The quantitative desorption of Rh(III) accompanied with 4-butylaniline hydrochloride from BuIRs was also achieved by Soxhlet extraction using methanol. UV-Vis absorption measurements of Rh(III)-containing solutions showed that the equilibrium shift of Rh(III)-based species in HCl solutions is slow, and heating of the solutions is effective for equilibrating. The BuIRs obtained in this study effectively recovered the Rh(III) chloro-complex anion ($[\text{RhCl}_6]^{3-}$) from low Rh(III) concentration solutions, and can be useful in the Rh(III) recovery process.

Keywords : platinum group metals / rhodium / adsorption / 4-alkylaniline / porous resin

1 INTRODUCTION

Rhodium (Rh) is a platinum-group metal (PGM) and is mainly used for automobile exhaust catalysts [1–3]. The recycling of PGMs, especially for Rh, is essential because of their scarcity and high price as well as for effective resource use. However, it is widely recognized that efficient recovery of Rh is difficult and remains a large problem [4].

PGM separation and recovery are generally performed by solvent extraction from metal-containing solutions via two different extraction mechanisms: ligand-metal coordination and ion-pair formation [5]. Palladium (Pd) and platinum (Pt), which are used as automobile exhaust catalysts along with Rh, can be extracted using various kinds of extractants, such as secondary and tertiary amines [6–9], organosulfides [10,11], and organophosphates [12–14]. However, extraction of Rh is known to be complicated regardless of the extraction mechanism. For example, Rh(III) extraction via a coordination mechanism is regarded to be kinetically inert and Rh(III) is nearly impossible to extract by an ion-pair mechanism [15,16]. Therefore, selective extraction as well as efficient extraction of Rh is one of the most challenging issues.

Recently, we developed selective Rh(III) recovery methods by precipitation using aromatic primary amines [17–19]. Preferential and selective precipitation of Rh(III) from the mixture of Pd(II), Pt(IV), and Rh(III) in hydrochloric acid (HCl) solutions was successfully achieved using aromatic primary monoamines or diamines as precipitants. However, the recovery percentages of Rh(III) by the precipitation methods were at most approximately 90% from 100 ppm Rh(III) solutions because some of the Rh(III)-containing precipitates were dissolved in the solutions. As a result, Rh(III) remained in the solution at a low concentration of approximately 10 ppm. Furthermore, some of leaching solutions

of spent catalysts contained low-concentration of Rh(III) less than 50 ppm [20,21]. Since PGMs are high price and precious metals, quantitative recovery of PGMs as far as possible is required. Therefore, a new recovery method that enables efficient recovery of Rh(III) from low-concentration Rh(III) solutions (ca. 10 ppm) is necessary. In this study, we focused on the use of aromatic primary amine-impregnated resins for Rh(III) recovery. It has been reported that extractant-impregnated resins are good adsorbents for metals and are advantageous in terms of low toxicity and high economic efficiency compared to solvent extractions [22–24]. Immobilization of precipitants on porous resins is expected to improve the efficiency of Rh(III) recovery from low metal concentration solutions because of the insolubility of the resins as well as the high surface area.

Herein, we present the preparation of 4-alkylaniline-impregnated resins and the Rh(III) recovery from HCl solutions. 4-Butylaniline was successfully immobilized on porous resins by soaking the resins in aqueous solutions of 4-butylaniline hydrochloride. The amine-impregnated resins adsorbed Rh(III) in high percentages even from 10 ppm Rh(III) solutions. Furthermore, adsorbed Rh(III) was successfully recovered from the resins by washing with methanol. The analysis of Rh(III) chloro-complexes in HCl was also conducted.

2 EXPERIMENTAL

2.1 Materials

4-Butylaniline was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and used as received. 4-Butylaniline hydrochloride was prepared by mixing 4-butylaniline and a 1 M HCl solution, followed by evaporation of water. The Rh(III) standard solution was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and used as received. Pd(II) and Pt(IV) standard solutions were

purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used as received. Hydrophobic porous resins (Sepabeads SP700) and anion-exchange resins (AERs, Diaion PA308) were supplied by Mitsubishi Chemical Corp. (Tokyo, Japan). The hydrophobic porous resins were thoroughly washed with water and methanol, and then dried at 50°C for 24 h under vacuum before use. The anion-exchange resins were soaked in 1 M NaOH solution for 12 h, thoroughly washed with water, and then dried at 50°C for 24 h under vacuum before use.

2.2 Preparation of 4-butylaniline-impregnated resins (BuIRs)

Dried porous resins (Sepabeads SP700, 3 g) were soaked in a 1.0 M aqueous solution of 4-butylaniline hydrochloride (18 mL) and shaken for 1 h at room temperature. The resins were collected by filtration, washed with water, and dried at 50°C for 12 h to yield BuIRs. The amount of amine on the resulting BuIRs was determined to be 0.97 mmol/g from the difference in weight of the resins before and after impregnation of the amine.

The BuIRs with different densities of the immobilized amines were prepared by the similar procedure described above using 0.12 M, 0.19 M, and 0.27 M aqueous solutions of 4-butylaniline hydrochloride, and the amounts of the amines on the resulting BuIRs were determined to be 0.39 mmol/g, 0.61 mmol/g, and 0.80 mmol/g, respectively.

2.3 Metal adsorption experiments

BuIRs were added to a 4 mL HCl solution containing 10 ppm of Rh(III) and the mixture was shaken vigorously. The metal concentration in the supernatant was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The HCl concentration, loading amount of BuIRs, shaking time, and density of the immobilized amines on BuIRs were changed in the metal adsorption experiments. BuIRs with 0.97 mmol/g were used except for the experiments changing the density of the amines on BuIRs. Rh(III), Pd(II), or Pt(IV) adsorption experiments using anion-exchange resins (1.0 mequiv./g) were performed using a similar method.

2.4 Rh(III) desorption from BuIRs

Rh(III)-adsorbed BuIRs were prepared using 6 M HCl solutions containing 100 ppm of Rh(III) using a procedure similar to that described in the metal adsorption experiments, and the adsorbed amount of Rh(III) was determined by ICP-AES of the solution after Rh(III) adsorption. Rh(III)-adsorbed BuIRs (0.1 g) were added to a 1 mL of 10 M NH_4OH solution or methanol and the mixture was shaken vigorously for 1 h. The metal concentration in the supernatant was determined by ICP-AES.

For Soxhlet extraction, Rh(III)-adsorbed BuIRs (0.3 g) were placed into an extraction thimble and inserted into a Soxhlet assembly fitted with a flask. Thereafter, 150 mL of methanol was added to the flask and refluxed for 12 h. The resulting methanol solution was evaporated and dried in vacuo. The obtained solid was dissolved in 1 M HCl, and the metal concentration in the solution was determined by ICP-AES.

2.5 UV-Vis absorption measurements

Rh(III)-containing solutions after Rh(III) adsorption experiments were prepared as follows. First, 0.4 g of BuIRs (0.97 mmol/g) were added to a 4 mL of 6 M HCl solution containing 100 ppm of Rh(III)

and the mixture was shaken vigorously for 1 h. Subsequently, BuIRs were removed from the solution, and another 0.5 g of BuIRs were added to the solution. After vigorous shaking for 1 h, the supernatant was used for the UV-Vis absorption measurements.

2.6 Measurements

An ICP-AES instrument (SPS5510, Hitachi High-Tech Science Corp., Tokyo, Japan) was used for the metal concentration measurements. ^1H NMR spectra were recorded using a JEOL JNM-ECX 500 NMR spectrometer (Jeol Co., Tokyo, Japan). UV-Vis absorption spectra were collected using a UV-Vis spectrophotometer (Model V-750, Jasco co., Tokyo, Japan).

3 RESULTS AND DISCUSSION

3.1 Rh(III) adsorption experiments

In this study, we used 4-butylaniline as an aromatic primary amine because the amine is reported to precipitate the Rh(III) chloro-complex anion ($[\text{RhCl}_6]^{3-}$) from HCl solutions [17]. As amine supports, hydrophobic porous resins based on styrene and divinylbenzene were selected because of their high stability in acidic solutions. 4-Butylaniline-impregnated resins (BuIRs) were prepared by soaking the resins in aqueous solutions of 4-butylaniline hydrochloride. The amount of amine immobilized on the resins was evaluated from the difference in weight of the resins before and after impregnation of the amine. The saturation adsorption capacity of the amine on the resin was approximately 1.0 mmol/g.

Rh(III) adsorption experiments were performed by adding BuIRs to Rh(III)-containing HCl solutions (Rh(III): 10 ppm) and shaking. The adsorption percentages of Rh(III) were evaluated by ICP-AES of the solutions after removal of the resins. Figure 1a shows the relationship between Rh(III) adsorption and HCl concentrations. The Rh(III) adsorption increased with increasing HCl concentration, reaching 70% at 5 M HCl. It is noteworthy

Figure 1 The effect of (a) HCl concentration (0.4 g of BuIRs, 1 h of shaking), (b) loading concentration of BuIRs (6 M HCl, 1 h of shaking), (c) shaking time (6 M HCl, 0.4 g of BuIRs), and (d) density of amines on BuIRs (6 M HCl, amine/Rh = 1000 mol/mol, 1 h of shaking) on Rh(III) adsorption.

Figure 2 The Rh(III) adsorption results from 10 ppm Rh(III) solutions using BuIRs or AERs.

that BuIRs successfully achieved high Rh(III) adsorption (71% at 6 M HCl) from low-concentration Rh(III) solutions. The Rh(III) adsorption behavior according to the loading amount of BuIRs is shown in Figure 1b. The Rh(III) adsorption percentages increased with an increase in BuIRs loading, and reached a plateau at 0.4 g/mL, which was 4-butylaniline on BuIRs/Rh = 1000 mol/mol. The effect of shaking time on Rh(III) adsorption was also investigated (Figure 1c). Rh(III) adsorption was completed after 1 h of shaking. Prolonged shaking did not induce an increase in Rh(III) adsorption.

The Rh(III) adsorption experiments were performed by varying the density of the immobilized amines on BuIRs (0.39–0.97 mmol/g). As shown in Figure 1d, the Rh(III) adsorption percentages increased in proportion to the density of the amines on the BuIRs, even though the loading amount of the amine on BuIRs was constant (amine/Rh = 1000 mol/mol). This result indicates that several amines are involved in the adsorption of one Rh(III) chloro-complex anion ($[\text{RhCl}_6]^{3-}$). In our previous paper, it was revealed that Rh(III) was precipitated using 4-alkylanilines by forming unique ion-pair complexes in which one $[\text{RhCl}_6]^{3-}$ was surrounded by six anilinium cations [17]. Therefore, Rh(III) adsorption occurs by the surrounding of $[\text{RhCl}_6]^{3-}$ with several amines on the BuIRs.

The Rh(III) adsorption ability of BuIRs was compared with that of typical anion exchange resins possessing quaternary ammonium groups (AERs). The AERs used in this study showed high adsorption ability toward Pd(II) and Pt(IV): 89% and 98% of Pd(II) and Pt(IV) from 6 M HCl solutions (Pd(II), Pt(IV): 1 mM each), respectively. Figure 2 shows the Rh(III) adsorption results from 10 ppm Rh(III) solutions using BuIRs and AERs. The Rh(III) adsorption using AERs was very low (16%), whereas that using BuIRs was high (75%). This result clearly indicates that BuIRs possessing primary amines have a much higher Rh(III) adsorption ability than conventional PGM adsorbents possessing quaternary ammonium groups. Although the BuIRs successfully adsorbed Rh(III), complete adsorption of Rh(III) was not achieved even when a large amount of BuIRs was used, as shown in Figure 1b. One possibility is that the Rh(III)-containing solution used in this study contains Rh species that are inactive for recovery by 4-alkylanilines, such as $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$.

3.2 Rh(III) Desorption from Resins

It has been reported that Rh(III) quantitatively desorbed from Rh(III)-containing precipitates composed of $[\text{RhCl}_6]^{3-}$ and aromatic primary diamines by adding NH_4OH solutions [18]. The successful desorption of Rh(III) would be due to the collapse of the ion-pairs composed of $[\text{RhCl}_6]^{3-}$ and ammonium cations of the diamines. Therefore, the desorption of Rh(III) from BuIRs

Figure 3 ^1H NMR spectra of 4-butylaniline hydrochloride (a) as prepared, and (b) after recovery by sublimation.

was studied using NH_4OH solutions. However, the desorption efficiency of Rh(III) from BuIRs was only 60%, despite the use of a 10 M NH_4OH solution. This result may be due to the low contact efficiency of the NH_4OH solution with the immobilized amines on BuIRs. Subsequently, we used methanol for the Rh(III) desorption experiments. In addition to Rh(III), 4-butylaniline hydrochloride was desorbed from BuIRs, resulting in a Rh(III) desorption efficiency of 66% and 71% using methanol and hot methanol, respectively. Based on this result, Soxhlet extraction of BuIRs using methanol was conducted for 12 h, and the quantitative desorption of Rh(III) (> 99%) was successfully achieved. It is noteworthy that desorbed 4-butylaniline hydrochloride was easily recovered by sublimation from the desorbed mixture, and its chemical structure was unchanged according to the ^1H NMR spectra (Figure 3). Furthermore, the porous resins after desorption using methanol were not damaged. It is possible to repeatedly reuse both 4-butylaniline hydrochloride and porous resins.

3.3 Distribution of Rh(III)-based species and equilibrium shifts

The distribution of Rh(III)-based species in a 6 M HCl solution was evaluated by UV-Vis spectroscopy. It is reported that the absorption peaks of Rh(III) chloro-complex anions are observed in the range of 350–650 nm (488 nm and 385 nm for $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$, 507 nm and 402 nm for $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$, 518 nm and 411 nm for $[\text{RhCl}_6]^{3-}$) [25,26]. The abundance ratio of the Rh(III)-based species was calculated from the waveform separation of the spectrum shown in Figure 4a. It was found that the solution contained 83% $[\text{RhCl}_6]^{3-}$, 10% $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$, and 7% $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$. However, previous papers have reported that $[\text{RhCl}_6]^{3-}$ accounts for approximately 90%, and $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ does not exist in 6 M HCl solutions [4,17,19]. We assumed that the Rh(III)-based species in the HCl solution used was not in an equilibrium state. Therefore, we performed heating (80°C for 24 h) of a 6 M HCl solution containing 100 ppm of Rh(III), and the distribution of Rh(III)-based species in the solution was evaluated by UV-Vis spectroscopy (Figure 4b). As a result, the solution contained 91% of $[\text{RhCl}_6]^{3-}$ and 9% of $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$, and this abundance ratio matched well with previous reports. Then, the equilibrium shift from $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ to $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ or $[\text{RhCl}_6]^{3-}$ was investigated by heating Rh(III)-containing HCl solutions. We used Rh(III)-containing solutions after Rh(III) adsorption experiments, and the solution contained

Figure 4 UV-Vis absorption spectra of 100 ppm Rh(III) solution (6 M HCl) (a) before and (b) after heating at 80°C for 24 h. $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$, $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$, and $[\text{RhCl}_6]^{3-}$ are shown in pink, yellow, and green, respectively.

Figure 5 UV-Vis absorption spectra (a) before and (b) after heating (80°C for 24 h) of Rh(III)-containing solution after Rh(III) adsorption experiments.

Figure 6 The relationship between heating time and peak top wavelength in absorption spectra.

only $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ in spite of the 6 M HCl condition (Figure 5a). As shown in Figures 5b and 6, $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ changed to $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ or $[\text{RhCl}_6]^{3-}$ upon heating at 60°C or 80°C, and the transformation to $[\text{RhCl}_6]^{3-}$ was almost complete after 10 h of heating at 80°C. However, heating at 40°C did not induce an equilibrium shift of $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ even after 24 h. This result evidently shows that the equilibrium shift of $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ without heating is very slow, and the heating at 80°C is effective

for the equilibrium shift of Rh(III)-based species.

Finally, the Rh(III) adsorption was evaluated using BuIRs and a 10 ppm Rh(III) solution (6 M HCl) after heating at 80°C for 24 h. The Rh(III) adsorption percentage reached high value of 89%, which corresponds to the abundance ratio of $[\text{RhCl}_6]^{3-}$ (91%). This result evidently indicates that BuIRs can efficiently recover $[\text{RhCl}_6]^{3-}$ from low metal concentration solutions.

4 CONCLUSION

The BuIRs were prepared by soaking the porous resins in aqueous solutions of 4-butaniline hydrochloride. Rh(III) was successfully adsorbed by BuIRs from 10 ppm Rh(III) solutions (6 M HCl). The quantitative desorption of Rh(III) accompanied with 4-butaniline hydrochloride from BuIRs was also achieved by Soxhlet extraction using methanol. Furthermore, it is possible to repeatedly reuse both desorbed amine hydrochloride and porous resins. It was found that the equilibrium shift of Rh(III)-based species in HCl solutions is slow, and heating of the solutions is effective for equilibrating. We succeeded in the high adsorption (91%) of Rh(III) using BuIRs by equilibrating the 10 ppm Rh(III) solution. The BuIRs obtained in this study are promising for use in Rh(III) recovery from low Rh(III) concentration solutions.

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