Highly Selective Rh(III) Recovery from HCl Solutions Using Aromatic Primary Diamines via Formation of Three-Dimensional Ionic Crystals

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Supporting Information

ABSTRACT: A new Rh(III) separation method using metal-containing hydrochloric acid (HCl) solutions has been developed. This method includes Rh(III) precipitation with high selectivity using aromatic primary diamines as precipitants. The compound p-phenylene diamine dihydrochloride (PPDA) successfully precipitates only Rh(III) from HCl solutions containing Pd(II), Pt(IV), and Rh(III). Furthermore, highly selective Rh(III) recovery from the simulated spent catalyst leach solution, comprising Pd, Pt, Rh, Ce, Al, Ba, Zr, La, and Y in 5 M HCl, was achieved using PPDA. Single-crystal X-ray analysis revealed that the Rh(III)-containing precipitate using PPDA forms three-dimensional ionic crystals comprising the [RhCl6]3−/ammonium form of PPDA/chloride anion/H2O at a 1:2:1:2 ratio. Formation of these unique ionic crystals plays a key role in the highly selective Rh(III) recovery. This Rh(III) recovery method will be promising for use in the purification process of Rh as well as the practical Rh recovery from spent catalysts.

INTRODUCTION

Rhodium (Rh) is one of the most high-priced metals and a member of the platinum group metals (PGMs). Currently, Rh is mainly used in catalysts for automobile exhaust gas along with palladium (Pd) and platinum (Pt).1−3 Because of the scarcity and high price of PGMs, their recycling from spent catalysts and electronic scraps is essential for metal sustainability. However, it is known that separation and selective recovery of Rh from the mixture of PGMs (such as Pd and Pt) is quite difficult and still remains a challenging issue.4

In general, PGMs are separated individually by solvent extraction from the acid leach liquors of secondary resources.5−19 It is known that the extraction of Pd(II) and/or Pt(IV) from Rh(III)-containing solutions can be achieved using organic extractants, such as secondary or tertiary amines,10−12 sulfur-containing compounds,13−15 and organophosphorus compounds.16−19 This is because the extraction of PGMs occurs in the following order via the ligand−metal coordination mechanism or ion-pair formation mechanism.20 The PGMs can be extracted in the following order Pd(II) ≫ Rh(III) ≫ Pt(IV) via the ligand−metal coordination mechanism, and the extraction of Rh(III) and Pt(IV) hardly occurs because of their kinetically inert nature.21 Furthermore, the extraction of chloro-complexes of PGMs from hydrochloric acid (HCl) solutions via the ion-pair formation mechanism occurs in the order of [MCl4]2− ≈ [MCl6]2− > [MCl4]3− > aqua species.22 The chloro-complex anions of Pd(II) and Pt(IV), [PdCl4]2− and [PtCl6]3−, can be extracted, whereas that of Rh(III), [RhCl6]3−, is quite difficult to extract based on ion-pair formation. Therefore, Rh(III) is generally recovered from the raffinate after solvent extraction of leach liquors, even in industrial processes, owing to its inert nature.23 It is widely recognized that preferential and selective recovery of Rh(III) in preference to Pd(II) and Pt(IV) is one of the most difficult goals to achieve.

To date, several separation and recovery methods of Rh(III) via solvent extraction have been developed and employed. The extractability of Rh(III) can be enhanced by the addition of SnCl2.24−28 Tertiary amines and organophosphines can extract Rh(III) from SnCl2-containing HCl solutions, while Pt(IV) is coextracted. As a selective separation method of Rh, the selective back extraction of Rh(III) from an organic phase containing Pd(II), Pt(IV), and Rh(III) into a concentrated HCl solution was reported by Narita et al.29,30 This method requires two steps: extraction of Pd(II), Pt(IV), and Rh(III) into an organic phase and the back extraction of Rh(III) into a water phase. However, these Rh(III) separation methods cannot extract only Rh(III) in preference to Pd(II) and Pt(IV) in one step.

Recently, we have developed a new Rh(III) separation method using 4-alkylanilines as precipitants.31 Selective precipitation of Rh(III) from HCl solutions containing Pd(II), Pt(IV), and Rh(III) was successfully achieved based on the
formation of a unique ion-pair composed of $[\text{RhCl}_6]^{3-}$/anilinium/chloride ions in a 1:6:3 ratio. This separation method enabled selective and preferential Rh(III) recovery in preference to Pd(II) and Pt(IV) in a single precipitation step. However, the use of 4-alkylanilines as precipitants has a risk for coprecipitation of Pd(II) and Pt(IV) when the concentrations of Pd(II) and Pt(IV) are high. This is because the ion-pairs of Pd(II) and Pt(IV) are alkyl-terminated hydrophobic structures. Therefore, we focused on the use of aromatic primary diamines as precipitants for Rh(III) selective recovery. It is expected that the diamines selectively form a three-dimensional ion-pair network with $[\text{RhCl}_6]^{3-}$ based on the abovementioned unique ion-pair formation. On the other hand, the precipitation of Pd(II) and Pt(IV) is likely to be suppressed even in high concentrations because the ion-pairs of Pd(II) and Pt(IV) with diamines are expected to form ammonium-terminated hydrophilic structures.

Here, we present a highly selective Rh(III) recovery process from metal-containing HCl solutions, using aromatic primary diamines as precipitants. Highly selective Rh(III) separation from HCl solutions containing Pd(II), Pt(IV), and Rh(III) was achieved via selective formation of Rh(III)-containing precipitates. In addition, this method enabled the Rh(III)-selective recovery from the simulated spent catalyst leach solutions containing various types of metals, such as PGMs, base metals, and lanthanoids. We found that the key to the highly selective recovery of Rh(III) is the formation of three-dimensional ionic crystals comprising $[\text{RhCl}_6]^{3-}$ and aromatic primary diamines.

### RESULTS AND DISCUSSION

#### Rh(III) Precipitation Using Aromatic Primary Amines.

The Rh(III) precipitation experiments were carried out using Rh(III)-containing HCl solutions (300 mg/L) and aromatic primary amines. The precipitation percentages of Rh(III) were evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) of the supernatant. For this experiment, we used commercially available diamines: 4,4′-diaminodiphenyl ether (ODA), 1,4-bis(4-aminophenoxy)benzene (DPOP), and 4,4′-bis(4-aminophenoxy)biphenyl (DPOBP). Figure 1 shows the Rh(III) precipitation behaviors according to HCl concentration. The Rh(III) precipitation percentage increases with an increase in the HCl concentration, reaching a maximum at approximately 3–5 M HCl. At
high HCl concentrations over 6 M HCl, the Rh(III) precipitation percentages decrease. The increase in the Rh(III) precipitation below 5 M HCl would be caused by the increase in the amount of [RhCl₆]³⁻ present in the solutions. On the other hand, the decrease in the solubility of the diamines by temperature to 80 °C (38% for rt, 75% for 80 °C, Figure S1). As can be seen in Figure 1, DPOBP showed the best performance in terms of Rh(III) precipitation among the three diamines. Approximately 90% of Rh(III) was precipitated using DPOBP at 4–6 M HCl concentrations.

The Rh(III) precipitation experiments were carried out using DPOBP and 5 M HCl solutions by changing the loading amounts of DPOBP and the shaking time. The Rh(III) precipitation percentages increased in proportion to the loading amount, reaching a plateau at a DPOBP/Rh molar ratio of 4:1 (Figure 2a). Figure 2b shows the shaking time dependence of the Rh(III) precipitation at a feed ratio of DPOBP/Rh(III) = 5 mol/mol. The Rh(III) precipitation was completed after 1 h of shaking, and the prolonged shaking did not induce an increase in the Rh(III) precipitation percentage.

**Rh(III) Separation from Pd(II) and Pt(II) Using DPOBP.** The metal precipitation experiments from the HCl solutions containing Pd(II), Pt(IV), and Rh(III) (300 mg/L each) were performed using DPOBP as a precipitant. Figure 3 shows the relationship between metal precipitation percentages and HCl concentrations. The Rh(III) precipitation behavior was almost the same as that from Rh(III)-containing HCl solutions, as shown in Figure 1, indicating that Pd(II) and Pt(IV) do not disturb the precipitation of Rh(III). Although a small amount of Pt(IV) was precipitated accompanied by Pd(II) and Rh(III) at low HCl concentrations less than 3 M, no precipitation of Pt(IV) occurred at 4–9 M HCl concentrations. On the other hand, most of the Pd(II) was precipitated at low HCl concentrations, and the Pd(II) precipitation occurred at a wide range of HCl concentrations, up to 7 M. The precipitation of Pd(II) even at high HCl concentrations would be caused by high hydrophobicity of DPOBP. In fact, Pd(II) was not leached in 9 M HCl from the Pd(II) precipitate prepared in 2 M HCl, indicating that the hydrophobic nature of the Pd(II) precipitate prevents the exchange of [PdCl₄]²⁻ with chloride anions (Figure S2). The selective precipitation of Rh(III) using DPOBP was achieved in 8 M HCl: 82% for Rh(III), 0% for Pd(II), and 0% for Pt(IV). However, the use of DPOBP has a risk of coprecipitation of Pd(II) from high Pd(II) concentration solutions. Therefore, we selected p-phenylene diamine dihydrochloride (PPDA), which is the smallest aromatic diamine compound and has higher hydrophilicity than DPOBP (solubility in 5 M HCl: 0.18 mg/mL for DPOBP, 5.6 mg/mL for PPDA). The performance for selective Rh(III) recovery using PPDA was investigated in the following experiments.

**Selective Rh(III) Precipitation Using PPDA.** The Rh(III) precipitation experiments were carried out using PPDA as a precipitant by changing the HCl concentration and the PPDA loading. As shown in Figure 4a, Rh(III) was precipitated in 4–7 M HCl after 6 h of shaking, and the Rh(III) precipitation reached a maximum of 85% in 5 M HCl. It is noteworthy that the Rh(III)-containing precipitate prepared from 5 M HCl was easily soluble in 9 M HCl (Figure S2). This fact clearly indicates that the decrease in the Rh(III) precipitation at high HCl concentrations over 5 M is caused by the exchange of [RhCl₆]³⁻ with chloride anions. The effect of the loading amount of PPDA on the Rh(III) precipitation after 6 h of shaking was studied using 5 M HCl solutions. Rh(III) precipitation increased until PPDA/Rh = 15 mol/mol, and the precipitation percentages were not changed by further addition of PPDA (Figure 4b). Figure 4c shows the shaking time dependence of the Rh(III) precipitation at a feed ratio of PPDA/Rh(III) = 15 mol/mol. It took at least 3 h for Rh(III) precipitation using PPDA to become constant.

The separation of Rh(III) from Pd(II) and Pt(IV) was studied using PPDA. The dependence of the metal precipitation on the HCl concentration is shown in Figure 4d. Rh(III) precipitation occurred in 4–6 M HCl, and 82% of Rh(III) was precipitated at a 5 M HCl concentration. On the
other hand, Pd(II) and Pt(IV) were not precipitated under the studied conditions (1–9 M HCl). As we expected, a small aromatic diamine compound, PPDA, worked as a highly selective precipitant of Rh(III): 82% for Rh(III), 0% for Pd(II), and 0% for Pt(IV) in 5 M HCl.

**Desorption of Rh(III) from Precipitates.** We investigated the Rh(III) desorption from precipitates, using our precipitation method as a Rh(III) recovery strategy. The Rh(III) desorption experiments were performed by adding NH₄OH solution to the Rh(III)-containing precipitates. Rh(III) was quantitatively transferred from the Rh(III)-containing precipitates using NH₄OH solutions of 1–5 M (Figure S3a). On the other hand, high-concentration NH₄OH solutions over 6 M were required for the quantitative Rh(III) desorption from the Rh(III)-containing precipitates using DPOBP (Rh-DPOBP), as shown in Figure S3b. The successful desorption of Rh(III) would be due to the collapse of the ion-pairs composed of Rh(III) chloro-complex anions and ammonium cations of the diamines; ammonium cations of PPDA and DPOBP were transformed into free amines by NH₄OH. It is noteworthy that the chemical structure of the recovered DPOBP after Rh(III) desorption was unchanged (Figure S4). Unfortunately, the recovered amount of PPDA is too small for chemical structural analysis.

**Rh(III) Recovery from Simulated Spent Catalyst Leach Solutions.** To elucidate the practical utility of our Rh(III) separation method, Rh(III) recovery from simulated spent catalyst leach solutions was investigated. The simulated solutions (5 and 8 M HCl) containing PGMs (Pd, Pt, and Rh) and other metals such as base metals and lanthanoids (Ce, Al, Ba, Zr, La, and Y) were prepared based on the previously reported HCl leach solutions of automobile exhaust catalysts. Because of the saturation of Ba in 8 M HCl, the concentration of Ba in 8 M HCl is lower than that in 5 M HCl (Tables S1 and S2). The Rh(III) recovery experiments from the simulated solutions using DPOBP or PPDA were carried out. The metal recovery percentages were evaluated from the NH₄OH solutions after the desorption process by ICP-AES. In the case of using DPOBP, the metal precipitation percentages were also evaluated before the desorption process. The results of the Rh(III) recovery experiments are shown in Figures 5 and 6, and Tables S1 and S2. As shown in Figure 5, Rh(III) was selectively precipitated in a good yield (78%) using DPOBP from the simulated solution (8 M HCl), although Pd(II) was partially precipitated (21%). Other metals, except Pd(II), were not detected by ICP-AES. The precipitation of Pd(II) using DPOBP would be derived from poor hydrophilicity of DPOBP and high Pd(II) concentration. We have found that the desorption of Rh(III) using NH₄OH solutions is inefficient (Rh(III) desorption: 46%) when DPOBP is used as a precipitant (Table S1). The improvement of the low desorption efficiency is still in progress. On the other hand, PPDA enabled highly selective Rh(III) recovery from the simulated solution: 84% for Rh(III) and less than 2% for other metals (Figure 6 and Table S2). As a result, we have achieved highly selective Rh(III) recovery from the simulated spent catalyst leach solutions, using aromatic primary diamines. It is very surprising that only Rh(III) was selectively recovered in high yield using PPDA despite much higher concentrations of Pd(II), Pt(IV), and metals other than Rh(III) in the simulated solution.

**Characterization of Rh(III)-Containing Precipitates.** To elucidate the mechanism of Rh(III) selective recovery using aromatic primary diamines, the structural analyses of the Rh(III)-containing precipitates were carried out. Single crystals were prepared by adding DPOBP or PPDA into Rh(III)-containing HCl solutions. The addition of PPDA successfully yielded red-colored single crystals, while, unfortunately, single crystals were not obtained using DPOBP. Figure 7 shows the crystal structure of Rh-DPOBP. Two Rh(III) chloro-complex anions ([RhCl₆]³⁻) are linked by an ammonium form of PPDA via ionic bonds. One [RhCl₆]³⁻ interacts with four ammonium cations, and one chloro anion coexists to balance the total charge. The obtained three-dimensional ionic crystal is composed of the [RhCl₆]³⁻/ammonium form of PPDA/chloride ion/H₂O = 1:2:1:2. We have reported that aromatic primary monoamines and [RhCl₆]³⁻ form unique ion-pair complexes composed of [RhCl₆]³⁻/anilinium/chloride ions in a 1:6:3 ratio. The structure of the ionic crystals obtained in this study is completely different from the crystals obtained using aromatic monoamine. The ratios of Rh(III) and diamines in Rh-DPOBP and Rh-PPDA were confirmed by thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) analysis. Weight loss was observed in the range of 180–450 °C for both precipitates, which is attributed to the decomposition and volatilization of amines, chlorine, and water (Figure 8a,b). The residual weights at 800 °C were found to be 10.7 and 20.2% for Rh-DPOBP and Rh-PPDA, respectively. It is known that the combustion of RhCl₃ in air yields Rh₂O₃ below 900 °C. The resulting weight fractions of the residues by TGA coincide with the expected weight fractions of Rh₂O₃ after combustion of the ionic crystals, composed of the [RhCl₆]³⁻/ammonium form of diamine/chloride anion/H₂O in a 1:2:1:2 ratio. The weight fractions are calculated to be 11.2 and 20.9% for the ionic

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Metal precipitation from the simulated spent catalyst leach solution (8 M HCl, Pd: 937 mg/L, Pt: 617 mg/L, Rh: 303 mg/L, Ce: 5239 mg/L, Al: 2661 mg/L, Ba: 710 mg/L, Zr: 208 mg/L, La: 71 mg/L, and Y: 28 mg/L) using DPOBP.

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Metal recovery from the simulated spent catalyst leach solution (5 M HCl, Pd: 895 mg/L, Pt: 592 mg/L, Rh: 300 mg/L, Ce: 5494 mg/L, Al: 2785 mg/L, Ba: 2609 mg/L, Zr: 207 mg/L, La: 53 mg/L, and Y: 32 mg/L) using PPDA.
crystals using DPOBP and PPDA, respectively. The XPS spectra of the precipitates exhibit N 1s, Rh 3d, C 1s, Cl 2s, and Cl 2p signals (Figure 8c,d). The Rh/N/Cl atomic ratios were calculated to be 1.0:4.0:7.0 and 1.0:4.0:6.9 for Rh-DPOBP and Rh-PPDA, respectively. These atomic ratios are consistent with those of the ionic crystals comprising the $[\text{RhCl}_6]^{3-}/\text{ammonium form of diamine/chloride anion/H}_2\text{O}$ in a 1:2:1:2 ratio (Rh/N/Cl = 1:4:7). TGA and XPS results clearly indicate that the Rh(III)-containing precipitates using DPOBP and PPDA form ionic structures similar to the single-crystal structure shown in Figure 5.

The structure of Rh-PPDA in the precipitation experiments was also investigated by powder X-ray diffraction measurements in the $2\theta$ range of $5-30^\circ$. As shown in Figure 9, all of the peaks observed in the measured pattern were closely matched in position and relative intensity with the simulated pattern generated from the single-crystal diffraction data of Rh-PPDA. This result strongly supports that Rh(III) was precipitated using PPDA by forming unique three-dimensional ionic crystals.

**Mechanism of Selective Recovery of Rh(III).** The highly selective precipitation of Rh(III) was successfully achieved using PPDA even from the HCl solution containing various
kinds of metals, such as PGMs, base metals, and lanthanoids. The used metals except for PGMs are expected not to form ion-pairs with PPDA, that is, precipitates, because they basically form cations in HCl solutions. On the other hand, chloro-complex anions of Pd(II) and Pt(IV) have the possibility to be precipitated via ion-pair formation with PPDA. In our previous study, we revealed that the precipitates composed of $[\text{PdCl}_4]^{2-}$ or $[\text{PtCl}_6]^{2-}$ and ammonium cations of 4-alkylanilines are unstable in high-concentration HCl solutions and soluble by exchange of anilinium cations with protons.\(^{31}\) Therefore, the low stability of the ion-pairs of $[\text{PdCl}_4]^{2-}$ or $[\text{PtCl}_6]^{2-}$ and PPDA (Pd-PPDA, Pt-PPDA) in HCl solutions would be one reason for the lack of Pd(II) and Pt(IV) precipitation. Another reason would be the high hydrophilicity of Pd-PPDA and Pt-PPDA. This is because Pd-PPDA and Pt-PPDA are supposed to have ammonium-terminated ion-pairs, as shown in Figure 10. It is noteworthy that Pd(II) and Pt(IV) are precipitated using 4-butylaniline from HCl solutions (Pd(II), Pt(IV), and Rh(III): 300 mg/L each), even at high HCl concentrations (>5 M), while they are not precipitated from HCl solutions (Pd(II), Pt(IV), and Rh(III): 100 mg/L each) at 1–8 M (Figure S5).\(^{31}\) Because the ion-pairs composed of $[\text{PdCl}_4]^{2-}$ or $[\text{PtCl}_6]^{2-}$ and 4-butylanilines are alkyl-terminated hydrophobic structures, the high concentration of Pd(II) and Pt(IV) leads to precipitation despite the low stability of the ion-pairs in HCl solutions. Considering the results of 4-butylaniline, the high solubility of Pd- and Pt-PPDA in HCl solutions, which is attributed to their ion-pair structures contribute significantly to the highly selective precipitation of Rh(III) using PPDA. The selective precipitation of Rh(III) using DPOBP would be achieved by the same reasons, although Pd(II) is coprecipitated owing to high hydrophobicity of DPOBP.

Rh(III) precipitation occurs via formation of ionic crystals composed of the $[\text{RhCl}_6]^{3-}$/ammonium form of PPDA/chloride anion/H$_2$O in a 1:2:1:2 ratio. It should be noted that single crystals of Rh-PPDA were obtained even from the simulated spent catalyst leach solution by adding PPDA and leaving to stand for several days (Figure S6). This fact clearly indicates that the formation of ionic crystals between PPDA and $[\text{RhCl}_6]^{3-}$ is significantly selective regardless of the existence of other metal ions. Thus, the formation of the unique ionic crystals plays a key role in the highly selective recovery of Rh(III).

## CONCLUSIONS

Highly selective recovery of Rh(III) from metal-containing HCl solutions has been achieved using aromatic primary amines as precipitants. Rh(III) was preferentially and selectively precipitated from the HCl solutions and Rh(III) in the precipitate was transferred into NH$_4$OH solution. Highly selective recovery of Rh(III) from the simulated spent catalyst leach solution was successfully achieved using PPDA as a precipitant. Structural analysis revealed that the successful recovery of Rh(III) is attributed to the formation of ionic crystals comprising the $[\text{RhCl}_6]^{3-}$/ammonium form of diame/chloride anion/H$_2$O in a 1:2:1:2 ratio. This method will be promising for use in the purification process of Rh owing to significantly high selectivity of Rh as well as the practical Rh recovery from the spent catalysts.

## MATERIALS AND METHODS

### Materials

OA, DPOP, DPOBP, PPDA (hydrochloride form), and AlCl$_3$ were purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received. Pd(II), Pt(IV), and Y standard solutions and LaCl$_3$ were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. and used as received. Rh(III) standard solution, CeCl$_3$, BaCl$_2$, and ZrCl$_4$ were purchased from Kanto Chemical Co., Inc. and used as received. Simulated spent catalyst solutions were prepared by dissolving metal chlorides in HCl and mixing with metal standard solutions.

### Metal Precipitation Experiments Using Aromatic Primary Amines.

To the HCl solutions (1 mL) containing Rh(III) (300 mg/L) or Pd(II), Pt(IV), and Rh(III) (300 mg/L each) aromatic primary amines (ODA, DPOP, DPOBP, or PPDA) were added and the mixtures were shaken vigorously at room temperature. After centrifugation (7200 g, 10 min), the metal concentration in the supernatant was determined by ICP-AES. The HCl concentrations, the amount of precipitants, and the shaking time were changed in the metal precipitation experiments.

### Desorption of Rh(III) from Precipitates.

To 5 M HCl solutions (1 mL) containing Rh(III) (300 mg/L) or Pd(II), Pt(IV), and Rh(III) (300 mg/L each) aromatic primary amines (ODA, DPOP, DPOBP, or PPDA) were added and the mixtures were shaken vigorously at room temperature. The resulting solid was separated by centrifugation (7200 g, 10 min) and the supernatant was removed. After drying in vacuo at room temperature, NH$_4$OH solution (1 mL) was added to the solid and the mixture was shaken vigorously at room temperature. The remaining solid was removed by filtration and the metal concentration in the resulting filtrate was determined by ICP-AES.

### Rh(III) Recovery from Simulated Spent Catalyst Leach Solutions.

To a simulated spent catalyst leach solution (5 M HCl, 10 mL) PPDA (PdPA/Rh = 15 mol/mol) was added and the mixture was shaken vigorously for 6 h at room temperature. The resulting solid was collected by filtration and washed with PPDA-saturated 5 M HCl solution (ca. 5.6 mg/mL). To the solid 1 M NH$_4$OH solution was added (10 mL) and the mixture was shaken vigorously for 10 min at room temperature. After removal of the solid by filtration, the metal concentration in the resulting filtrate was determined by ICP-AES. The Rh(III) recovery experiment using DPOBP was...
performed in the similar manner. A simulated solution of 8 M HCl and DPOBP (DPOBP/Rh = 15 mol/mol, 3 h of shaking) was used and the resulting solid was washed with DPOBP-saturated 8 M HCl solution (ca. 0.10 mg/mL). In the desorption process, 8 M NH₄OH solution was used and the mixture was shaken vigorously for 1 h. The metal precipitation percentages were evaluated using the filtrate before the desorption process.

**Preparation of Rh-DPOBP and Rh-PPDA.** To a 5 M HCl solution (20 mL) containing Rh(III) (300 mg/L) DPOBP (DPOBP/Rh = 5 mol/mol) or PPDA (PPDA/Rh = 15 mol/mol) was added and the mixture was shaken vigorously at room temperature. The resulting solid was collected by filtration and washed with methanol to remove excess amine hydrochloride. The solid was dried for 24 h at room temperature in vacuo.

**Preparation of Single Crystals.** To a 5 M HCl solution (5 mL) containing Rh(III) (300 mg/L) PPDA (PPDA/Rh = 10 mol/mol) was added and the resulting solution was left to stand for several days. Single crystals were obtained as red-colored plates. Preparation of single crystals from a simulated spent catalyst leach solution (8 M HCl) using PPDA was performed in the same manner.

**Measurements.** ¹H NMR spectra were recorded using a JEOL JNM-ECX 500 NMR spectrometer (Jeol Co., Ltd.). An ICP-AES instrument (SPSS510, SII Nanotechnology Inc.) was used for the metal concentration measurements. X-ray photoelectron spectroscopy (XPS) measurements were performed using an AXIS-ULTRA X-ray photoelectron spectrometer (Kratos Analytical Ltd.). Element quantification was performed using the relative sensitivity factors supplied with instrument control software (N 1s: 0.477, Cl 2s: 0.493, Rh 3d: 4.822). TGA measurements were carried out using a STA7300 (Hitachi High-Tech Science Corp.) at a heating rate of 10 °C/min under air flow (200 mL/min). The powder X-ray diffraction measurements were conducted on a Rigaku Ultima IV. The single crystal X-ray diffraction data were collected using a Rigaku Saturn 724 CCD diffractometer with Mo Kα radiation (λ = 0.71075 Å). Table S3 lists the crystal data and structure refinement. Data collection, cell refinement, and data reduction were performed using CrysalisPro software. The structure was solved by direct methods using SHELXTL and refined by full-matrix least-squares methods on F₂ using SHELX2014. All materials for publication were prepared by Yadokari-XG 2009 software. Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures may be found from the Cambridge Crystallographic Centre by referencing the CCDC number 1922165.

**ASSOCIATED CONTENT**

*Supporting Information* The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02052.

Additional experimental data for the metal recovery and the characterization of Rh-containing precipitate (PDF)

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The manuscript was written through contributions of all authors.

**Notes**

The authors declare no competing financial interest.

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