

Hydrocarbonyl Processes for Conversion of Platinum-Rhodium-Palladium Alloys

Technological possibilities of a new process for pgms extraction

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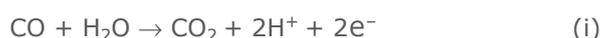
A novel process for the recovery of platinum group metals (pgms) from ternary alloys using a hydrocarbonyl process is proposed. The hydrocarbonyl process involves treatment of a chloride solution of the pgms with carbon monoxide at ambient pressure. The results demonstrate that the process can provide high purity pgms from a ternary platinum-rhodium-palladium alloy such as that obtained from palladium-nickel catchment alloys used with platinum-rhodium gauzes during high temperature ammonia oxidation.

1. Introduction

Ternary alloys of Pt with Rh and Pd are used for the preparation of catalysts for conversion of ammonia (NH₃). Such ternary alloys also form upon capture of Pt and Rh on catchment alloys of Pd with 5 mass% Ni. Long operation of catalysts made of binary Pt-Rh and ternary Pt-Rh-Pd alloys leads to formation of spent alloys of Pt with Rh and Pd in a broad compositional range. **Table I** shows compositions of several alloys of this type. Spent ternary alloys of Pt with Rh and Pd require refining for recovery of each precious metal. In most cases, the well-known hydrometallurgical process is applied, which involves dissolution of metals by hydrochlorination. Pt is separated by precipitation of the ammonium salt, ammonium hexachloroplatinate (NH₄)₂[PtCl₆], which is further

calcined to obtain sponge Pt. From the filtrate, Pd is extracted in the form [PdCl₂(NH₃)₂]. In the case of Rh, another method is used, which is known as a nitration process. Rh is precipitated as nitratorhodates of ammonium-sodium from a solution of nitrate complexes. This procedure introduces impurities of various non-ferrous and noble metals; therefore, the products require further purification (1).

JSC R&PC Supermetal proposes a new method of refining ternary Pt-Rh-Pd alloys based on hydrocarbonyl processes. The term 'hydrocarbonyl processes' implies chemical reactions taking place upon treatment of solutions of pgm chloride complexes by carbon monoxide (CO) at ambient pressure. Hydrocarbonyl processes are based on the high chemical activity of CO molecules in the inner spheres of carbonylchloride complexes. The activity of CO ligands can be demonstrated by the following redox reactions (Equations (i) and (ii)):



As a result, the central atom in the complex reduces to the lower (or zero) oxidation state. Pd, gold and silver are reduced to metals, whereas Pt

Table I Sample Compositions of Pt-Pd-Rh Alloys

Number	Composition ^a , mass%		
	Pt	Pd	Rh
1	84.48	8.79	6.01
2	44.20	55.03	0.55
3	71.97	19.85	8.15
4	21.20	76.83	1.96

^aIn ternary alloys formed as a result of capturing platinum group metals on catchment gauze of alloys of palladium and nickel (5 mass%), the sum of iron and non-ferrous metals admixtures can reach 0.1 mass%

can be either reduced to metal or, at temperature (T) $\leq 80^\circ\text{C}$, to polymeric bicarbonyl $[\text{Pt}(\text{CO})_2]_n$. The reduction proceeds stepwise:



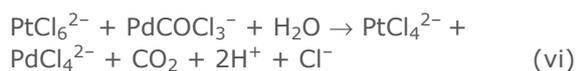
Rhodium, ruthenium and iridium are normally reduced to lower oxidation states: Rh(I), Ru(II), Ir(I) and form carbonylchloride anions: $\text{Rh}(\text{CO})_2\text{Cl}_2^-$, $\text{Ir}(\text{CO})_2\text{Cl}_2^-$, $\text{Ru}(\text{CO})_2\text{Cl}_4^{2-}$.

Hydrocarbonyl processes in multicomponent solutions of pgms include a number of reactions running parallel and in series including autocatalytic reactions. In particular, upon treating solutions of chloride complexes of Pt(IV) and Pd(II) by CO the following reactions proceed:

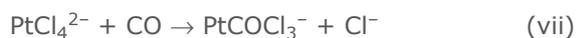
- formation of Pd(II) carbonylchloride (2)



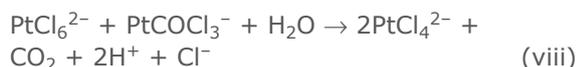
- reduction of Pt(IV) to Pt(II) owing to catalytic action of Pd(II) carbonylchloride anion



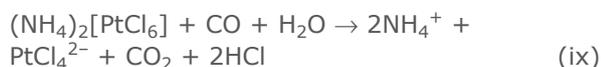
- formation of Pt(II) carbonylchloride



- regeneration of PdCOCl_3^- according to Equation (v)
- reduction of Pt(IV) to Pt(II) owing to catalytic action of Pt(II) carbonylchloride anion (3)



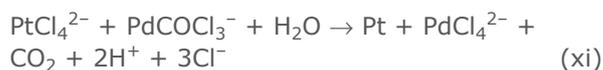
The Pt(IV) chloride complex in the form of $(\text{NH}_4)_2[\text{PtCl}_6]$ usually contains admixtures of Pd and other metals. It dissolves in the course of the hydrocarbonyl process (Equations (v)–(viii)) by reduction of Pt(IV) to Pt(II):



Once $(\text{NH}_4)_2[\text{PtCl}_6]$ dissolves, the system remains homogeneous for some time until precipitation of Pd (and Au, if present) starts due to redox decomposition of Pd(II) carbonylchloride, which can be expressed by Equation (x):

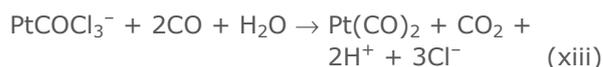


Simultaneously, in the initial period of the $(\text{NH}_4)_2[\text{PtCl}_6]$ reduction, a certain amount of Pt is reduced according to Equation (xi):



Accordingly, Pd precipitated by Equations (x) and (xi) typically contains small amounts of Pt.

The Pt(II) chloride complex formed by Equation (ix) transfers to the carbonylchloride anion upon treatment by CO following Equation (vii). It further undergoes inner sphere hydrolysis yielding Pt(0) or bicarbonyl $[\text{Pt}(\text{CO})_2]_n$ according to Equations (xii) and (xiii):



The kinetics and mechanism of the reaction of CO with solutions of chloride complexes of pgms have been discussed in detail (4–7). In particular, Equation (ix) was studied. $(\text{NH}_4)_2[\text{PtCl}_6]$ was isolated from a solution of chloride complexes upon leaching of industrial concentrate of pgms in the hydrochloric acid + dichlorine ($\text{HCl} + \text{Cl}_2$) system and contained 41.45% Pt and 0.65% Pd. Suspension of $(\text{NH}_4)_2[\text{PtCl}_6]$ in water with a solid-to-liquid ratio of 1:11 was treated by CO with vigorous stirring at fixed temperature. After 40 min, $(\text{NH}_4)_2[\text{PtCl}_6]$ dissolved totally forming a cherry red solution with subsequent slow precipitation of black. Afterwards, the black was separated and analysed to assess the Pt:Pd ratio, whereas the filtrate was probed to analyse the content of Pd and then was again treated by CO. The obtained results are presented in **Table II**.

The data show that the initial precipitate of black contained 25% Pt with respect to the mass of Pd. This can be explained by simultaneously running Equations (x) and (xi). As the content of the Pt(II) chloride complex in solution increases because of transition to carbonylchloride by Equation (vii), the rate of reaction of Equation (xi) decreases. Therefore, the Pd:Pt mass ratio in the precipitate also decreases owing to simultaneous precipitation of Pd and the increase in the rate of Pt precipitation according to Equations (xii) and (xiii) (5). Altogether this leads to complete precipitation of Pd during the initial stages of the process, whereas coprecipitation of Pt is limited to several per cent (**Table II**).

The results of this experiment showed that a hydrocarbonyl process could be used to obtain Pt from $(\text{NH}_4)_2[\text{PtCl}_6]$ extracted from multicomponent solutions. However, a complete analytical characterisation of the products was

Table II Results of the Treatment of the $(\text{NH}_4)_2[\text{PtCl}_6]$ Pulp by CO in Water^a

Number	Treatment conditions		Content in precipitate, mg (%) of extraction		Pd:Pt mass ratio in precipitate	Pd in filtrate	Rate of precipitation, % min ⁻¹	
	Temperature, °C	Time, min	Pd	Pt			Pd	Pt
1 ^b	90	45	21.8 (18.79)	5.4 (0.073)	4.00	+	3.76	$1.6 \cdot 10^{-3}$
2	95	15	13.1 (11.29)	7.5 (0.101)	1.75	+	0.75	$0.7 \cdot 10^{-3}$
3	25	10	62.6 (53.96)	74.9 (1.01)	0.83	+	5.40	0.10
4	25	10	15.2 (13.10)	232.6 (3.136)	0.07	-	1.31	0.31
5 ^c	90-100	~60	traces	146.4 (1.976)	0.00	-	-	-

^a The solid-to-liquid ratio is 1:11. 17.87 g of $(\text{NH}_4)_2[\text{PtCl}_6]$ contains 7.4071 g Pt and 0.1162 g Pd

^b After 40 min treatment $(\text{NH}_4)_2[\text{PtCl}_6]$ dissolved completely and black started to precipitate

^c Filtrate after operation number 4 was heated in air to observe formation of $\text{Pt}[(\text{CO})_2]_n$

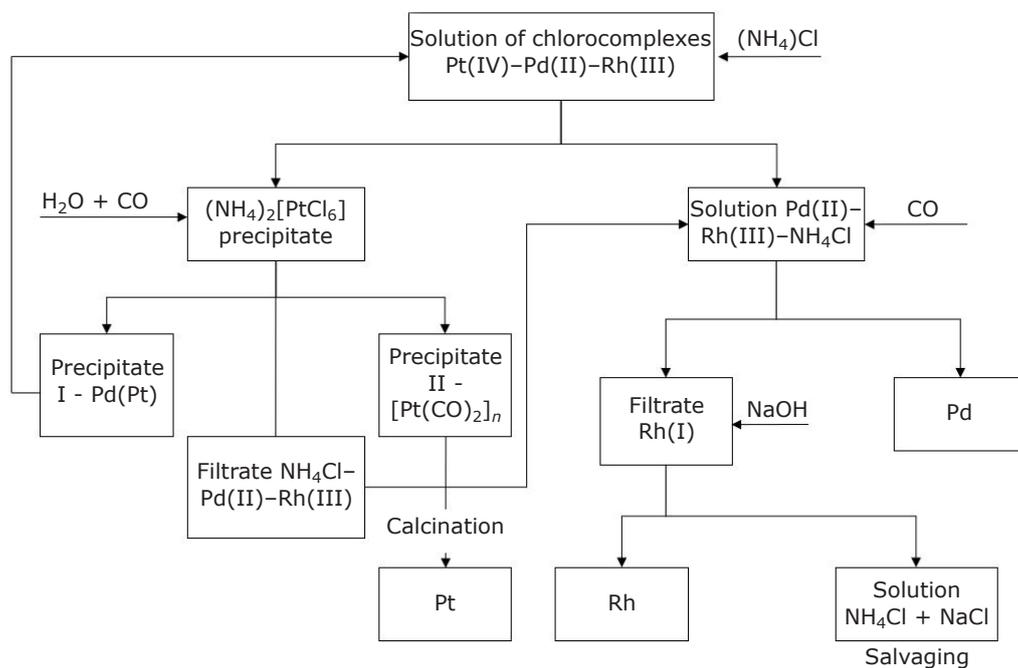


Fig. 1. Principal technological scheme of hydrocarbonyl process of the Pt-Pd-Rh alloy refinement

not performed. Therefore, the development of refinery technology for Pt-Rh-Pd alloys was further based on the extraction of Pt from the initial solution in the form of $(\text{NH}_4)_2[\text{PtCl}_6]$ followed by preparation of pure Pt according to the scheme presented in **Figure 1**.

2. Experimental

The analysis of sponge-like metals was performed using a diffraction spectrograph DFS-8 with arc excitation of a spectrum and multichannel analyser of the spectra in the concentration

range 0.0003–0.35% and atomic absorption spectrometer novAA[®] 330 (Analytik Jena, Germany) with flame atomisation for the mass concentration range of 0.01% to 10%. Residual content of Pt, Pd and Rh in solutions was determined by means of atomic absorption spectrometer AAS KVANT.Z with electrothermal atomisation. The detection limit was 0.20 µg l⁻¹ for Pt, 0.05 µg l⁻¹ for Pd and 0.03 µg l⁻¹ for Rh.

To assess the technological possibility of hydrocarbonyl processes for conversion of ternary Pt-Rh-Pd alloys, $(\text{NH}_4)_2[\text{PtCl}_6]$ was extracted from the chloride solution with the following content

Table III Composition of the Pt Sponge After Calcination of $(\text{NH}_4)_2[\text{PtCl}_6]$ at 1000°C

Element	Content, mass%	Element	Content, mass%	Element	Content, mass%
Platinum	98.5073	Iron	0.0025	Tin	0.0070
Rhodium	1.037	Nickel	0.0006	Aluminium	0.0028
Palladium	0.3598	Zinc	0.0061	Silver	0.0320
Gold	0.0188	Lead	0.0161	Cadmium	0.0032
Copper	0.0043	Magnesium	<0.0005	Calcium	0.0020

Table IV Composition of Precipitates Obtained by Carbonylation of $(\text{NH}_4)_2[\text{PtCl}_6]$

Element	Composition, mass%		Element	Composition, mass%		Element	Composition, mass%	
	Precipitate I 277.44 mg	Precipitate II 2889.12 mg		Precipitate I 277.44 mg	Precipitate II 2889.12 mg		Precipitate I 277.44 mg	Precipitate II 2889.12 mg
Platinum	95.7156	99.7098	Iron	0.3760	0.0050	Tin	0.0700	0.0011
Rhodium	0.3000	0.2100	Nickel	0.0060	0.0006	Aluminium	0.0330	0.0035
Palladium	2.8000	0.0150	Zinc	0.0260	0.0030	Silver	0.2500	0.0200
Gold	0.1250	<0.0003	Lead	0.0650	0.0200	Calcium	0.0210	0.0020
Copper	0.1850	0.0080	Magnesium	0.0104	0.0014	Cadmium	0.0170	<0.0003

Precipitate I: washed with 2 M HCl on a filter; Precipitate II: washed by suspending in 2 M HCl, filtered off and then washed on a filter

of metals: Pt 55.52 g l⁻¹; Pd 21.22 g l⁻¹; and Rh 5.27 g l⁻¹. For the chemical analysis of the product, a weighed portion of the salt was calcined in a muffle furnace at 1000°C. The residual mass of the resulting Pt sponge was 42.94% with respect to the mass of $(\text{NH}_4)_2[\text{PtCl}_6]$ (see **Table III**).

2.1 Extraction of Platinum from Ammonium Hexachloroplatinate

Suspension of 7.50 g of $(\text{NH}_4)_2[\text{PtCl}_6]$ in a 2 M solution of HCl (solid-to-liquid ratio 1:20) was treated by CO at ambient pressure and a temperature of 60°C. Gradual dissolution of $(\text{NH}_4)_2[\text{PtCl}_6]$ was observed with concomitant formation of a red solution of Pt(II) chloride complex according to Equation (ix). After 2.5 h, $(\text{NH}_4)_2[\text{PtCl}_6]$ was dissolved completely and Pt[(CO)₂]_n started to precipitate. After 1 h the treatment was stopped and the resulting solution was enclosed in a CO atmosphere for precipitate coagulation. After cleaning the solution, the precipitate was filtered off, washed with 2 M HCl and calcined in a muffle furnace at 1000°C. 277.44 mg of Pt sponge was obtained (Precipitate I).

Filtrate from Precipitate I together with the scourge was treated with CO at 40°C. After 30 min, platinum carbonyl [Pt(CO)₂]_n started to

Table V Distribution of the Admixtures Over Precipitates I and II

Sum of admixtures, mass%	Precipitate I	Precipitate II
Σ ₁	0.745	0.038
Σ ₂	0.068	0.007
Σ ₃	3.475	0.245
Σ _{1, 2}	0.813	0.045
Σ _{1, 2, 3}	4.288	0.290
Pt, %	95.712	99.710
Σ _{Pt, Rh} , %	96.012	99.920

Σ₁ = sum of heavy non-ferrous metals (Cu, Ni, Fe, Pb, Zn, Sn, Cd); Σ₂ = sum of light non-ferrous metals (Ca, Mg, Al); Σ₃ = sum of noble metals (Pd, Rh, Au, Ag)

form (Precipitate II). After 3 h, the gas treatment was stopped and the reactor was closed in a CO atmosphere for coagulation of Precipitate II. The solution was decanted and Precipitate II was suspended in 2 M HCl and then filtered off under vacuum and washed with 2 M HCl on a filter. Precipitate II was dried and calcined at 1000°C, which yielded 2289.12 mg of Pt sponge. Compositions of Precipitates I and II are given in **Table IV**, while **Table V** shows the distribution of the elements for these precipitates.

2.2 Extraction of Palladium from the Filtrate After Deposition of Ammonium Hexachloroplatinate

After sedimentation and filtration of $(\text{NH}_4)_2[\text{PtCl}_6]$, the solution contains chloride complexes of Pd(II) and Rh(III) together with residual Pt(IV), which was determined by a solubility equilibrium of $(\text{NH}_4)_2[\text{PtCl}_6]$ and concentration of NH_4Cl . For extraction of Pd, the filtrate was treated by CO at ambient pressure and a T of 50–70°C. Blackening of the solution was noticeable in 2–3 min. After 3 h 15 min of treatment, the reactor was closed under CO atmosphere for coagulation of Pd black. The solution was decanted and the precipitate was suspended in 2 M HCl, filtered off and washed on a filter with 2 M HCl, after which the filtrate was closed in a flask under CO atmosphere.

2.3 Extraction of Rhodium After Precipitation of Palladium

After extraction of Pd the remaining filtrate has yellowish-green colour, a characteristic of Rh(I) ($\text{Rh}(\text{CO})_2\text{Cl}_2^-$), which is stable only in highly acidic media and decomposes in basic media. Consequently, upon adding alkali to the solution of Rh(I) carbonyl chloride, blackening was observed. Heating the pulp led to coagulation and sedimentation of Rh black. The precipitate was filtered, suspended in 2 M HCl and filtered again. The obtained Rh black easily dissolved in the HCl + hydrogen peroxide (H_2O_2) mixture with formation of a pink solution typical for H_3RhCl_6 . The analysis of the filtrate showed that it did not contain Pt, Pd or Rh.

3. Discussion of the Results

The results of extraction of Pt from the $(\text{NH}_4)_2[\text{PtCl}_6]$ pulp by treating with CO were analysed. The content of Pt in Precipitates I and II amounted to 95.712% and 99.710%, whereas the rates of extraction for $(\text{NH}_4)_2[\text{PtCl}_6]$ were 8.37% and 90.81%, respectively. The analysis of the filtrate showed that the total extraction of Pt into Precipitates I and II was equal to 99.96%. The content of heavy non-ferrous metals (Σ_1) in Precipitate II was more than an order of magnitude less than in Precipitate I, whereas the content of light non-ferrous elements (Σ_2) in Precipitate II was almost one order of magnitude less than in Precipitate I. The content of noble metals in Precipitates I and II (Σ_3) showed a 14 times decrease owing to extraction of sizable

amounts of Au, Ag and Pd into Precipitate I. At the same time, the content of Rh in Precipitates I and II was 0.30% and 0.20%, respectively, meaning that Rh remains the principal admixing element; the combined content of Pt and Rh ($\Sigma_{\text{Pt, Rh}}$) in Precipitates I and II amounted to 96.012% and 99.920%, respectively. This appears to be due to accumulation of Rh in solution in the form of Rh(I) carbonylchloride ($\text{Rh}(\text{CO})_2\text{Cl}_2^-$) and its adsorption of Pt carbonyl. Complete removal of Rh is possible by oxidative washing of the precipitate due to formation of Rh(III) chloride complex. In particular, suspending Precipitate II in 2 M HCl in air leads to pink colour of the filtrate, indicating the presence of H_3RhCl_6 . Also, one can speculate that higher content of non-ferrous metals in Precipitate I might be a consequence of insufficient washing.

4. Conclusion

The performed study has shown that hydrocarbonyl processes can be used for the individual recovery of precious metals from ternary Pt-Rh-Pd alloys. It is also shown that the hydrocarbonyl process can be used for conversion of $(\text{NH}_4)_2[\text{PtCl}_6]$ into pure Pt, which can be exploited for production of Pt from technogenic and natural products. It should be stressed that hydrocarbonyl processes have vast potential in technology and application of pgms and can be used for concentrating as $\Sigma_{\text{Pt, Pd, Au, Ag, Si, Te}}$ or $\Sigma_{\text{Rh, Ru, Ir}}$ from multicomponent industrial products based on non-ferrous metals (6–9); upon refining concentrates and various alloys (10, 11); and in manufacturing powders of pgms with desired physicochemical properties and deposited catalysts, including those for neutralisation of exhaust gases of combustion engines (12).

It is expected that further investigation of the processes of hydrocarbonylation of pgm chloride complexes will lead to preparation of new composite materials containing one or more pgms together with carbon in either form (13).

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