

SORPTION
AND ION EXCHANGE PROCESSES

Propiconazole and Penconazole as Effective Extractants for Selective Recovery and Concentration of Platinum(IV) and Palladium(II) from Hydrochloric Acid Solutions Formed in Leaching of Spent Aluminoplatinum and Aluminopalladium Catalysts

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Received December 17, 2015

Abstract—Selective recovery and concentration of platinum(IV) and palladium(II) from hydrochloric acid solutions of varied composition was studied using commercial reagents propiconazole and penconazole as extractants. The ranges of hydrochloric acid concentrations for effective extraction and highly selective separation of platinum metals from Al(III) and Ni(II) with propiconazole (toluene with 15 vol % *n*-decanol as deluent) and penconazole (chloroform) were determined. The conditions for 10-fold selective concentration of platinum metals with recovery of more than 99.9% of metal ions into the organic phase were found. The conditions for quantitative (>99%) stripping of platinum(IV) with a hydrochloric acid solution of thiourea and palladium(II) with ammonia solution were determined. The results obtained can be used for optimizing the modes of selective recovery of platinum(IV) and palladium(II) from hydrochloric acid solutions formed in leaching of alumina-supported platinum-rhenium, platinum-nickel, and palladium catalysts.

DOI: 10.1134/S1070427216020075

The world's consumption of platinum metals annually grows and exceeds the amount of their production from primary (ore) sources of raw materials [1, 2]. More than 70% of the consumed amount of palladium and more than 40% of platinum is used in various industries as oxide-supported metal catalysts (oxide supports Al₂O₃, SiO₂, etc.) [1, 3]. Spent catalysts serve as an important secondary raw-material source of platinum metals and are to be processed to recovery valuable components.

There is no versatile technological scheme for processing of oxide-supported platinum and palladium catalysts. At a number of foreign and domestic plants, platinum metals are recovered from spent catalysts by multistage energy-, reagent-, and labor-intensive pyrohydrometallurgical method [3–5]. There have been numerous reports concerned with development of less energy-intensive hydrometallurgical methods for recovery of platinum metal from spent catalysts [3, 5–8].

As a rule, the suggested hydrometallurgical processing schemes with acid leaching of a catalyst include the following stages: oxidative calcination to remove carbon black and organic compounds from the surface at 300–800°C; grinding, when necessary, to particle size of 0.1–0.5 mm; leaching with aqua regia or hydrochloric acid solutions in the presence of oxidizing agents (nitric acid, sodium hypochlorite, or hydrogen peroxide) under heating; and recovery of platinum metals from the leach solution by reagent-induced precipitation or reduction, anion-exchange sorption, or solvent extraction. At present, leaching with diluted solutions of hydrochloric acid (4–7 M) in the presence of hydrogen peroxide (0.5–4 M) is considered to be the most economical and ecologically safe [3, 6, 8].

Solvent extraction is promising for selective recovery, separation, and concentration of platinum(IV) and palladium(II) from hydrochloric acid solutions formed

in leaching of catalysts. The extraction method is more technologically convenient and can increase the recovery and purity of noble metals, compared with precipitation techniques and cementation. Commercial extractants, such as TBP, trioctylphosphine oxide (Cyanex 921), tertiary amines (Alamine 300, Alamine 336), and chloride of a quaternary ammonium base (Aliquat 336), have been suggested for extraction of platinum(IV) and palladium(II) from hydrochloric acid solutions formed in leaching of automobile and commercial catalysts, but a search for more selective and effective extractants for recovery of platinum metals from strongly acid solutions with a substantial salt background remains a topical issue [2, 9].

The compounds 1- $\{[2-(2,4\text{-dichlorophenyl})-4\text{-propyl-1,3-dioxolan-2-yl}]\text{-methyl}\}$ -1*H*-1,2,4-triazole (propiconazole) and (*RS*)-1- $[2-(2,4\text{-dichlorophenyl})\text{-pentyl}]\text{-1H-1,2,4-triazole}$ (penconazole) are manufactured on industrial scale and widely used in agriculture as low-toxic fungicides. At the same time, the properties of these compounds satisfy the requirements to commercial extractants. It has been found previously that propiconazole effectively extracts palladium(II) and platinum(IV), and penconazole, palladium(II) from hydrochloric acid solutions [10, 11].

The goal of our study was to optimize the conditions of selective recovery and concentration of platinum(IV) and palladium(II) from hydrochloric acid solutions, by solvent extraction with propiconazole and penconazole, and to assess the prospects of the suggested approach in recovery of platinum metals from solutions formed in leaching of spent alumina-supported platinum-rhenium, platinum-nickel, and palladium catalysts.

EXPERIMENTAL

We used the reagents propiconazole TC (98%) and penconazole TC (95%), manufactured by Kingtai Chemicals Co., Ltd (China). The solutions of extractants were prepared by dissolution of precisely weighed portions of the reagents in chloroform or in a mixture of toluene with 15 vol % *n*-decanol (the solvents were of analytically pure grade).

Aqueous solutions for studying the extraction and stripping of metal ions were prepared using PdCl_2 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ of pure grade, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and hydrochloric acid of chemically pure grade, and thiourea and ammonia of analytically pure grade.

As model objects were taken the solutions that can be obtained in leaching of calcined and ground (0.1–0.5 mm) catalysts with a 5–6 M HCl solution in the presence of hydrogen peroxide (0.5–1.4 M) at a temperature $T \approx 100^\circ\text{C}$ and solid (g) to liquid (cm^3) phase ratio $S : L = 1 : 5$ (aluminoplatinum catalysts) or $1 : 10$ (aluminopalladium catalyst), followed by washing of the cake with a 2–3 M HCl solution at $S : L = 1 : 2$. This scheme of hydrochloric leaching of aluminoplatinum and aluminopalladium catalysts, suggested on the basis of published data [6–8, 12, 13], provides a 98–99% recovery of platinum metals into a hydrochloric acid solution. Further, the leach solution of catalyst (upon filtering of the slurry), combined with the solution used to wash the cake, is named “model leach solution.” The content of Al(III) in the leach solution of catalyst depends on the calcination temperature [7].

In the case of platinum-rhenium catalysts, it is advisable to separate rhenium in the calcination stage [4, 7]. For example, more than 99.9% of rhenium is recovered into the gas phase when KR-110 catalyst is calcined in the presence of air at $1200\text{--}1300^\circ\text{C}$ for 1 h. In the process, the γ -form of alumina is converted to the α -form insoluble in acids and an insignificant amount (0.12%) of aluminum is dissolved in the course of leaching [7]. We suggest calcining the platinum-nickel catalyst at 1000°C , which will provide conversion of most part of $\gamma\text{-Al}_2\text{O}_3$ to the α -form. More than 6% of aluminum and 90–95% of nickel may pass into solution in the course of leaching of calcined catalyst [7, 13]. It is advisable to perform the calcination of the aluminopalladium catalyst at 800°C , with a significant amount of aluminum possibly passing into the leaching solution.

When calculating the composition of model leach solutions, we assumed that the composition of calcined catalysts is the same as that of the starting commercial catalysts (Table 1). The concentrations of aluminum(III) and nickel(II) in the model solutions were evaluated with consideration for the catalyst calcination temperature in the above-suggested hydrochloride leaching scheme.

The concentrations of platinum(IV) and palladium(II) in individual and complex aqueous solutions were determined by spectrophotometric methods with tin(II) chloride on a Specord M40 spectrophotometer, and those in thiourea and ammonia re-extracts, in a similar way upon conversion of re-extract aliquots to hydrochloric acid solutions by the known method [14]. The concentrations of nickel(II) and aluminum(III) in individual aqueous

Table 1. Composition of commercial oxide-supported metal catalysts and the calculated composition of model leach solutions of spent catalysts

Catalyst	Catalyst composition, %	$T_{\text{calcination}}, ^\circ\text{C}$	Composition of the model solution, M
Platinum-rhenium reforming catalysts E-603, KR-110	Pt 0.28–0.32 Re 0.27–0.33 SiO ₂ 0.73 Al ₂ O ₃	1200–1300	HCl 3–5 Pt 0.0020–0.0023 Al 0.003
Platinum-nickel catalyst for isomerization and hydrogenation of hydrocarbons	Pt 0.2–0.3 Ni 0.5–2.5 Al ₂ O ₃	1000	HCl 3–5 Pt 0.0015–0.0022 Ni 0.012–0.058 Al > 0.15
Aluminopalladium catalyst APK-2 for purification of effluent gases formed in manufacture of nitric acid to remove nitrogen oxides	Pd 1.8–2.0 Al ₂ O ₃	800	HCl 3–4 Pd 0.014–0.016 Al > 0.2

solutions were determined by the complexometric method, using Murexide [15] and Xylenol Orange [16], respectively, as indicators. The concentration of nickel(II) in aqueous solutions containing platinum(IV) was determined by the atomic absorption spectroscopy method on a Hitachi 508 spectrophotometer (acetylene-air flame, wavelength 232.1 nm). The concentration of metal ions in the organic phase was calculated from the difference between the metal ion concentrations in the starting aqueous solution and in the raffinate with consideration for the volume ratio between the aqueous and organic phases, A : O.

The extraction and stripping of metal ions was performed in separating funnels at a temperature of $23 \pm 1^\circ\text{C}$ and preset A : O ratio under vigorous shaking for 15–30 min (extraction) and 10–15 min (stripping).

RESULTS AND DISCUSSION

To determine the optimal conditions for effective and selective extraction of platinum(IV) and palladium(II) from hydrochloric acid solutions formed in leaching of aluminoplatinum and aluminopalladium catalysts, we studied the dependence of the degree of extraction of a number of metals, catalyst components (Table 1), with propiconazole and penconazole on the initial concentration of hydrochloric acid in the aqueous phase (Fig. 1) at a phase contact duration sufficient [10, 11] for equilibrium to be attained in the extraction of platinum metals.

Propiconazole extracts palladium(II) with high efficiency ($E > 97\%$) in a wide range of concentrations of the acid (0.1–7 M), and platinum(IV), at 3–7 M HCl (Fig. 1a). Penconazole extracts the most effectively ($E > 95\%$) palladium(II) from 0.1 and 2–8 M HCl solutions, and platinum(IV), from 4–10 M HCl solutions (Fig. 1b). In the HCl concentration range 0.1–10 M, aluminum(III) is hardly extracted by the reagents (distribution coefficient $D_{\text{Al}} < 0.01$ at $c_{\text{Al}} = 0.02$ M and $c_{\text{L}} = 0.06$ M). This is indicative of a high selectivity of 1,2,4-triazole derivatives toward platinum metals over aluminum(III). At an aqueous phase acidity of less than 5 M HCl, palladium(II) and platinum(IV) can be separated from nickel(II) with high selectivity by extraction with propiconazole because nickel(II) is not extracted in this range (Fig. 1a). Within the determination error, no extraction of nickel(II) with penconazole is observed in the HCl concentration range under study (Fig. 1b). Consequently, penconazole is characterized by high selectivity toward palladium(II) and platinum(IV) over nickel(II), in a wider concentration range of the acid than that for propiconazole. The high selectivity and efficiency of the reagents indicates that they are promising for extractive separation of platinum(IV) from nickel(II) in hydrometallurgical processing of platinum-nickel catalysts and for separation of palladium(II) and platinum(IV) from nickel(II) in processing of automobile catalysts. It follows from the Fig. 1 that the concentration of hydrochloric acid in model solutions formed in leaching of spent aluminoplatinum and aluminopalladium catalysts (Table 1) corresponds to

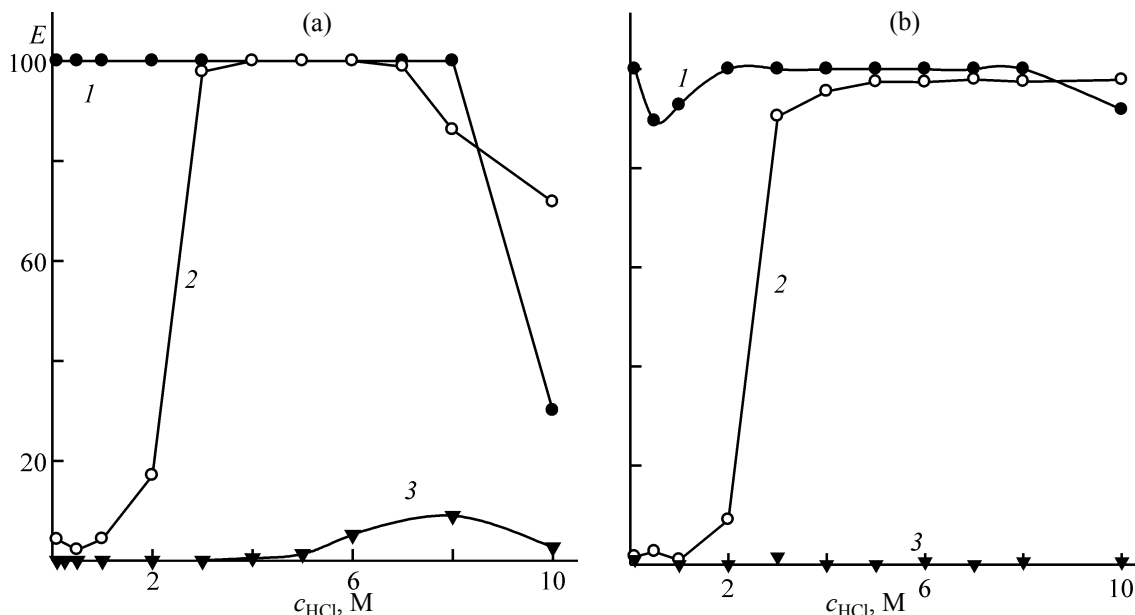


Fig. 1. The dependence of extraction E , % of (1) palladium(II), (2) platinum(IV), and (3) nickel(II) with (a) propiconazole (toluene with 15 vol % *n*-decanol) and (b) penconazole (chloroform) from individual solutions on the hydrochloric acid concentration c_{HCl} , M, in the aqueous phase. A : O = 1 : 1; concentration of metal ions in the aqueous phase; $c_{\text{Pd,Pt}} = 0.005$ M; reagent concentration in the organic phase, $c_{\text{L}} = 0.05$ M; $c_{\text{Ni}} = 0.02$ M; $c_{\text{L}} = 0.06$ M; phase contact duration: (a) 20 and (b) 30 min.

the optimal concentration for selective and effective extraction of platinum metals with 1,2,4-triazole derivatives.

We also studied the influence exerted by the concentrations of hydrochloric acid, nickel(II) and aluminum(III) chlorides in the aqueous phase, composition of the extractive agent, and A : O ratio on the degree of extraction of platinum metals from solutions modeling the composition of combined catalyst-leaching and cake-washing solutions in a number of components (Table 2). It was found that, at a reagent concentration in the organic phase of 0.25 M and A : O = 5 : 1, platinum(IV) is completely recovered from model leach solutions of aluminoplatinum catalysts with propiconazole (toluene with 15 vol % *n*-decanol) and penconazole (chloroform) with 5-fold concentration in the extract, irrespective of the acidity of the aqueous phase. At A : O = 10 : 1, the extraction of platinum(IV) with propiconazole is accompanied by the formation of a yellow precipitate at the phase boundary, which is probably due to the limited solubility of the extracted compound in the given diluent. Replacement of the diluent with chloroform fails to provide full extraction of platinum(IV) with propiconazole from 3–4 M HCl solutions in a single stage even at a smaller A : O ratio of 5 : 1. The complete extraction of platinum(IV), with 10-fold concentration in the extract, is reached in a single stage of extraction with

penconazole (chloroform) at A : O = 10 : 1. The presence of nickel(II) and aluminum(III) in model leach solutions of the platinum-nickel catalyst in amounts corresponding to the 100% dissolution of nickel and to 10 and 20% dissolution of Al_2O_3 does not affect the extent to which platinum(IV) is recovered by extraction with the reagents under the optimal conditions. The fact that nickel(II) is not extracted from the model solution confirms the high selectivity of the extractants toward platinum(IV). It should be noted that the raffinate remaining after the extractive recovery of platinum(IV) can be used to prepare hydrochloric acid solutions for leaching of a spent aluminoplatinum catalyst or for washing the cake.

Palladium(II) is completely recovered from model leach solutions formed in leaching of the aluminopalladium catalyst with 0.5 M propiconazole and penconazole solutions, with 10-fold concentration in the extracts in a single stage at acidity of the aqueous phase of 3–4 M HCl. Aluminum(III) in the amount corresponding to the dissolution of 20 and 40% of Al_2O_3 in leaching has no effect on the efficiency of palladium(II) extraction from model solutions with 1,2,4-triazole derivatives. The Al(III)-containing raffinate remaining after the extractive recovery of palladium(II) can be used to prepare a solution for leaching of the aluminopalladium catalyst [2].

Table 2. Effect of extraction conditions on the extraction E of platinum(IV) and palladium(II) from model leach solutions formed from spent aluminoplatinum and aluminopalladium catalysts. Phase contact duration: 20 min in extraction of platinum(IV) and 15 min in extraction of palladium(II)

Composition of a model solution, M		Extractant composition	A : O	E , %
c_M	c_{HCl}			
Pt 0.0022	3	0.25 M propiconazole (chloroform)	5 : 1	78.2
Pt 0.0022	4	0.25 M propiconazole (chloroform)	5 : 1	97.4
Pt 0.0022	5	0.25 M propiconazole (chloroform)	5 : 1	99.9
Pt 0.0022	3–5	0.25 M propiconazole (toluene with 15 vol % <i>n</i> -decanol)	5 : 1	>99.9
Pt 0.0022 Ni 0.059	4	0.25 M propiconazole (toluene with 15 vol % <i>n</i> -decanol)	5 : 1	>99.9
Pt 0.0022 Al 0.27; 0.53	4	0.25 M propiconazole (toluene with 15 vol % <i>n</i> -decanol)	5 : 1	>99.9
Pt 0.0022	3–5	0.25 M penconazole (chloroform)	5 : 1	>99.9
Pt 0.0022	4	0.25 M penconazole (chloroform)	10 : 1	>99.9
Pt 0.0022 Ni 0.059	4	0.25 M penconazole (chloroform)	10 : 1	>99.9
Pt 0.0022 Al 0.27; 0.53	4	0.25 M penconazole (chloroform)	10 : 1	>99.9
Pd 0.0148	3–4	0.50 M propiconazole (toluene with 15 vol % <i>n</i> -decanol)	10 : 1	>99.9
Pd 0.0163 Al 0.32; 0.64	3.5	0.50 M propiconazole (toluene with 15 vol % <i>n</i> -decanol)	10 : 1	>99.9
Pd 0.0148	3–4	0.50 M penconazole (chloroform)	10 : 1	>99.9
Pd 0.0163 Al 0.32; 0.64	3.5	0.50 M penconazole (chloroform)	10 : 1	>99.9

The recycling of the raffinate in the scheme for processing of catalysts with solvent extraction of a platinum metal from the hydrochloric acid leach solution with 1,2,4-triazole derivatives will make it possible to reduce the expenditure of hydrochloric acid and the volume of liquid waste and its contamination, compared with the precipitation methods and cementation.

It follows from the results presented in Table 3 that more than 99% of platinum(IV) and 100% of palladium(II) is stripped with a 5% thiourea solution in 0.1 M hydrochloric acid and with a 4 M NaOH solution, respectively, at A : O = 1 : 1. Consequently, the extractants can be used in the cyclic extraction–stripping mode. The re-extracts are precursors for obtaining pure platinum metals or their compounds. It should be noted that

ammonia re-extracts of palladium(II) well fit in modern technological schemes of affinage.

CONCLUSIONS

(1) It was found that the available commercial reagents propiconazole and penconazole are highly effective extractants for recovery of platinum(IV) and palladium(II) from model hydrochloric acid leach solutions of spent alumina-supported platinum-rhenium, platinum-nickel, and palladium catalysts. The reagents can be used to separate with high selectivity platinum(IV) from aluminum(III) and nickel(II), and palladium(II) from aluminum(III).

(2) The possibility of a 10-fold extractive concentration of platinum(IV) with a 0.25 M solution of penconazole in

Table 3. Stripping S of platinum(IV) and palladium(II). A : O = 1 : 1, phase contact duration in stripping of platinum(IV) 15 min, and that for palladium(II), 10 min

Extract			Stripping		
extractant composition	metal	$c_{M.org}$, M	stripping solution	$c_{M.aq}$, M	S, %
0.25 M propiconazole (toluene with 15 vol % <i>n</i> -decanol)	Pt	0.0109	5% TM, 0.1 M HCl	0.0108	99.2
0.25 M penconazole (chloroform)	Pt	0.0217	5% TM, 0.1 M HCl	0.0216	99.5
0.50 M propiconazole (toluene with 15 vol % <i>n</i> -decanol)	Pd	0.148	4 M NH ₄ OH	0.148	>99.9
0.50 M penconazole (chloroform)	Pd	0.148	4 M NH ₄ OH	0.148	>99.9

chloroform and that of palladium(II) with a 0.5 M solution of propiconazole in toluene with 15 vol % *n*-decanol or penconazole in chloroform, with complete recovery of a platinum metal from model leach solutions of spent catalysts in a single extraction stage was shown.

(3) More than 99% of platinum(IV) is stripped with a 5% solution of thiourea in 0.1 M hydrochloric acid, and 100% of palladium(II), with a 4 M NH₄OH solution, which enables use of the extractants in the cyclic extraction–stripping mode.

(4) The inclusion of the stage of concentration of a platinum metal by solvent extraction with propiconazole or penconazole into the hydrometallurgical scheme for processing of spent aluminoplatinum and aluminopalladium catalysts will make it possible to selectively recover into the re-extract more than 98% of platinum or 99% of palladium upon dissolution of 99% of the platinum metal in the course of leaching.

ACKNOWLEDGMENTS

The study was financially supported by OKhNM-5 Program of the Department of Chemistry and Materials Science, Russian Academy of Sciences. The authors are grateful to the Russian Foundation for Basic Research (grant no. 13-00-14056 IR) for financing the access to information resources of foreign publishing houses.

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