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The Extraction of Platinum and Palladium from Supported over Al_2O_3 Spent Catalysts Using Alternating Current

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Abstract

The results of investigation of extraction of platinum and palladium from spent catalysts of gases of gasoline and diesel engines and oil refining purification into solution of HCl at anodic polarization of graphite electrodes by alternating current are demonstrated. Influence of temperature, current density, concentration of HCl and other factors have been studied. The optimal parameters of electrolysis with extraction into solution of 98-100% noble metals have been determined. feedstocks to desirable higher added-value products.

Introduction

The new electrochemical method for extraction of platinum and palladium from supported over Al_2O_3 spent catalysts of transport and oil refining using alternating current from net 220V with frequency 50 Hertz was developed. 99-100% extraction of platinum and palladium is achieved in 25-36% HCl at current density 6300-9500 A/m^2 and temperature 328-343K.

Electrochemical dissolving using alternating current is well known. It is used for dissolving of platinum metals or extraction of them from concentrates [1-4]. It is reported that alternating current used for industrial processing of waste of electrochemical productions into salts of Rh, Ir, Pd, Ru chloride of high purity and catalysts [5,6]. Maximum platinum content (40,48 %) in obtained product (K_2PtCl_6) is achieved at current strength 5 A and temperature 353-363K. Density of alternating current 1,3-1,5A/sm^2, temperature 373-383K are optimal conditions for dissolving of alloy of platinum metals in 20 % hydrochloric acid [3]. The dissolving rate achieves 2g of metal per hour and is used for preparation of particular pure chlorides of precious metals at such conditions.

We use alternating current for extraction of platinum and palladium from supported over Al_2O_3 spent catalysts of transport and oil refiring.

Methods

The spent in neutralizer of internal-combustion engine the palladium SHPAK-0,5 SHPK-0,5 (0,5 mas. % Pd), platinum SHPK-1(0,1 mas. % Pt) contacts and spent platinum catalyst AP-64 (0,64 mas. % Pt) of Shymkent oil refiner were used as catalysts.

The following requirements were taken into account at selecting of electrolyte composition for electrochemical processing of platinum-and palladium-containing spent catalysts:

-electrolyte solution must provide complete dissolving of platinum and palladium as stable compounds;

-electrolyte under effect of electric current must get strong oxidizing properties;

-electrolyte must have high electric conductivity;

-electrolyte must interact smallestly with the base of catalyst - alumina.

Solutions of hydrochloric acid meet these requirements in the best way. They have sufficient electric conductivity and permit to obtain the stable complex platinum ions of $[PtCl_6]^{2-}$ type and palladium $[PdCl_4]^{2-}$. They get strong oxidizing properties under effect of current owing to chlorine formation.

Alternating current from net 220 V with frequency 50 hertz was used fot experiments. Methods were described in [7].

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Results and discussion

Influence of concentration of hudrochloric acid on extraction of platinum and palladium from spent catalysts SHPAK-0,5 and AP-64 at current density 9500A/m^2 and temperature 343K is shown on fig. 1. As Fig.1 shows the increasing of concentration of hydrochloric acid from 15 to 36 % results in increasing of extractable per 1 hour content of both palladium and platinum. Maximum quantity of palladium (82 %) and platinum (87 %) is extracted in 36 % HCl. Thus, platinum from spent catalyst of oil refining is extracted more easily than palladium from spent catalyst of transport at the same conditions.

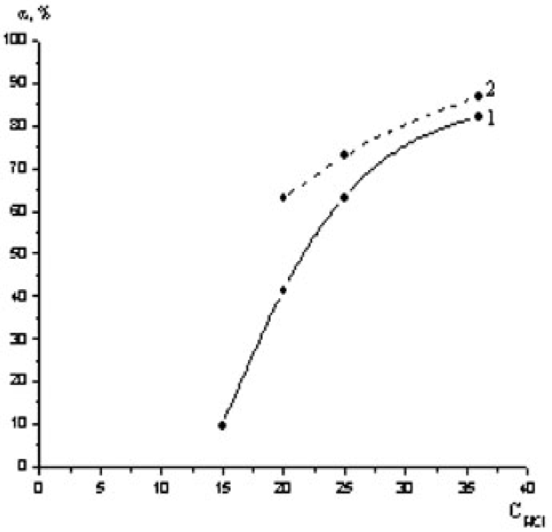

Fig.1. Influence of HCl concentration on Pd and Pt extraction from spent catalyst SHPAK-0,5 (1) and AP-64 (2) at current density 9500 A/m^2 and temperature 343K.

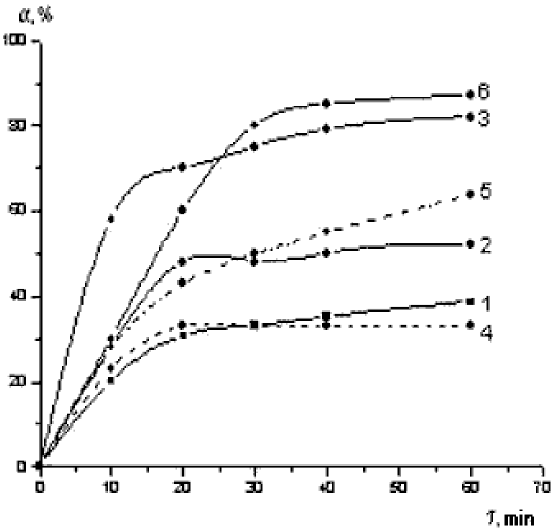

Fig.2. Kinetic curves of Pd and Pt extraction from spent catalysts SHPAK-0,5 (1-3) and AP-64 (4-6) in 36 % HCl at temperature 343K: 1,4 - without current; 2,5 - 6300 A/m^2, 3,6 - 9500 A/m^2.

According to Fig.2 the extent of platinum and palladium extraction increase and achieves maximum in 50-60 min. Increasing of density of alternating current from 6300 to 9500 A/m^2 results in increasing of extraction of palladium from 52,6 to 82 %, platinum - from 64 to 87 %. Further increasing of current density is pointless, because it results in increasing of electrolyte temperature due to expense of electric energy for its heating. Platinum and palladium in 36 % HCl without using of current were extracted only 35-39 %.

Influence of conditions of preliminary processing of spent catalysts SHPAK-0,5 and AP-64 on kinetics of platinum and palladium extraction in 36 % HCl was investigated.

It is shown from Fig.3 that 72,7 % extraction of palladium from spent catalyst SHPAK-0,5 is achieved per 1 hour using ethanol as reducer. Reduction of this catalyst in hydrogen or by formaldehyde decreases the extent of palladium extraction (to 10-15 %).It is known [8] that formaldehyde is polymerized at the temperature below 373K. Probably, partial polymerization over catalytic surface occurs in our case. This fact prevents for palladium extraction. Palladium is not only reduced, but also able to adsorb hydrogen during processing of spent out catalyst SHPAK-0,5

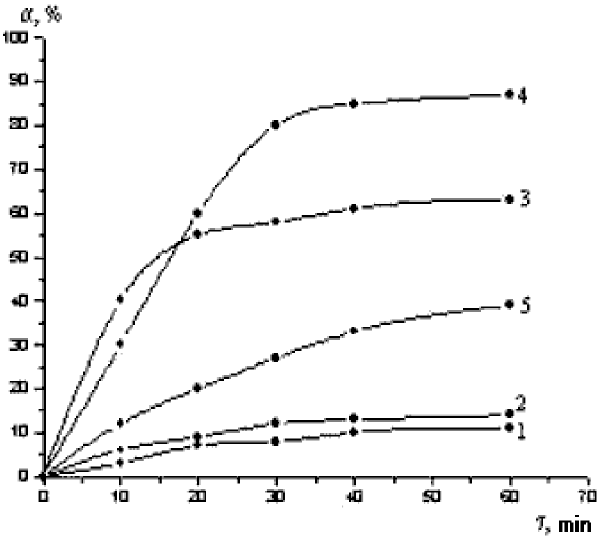

Fig.3. Influence of nature of reducer on kinetic curves of Pd and Pt extraction from spent catalysts SHPAK-0,5 (1-3) and AP-64(4,5) in 36 % HCl at current density 9500 A/m^2 and temperature 343K; 1,4- H_2; 2-CH_2O; 3,5 - C_2H_5OH.

by hydrogen. Probably, hydrogen makes anodic oxidation of palladium difficult during electrolysis by alternating current. Probably owing to it the low extent of palladium extraction to solution is observed.

Observed in experiments (Fig.2 and 3) comparatively high extent of platinum extraction (87 %) from samples AP-64 is explained by presence of platinum in spent catalysts of oil refining in reducing condition basically [9,10], because the reforming process is carried out at hydrogen pressure and temperature 773K.

It should be noted that heating of catalyst AP-64 at 973K on air decreases the extent of platinum extraction up to 59,1 % in comparison with reduced sample in hydrogen (87 %). Evidently, not only burning out on the surface of carbonic sediments, but also oxidation of platinum and diffusion of it into internal layers of alumina granule occur “as a result of heating of catalyst on air at high temperature. This process makes the electrochemical dissolving difficult. In [11] it was indicated that penetration of oxygen at high temperatures of interaction (>573K) into crystal lattice of platinum catalysts occurs with forming of oxide films and appearance of platinum complexes with oxygen of PtO_2-Al_2O_3 type.

To achieve more complete palladium and platinum extraction from spent catalysts the conditions of preliminary processing and regime for conducting of electrochemical process of regeneration were varied.

Optimal conditions for preliminary preparation of spent catalysts for purification of exhaust gas of internal-combustion engine were determined. It was found, that high extraction rate of palladium and platinum from spent catalysts of transport SHPAK-0,5, SHPK-0,5 and SHPK-0,1 is achieved after removing of formed during long usage sulfate complexes from its surface. Besides, platinum and palladium are in oxidized states in spent catalysts of transport, because palladium is oxidized beginning from 423K and platina - from 575-773K [12]. For 99-100 % extraction of such metals with the help of alternating current it is necessary to reduce it to specific state.

Platinum of reforming catalyst is in reduced state. The low rate of extraction of platinum in comparison with palladium from SHPAK-0,5 is due to partial interaction of it with carrier and presence of admixtures of other elements. Rising of electrolysis temperature at current density 6300 A/m^2 to 363 K result in considerable (two times) increase in platinum concentration in solution already on thirtieth minute, but boiling of electrolyte and formation of HCl vapors were observed near the electrodes. Grinding of catalytic granules AP-64 increased the rate of dissolving of platinum in initial period (in first 15 minutes by 20%), especially at current density 6300 A/m^2 a little, but did not change the total quantity of extracted for 1 hour platinum. Grinding of catalyst promotes partial dissolving of Al_2O_3 in acid to $AlCl_3$. $AlCl_3$ is hydrolized with forming of colloidal sediments. This is negative phenomenon, because separation of electrolyte from carrier of catalyst is deteriorated. Thus, neither increase in temperature, nor grinding of catalyst AP-64 permit to extract the platinum from catalyst completely.

Complete extraction of platinum from spent catalyst of oil refining is realized by two stage electrochemical dissolving using fresh electrolyte of diminished volume on each stage or circulation of electrolyte [13,14] in contrast to investigated catalyst of transport. Thus, selection of conditions for the preliminary preparation of the samples and optimizing of technological regimes of the process permit to realize 99-100 % extraction of palladium and platinum in 25-36 % HCl at density of alternating current 6300-9500A/m^2 and temperature 328-343K (Table 1).

Electrode is depolarized in anodic semiperiod, but inverse process is inhibited in the following semiperiod. It is the principal reason of possible oxidation of substances in solution at alternating current. Therefore the anodic process is accelerated, electrolyte gets strong oxidizing properties owing to forming of atomic chlorine:

anodic semiperiod

$$Cl^-_{(s)} \rightarrow Cl^o_{(s)} + e,$$

$$Cl^o_{(s)} + Cl^o_{(s)} \rightarrow Cl_{2(s)} \rightarrow Cl_{2(g)}$$

catodic semiperiod

$$H^+_{(s)} + e \rightarrow H^o_{(s)}$$

$$H^o_{(s)} + H^o_{(s)} \rightarrow H_{2(s)} \rightarrow H_{2(g)}$$

Atomic chlorine is the strongest oxidant. Therefore the part of atomic chlorine succeeds to enter into reaction: $Cl^o_{(s)} + Red_{(h)} \rightarrow Cl^-_{(s)} + Ox_{(s)}$, where $Red_{(h)}$, $Ox_{(s)}$ are reduced and oxidized components of spent catalyst (platinum, palladium et al.).

Molecules of chlorine are produced from other part of atomic chlorine. Molecular chlorine, dissolved in electrolyte, is also an oxidant with respect to reduced

Table 1

Regeneration of noble metals from spent catalysts (10 g) at anodic polarization by alternating current in HCl and temperature 343 K

Catalyst	Pretreatment conditions	Electrolysis conditions		Degree for Extraction of metals, % per 1h
		concentration of HCl (%) HCl	Current density, P, A/m^2	
SHPK - 0,5	[7]	36	9500	100
SHPAK-0,5	[7]	36	9500	100
SHPK-1	[7]	26	790	100
AP-64 (SHNPZ)	Without treatment		9500 7900-9500	86
AP-6 (SHNPZ)	Without treatment	20-36 sub-stitution of electrolyte Pv =120 A/l		98,4-100 per 45 min
AP-64 (PNPZ)	heating at 773K	36, circulation of electrolyte	14800	79
AP-56	heating at 773K	36, circulation of electrolyte	9300	93

platinum and palladium. But it is less active, than atomic chlorine. Therefore electrochemical reduction has an advantage in comparison with direct using of gaseous chlorine. Evaluation of atomic chlorine depends on size of electrode potential and concentration of chlorine ions near the surface of electrode. Increasing of the process temperature, increasing of electrolyte concentration, intencity of mixing of solution are of great significance. They cause reduction catodic polarization [15-17].

Thus, on the electrode high gradient of potential, that is rectifying of current originates at laying on of alternating current of high density at anodic semiperiod. This fact results in intensive evaluation of atomic chlorine. Evaluation of chlorine can activate the following after evaluation of atomic chlorine process of oxidation of platinum and palladium with extraction of them from spent catalyst to solution of hydrochloric acid.

The developed new electrochemical method of extraction of precious metals from supported spent catalysts using alternating current permits to reuse the support (Al_2O_3) for preparation of new catalysts of gas purification [7]. Consequently the technology with the exception of waste for application of metallic catalysts over supports can be carried out. Pollution of environment by secondary raw-material may be prevented.

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