The Extraction of Platinum and Palladium from Supported over Al₂O₃ 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 Al₂O₃ 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/m² 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 (K₂PtCl₆) is achieved at current strength 5 A and temperature 353-363K. Density of alternating current 1,3-1,5A/sm², 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 Al₂O₃ spent catalysts of transport and oil refining.

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 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 [PtCl₆]²⁻ type and palladium [PdCl₄]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 for experiments. Methods were described in [7].
Results and discussion

Influence of concentration of hydrochloric acid on extraction of platinum and palladium from spent catalysts SHPAK-0,5 and AP-64 at current density 9500 A/m² 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.

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/m² 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.
but boiling of electrolyte and formation of HCl va-

cence  in solution already on thirtieth minute, con-
siderable (two times) increase in platinum at cur-
rent density 6300 A/m² to 363 K result in

of other elements. Rising of electrolysis temperature

teraction of it with carrier and presence of admix-
tures in solution at alternating current. Therefore

It should be noted that heating of catalyst AP-64 at
973K on air decreases the extent of platinum extrac-
tion 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 oxida-
tion 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 tempera-
tures of interaction (>573K) into crystal lattice of plati-
num catalysts occurs with forming of oxide films and
appearance of platinum complexes with oxygen of
PtO₂-Al₂O₃ type.

To achieve more complete palladium and platinum
extraction from spent catalysts the conditions of pre-
liminary processing and regime for conducting of elec-
trochemical process of regeneration were varied.

Optimal conditions for preliminary preparation of
spent catalysts for purification of exhaust gas of in-
ternal-combustion engine were determined. It was
found, that high extraction rate of palladium and plati-
num 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 plati-
num - 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 in-
teraction of it with carrier and presence of admix-
tures of other elements. Rising of electrolysis temperature
at current density 6300 A/m² to 363 K result in
considerable (two times) increase in platinum concen-
tration in solution already on thirtieth minute, but boiling of electrolyte and formation of HCl va-
pors were observed near the electrodes. Grinding of
catalytic granules AP-64 increased the rate of dissolv-
ing of platinum in initial period (in first 15 minutes by
20%), especially at current density 6300 A/m². a little,
but did not change the total quantity of extracted for 1
hour platinum. Grinding of catalyst promotes partial
dissolving of Al₂O₃ in acid to AlCl₃. AlCl₃ is hydrolized
with forming of colloidal sediments. This is negative
phenomenon, because separation of electrolyte from
carrier of catalyst is deteriorated. Thus, neither in-
crease 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 elec-
trochemical 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 alter-
nating current 6300-9500A/m² 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 sub-
stances in solution at alternating current. Therefore
the anodic process is accelerated, electrolyte gets
strong oxidizing properties owing to forming of atomic
chlorine:

\[
\begin{align*}
\text{anodic semiperiod} \\
\text{Cl}^- + e \rightarrow \text{Cl}^0, \\
\text{Cl}^0 + \text{H}^+ \rightarrow \text{H}_2, \\
\text{catodic semiperiod} \\
\text{H}^+ + e \rightarrow \text{H}_2
\end{align*}
\]

Atomic chlorine is the strongest oxidant. Therefore
the part of atomic chlorine succeeds to enter into
reaction: Cl⁻ + Red₂ → Cl⁻ + Ox₂, where Red₂, Ox₂ 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

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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 |
|----------------|-------------------------|-------------------------|------------------------------------------|
| SHPK - 0.5     | [7]                     | 36, concentration of HCl (%) | 9500                                     | 100                                      |
| SHPAK-0.5      | [7]                     | 36, concentration of HCl (%) | 9500                                     | 100                                      |
| SHPK-1         | [7]                     | 26, concentration of HCl (%) | 790                                      | 100                                      |
| AP-64 (SHNPZ)  | Without treatment       | 20-36 sub-stitution of electrolyte P =120 A/l | 9500                                     | 86                                       |
| AP-6 (SHNPZ)   | Without treatment       | 36, circulation of electrolyte | 7900-9500                               | 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, intensity 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 semi-period. 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 (Al₂O₃) 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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