Russian Journal of Applied Chemistry, Vol. 75, No. 3, 2002, pp. 402–407. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 3, 2002, pp. 413–418.
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SORPTION AND ION-EXCHANGE PROCESSES

Recovery of Platinum with Calcium Oxide Sorbent in Ammonia Oxidation

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Received June 26, 2001

Abstract—The reaction of granulated CaO sorbent with platinum lost in high-temperature oxidation of ammonia was studied. Physicochemical properties of the product and conditions and mechanism of its formation are considered.

Catalytic oxidation of ammonia to nitrogen(II) oxide is the key stage in industrial synthesis of nitric acid [1]. Commercial catalysts (Pt, Rh, and Pd alloys) undergo physicochemical transformations in the process, with their surface structure and chemical composition changed [1–6]. A set of transformations of this kind results in loss of deficient and expensive platinum-group metals. An effective way to reduce the loss of platinum metals is their partial recovery by sorbents mainly based on calcium oxide [1, 7–15].

The mechanism of platinum recovery by calcium-containing sorbents and the chemical aspect of the process are debated in the scientific literature. Atroshchenko *et al*. [9] came to a conclusion that platinum is bound on the surface of the oxide sorbent to form an $x\mathrm{CaO}\cdot y\mathrm{Pt}$ compound. In other studies [10, 11], platinum was found in the sorbent bulk as $4\mathrm{CaO}\cdot\mathrm{PtO_2}$ and $\mathrm{CaO}\cdot\mathrm{Pt_2}$ compounds. In [12, 16], platinum compounds in the sorbent bulk were identified as $\mathrm{Ca_4PtO_6}$ and PtO.

This study is concerned with recovery by calcium oxide of platinum lost in high-temperature oxidation of ammonia and with identification of products formed in the reaction of the lost platinum with calcium oxide.

The calcium oxide sorbent was prepared as follows. As starting compound served calcium oxide of chemically pure grade, which was treated with 80% ethanol (2–3% relative to sorbent weight) and compacted into pellets under a pressure of 150 MPa. Step-like thermal treatment of the sorbent was done in a muffle furnace in air at 473, 673, 873, and 1073 K (for 2 h in each stage). The sorbent was crushed into grains, and fraction with a grain size of $(2\text{–}3)\times 10^{-3}$ m was selected.

Since the lost platinum is mainly caught by the surface layer of sorbents [1, 7–14, 17], sorbent grains were ground and subjected to additional forming and thermal treatment in inert medium (argon) following the above scheme in order to intensify the process and raise the yield of the chemical compounds obtained.

The processes of platinum recovery were studied on a flow-through installation with a quartz reactor 5×10^{-1} m in diameter. As catalyst was used platinum in the form of a package of five meshes with a wire diameter of 7.5×10^{-5} m (industrial platinoid alloy nos. 1 and 5 were not used, because Rh and Pd contained in these alloys in addition to Pt would complicate the interpretation of the experimental results). A bed of sorbent grains, of height 1.7×10^{-1} m, was placed directly after the catalyst meshes at a distance of 8.0×10^{-3} m from them.

The temperature of catalytic oxidation of ammonia was maintained at 1073 K, and the pressure in the system, at 0.101 MPa. The content of ammonia in the air–ammonia mixture (AAM) was about 11.5 vol %. The linear flow velocity of AAM was 0.40 m s^{-1} (normal conditions).

X-ray phase analysis of the compounds obtained was carried out on a Siemens D-500 diffractometer with CuK_α radiation and graphite monochromator used to analyze the diffracted beam. The phases observed in the diffraction patterns were identified using the JCPDS file contained in the mathematical software package of the diffractometer; some X-ray diffraction pattern were compared with the data of the ASTM file [18].

IR absorption spectra were measured on a Perkin–Elmer 577 spectrometer in the range 200–2000 cm^{-1} with CsI pellets used as matrices.

Differential thermal analysis was made on an

MOM Q-derivatograph (Hungary). The temperature was raised at a rate of 300 deg h^{-1} in the interval 293–1273 K, the sample weight was 1×10^{-4} kg, and the duration of catalyst operation and of tests with absorption mass constituted 500 h.

During reactor shutdowns (especially in the final stage of a prolonged experiment), measures were taken for preventing to the maximum possible extent the moisture absorption by the sorbent, leading to its conversion into $Ca(OH)_2$, by purging the reactor at high temperature with dried argon and isolating the argon-filled reactor from humid air by means of moisture absorbents. After being discharged from the reactor, the sorbent was stored in a hermetically sealed vessel filled with dried argon.

X-ray phase analysis of used up sorbent demonstrated that it contained calcium oxide, platinum, and a compound of unknown composition with low line intensities (Fig. 1); no platinum dioxide PtO_2 was found. To confirm the results of X-ray phase analysis, sorbent samples were treated with a 48% solution of HBr at 293 K (PtO_2 dissolves in this reagent, whereas Pt and other its compounds do not [5]). The presence of platinum in solution was determined by the atomic absorption method. Experiments demonstrated that, indeed, there was no platinum dioxide in the sorbent.

Identification of X-ray patterns of a multicomponent mixture is difficult (especially in the cases when lines are closely spaced or insufficiently intense at low concentrations of substances). For this reason, the system was separated into components, with their subsequent identification.

To eliminate the influence of unchanged sorbent on the X-ray patterns of a complex system, the formulation was dissolved in HNO_3 (25 wt %, chemically pure grade) at 308 K. In doing so, account was taken of the fact that neither Pt nor its compounds dissolve at moderate temperatures [5, 19, 20]. The liquid phase was separated from solids and discharged. The solid phase was thoroughly and repeatedly washed with hot double-distilled water (to absence of Ca^{2+} and NO_3^- ions in washing water) and subjected to thermal treatment in inert medium (Ar) at 473–523 K to constant weight.

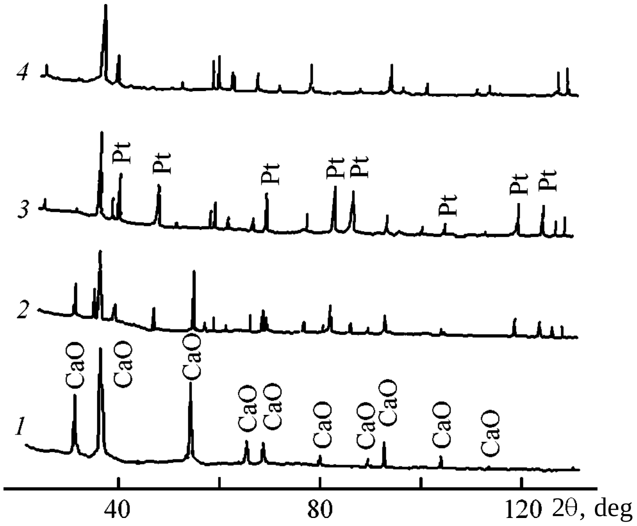

Fig. 1. X-ray patterns of the sorbent and products of platinum recovery. (2θ) Bragg angle. Sorbent: (*1*) starting, (*2*) after 500 h of catalyst operation, and (*3*) after treatment with HNO_3; (*4*) product of sorbent reaction with Pt compounds.

The X-ray patterns of the solid residue (after dissolution and removal of the unchanged part of the sorbent) contained only line sets with interplanar spacings characteristic of platinum, and less intense lines of a compound of unknown composition (Fig. 1). Based on characteristics of the lines, an assumption was made that the unknown compound belongs to the structural type $M_xPt_3O_4$, where M is Ca, i.e., $Ca_xPt_3O_4$. Since this compound does not dissolve even in boiling aqua regia [19], the following analytical procedure was used to isolate it as individual phase. The residue after dissolving CaO was treated with aqua regia at 318 K to recover platinum dissolving under these conditions [5, 19, 20]. The liquid phase was separated, and the solid phase was thoroughly washed in hot double-distilled water (to absence of Ca^{2+} and NO_3^- ions in washing water) and subjected to thermal treatment by the scheme described above. Characteristics of X-ray patterns of the given compound are presented in Table 1.

Table 1. Characteristics of X-ray patterns of the compound $Ca_xPt_3O_4$ ($x = 1$) found in the sorbent

hkl	*d*, nm	*I*, %	*hkl*	*d*, nm	*I*, %
110	0.4052	18.7	332	0.1222	3.2
200	0.2879	5.5	422	0.1170	3.1
210	0.2564	100.0	510/431	0.1124	6.1
211	0.2340	28.8	520/432	0.1065	26.1
220	0.2028	3.7	521	0.1047	6.7
310	0.1813	7.0	440	0.1013	11.2
222	0.1655	28.5	530/433	0.0983	2.0
320	0.1590	31.0	600/442	0.0955	0.5
321	0.1531	18.1	610	0.0942	6.3
400	0.1433	16.8	611/532	0.0930	7.1
411/330	0.1351	3.9	541	0.0885	2.6
420	0.1283	2.8	622	0.0864	19.8
421	0.1251	26.3	630/542	0.0855	25.0

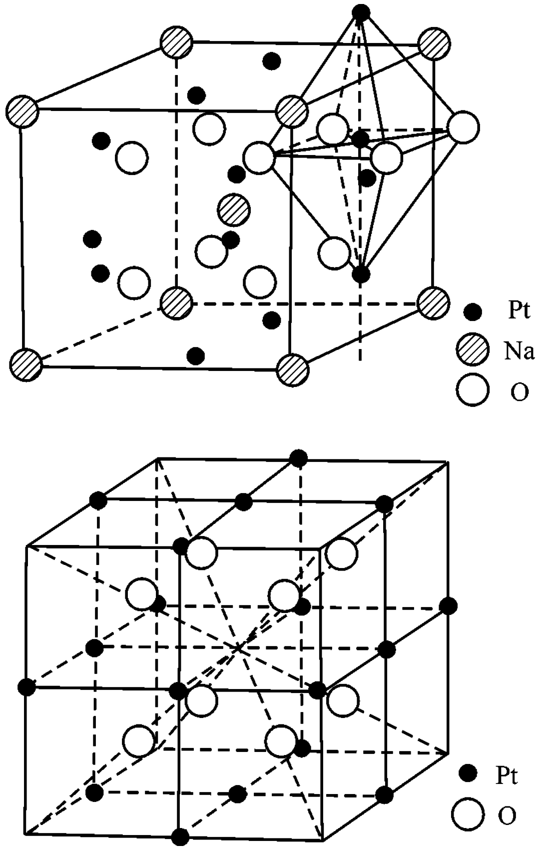

Fig. 2. $Na_xPt_3O_4$ structure by Muller and Roy [21].

The set of lines in X-ray patterns (interplanar spacings, intensities), which is in good agreement with the data of [19] and JCPDS and ASTM files [18], indicates the formation in the sorbent of a chemical compound, $Ca_xPt_3O_4$, having a simple cubic lattice (a = 0.5739 nm) with space group $Pm3n\text{–}O_h^3$. The compound $Ca_xPt_3O_4$ belongs to the structural type $Na_xPt_3O_4$ (with x varying between 0 and 1) and is a nonstoichiometric intercalation compound of platinum oxide (Pt_3O_4) [19, 21]. The cubic structure of Pt_3O_4 is constituted by square oxygen prisms occupied by Pt atoms and arranged perpendicularly to one another (Fig. 2). Oxygen atoms occupy cube vertices. Pt atoms center each oxygen face in these prisms. Cubic voids formed by prism intersection are empty. This structure corresponds to the ideal composition $PtO_{1.33}$ [21]. Deviations from the ideal composition Pt_3O_4 can be attributed to formation of interstitial solid solutions. Excess, with respect to the $PtO_{1.33}$, platinum atoms, and also impurity ions Na^+, K^+, Ca^{2+}, and Mg^+, may be introduced into cubic voids of the structure, forming stable nonstoichiometric intercalation compounds of the structural type $Na_xPt_3O_4$ [19, 22, 23]. Compounds with this structure are stable even at a very small number of atoms introduced [19, 22, 23]. In the given case, the compound $Ca_xPt_3O_4$ of the same structural type was formed when Ca^{2+} ions were present in excess.

Table 2. Analytical data for the composition of $Ca_xPt_3O_4$ (x = 1) found in the sorbent

Sample weight, g	Content,* wt %				
	O			Pt (4)	Ca (5)
	1	2	3		
0.3010	–	9.31	–	84.91	–
0.2543	–	9.25	–	84.89	–
0.2855	–	9.28	–	84.90	–
0.1015	9.29	–	–	84.89	5.82
0.0876	9.27	–	–	84.91	5.82
0.1000	–	–	9.30	–	5.79
0.1000	–	–	9.26	–	5.85
Average	9.28	9.28	9.28	84.90	5.82

* Determination method: (*1*) gravimetric, (*2*) volumetric, (*3*) thermogravimetric, (*4*) atomic-absorption, and (*5*) chemical.

The IR spectrum of the compound contains absorption bands at 707, 683, 599, 479, 367, and 230 cm^{-1}, characteristic of the compound of this structural type [24]. The absorption bands at 707 and 599 cm^{-1} can be assigned to Pt–O stretching vibrations, and those at 683 and 479 cm^{-1}, to Ca–O stretching vibrations. The absorption bands at 367 and 230 cm^{-1} characterize O–Pt–O bending vibrations.

To confirm the quantitative composition of nonstoichiometric $Ca_xPt_3O_4$, this compound was analyzed for the content of all the constituent elements by various techniques. The results obtained are presented in Table 2.

The stoichiometric compound $Ca_xPt_3O_4$ (x = 1) must contain (wt %): Pt 84.90, Ca 5.82, and oxygen 9.28. The content of oxygen was determined as an average of the values yielded by three analytical methods: gas-volumetric, thermogravimetric (decomposition of the compound), and from the difference when determining the content of platinum and calcium.

A thermogravigram of the compound $Ca_xPt_3O_4$ is shown in Fig. 3. Heating of the substance (in argon, to prevent high-temperature oxidation of platinum and its sublimation as platinum dioxide vapor [1–5, 20]) in the interval 1183–1223 K leads to the weight loss (6.96%), associated with endothermic decomposition of the compound in accordance with the equation

$$2Ca_xPt_3O_4 = 2xCaO + 6Pt + (4 - x)O_2. \tag{1}$$

The products of dissociation of the compound are calcium oxide, metallic platinum, and oxygen, which is characteristic of double oxides including a noble metal [25]. The endothermic peak in the DTA curve lies at 1203 ± 5 K.

The X-ray patterns of products of $Ca_xPt_3O_4$ decomposition, cooled in inert medium (Ar), contain, in addition to reflections associated with calcium oxide (0.276, 0.239, 0.169, 0.1447, 0.1383, 0.1203, 0.1072, and 0.0980 nm), also those associated with metallic platinum (0.227, 0.1957, 0.1386, 0.1179, 0.1132, 0.0979, 0.0898, 0.0875, 0.0799, and 0.0754 nm).

For the compound $Ca_xPt_3O_4$, the weight loss in decomposition virtually did not exceed the expected value calculated by Eq. (1) at $x = 1$, which indicates that the influence of platinum sublimation in the form of dioxide

$$Pt(c) + O_2(g) = PtO_2(g) \tag{2}$$

is eliminated in the inert medium. A chemical analysis of the solid residue after $Ca_xPt_3O_4$ decomposition was made by dissolving the mixture in boiling aqua regia and then determining the platinum content in solution by the atomic-absorption method [26]. The content of calcium(II) was found gravimetrically by a standard procedure in the form of calcium carbonate after solution neutralization.

The oxygen content in $Ca_xPt_3O_4$ was determined volumetrically by thermal decomposition of a sample in a sealed ampule placed in a muffle furnace (1273 K, 1.5 h). After fast cooling of the ampule to room temperature, the volume of evolved oxygen was measured with a gas burette. The gas-volumetric analysis confirmed the data of thermogravimetric and chemical methods as regards the content of oxygen in a $Ca_xPt_3O_4$ sample at $x = 1$ (Table 2). Thus, chemical analysis of condensed products of $Ca_xPt_3O_4$ decomposition, and also analysis for the content of oxygen by various techniques, made it possible to determine unambiguously the composition of the compound obtained: $CaPt_3O_4$, i.e., $x = 1$.

The formation of $Ca_xPt_3O_4$ in the sorbent can be accounted for on the basis of a comparative analysis of the conditions of platinum recovery and synthesis of this compound. In [19], $Ca_xPt_3O_4$ ($x = 1$) was synthesized upon prolonged heating in air (823–973 K, $P = 0.101$ MPa) of a mixture of platinum dioxide and calcium nitrate. In [27], the same compound was obtained by heating a mixture of platinum dioxide, platinum black, and calcium oxide (673–773 K, $P = 0.202$–0.808 MPa) for 300–340 h. $Ca_xPt_3O_4$ was synthesized by introducing calcium ions into voids of the cubic lattice of Pt_3O_4 of the structural type $Na_xPt_3O_4$ [19, 21–23], which is stable at $T \le 1073$ K. Consequently, formation of $Ca_xPt_3O_4$ assumes the presence of platinum oxide Pt_3O_4 in the starting reaction mixture or formation of this substance in some stage of a complex process.

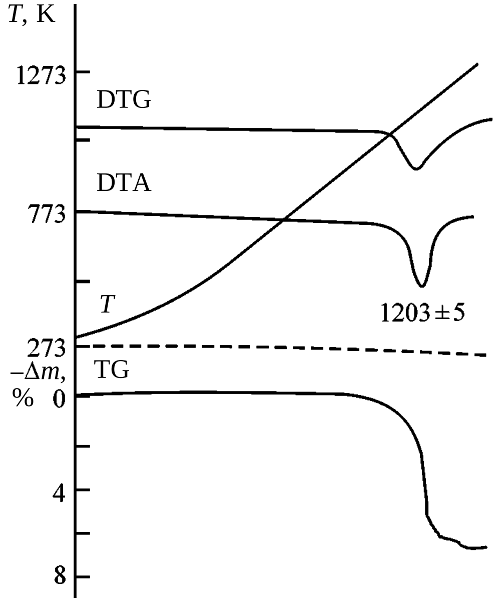

Fig. 3. Thermogravigram of $CaPt_3O_4$. Substance weight 1×10^{-4} kg, heating rate 300 deg h^{-1}. (*T*) Temperature and (Δm) weight change.

Introduction of platinum atoms or calcium ions (and also, according to [19, 21–23], of microscopic amounts of Na^+, K^+, Mg^{2+}, Zn^{2+}, and Li^+) leads to formation of a thermally stable nonstoichiometric compound $Ca_xPt_3O_4$ of the structural type $Na_xPt_3O_4$. The composition of $Ca_xPt_3O_4$ varies depending on the concentration of ions introduced into the substance structure (this concentration grows, at constant temperature and pressure, with increasing process time).

Platinum oxide Pt_3O_4 can be obtained by various methods [24, 28]; in particular, by thermal decomposition of platinum dioxide in accordance with the equation

$$3PtO_2 = Pt_3O_4 + O_2. \tag{3}$$

The optimal decomposition temperature is 923–953 K; at higher temperature, platinum dioxide intensively dissociates into platinum and oxygen (at 1173 PtO_2 dissociates completely [28]).

Platinum oxide Pt_3O_4 can also be obtained by oxidation of highly dispersed platinum (platinum black) in oxygen [24, 27] (especially under elevated pressure):

$$3Pt + 2O_2 = Pt_3O_4. \tag{4}$$

In the course of high-temperature oxidation of ammonia, the platinum catalyst undergoes a number of physicochemical transformations [1–6, 20]; in particular, platinum and platinum dioxide appear in the gas phase:

$$Pt(c) = Pt(g), \tag{5}$$

$$Pt(g) + O_2(g) = PtO_2(g). \tag{6}$$

To this should be added sublimation of platinum as platinum dioxide in accordance with Eq. (2).

The products of reactions (2), (5), and (6), Pt and PtO_2, are starting substances in processes used to obtain Pt_3O_4 (in gas phase or on the sorbent surface). Introduction of atoms (ions) of platinum and calcium (or microscopic amounts of K^+, Na^+, Mg^{2+}, and Zn^{2+}, present in the sorbent as impurities and, in part, coming from AAM as contaminants, despite the reagent purification to remove them) into voids in platinum oxide Pt_3O_4 stabilizes a compound of the structural type $Na_xPt_3O_4$ and improves its thermal resistance. The temperature of PtO_2 dissociation should not be exceeded only in the initial stage of synthesis. In later stages, this limitation is lifted since a higher-temperature process of Ca^{2+} ion introduction into the crystal lattice of a compound of the structural type $Na_xPt_3O_4$ occurs, i.e., $Ca_xPt_3O_4$ is formed in accordance with the equation

$$Pt_3O_4 + xCa^{2+} = Ca_xPt_3O_4, \tag{7}$$

where $0 \le x \le 1$.

Analysis of the conditions for absorption by the CaO sorbent of products formed in conversion of the platinum catalyst leads to the following important practical recommendations.

(1) It is necessary to satisfy certain temperature conditions of sorbent operation. The sorbent should be placed at a distance from the catalyst meshes at which its temperature does not exceed the temperature of complete PtO_2 dissociation ($T \le 1173$ K) or the temperature of Pt_3O_4 dissociation. Beginning with the instant of time when a nonstoichiometric compound $Ca_xPt_3O_4$ is synthesized in the sorbent, the sorbent temperature should not exceed the dissociation temperature of this compound (1183–1203 K).

(2) Since the nonstoichiometric compound $Ca_xPt_3O_4$ is formed in the sorbent at the phase boundary CaO–Pt_3O_4, it is necessary to have well-developed interface for accelerating the process. Low rate of the topochemical process leads to accumulation on the sorbent surface of products formed in transformations of the platinum catalyst [Eqs. (2), (4)–(6)]. Dissociation of these compounds enriches the sorbent surface with platinum, and the rate of $Ca_xPt_3O_4$ formation falls. Consequently, the sorbent taken in the form of pellets, coarse grains, or cylinders is inefficient in chemical recovery of products of platinum conversion, since only a small part of its outer surface is used in reaction (7), with deep layers of the sorbent virtually not involved in sorption at all.

(3) To make faster the chemical absorption of platinum-containing components by the sorbent, it is necessary to stabilize platinum oxide Pt_3O_4, i.e., to obtain a nonstoichiometric intercalation compound of the type $Na_xPt_3O_4$. Consequently, the presence in the calcium-containing sorbent of even minor concentrations of ions with small radius and high mobility (e.g., Li^+, Na^+, Mg^{2+}, Zn^{2+}, etc.), which readily penetrate into voids of the cubic lattice of Pt_3O_4 and stabilize it, must exert positive influence on the efficiency of platinum recovery in the form of the chemical compound $Ca_xPt_3O_4$ ($0 \le x \le 1$). When present in the sorbent, ions with larger radius (e.g., Ba^{2+}, Sr^{2+}, Cs^+, Rb^+, etc.) will adversely affect the efficiency of platinum recovery.

(4) In recovery of platinum from a calcium-containing sorbent, account should be taken of the high thermal and chemical stability of the compound $Ca_xPt_3O_4$, and appropriate temperature ($T \ge 1223$ K) and reagents should be used.

CONCLUSIONS

(1) It is established that conversion products of platinum lost in high-temperature oxidation of ammonia are bound chemically by a calcium-containing sorbent to give a nonstoichiometric compound $Ca_xPt_3O_4$ ($0 \le x \le 1$). The extent to which the compound is nonstoichiometric depends on the time of sorbent operation and process parameters.

(2) Data on chemical mechanisms of recovery of platinum lost in high-temperature oxidation of am-

monia by a calcium-containing sorbent can be used to develop theoretical prerequisites for synthesis of effective sorbents.

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