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Trapping of Transformation Products of a Palladium Catalyst for Ammonia Oxidation by a Calcium Oxide Absorbent

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Abstract—The chemical regularities of trapping palladium and its compounds lost in the process of high-temperature ammonia oxidation by a calcium oxide absorbent are studied. In the interaction with the absorbent, the products of palladium catalyst transformation form $CaPd_3O_4$, which is a derivative of the nonstoichiometric intercalation compound $Ca_xPd_3O_4$, where $0 \leq x \leq 1$. Physicochemical properties of this compound and the conditions of its formation are considered.

INTRODUCTION

Catalytic ammonia oxidation to NO forms the basis for the commercial manufacturing of nitric acid [1]. In technological processes, commercial catalysts (Pt, Rh, and Pd alloys) undergo physicochemical transformations with changes in the structures of the catalyst surfaces and their chemical compositions [1–5]. A set of such transformations results in the loss of deficient and expensive platinum group metals. One efficient method to diminish the loss of platinum-group metals is their partial trapping by absorption masses that basically containing calcium oxide [1, 6–13].

The chemistry of platinum trapping by a calcium oxide absorbent has been studied extensively [8–11], but the mechanism of the process remains a debatable topic. There are no data on the mechanism of trapping palladium contained in the commercial catalysts for ammonia oxidation by a calcium oxide absorbent (commercial alloys nos. 1 and 5 contain 4.0 and 15.0 wt % palladium, respectively [1]) [1, 5, 6]. There are no data on the nature of chemical compounds formed when the catalysts react with a calcium oxide absorbent.

This work is devoted to the study of the trapping process for the products of palladium catalyst transformation in the reaction of high-temperature ammonia oxidation by a calcium oxide absorbent and to the identification of products of interaction between palladium-containing components with calcium oxide.

EXPERIMENTAL

A calcium oxide absorbent was prepared as follows. Chemically pure calcium oxide was used as a starting material. The ground reagent was treated with a 70% aqueous solution of ethanol (2–3% of the absorbent weight) and palletized under a pressure of 150 MPa. The stepped thermal treatment of the absorbent was carried out in a muffle furnace in air at 473, 673, 873, 1073, and 1123 K (2 h at each temperature). Then, the absorbent was ground and the 2–3 mm fraction was separated.

Because the surface layer is largely responsible for the trapping of metals and their compounds [1, 6, 9–11], absorbent granules were ground, formed, and thermally treated in argon according to the above scheme every 40 h to intensify the process and increase the yield of chemical compounds.

The catalytic process of ammonia oxidation was carried out in a flow-type setup with a quartz reactor (diameter, 50 cm). The catalyst was a package of palladium grids with 0.09-mm threads (commercial platinum alloys nos. 1 and 5 were not used, because they contain Pt and Rh in addition to Pd [1] and their use would make it difficult to interpret the results of experiments). A 17-cm bed of absorbent granules was placed immediately after the catalyst grids at a distance of 0.8 cm.

The temperature of the catalytic ammonia oxidation was kept at the level of 1123 K, and the pressure in the system was 0.101 MPa. The concentration of ammonium in the ammonia–air mixture was ~11.5 vol %. The linear flow rate of the mixture was 0.40 m/s (at the normal pressure and temperature).

X-ray analysis of the resulting compounds was carried out using a Siemens D-500 diffractometer, CuK_α irradiation, and a graphite monochromator. Phases observed with X-ray diffraction patterns were identified using JCPDC files contained in the package supplied with the diffractometer. Some X-ray diffraction patterns were compared with data of ASTM files [14].

Differential thermal analysis was carried out using an MOM Q-derivatograph (Hungary). The temperature was increased at a rate of 5 K/min in the range 293–1373 K. Samples weighed 0.1 g.

The time-on-stream of the catalyst and the time of testing the absorption material was 700 h.

When the reactor operation was stopped, necessary steps were taken to exclude absorption of moisture by

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Table 1. Maximal distances (*d*) and intensities *I* of signals in X-ray diffraction patterns of the compound $CaPd_3O_4$

d, nm	*I*, %	*d*, nm	*I*, %
0.4059	16	0.1067	16
0.2870	6	0.1048	6
0.2568	100	0.1016	10
0.2349	35	0.0985	<1
0.2025	<1	0.0958	<1
0.1815	4	0.0945	6
0.1658	20	0.0934	6
0.1593	20	0.0887	<1
0.1535	18	0.0866	12
0.1436	14	0.0857	16
0.1354	2	0.0847	4
0.1284	2	0.0829	8
0.1254	18	0.0812	4
0.1225	4	0.0797	2
0.1173	<1	0.0789	30
0.1126	2	0.0782	20

the absorbent and its transformation into $Ca(OH)_2$: the reactor was purged with dried argon at a high temperature, and the reactor filled with argon was isolated from moist air using a system for moisture absorption. After discharging, the absorbent was kept in hermetically sealed volumes filled with dried argon.

RESULTS AND DISCUSSION

X-ray phase analysis of the absorbent after its operation showed that it contains calcium oxide, palladium, and a compound with an unknown composition with low-intensity signals (Fig. 1). Palladium oxide (PdO) was not detected. To check the latter result of X-ray diffraction analysis, the absorbent samples were treated in 48% HBr at 293 K (this reagent dissolves PdO but it does not dissolve Pd^0 and other palladium compounds [5, 15, 16]). The presence of palladium in the solution was determined by the atomic absorption method [17]. Experiments confirmed the absence of PdO.

Because the deciphering of X-ray diffraction patterns of multicomponent mixtures is rather difficult (especially if the signals of X-ray patterns are close and nonintense because of the low concentrations of substances), we used the method of separating the system into components with their further identification.

To remove the signals from the unreacted absorbent, the sample was dissolved in 25 wt % HNO_3 (chemically pure) at 308 K. We took into account that neither Pd^0 nor its compounds cannot be dissolved in 25% nitric acid at a moderate temperature [5, 15, 16]. The liquid phase was separated from the solid and removed. The solid phase was thoroughly washed with hot, doubly distilled water many times until the Ca^{2+} and NO_3^- disappeared from the wash water) and thermally treated in an inert (argon) medium at 473–523 K to a constant weight. The weight of the solid phase after dissolving calcium oxide was 0.10% of the initial absorbent sample weight.

X-ray diffraction patterns of the remaining solid phase (after the dissolution and removal of the unreacted absorbent portion) contained only signals corresponding to the interplanar distances that were characteristic of palladium and those of a compound of unknown composition (Fig. 1). The characteristics of the signals allowed us to assume that the unknown product is one of the compounds with the general formula $Ca_xPd_3O_4$, where *x* may range from 0 to 1 in the general case. Because the compound $Ca_xPd_3O_4$ (independently of the *x* value) is chemically stable and is not dissolvable in boiling concentrated nitric acid [15], we used the following analytical method for its isolation as an individual phase. The composition of substances was treated with boiling concentrated HNO_3 until the palladium, which is soluble in this acid, is removed from the system [5, 15, 16]. Then, the liquid phase was separated from the solid phase and removed. The solid phase was thoroughly washed in hot, doubly distilled water until NO_3^- was removed from the wash water and thermally treated according to the scheme described above. The characteristics of the X-ray patterns of this compound are shown in Table 1.

Data in Table 1 agree well with data reported in [15] and JCPDS and ASTM files [14]. They suggest the formation of $CaPd_3O_4$ in the absorbent; that is, $x = 1$ in $Ca_xPd_3O_4$. The $CaPd_3O_4$ compound has a cubic lattice ($a = 0.5746$ nm) with a $Pm3n$–O^3h spatial group and belongs to the $Na_xPt_3O_4$ structural type ($0 \le x \le 1$). $Na_xPt_3O_4$ is a nonstoichiometric intercalation compound of the Pt(II, III) oxide (Pt_3O_4) [15, 18].

Compounds of the $Na_xPt_3O_4$ structural type are based on the cubic lattice of the B_3O_4 type (B = Pt, Pd). The cubic structure of B_3O_4 is built of perpendicular square oxygen prisms filled with platinum (palladium) ions (Fig. 2). Oxygen ions are in the corners of a cube. Palladium (platinum) ions are in the center of each oxygen square of these prisms. The cavities of cubes formed by the intersections of prisms are empty. This structure corresponds to the ideal composition $BO_{1.33}$ [18]. Deviations from the ideal composition B_3O_4 are explained by the formation of solid intercalation solutions. Overstoichiometric (with respect to the $BO_{1.33}$ composition) platinum and palladium ions, as well as foreign ions (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) may embed into the cubic cavities of the structure and form stable nonstoichiometric intercalation compounds of the $Na_xPt_3O_4$ structural type [15, 19, 20]. Compounds with such a structure are stable even if the amount of intercalated ions is small [15, 19, 20].

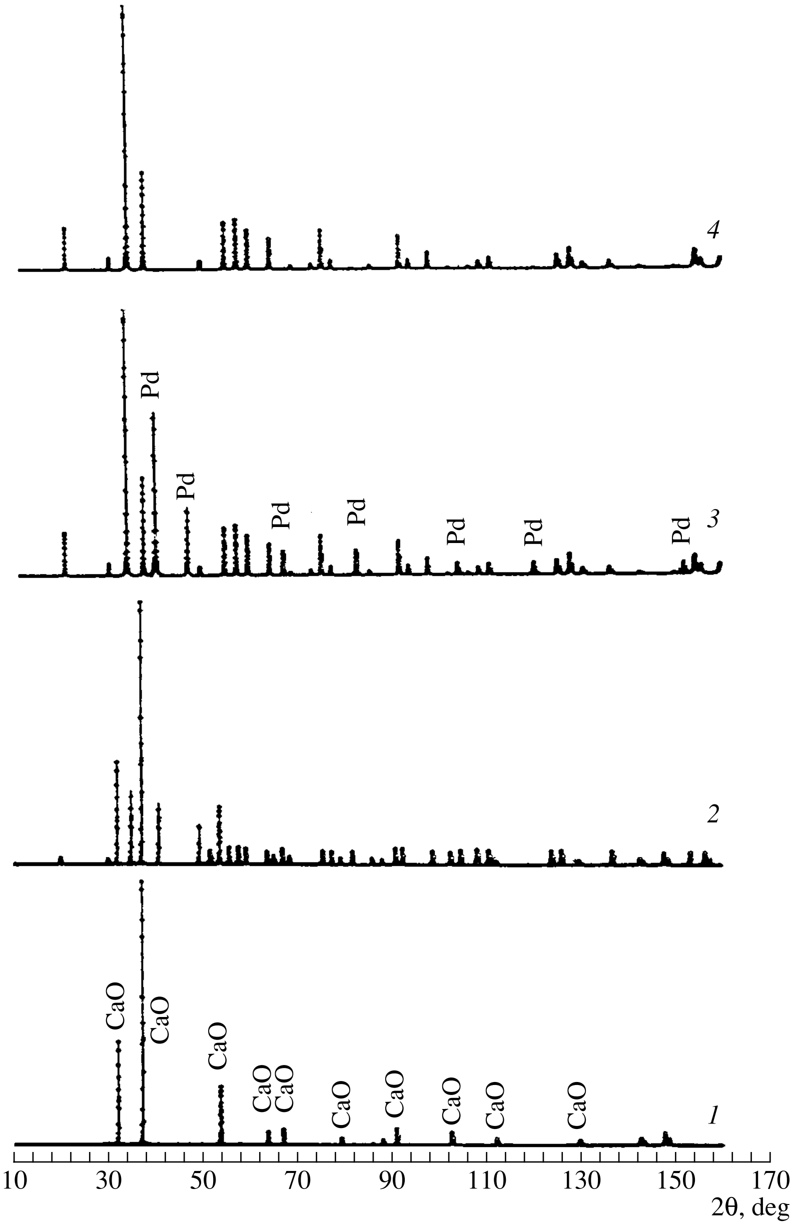

Fig. 1. X-ray diffraction patterns of the absorbent and the products of palladium trapping: (*1*) initial absorbent; (*2*) absorbent after 700 h on stream; (*3*) spent absorbent after treatment in HNO_3; (*4*) product of absorbent interaction with the palladium compounds ($CaPd_3O_4$).

In this case when there are excess Ca^{2+} ions, the compound $CaPd_3O_4$ forms in the reaction medium, and this compound is the intercalation structure in the cubic lattice of B_3O_4.

To determine the quantitative composition of this compound, it was subjected to elemental analyses to determine all the elements by different methods. The results are shown in Table 2.

The stoichiometric compound $CaPd_3O_4$ should have the following composition (wt %): Pd, 75.41; Ca, 9.47; and O, 15.12. The concentration of oxygen was determined as an average of the results of three analytical methods: volumetric, derivatography (compound decomposition), and using the difference after determining the concentration of palladium and calcium in the substance.

Figure 3 shows data of the thermal analysis of $CaPd_3O_4$. When the substance is heated in an inert (argon) medium to prevent high-temperature palladium oxidation and its sublimation in the form of PdO vapors [1–5, 16]), a weight loss (11.34%) is observed in the interval 1283–1323 K. This weight loss is associated with the endothermic decomposition of compounds according to the equation

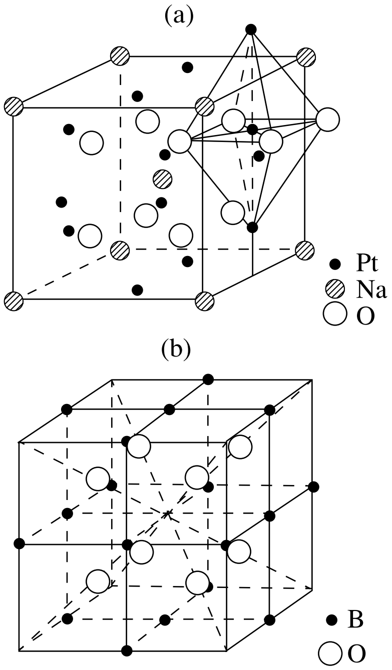

Fig. 2. The structures of (a) $Na_xPt_3O_4$ and (b) B_3O_4 (B = Pd, Pt) according to Muller and Roy [18].

$$2CaPd_3O_4 = 2CaO + 6Pd + 3O_2. \qquad (I)$$

The products of decomposition are calcium oxide, metallic palladium, and oxygen, which are characteristic of binary oxides involving a noble metal [21]. Indeed, the diffraction patterns of $CaPd_3O_4$ decomposition products cooled in an inert (argon) medium contain reflections belonging to calcium oxide (0.2760, 0.2390, 0.1690, 0.1447, 0.1383, 0.1203, 0.1072, and 0.0980 nm) and metallic palladium (0.2230, 0.1941, 0.1372, 0.1171, 0.1120, 0.0972, 0.0891, 0.0870, 0.0795, and 0.0750 nm).

For the compound $CaPd_3O_4$, the weight loss in the decomposition was not higher than the expected value calculated according to Eq. (I). This fact pointed to the absence of the effect of palladium sublimation in the form of oxide in an inert medium:

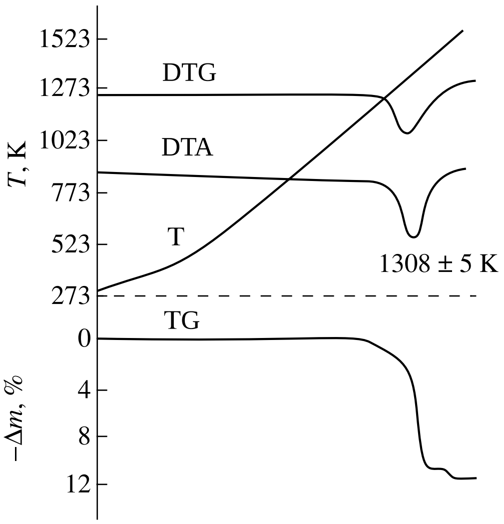

Fig. 3. Data of thermal analysis of $CaPd_3O_4$ (sample weight, 100 mg; heating rate 5 K/min; medium, argon).

$$2Pd_{(solid)} + O_{2(gas)} = 2PdO_{(gas)}. \qquad (II)$$

The solid residue after $CaPd_3O_4$ decomposition was chemically analyzed by dissolving the mixture in boiling concentrated nitric acid with further determination of the palladium concentration in the solution using the atomic absorption method [17]. The concentration of calcium was determined in the form of carbonate after solution neutralization by gravimetry according to the standard procedure.

The volumetric measurement of the oxygen concentration in the $CaPd_3O_4$ samples was carried out by the thermal decomposition of the sample in soldered quartz ampules in the muffle furnace (T = 1372 K, 1.5 h). After fast cooling the ampule to room temperature, the volume of oxygen formed was determined using a gas

Table 2. Results of elemental analysis of the compound $CaPd_3O_4$ found in the absorbent

Weight of the $CaPd_3O_4$ sample, g	Concentrations of elements according to the results of analysis, wt %				
	oxygen			palladium	calcium
	gravimetry	volumetric analysis	derivatography	atomic absorption	chemical analysis
0.3112	–	15.16	–	75.42	–
0.2833	–	15.09	–	75.40	–
0.2617	–	15.11	–	75.41	–
0.1026	15.13	–	–	75.42	9.48
0.0895	15.11	–	–	75.40	9.45
0.1000	–	–	15.14	–	9.51
0.1000	–	–	15.10	–	9.44
Average	15.12	15.12	15.12	75.12	9.47

burette. Volumetric analysis supported data obtained by derivatography and chemical methods for oxygen in the $CaPd_3O_4$ samples (Table 2).

Thus, the chemical analysis of condensed products of $Ca_xPd_3O_4$ decomposition, as well as data of different methods on the concentration of oxygen, enabled one to determine unambiguously the composition of the obtained compound: $CaPd_3O_4$; that is, $x = 1$.

The formation of $CaPd_3O_4$ in the absorbent can be explained proceeding from a comparative analysis of conditions for ammonia oxidation on the palladium catalyst and conditions for the synthesis of this compound. Bergner and Kohlhaas [15] synthesized $CaPd_3O_4$ by the prolonged heating of the mixture of Ca and Pd(II) nitrate decomposition products in air (temperature, 1023–1073 K; pressure, 0.101 MPa). Lazarev and Shaplygin [22] obtained the same compound by heating a mixture of PdO and calcium carbonate ($T = 1073$; $P = 0.101$ MPa) for 400 h.

The synthesis of $CaPd_3O_4$ was carried out by the intercalation of calcium and palladium ions into the cavities of the B_3O_4 cubic lattice considered above (see Fig. 2). The formation of the B_3O_4 structure can be considered as a result of the transformation of the tetragonal lattice of Pd(II) oxide [15, 18–20], which is introduced into the initial reaction mixture or formed in the decomposition of palladium compounds. The authors of [15, 18–20] do not exclude the possibility of B_3O_4 structure formation also in the direct interaction of palladium with oxygen in the reaction mixture. Under the action of intercalated calcium and palladium ions, as well as microamounts of Na^+, K^+, Mg^{2+}, Zn^{2+}, and Li^+ ions, the B_3O_4 lattice is stabilized and the nonstoichiometric compound $Ca_xPd_3O_4$ ($0 \le x \le 1$) of the $Na_xPt_3O_4$ structural type is formed [15, 18–20]. Then, the composition of the compound $Ca_xPd_3O_4$ changes depending on the concentration of intercalated Ca^{2+} ions [15, 23], which are present in the reaction mixture in excess. The concentration of intercalated calcium ions at a constant temperature and pressure increases with time.

In the process of high-temperature ammonia oxidation, the palladium catalyst undergoes a series of physicochemical transformations [1–5, 16] according to the equations

$$2Pd_{(solid)} + O_{2(gas)} = 2PdO_{(solid)}, \tag{III}$$

$$Pd_{(solid)} = Pd_{(gas)}, \tag{IV}$$

$$2Pd_{(gas)} + O_{2(gas)} = 2PdO_{(gas)}. \tag{V}$$

Also, to this it is necessary to add the process of palladium sublimation in the form of PdO according to Eq. (II). According to [16, 24], at $T = 1073$–1273 K, palladium is largely sublimated in metallic form rather than in the form of PdO; that is, process (IV) dominates over process (II). Condensed PdO starts to decompose into simple substances at $T = 1078$ K [16, 22]. At 1173 K, PdO decomposes completely [16], that is, at a process temperature equal to 1123 K, the gas phase after the catalyst contains both palladium and palladium(II) oxide [16, 24]. The products of reactions (II)–(V), Pd and PdO, are carried away by the gaseous flow of the reaction mixture and are the starting materials in the processes of $Ca_xPd_3O_4$ formation on the absorbent surface. The participation of palladium dioxide in the formation of $Ca_xPd_3O_4$ is improbable at a high temperature, because PdO_2 decomposes into simple substances at $T = 373$ K [16, 22].

The intercalation of palladium and calcium ions or microamounts of K^+, Na^+, Mg^{2+}, and Zn^{2+} ions, which are available in the absorbent as admixtures, into the cavities of the B_3O_4-type lattice results in the formation of the compound $Ca_xPd_3O_4$ ($0 \le x \le 1$) of the $Na_xPt_3O_4$ structural type.

A long process of absorbent Ca^{2+} ion intercalation into the lattice of the stabilized nonstoichiometric compound further occurs according to the equation

$$\begin{aligned} &Ca_xPd_3O_4 + (1-x)CaO \\ &= CaPd_3O_4 + \frac{1}{2}(1-x)O_2, \end{aligned} \tag{VI}$$

where $0 \le x \le 1$. Oxygen from the CaO lattice is partly carried away to the gas phase, and anionic vacancies appear in the oxide.

When the process time is long, the compound $Ca_xPd_3O_4$, which was found in the absorbent, is formed.

The dynamics of formation of new phases was monitored by sight using optical (MIM) and electron (JEM-7Y) microscopes. The study of thin sections of absorbent granules showed that new compounds are formed in the surface layers of the absorbent (structural features of new compounds, their color, and the forms of crystallites differ from those of calcium oxide). Indeed, heterogeneous reaction (VI) of the fixed bed of the solid absorbent with the transformation products of the palladium catalyst occurs at the interface of phases of the absorbent–catalyst transformation products (CaO–Pd and CaO–PdO). The porosity of the absorbent sizes of the reagent particles were such that chemical reactions were localized on the absorbent surface. The authors of [1, 6, 9–11] came to analogous conclusions.

The study carried out in this work provides the following practical recommendations:

1. To accelerate the process, it is necessary to have a developed interface boundary. The low rate of the topochemical process results in the acceleration of the products of palladium catalyst transformation on the absorbent surface (Eqs. (II)–(V)). The decomposition of PdO leads to a higher concentration of palladium on the absorbent surface. Therefore, the use of the absorbent in the form of pellets or large granules is inefficient for the chemical trapping of the products of palladium transformations. Only their small portion on the outer surface participates in the process. Deeper layers are not used in this case.

2. For the chemical process of absorption of palladium-containing components, it is necessary to stabi-

lize the nonstoichiometric intercalation compound $Ca_xPd_3O_4$ at an early stage of the reaction. Therefore, the presence of small mobile ions (e.g., Li^+, Na^+, Mg^{2+}, and Zn^{2+}), which readily intercalate into the cavities of the cubic lattice of the B_3O_4 type [15, 18–20, 23] and transform it into a stabilized nonstoichiometric compound of the $Na_xPt_3O_4$ structural type, should affect the efficiency of trapping of the products of palladium catalyst transformation in the form of the compound $Ca_xPd_3O_4$ ($0 \le x \le 1$) even when the concentrations of these ions in the calcium oxide are low.

Large, poorly mobile ions in the composition of absorbents (e.g., Ba^{2+}, Sr^{2+}, Cs^+, and Rb^+) have an opposite effect on the efficiency of palladium component trapping.

3. When palladium is extracted from a calcium oxide sorbent, it is necessary to take into account the high chemical and thermal stabilities of $CaPd_3O_4$ and use the corresponding temperature ($T \ge 1308$ K) and reagents.

Data on the chemical regularities of trapping the products of palladium catalyst transformation in the process of high-temperature ammonia oxidation can be used to develop theoretical bases for designing efficient absorbents.

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