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SORPTION
AND ION-EXCHANGE PROCESSES

Recovery with Calcium Oxide Sorbent of Conversion Products of Rhodium Catalyst for Ammonia Oxidation

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Abstract—The chemical aspects of recovery with a calcium oxide sorbent of rhodium lost in high-temperature oxidation of ammonia were studied. The physicochemical properties of this compound and conditions of its formation were considered.

Catalytic oxidation of ammonia to nitrogen(II) oxide underlies the industrial method for manufacture of nitric acid [1]. Industrial catalysts (Pt, Rh, and Pd alloys) undergo physicochemical transformations in technological processes, with the surface structure and the chemical composition of the catalysts changed [1–6]. A set of such transformations of platinoid catalysts leads to loss of deficient and expensive metals of the platinum group. An effective way to diminish the loss of platinum metals is their partial recovery by sorption masses mainly based on calcium oxide [1, 7–17].

The mechanism of platinum recovery with calcium-containing sorbents and the chemical aspect of the process are rather extensively covered in the scientific literature [1, 7–20]. At the same time, there is no evidence concerning the mechanism of recovery of rhodium, entering into the composition of industrial catalysts for ammonia oxidation (alloy nos. 1 and 5), with a calcium oxide sorbent; there are no data, either, on what kind of chemical compounds are formed in interaction between the products of conversion of rhodium catalysts and sorbents [1].

The present communication reports the results obtained in studying the recovery with a calcium oxide sorbent of rhodium lost in high-temperature oxidation of ammonia.

As a starting compound for preparing the sorbent was used calcium oxide of chemically pure grade. The reagent was ground and treated with a 70% aqueous solution of ethynol (2–3% relative to the sorbent mass) and compacted into pellets under pressure of 150 MPa. After thermal treatment of the mass in air at 473, 673, 873, and 1253 K (2 h at each temperature), the sorbent was crashed into grains and a fraction with grain size of 2 × 3 mm was selected.

Since recovery of lost metals and their compounds is mainly effected by the surface layer of sorbents [1, 7–16, 18–20], the sorbent grains were ground after every 40 h of operation and subjected to repeated forming and thermal treatment in an inert medium (Ar) in accordance with the scheme considered above.

The catalytic process of ammonia oxidation was carried out in a flow-through installation with quartz reactor 50 cm in diameter. As a catalyst served rhodium in the form of a package of five grids with thread diameter of 0.06 mm. The 17-cm-high bed of sorbent grains was placed at a distance of 0.8 cm from the catalyst grids.

The temperature of ammonia oxidation was 1253 K; the pressure in the system, 0.101 MPa; the content of ammonia in the ammonia–air mixture, 11.5 vol %; and the linear flow velocity of the mixture, 0.40 m s^{-1}. The time of catalyst operation and absorption mass testing was 600 h. An X-ray phase analysis of the compounds was made on a Siemens D-500 diffractometer with Cu_{K_α} radiation. A differential-thermal analysis was done on an MOM Q-derivatograph (Hungary). The heating rate was 5 deg min^{-1} in the temperature range 293–1773 K.

During reactor shutdowns, the system was purged with dried argon and isolated from air with moisture absorbers. After being discharged from the reactor, the sorbent was stored in hermetically sealed vessels filled with dried argon.

The X-ray phase analysis of the sorbent demonstrated that it contains CaO and a rhodium compound of unknown composition (Fig. 1). To eliminate the effect of unreacted sorbent on the X-ray diffraction patterns obtained, the sorbent was dissolved in 25% HNO_3 of chemically pure grade at 308 K. In doing so, account was taken of the fact that rhodium compounds do not dissolve in HNO_3 of this concentration at moderate temperatures [21]. The liquid phase was separated from the solid phase and removed. The solid phase was thoroughly and repeatedly washed with hot twice-distilled water (antil no Ca^{2+} and NO_3^- ions were contained in washing water) and subjected to thermal treatment in an inert medium (Ar) at 473–523 K to constant weight.

The X-ray diffraction patterns of the solid residue contained only lines characteristic of the compound $CaRh_2O_4$ (Fig. 1). The parameters of the X-ray patterns of this compound are presented in the table.

The set of lines in the diffraction patterns (interplanar spacings *d* and intensities *I*) is in good agreement with data from the ASTM file [22], which indicates that the chemical compound $CaRh_2O_4$, having rhombic lattice (a = 0.9169, b = 1.0747, c = 0.3087 nm) of the $CaFe_2O_4$ structural type with Pnam space group, is formed in the sorbent.

The composition of the $CaRh_2O_4$ compound was confirmed by X-ray phase and chemical analyses [23].

A thermogram of the compound $CaRh_2O_4$ is presented in Fig. 2.

When the substance is heated in an inert medium (argon) to prevent high-temperature oxidation of Rh and its sublimation in the form of rhodium(III) oxide [21, 23] in the temperature range 1713–1763 K, loss of mass (15.49%) is observed, associated with endothermic decomposition of the compound by the equation

$$2CaRh_2O_4 = 2CaO + 4Rh + 3O_2. \qquad (1)$$

The products of dissociation are calcium oxide, rhodium metal, and oxygen, which is characteristic of double oxides including a noble metal [23]. The X-ray diffraction patterns of products of $CaRh_2O_4$ decomposition, cooled in an inert medium (Ar), contain, in addition to reflections related to calcium oxide (0.276, 0.239, 0.169, 0.1447, 0.1383, 0.1203, 0.1072, 0.0980 nm), also reflections from metallic rhodium (0.2196, 0.1902, 0.1345, 0.1147, 0.1098, 0.0951, 0.0872, 0.0850 nm). An endothermic peak appears in the DTA curve at 1743 ± 10 K.

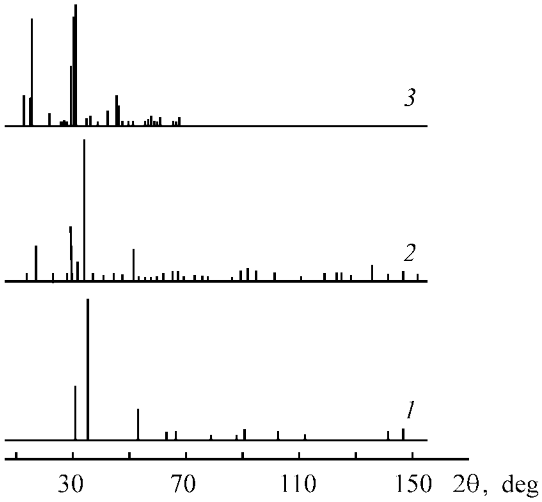

Fig. 1. X-ray diffraction patterns of the sorbents and products of rhodium recovery. (2θ) Bragg angle. (*1*) Initial sorbent, (*2*) sorbent after 600 h of catalyst operation, and (*3*) product of interaction between the sorbent and rhodium compounds ($CaRh_2O_4$).

For the $CaRh_2O_4$ compound, the loss of mass in decomposition virtually did not exceed the expected value calculated using Eq. (1), which indicates that the inert medium rules out any influence of rhodium sublimation in the form of rhodium(III) oxide [21, 23].

The formation of $CaRh_2O_4$ in the sorbent can be accounted for on the basis of a comparative analysis of the conditions under which the products of rhodium catalyst conversion are recovered and the conditions of synthesis of the given compound.

The authors of [24] synthesized $CaRh_2O_4$ by prolonged (for no less than 150°C) heating in air

Characteristics of X-ray diffraction patterns of the $CaRh_2O_4$ compound found in the sorbent

d, nm	*I*, %	*d*, nm	*I*, %
0.5373	12	0.1978	17
0.4617	24	0.1850	34
0.4515	49	0.1823	25
0.3456	8	0.1797	7
0.3329	1	0.1711	8
0.2972	3	0.1664	10
0.2822	3	0.1624	3
0.2686	49	0.1546	16
0.2626	91	0.1539	9
0.2569	100	0.1527	13
0.2551	43	0.1508	22
0.2308	7	0.1497	11
0.2265	11	0.1340	9
0.2114	4	0.1277	7
0.2001	9		

(T = 1173–1373 K, P = 0.101 MPa) of a mixture of rhodium(III) oxide (or rhodium metal) with calcium oxide (carbonate). Under these conditions, metallic rhodium is converted into rhodium(III) oxide [21, 23, 24].

In high-temperature oxidation of ammonium, the rhodium catalyst undergoes a number of physicochemical transformations [1, 25] in accordance with the reaction equations

$$4Rh_{(c)} + 3O_{2(g)} = 2Rh_2O_{3(c)}, \quad (2)$$

$$Rh_{(c)} = Rh_{(g)}, \quad (3)$$

$$4Rh_{(c)} + 3O_{2(g)} = 2Rh_2O_{3(g)}, \quad (4)$$

$$4Rh_{(g)} + 3O_{2(g)} = 2Rh_2O_{3(g)}. \quad (5)$$

At a process temperature of 1253 K rhodium sublimates predominantly in the form of rhodium(III) oxide [21, 26]. However, in the gas phase too, rhodium is readily oxidized by the oxygen present in the reaction medium to rhodium(III) oxide. Rhodium(III) oxide dissociates at 1333 K [21], being, therefore, stable at the reaction temperature.

The forming products of reactions (2)–(5), Rh and Rh_2O_3, carried away by the flow of the reaction mixture, are starting compounds in processes yielding the $CaRh_2O_4$ compound on the sorbent surface in accordance with the reaction equations

$$Rh_2O_3 + CaO = CaRh_2O_4, \quad (6)$$

$$4Rh + 3O_2 + 2CaO = 2CaRh_2O_4. \quad (7)$$

Thus, the products of conversion of the rhodium catalyst in high-temperature oxidation of ammonia are bound by the calcium oxide sorbent into the compound $CaRh_2O_4$. This fact is to be taken into account when using industrial catalysts for ammonia oxidation (with sorbents based on calcium oxide) containing rhodium. In rhodium recovery from calcium-containing sorbents, account should be taken of the high thermal and chemical stability of the $CaRh_2O_4$ compound [24], and the appropriate temperature and reagents should be used.

CONCLUSIONS

(1) The products of conversion of rhodium lost in high-temperature oxidation of ammonia are bound by the calcium oxide sorbent into the $CaRh_2O_4$ compound.

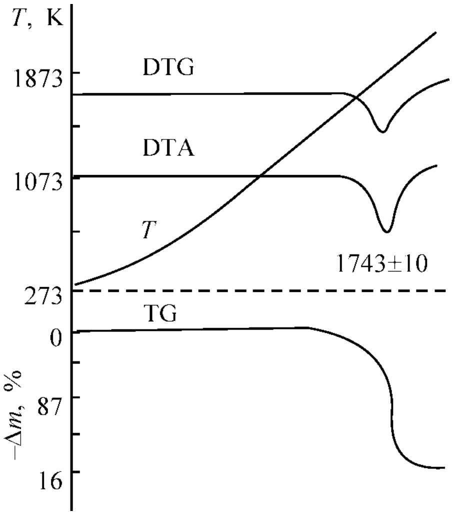

Fig. 2. Thermogram of $CaRh_2O_4$. Substance mass 100 mg, heating rate 5 deg min^{-1}. (T) Temperature and (Δm) mass change.

(2) Data on chemical aspects of recovery with the calcium oxide sorbent of rhodium lost in high-temperature oxidation of ammonia can be used in developing theoretical foundations for creation of effective sorption masses.

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