PLATINUM CAPTURE BY OXIDE SORBENTS IN THE PROCESS OF HIGH-TEMPERATURE CATALYTIC OXIDATION OF AMMONIA: MODERN PHYSICO-CHEMICAL APPROACHES AND RESOURCE-SAVING TECHNOLOGIES

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Abstract. The paper investigates the physico-chemical regularities of platinum capture by oxide sorbents in the process of high-temperature ammonia oxidation. The formation of the non-stoichiometric compound $Ca_xPt_3O_4$ has been established. The possibility of effective return of platinum to the technological cycle is demonstrated. Recommendations for optimizing the composition of sorbents and their operating conditions have been developed.

Keywords: platinum, capture, oxide sorbents, $Ca_xPt_3O_4$, ammonia oxidation, catalyst recycling, circular economy.

Introduction. Platinum losses during the catalytic oxidation of ammonia remain one of the most acute problems in the nitric acid industry. Annual irreversible platinum losses on a global scale are estimated at hundreds of kilograms, leading to significant economic losses and increasing dependence on primary raw materials. In the context of the global shortage of platinum group metals and the transition to a circular economy, the development of effective technologies for platinum capture and recycling is of strategic importance.

Literature Review

Over the past three years (2023–2026), research on the capture and recycling of platinum group metals from spent catalysts has significantly intensified.

In the work of Zhang et al. (2024), a new concept of composite oxide sorbents based on $CaO–CeO_2–ZrO_2$ was proposed, which increased the degree of platinum capture to 94.7% at 900–950°C [1]. The authors note that the introduction of rare earth elements stabilizes the Pt_3O_4 structure and reduces platinum entrainment into the gas phase.

Studies by the European group (2025) demonstrated the high efficiency of magnesium- and strontium-containing sorbents for the formation of stable platinates of the $M_xPt_3O_4$ type [2]. It was found that the non-stoichiometry of the compounds significantly depends on temperature and oxygen partial pressure.

In domestic studies (2023–2025), special attention is paid to calcium oxide sorbents modified with oxides of alkaline earth and rare earth metals. It has been shown that the introduction of small additives of Na_2O and K_2O increases the sorption capacity for platinum by 18–25% [3, 4].

Despite significant progress, the mechanisms of high-temperature interaction of PtO_2 with oxide matrices and the kinetics of formation of non-stoichiometric $Ca_xPt_3O_4$ phases under real conditions of industrial ammonia oxidation units remain insufficiently studied. This work aims to fill these gaps.

Experimental Part and Results

The studies were conducted on model and industrial samples of platinum catalysts for ammonia oxidation at a temperature of 1073 K for 300–500 hours. Calcium oxide modified with various additives (Na_2O, MgO, CeO_2) was used as a sorbent.

Phase transformations on the sorbent surface were studied using X-ray phase analysis (XRD), scanning electron microscopy (SEM) with energy-dispersive analysis (EDS), and differential thermal analysis (DTA).

It was established that a compound of the structural type $Na_xPt_3O_4$ with variable composition $Ca_xPt_3O_4$ ($0.6 \leq x \leq 1.2$) is formed in the surface layers of the sorbent. The

degree of non-stoichiometry depends on the operating time of the sorbent and the content of impurity ions.

Main chemical processes:

- $Pt(s) \rightleftharpoons Pt(g)$
- $Pt(s) + O_2(g) \rightleftharpoons PtO_2(g)$
- $3PtO_2(g) \rightleftharpoons Pt_3O_4(s) + O_2(g)$
- $Pt_3O_4 + xCaO \rightarrow Ca_xPt_3O_4$

The thermal stability of $Ca_xPt_3O_4$ is high: the decomposition temperature ranges from 1183 to 1223 K. Upon heating, the compound decomposes with the release of metallic platinum according to the equation:

$$2Ca_xPt_3O_4(s) \rightarrow 2xCaO(s) + 6Pt(s) + (4–x)O_2(g)$$

It has been experimentally shown that the optimal operating temperature of the sorbent lies in the range of 1073–1123 K. At higher temperatures, significant platinum entrainment into the gas phase is observed, while at lower temperatures, the rate of $Ca_xPt_3O_4$ formation decreases.

Modification of the sorbent with magnesium and cerium oxides made it possible to increase the degree of platinum capture from 78% (pure CaO) to 92–94%.

Conclusion. The conducted studies made it possible to establish the physico-chemical regularities of high-temperature platinum capture by oxide sorbents and to propose scientifically substantiated recommendations for optimizing their composition and operating conditions. The developed approaches open up prospects for creating highly efficient sorption systems that ensure a significant reduction in irreversible platinum losses in the nitric acid industry.

References

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