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## PdO IMPACT ON THE ACTIVITY OF HYDROCARBON OXIDATION WITH OXIDE CATALYSTS

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### ABSTRACT

The palladium component influence on the catalytic activity of a catalyst was investigated based on transition-metal oxides deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> carrier in the process of hydrocarbon catalytic thermal destruction. It has been determined that the value of surface concentrations of PdO deposited on Co<sub>3</sub>O<sub>4</sub> doesn't effect on the achievable conversion degree when using the obtained catalytic converter. It is suggested that PdO facilitates the interfacial diffusion of atomic oxygen on the catalyst oxide component due to support it in an oxidized state. Adsorbed on palladium oxygen migrates on cobalt oxide in the composition of this catalyst. At the expense of this process oxygen passivation of Pd-Co<sub>3</sub>O<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is overcome and its high reaction activity is ensured. Our research is evidence that Co<sub>3</sub>O<sub>4</sub> performs the role of active centers on a corundum carrier in the reaction of catalytic thermal hydrocarbon oxidation. Additionally injected PdO into the catalyst composition promotes to the cobalt phase enrichment by oxygen.

*Keywords:* gas emissions, catalytic conversion, catalyst unit, hydrocarbon conversion, transition-metal oxides, palladium oxide.

### INTRODUCTION

Platinum group metals are widely used as catalysts in the chemical industry (ammonia oxidation [1, 2], methane combustion in gas turbines [3]) and also in exhaust gases' converters of automobile transport [4-7]. The relatively low price of palladium among metals of this group and its high catalytic activity in reactions of hydrocarbon and CO oxidation, NO<sub>x</sub> reduction [8] at the same time determine the actuality of its compounds usage for the manufacture of gas purification catalysts.

But precious metal reserves on the Planet are limited and demand for them increases year by year. More than 45% of all mined platinum group metals were spent to 1994 only for production of catalysts used to protect the environment [9]. Their cost steady growth is the reason for an active search of alternatives for effective catalyst synthesis. Therefore a certain tendency of increasing the research focused on the use of transition metals in the process of gas purification from toxic substances is observed [10-13].

Commercially produced gas emission cleaning catalysts can be divided into three main groups [14]:

- catalysts containing platinum group metals;
- catalysts based on transition-metal oxides;
- mixed catalysts consisting of transition-element oxides and compounds of platinum group metals.

The effect of palladium component addition on the activity of an oxide catalyst deposited on a carrier - molten corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) in a process of catalytic thermal hydrocarbon destruction was studied in the present research.

#### **MATERIALS AND METHODS**

Corundum grains of 0.3-0.4 mm fraction were used as a carrier; the grains were subjected to a multi-stage impregnation with saturated water solutions of nitrates  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . The catalyst active centers on the carrier were formed in the subsequent two-hour drying at  $130^\circ\text{C}$  and heat treatment for 4 hours at the temperature of  $400^\circ\text{C}$  [12].

The identification of formed active centers, conducted by X-ray phase analysis using DRON-2.0 diffractometer showed that the nitrate salts were subjected to decomposition with  $\text{Co}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{NiO}$  formation (Fig. 1) on the corundum surface[13].

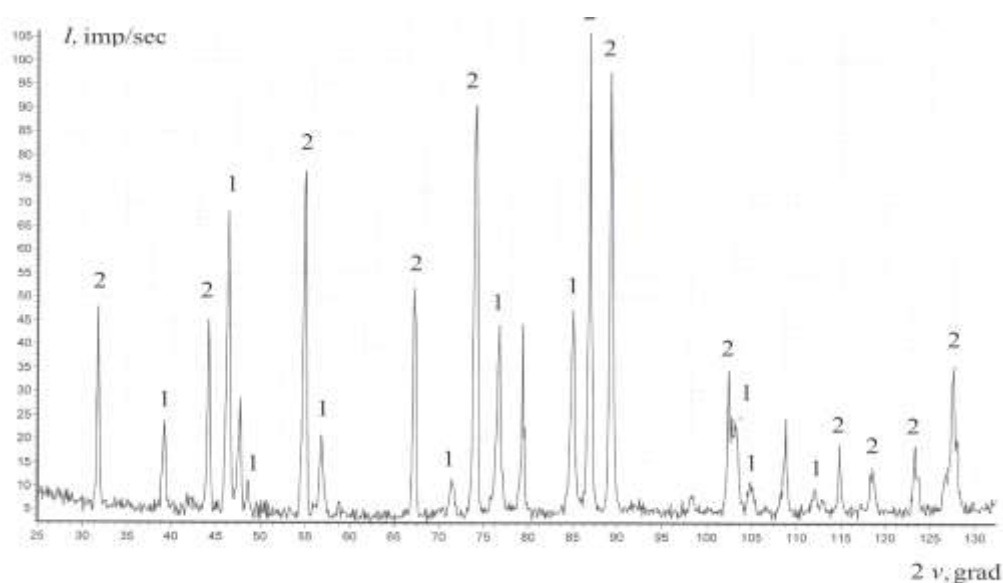


Fig. 1. The XRD of coated samples on the corundum: peaks proper to 1 –  $\text{Co}_3\text{O}_4$ ; 2 –  $\alpha\text{-Al}_2\text{O}_3$

The carrier  $\alpha\text{-Al}_2\text{O}_3$  samples with supported catalysts of given compositions and without them were treated with  $\text{Pd}(\text{NO}_3)_2$  saturated water solution of  $2 \text{ g/cm}^3$  density by the same method. The samples were also subjected to thermal decomposition. The results of X-ray analysis (Fig. 2) showed that palladium nitrate destruction on corundum grains led to  $\text{PdO}$  formation.

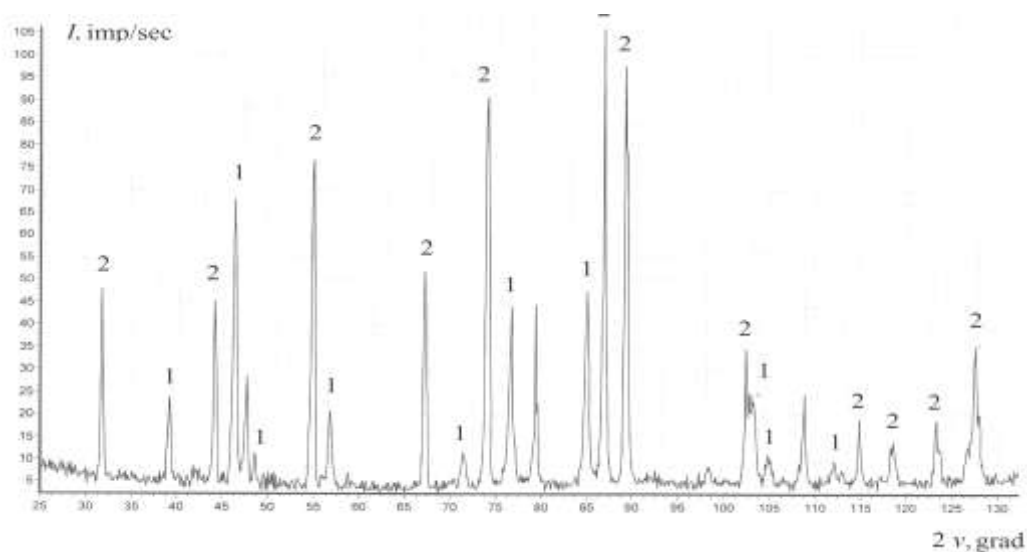


Fig. 2. The XRD of coated samples on the corundum: 1 – peaks proper to PdO; 2 –  $\alpha$ - $\text{Al}_2\text{O}_3$

The effectiveness of using a certain type of gas purification catalyst was determined by studying the process of catalytic thermal hydrocarbon destruction (Fig. 3-6) on the lab bench [15]. Benzene vapors in air medium were used as a model hydrocarbon mixture [16].

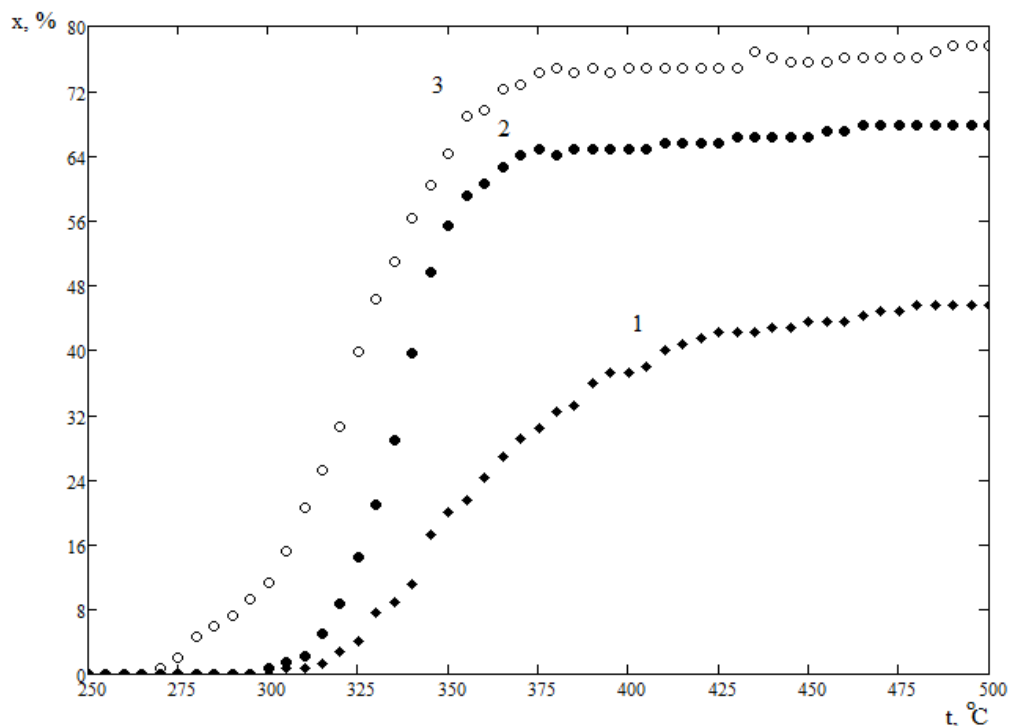


Fig. 3. Temperature dependences of benzene vapor conversion degree (%) obtained using compositions  $\text{Co}_3\text{O}_4$  - PdO with surface concentration on the carrier ( $\text{mg}/\text{cm}^2$ ):  $\text{Co}_3\text{O}_4$  – 5, PdO – 1 (1);  $\text{Co}_3\text{O}_4$  – 10, PdO – 1 (2); PdO – 1 (3)

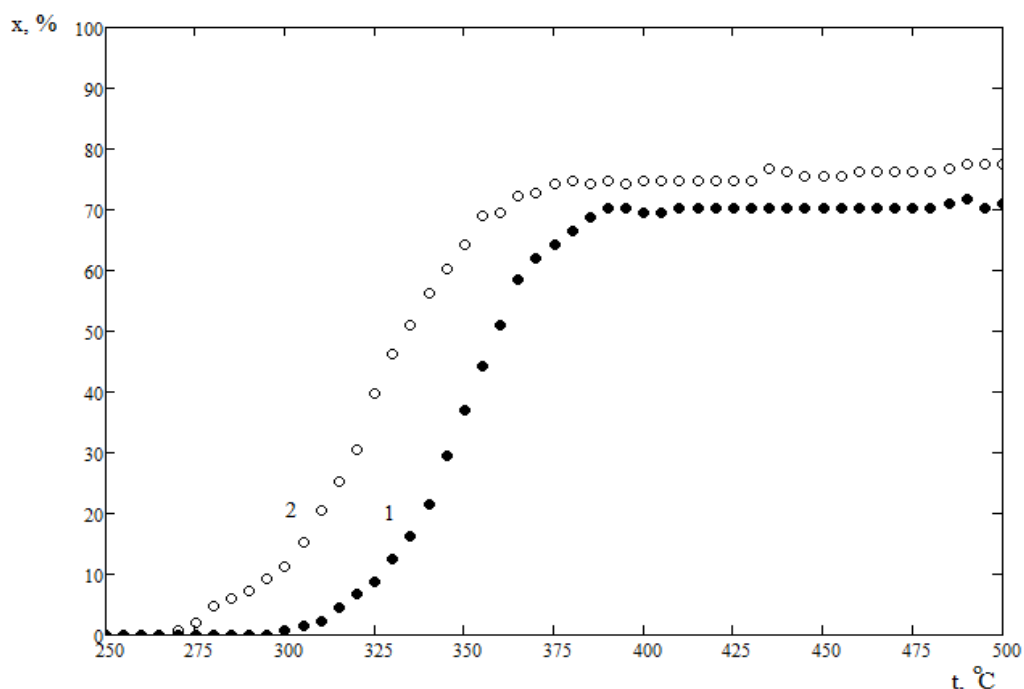


Fig. 4. Temperature dependences of benzene vapor conversion degree (%) obtained using compositions  $\text{Cr}_2\text{O}_3 - \text{PdO}$  with surface concentration on the carrier ( $\text{mg}/\text{cm}^2$ ):  $\text{Cr}_2\text{O}_3 - 10$ ;  $\text{PdO} - 1$  (1);  $\text{PdO} - 1$  (2)

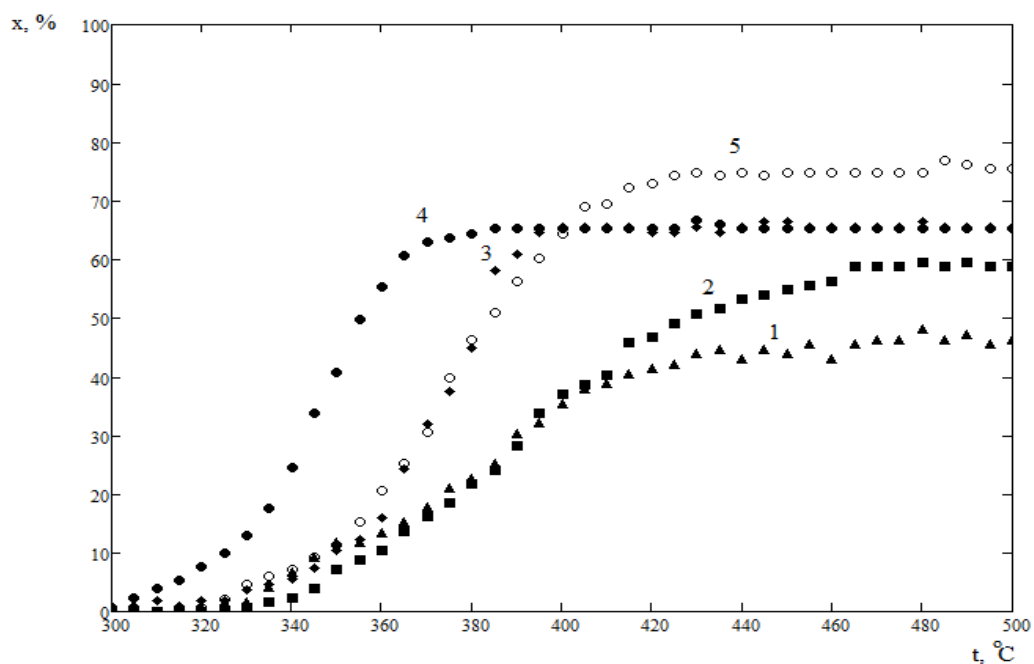


Fig. 5. Temperature dependences of benzene vapor conversion degree (%) obtained using compositions  $\text{CuO} - \text{PdO}$  with surface concentration on the carrier ( $\text{mg}/\text{cm}^2$ ):  $\text{CuO} - 3$ ,  $\text{PdO} - 1$  (1);  $\text{CuO} - 5$ ,  $\text{PdO} - 1$  (2);  $\text{CuO} - 7$ ,  $\text{PdO} - 1$  (3);  $\text{CuO} - 10$ ,  $\text{PdO} - 1$  (4);  $\text{PdO} - 1$  (5)

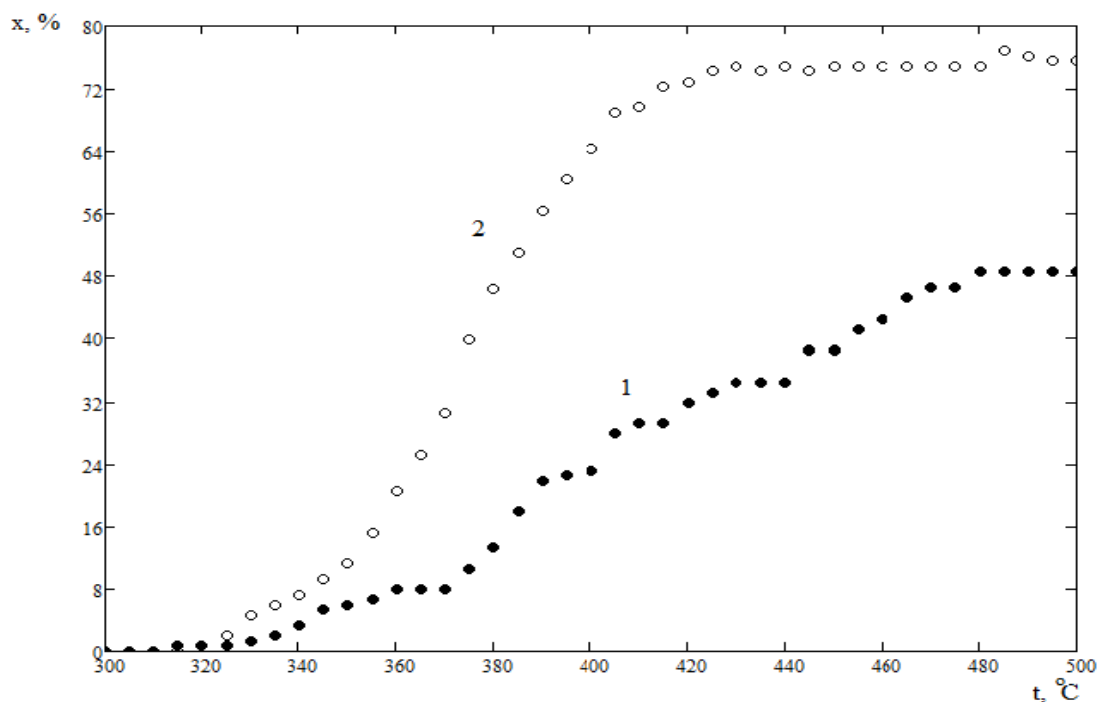


Fig. 6. Temperature dependences of benzene vapor conversion degree (%) obtained using compositions NiO – PdO with surface concentration on the carrier (mg/cm<sup>2</sup>): NiO – 10; PdO – 1 (1); PdO – 1 (2)

### RESULTS AND DISCUSSION

Temperature dependences (Fig. 2-5) show maximum values of benzene vapor conversion degrees, presented in Table 1.

Table 1. Values of surface concentrations of catalyst active centers and maximum benzene vapor conversion degree

Surface concentrations of catalyst active centers, mg/cm <sup>2</sup>	Maximum benzene vapor conversion degree, %
Co <sub>3</sub> O <sub>4</sub> – 5; PdO – 1	46
Co <sub>3</sub> O <sub>4</sub> – 10; PdO – 1	68
Cr <sub>2</sub> O <sub>3</sub> – 10; PdO – 1	70
CuO – 3; PdO – 1	46
CuO – 5; PdO – 1	60
CuO – 7; PdO – 1	66
CuO – 10; PdO – 1	66
NiO – 10; PdO – 1.	49
PdO – 1	75

Data in Table 1 testifies that the highest degree of catalytic neutralization is reached using PdO catalyst active centers with surface concentration of 1 mg/cm<sup>2</sup>. Pre-coating of

transition-metal oxides (in amounts specified by surface concentration limits) on the carrier decreases the catalyst activity.

The experiments for determination of the effect of palladium oxide amount in the complex catalyst  $\text{Co}_3\text{O}_4\text{-PdO}/\alpha\text{-Al}_2\text{O}_3$  composition on its activity were conducted in parallel. Data of surface concentrations of supported catalysts on corundum grains and reached maximum benzene vapor conversion degree at their usage is given in Table. 2.

Table 2. Dependences of values of maximum benzene vapor conversion degree on surface concentrations of catalyst active elements

Surface concentrations of catalyst active centers, $\text{mg}/\text{cm}^2$	Maximum benzene vapor conversion degree, %
PdO – 0.1	28
$\text{Co}_3\text{O}_4$ – 10	56
$\text{Co}_3\text{O}_4$ – 10, PdO – 0.1	67

Data in Table 2 testifies that the lowest benzene vapor conversion degree is reached using PdO as catalyst active centers with  $0.1 \text{ mg}/\text{cm}^2$  surface concentration on the carrier. Using  $\text{Co}_3\text{O}_4$  catalyst with  $10 \text{ mg}/\text{cm}^2$  surface concentration allows to reach maximum benzene vapors conversion degree of 56%. The conversion degree increases up to 67% upon subsequent PdO depositing with the surface concentration of  $0.1 \text{ mg}/\text{cm}^2$  (Table 2). However according to the Table 1 maximum benzene vapor conversion degree equal to 68% was obtained when depositing on the corundum  $\text{Co}_3\text{O}_4$  surface with surface concentration of  $10 \text{ mg}/\text{cm}^2$  and PdO  $1 \text{ mg}/\text{cm}^2$ . Thus it is established that at subsequent PdO compound deposition on  $\text{Co}_3\text{O}_4$  with the surface concentration in the range  $0.1\text{-}1 \text{ mg}/\text{cm}^2$  the maximum conversion degree is not significantly changed when using the catalyst of such compositions.

### CONCLUSIONS

PdO role in the composition of  $\text{Co}_3\text{O}_4\text{-PdO}/\alpha\text{-Al}_2\text{O}_3$  catalyst is shown, apparently, in increasing  $\text{Co}_3\text{O}_4$  phase stability. This may be conditioned by the fact that PdO facilitates interfacial diffusion of atomic oxygen on catalyst oxide component and maintains it in oxidized state. This provision is confirmed by the results of NO and CO catalytic conversion research [17] on the  $\text{Pd-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$  catalyst.

The research [17] showed that oxygen adsorbed on palladium migrates on cobalt oxide in the composition of this catalyst. At the expense of this process oxygen passivation of  $\text{Pd-Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$  catalyst is overcome and its high reaction activity is ensured. Our research is evidence that  $\text{Co}_3\text{O}_4$  performs the role of active centers on a corundum carrier in the reaction of catalytic thermal hydrocarbon oxidation. Additionally injected PdO into the catalyst composition promotes to the cobalt phase enrichment with oxygen.

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