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RESEARCH ARTICLE

# Features of the Mechanism of Catalytic Oxidation of Carbon Monoxide on Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts

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## Abstract

The mechanism of catalytic low-temperature oxidation of CO on Pd/Al<sub>2</sub>O<sub>3</sub> was studied. A combined reaction mechanism through the formation and decomposition of carboxyl-type structures was proposed, in which adsorbed oxygen reoxidizes reduced palladium atoms and ensures the decomposition of carboxyl structures with the formation of CO<sub>2</sub> and the regeneration of OH groups. It was shown that with a small addition of Pd the activity of the catalyst increases significantly. The positive effect is due to the activation of CO or a change in the state of oxygen on the surface of the catalyst. Palladium was estimated by the value of hydrogen adsorption at 70°C. The reaction rate of catalytic oxidation of carbon monoxide, as the main characteristic of the activity and efficiency of the studied catalysts, was measured on a circulation-static unit using the method of continuous analysis of the gas mixture. The higher SCA of supported palladium in comparison with massive palladium in the reaction of low-temperature oxidation of CO may be associated with the written-off mechanism. This assumption is consistent with the TDA data. Close values of the adsorption energy of CO on the compared objects indicate a practically identical state of adsorbed CO on supported and massive palladium. However, the concentration of this form of CO, active in the oxidation reaction, on Pd/Al<sub>2</sub>O<sub>3</sub> is approximately two orders of magnitude higher. Pd black adsorbs CO mainly in a weakly bound, low-activity form, which is reversible already at 100°C. For Pd black, which has no hydroxyl coating, a mechanism is realized with the participation of CO molecules and adsorbed oxygen atoms in intermediate complexes. The decomposition of these complexes is consistent with the high activation energy. The effect of superadditive adsorption capacity for carbon monoxide and specific catalytic activity in the reaction of low-temperature oxidation of CO was found. It was also discovered that the low-temperature oxidation reaction of CO on catalysts of the Pd/Al<sub>2</sub>O<sub>3</sub> system can proceed *via* a non-trivial mechanism, which includes the participation of hydroxyl groups of the Al<sub>2</sub>O<sub>3</sub> surface, coordinated by palladium, in the reaction.

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## Introduction

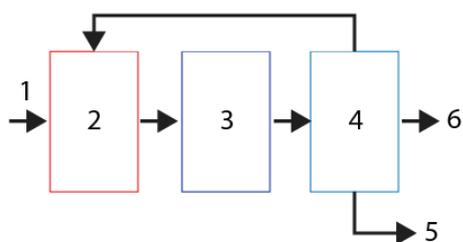
The “poison gas” CO gets into the air with gas emissions from industrial enterprises and motor vehicles, as a result of fires, volcanic eruptions, etc. To protect against it, respirators and gas masks with a catalyst for the oxidation of carbon monoxide to harmless dioxide are used. The positive effect is due to the activation of CO or a change in the state of oxygen on the surface of the catalyst. A large number of publications, both previously and recently, have been devoted to their development and study [1-6]. Figure 1 shows simplified diagram of catalytic gas purification.

Catalysts based on platinum metals (Pt, Pd, Rh) are often used [7-10]. These catalysts are effective in the processes of simultaneous neutralization of CO, NO and hydrocarbons, but are also quite expensive. A significant part of the annually mined platinum metals is spent on their manufacture

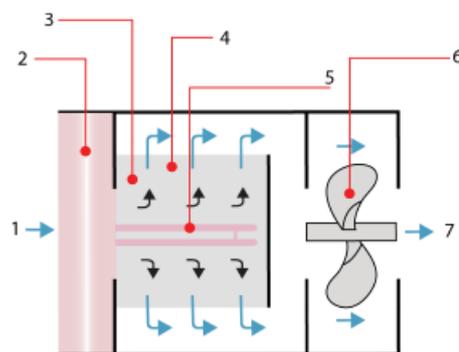
Therefore, minimizing the content of platinum metals in the composition of catalysts is currently one of the most important tasks of scientific research and practical development. The mechanism of carbon monoxide oxidation on palladium or platinum catalysts has been studied in a number of works [11-14].

## Experimental

The reaction rate ( $r$ ) of catalytic oxidation of carbon monoxide, as the main characteristic



**Figure 1** Scheme of catalytic gas cleaning apparatus: 1 – inlet gas, 2 – heater, 3 – catalytic column, 4 – heat exchanger, 5 – cold air, 6 – purified gas.



**Figure 2** Purification scheme with photocatalyst: 1 – inlet gas, 2 – filter, 3 – catalyst, 4 – coal, 5 – UV lamp, 6 – fan, 7 – purified gas.

of the activity and efficiency of the studied catalysts, was measured on a circulation-static unit using the method of continuous analysis of the gas mixture with a mass spectrometric analyzer of partial pressures APDM-1.

Palladium was estimated by the value of hydrogen adsorption at 70°C. For comparison, palladium black was used, obtained by precipitation from a solution of  $RdCl_2$  with a 10% solution of sodium formate upon heating it to boiling. The oxidation reaction of CO was carried out at (70-180)°C. The labeled oxygen ( $O_2$ ) content was 80 at. %. Analysis of the reaction mixture and the isotopic composition of the reagents was carried out during the reaction by mass-spectrometry. The reaction rate was calculated based on the dependence of the intensity of the mass spectrometric peak of CO on the reaction time. Differential Thermal Analysis (DTA) of the adsorbed phase was carried out at a constant heating rate (48°C/min) of the sample to 500°C in a cell continuously pumped out through the inlet valve of the mass spectrometer. DTA was carried out after the reaction or adsorption of reagents at 150°C, cooling the sample to 0°C and then pumping the cell down to a pressure of  $10^{-7}$  mm Hg. The state of the adsorbed CO was characterized by the temperatures of the maxima of the thermal desorption peaks ( $T_{max}$ ), from which the desorption activation energy ( $E_{des}$ ) was estimated using the equation:

$$\frac{E_{\text{des}}}{RT} = \ln \frac{v}{b} + \ln \left[ \frac{T_{\text{max}}}{\ln \frac{v}{b}} \right]$$

( $R$  – gas constant,  $v \approx 5 \cdot 10^{12} \text{ c}^{-1}$ ,  $b = dT/d\tau$ ,  $T$  – absolute temperature,  $\tau$  – time). The degree of coverage of the catalyst surface with adsorbed oxygen was estimated based on the material balance of the label in the Isotope Exchange (IE) reaction of oxygen in the  $\text{O}_2^*$ -catalyst system, carried out in the thermal desorption mode up to  $200^\circ\text{C}$ .

## Results and Discussion

Aluminum oxide does not exhibit noticeable catalytic activity in the CO oxidation reaction at the temperatures studied. The  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst is active at these temperatures. At  $t > 100^\circ\text{C}$ , a virtually steady-state activity value is established in  $\sim 10$  s. The initial velocity value remains unchanged with repeated injections. It does not change with preliminary injection of CO or  $\text{O}_2$  onto the sample, or in the presence of water vapor. The degree of utilization of the internal surface of the catalyst under the conditions studied is close to complete. Under these conditions, the specific (per unit palladium surface area) catalytic activity (SCA) of  $\text{Pd}/\text{Al}_2\text{O}_3$  is significantly higher than that of Pd-black. The kinetic characteristics of the reaction on these catalysts are given in table 1.

To test the possible influence of oxygen on the label content in the formed  $\text{CO}_2$ , CO oxidation was carried out by freezing  $\text{CO}_2$  at the reactor outlet. No significant change in the value of  $\alpha_{\text{CO}}$  occurred. This suggests the absence of a noticeable label transfer between  $\text{CO}_2$  and the catalyst under the reaction conditions. This assumption is confirmed by the data of experiments in which the change in  $\alpha_{\text{CO}}$  was determined for one pass of  $\text{CO}_2^*$  through the catalyst bed, which was carried out by refreezing  $\text{CO}_2$  from a trap located in front of the reactor to a trap behind the reactor.

With CO labeled with oxygen, the  $\alpha_{\text{CO}_2}$  value remains unexpectedly low even with a relatively high oxygen consumption during the reaction. Since the label content in  $\text{O}_2$  and CO ( $\alpha_{\text{CO}} = 0.25$  at. %) does not change, the low  $\alpha_{\text{CO}_2}$  value may be due either to the participation of the oxygen of the catalyst in the reaction, which initially had a natural isotopic composition (0.2%  $^{18}\text{O}$ ), or to rapid isotopic exchange of oxygen between  $\text{CO}_2$  and the catalyst.

Thus, under the conditions of the CO oxidation reaction, it is possible to exclude a noticeable effect of the oxygen on the content of the label in  $\text{CO}_2$  formed in the reaction. Consequently, the low value of CO observed in the reaction can only be explained by the participation in the formation of  $\text{CO}_2$  of oxygen atoms of the catalyst, which had a natural isotopic composition before the start of the reaction. Such oxygen atoms can belong either to the supported palladium or to the carrier. According to the preparation conditions, palladium supported on  $\text{Al}_2\text{O}_3$  should not contain noticeable amounts of adsorbed or dissolved oxygen, which is confirmed by the absence of oxygen between  $\text{O}_2^*$  and the catalyst at  $T \leq 400^\circ\text{C}$ , as well as the absence of oxygen peaks in the thermal desorption spectrum at  $T \leq 450^\circ\text{C}$ . The introduction of the reaction mixture onto  $\text{Pd}/\text{Al}_2\text{O}_3$  is accompanied by the adsorption of CO and oxygen. The oxygen adsorbed under these conditions is removed during the TD process only in the form of  $\text{CO}_2$  (Table 3). The amount of this oxygen, according to the change of  $\alpha_{\text{O}_2^*}$  during Isotopic Exchange (IE), carried out in the TD mode of the adsorbed phase, corresponds approximately to a monolayer coating of the palladium surface. If CO interacts with adsorbed oxygen, then preliminary treatment of the catalyst with a mixture of CO +  $^{16}\text{O}_2$  can, in principle, reduce CO, with subsequent use of  $\text{O}_2$  in the reaction. However, the oxygen adsorbed on palladium is insufficient to explain the observed low value of CO, since already at (25–30) % conversion of CO, the adsorbed oxygen

**Table 1:** The values of specific surface area (S), activation energy and rate of the process (E and r, respectively), reaction order (n).

Sample	S, m <sup>2</sup> /g (Pd)	E, kJ/mol	r, molec <sub>CO</sub> /cm <sup>2</sup> (Pd/c, 100°C)	n	
				by CO	by O <sub>2</sub>
Pd/Al <sub>2</sub> O <sub>3</sub>	30	29.3	(0.5-1)·10 <sup>14</sup>	1	0
Pd/c	3.3	40.1	10 <sup>12</sup>	1	0

**Note:** E was determined from the temperature dependence of r.

**Table 2:** Thermal desorption after adsorption of CO (ads) and reaction (re) at t = 150°C, P<sub>CO</sub> = 2 mm Hg.

Sample	CO (ads)			CO (re)			CO <sub>2</sub> (re)	
	t <sub>max</sub> , °C	I, rel. un	E <sub>des</sub> , kJ/mol	t <sub>max</sub> , °C	I, rel. un	E <sub>des</sub> , kJ/mol	t <sub>max</sub> , °C	I, rel. un
Pd/Al <sub>2</sub> O <sub>3</sub>	90	100	97	0	100	97	100	1000
Pd/c	70	1	91	80	1	94	150	0.8

**Table 3:** Effective concentration of reactive OH groups.

t, °C	P <sub>CO</sub>	P <sub>CO2</sub>	10 <sup>-17</sup> ·n <sub>OH</sub> , groups/m <sup>3</sup>	n <sub>OH</sub> , % monolayer
	mm Hg			
102	3	21	3.16	6.3
102	9.3	62	3.01	6
169	3	80	3.04	6.1

is renewed due to the gas phase more than 10 times. The presented facts allow us to conclude that in the case of Pd /Al<sub>2</sub>O<sub>3</sub>.

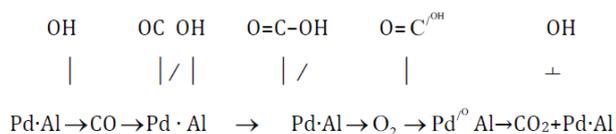
Oxygen atoms entering the CO oxidation product do not directly belong to either gaseous, adsorbed, or dissolved oxygen and, therefore, are included in one form or another in the composition of the carrier. The participation of the catalyst oxygen in the oxidation of CO suggests the possibility of this reaction occurring in the mode of catalyst reduction with carbon monoxide. It turned out that the reaction of CO oxidation actually occurs on Pd/Al<sub>2</sub>O<sub>3</sub> in the absence of oxygen in the gas phase, but its rate becomes noticeable only at t ≥ 350°C. It was also established that during CO oxidation in the mode of catalyst reduction, the formation of CO<sub>2</sub> is accompanied by the release of hydrogen. This fact leads to the conclusion that the oxygen-containing form interacting with CO are hydroxyl groups Al<sub>2</sub>O<sub>3</sub> [15,16]. It is natural to assume that in the catalytic mode, CO oxidation is also carried out with the participation of these OH groups. This assumption is supported

by a certain effect that a change in the content of surface OH groups has on the activity of the catalyst as a result of vacuum training of the sample and its treatment with water vapor.

This conclusion is also supported by the results of an experiment in which the reaction CO + <sup>16</sup>O<sub>2</sub> was carried out on a standardly trained catalyst sample, pre-enriched with a label by treating it at 20°C with water vapor containing 75% <sup>18</sup>O [17-19].

The concentration of the label in CO<sub>2</sub> frozen out during the reaction was 36%. It is known that Al<sub>2</sub>O<sub>3</sub> is characterized by the formation of hydrogen bonds between water molecules and OH groups of the oxide, i.e. the formation-oxidation reactions by a stepwise mechanism [20-23]. In the case under consideration, although the oxygen of the catalyst (OH groups of Al<sub>2</sub>O<sub>3</sub>) is included in the reaction product, this conclusion is contradicted by the large difference in CO oxidation temperatures with comparable rates in the catalysis and reduction modes and, consequently, the need (within the framework of the stepwise mechanism) to break strong

O - H bonds at low catalysis temperatures. The reason for this difference is apparently that in the catalysis mode the reaction is carried out with the participation of molecular oxygen in the intermediate complex, although it is not included in the reaction product  $\text{CO}_2$ . This circumstance removes the need to break O - H bonds during catalysis if the formation of  $\text{CO}_2$  and the regeneration of OH groups occur by redistribution of bonds in the intermediate complex. Under the studied conditions, when the first order of the reaction rate with respect to CO and zero order with respect to  $\text{O}_2$  is realized, it can be assumed that the rate-determining stage of the reaction is the adsorption of CO, accompanied by the formation of surface structures of the carboxyl type with the participation of OH groups. Under these conditions, the stages of oxygen adsorption and the subsequent decomposition of the intermediate complex are carried out as fast. The adsorbed oxygen reoxidizes the reduced palladium atoms and stimulates the decomposition of the carboxyl structure with the formation of  $\text{CO}_2$  and the regeneration of the OH group. The possibility of such a combined mechanism is consistent with a similar phenomenon of initiation of the decomposition of surface structures of the carbonate-carboxylate type by molecular oxygen [24,25]. This mechanism is consistent with the observed earlier in [25,26] symbiosis in the rates of consumption of CO and anion-radicals  $\text{O}_2^-$  on the surface of  $\text{Pd}/\text{Al}_2\text{O}_3$ . With regard to one palladium atom, the reaction of CO oxidation on this catalyst can be represented in accordance with the proposed mechanism by the following scheme:



A similar mechanism of the reaction of CO oxidation with the participation of OH-groups is proposed for homogeneous catalysis

by metal complexes [26]. The possibility of participation of OH-groups of the oxide surface in heterogeneous-catalytic oxidation has been established, for example, in the reaction of low-temperature oxidation of propylene to acetone in the presence of water vapor [26-29]. The higher SCA of supported palladium in comparison with massive palladium in the reaction of low-temperature oxidation of CO may be associated with the written-off mechanism. This assumption is consistent with the TDA data (Table 3). Close values of the adsorption energy of CO on the compared objects indicate a practically identical state of adsorbed CO on supported and massive palladium. However, the concentration of this form of CO, active in the oxidation reaction, on  $\text{Pd}/\text{Al}_2\text{O}_3$  is approximately two orders of magnitude higher. Pd black adsorbs CO mainly in a weakly bound, low-activity form, which is reversible already at  $100^\circ\text{C}$ . For Pd black, which has no hydroxyl coating, a mechanism is realized with the participation of CO molecules and adsorbed oxygen atoms in intermediate complexes [30-34]. The decomposition of these complexes is consistent with the high activation energy.

## Conclusion

For the  $\text{Pd}/\text{Al}_2\text{O}_3$  system, relative to Pd black and  $\text{Al}_2\text{O}_3$ , the effect of superadditive adsorption capacity for carbon monoxide and specific catalytic activity in the reaction of low-temperature ( $T \leq 423 \text{ K}$ ) oxidation of CO was found. It was also discovered that the low-temperature oxidation reaction of CO on catalysts of the  $\text{Pd}/\text{Al}_2\text{O}_3$  system can proceed via a non-trivial mechanism, which includes the participation of hydroxyl groups of the  $\text{Al}_2\text{O}_3$  surface, coordinated by palladium, in the reaction.

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the participation of hydroxyl groups of the  $\text{Al}_2\text{O}_3$  surface, coordinated by palladium, in the reaction.

The magnitude of the specific catalytic activity of the supported palladium depends on both the nature of the carrier and the dispersion of the supported palladium (Appendix).

## Conflict of Interest

The authors declare that there is no conflict of interest.

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