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Features of the Mechanism of Catalityc Oxidation of Carbon Monoxide on Pd/Al_2O_3 Catalysts

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The mechanism of catalytic low-temperature (T≤150 °C) oxidation of CO on Pd/Al_2O_3 was studied using labeled oxygen and thermal desorption analysis. It was found that the reaction proceeds through interaction in intermediate complexes of CO molecules with hydroxyl groups of Al_2O_3. 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_2 and the regeneration of OH groups. It was shown that with a small addition of Pd (0.04-0.1 wt.%) 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.

Keywords: carbon monoxide; palladium; alumina; catalysis

1. 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].

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 catalysts has been studied in a number of works [11–14].

2. Experimental

The reaction rate (r) 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 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 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:

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

(R—gas constant, $\upsilon \approx 5 \cdot 10^{12}$ c^{-1}, $b = dT/d\tau$, T—absolute temperatute, τ—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 O_2^*-catalyst system, carried out in the thermal desorption mode up to 200 °C.

3. Results and Discussion

Aluminum oxide does not exhibit noticeable catalytic activity in the CO oxidation reaction at the temperatures studied. The Pd/Al_2O_3 catalyst is active at these temperatures. At t>100 °C, a virtually steady-state activity value is established in ~10 s. The initial velocity value remains unchanged with repeated injections. It does not change with preliminary injection of CO or 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 Pd/Al_2O_3 is significantly higher than that of Pd-black. The kinetic characteristics of the reaction on these catalysts are given in Table 1.

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

sample	S, m^2/g (Pd)	E, kJ/mol	r,$molec_{CO}/cm^2$ (Pd/c, 100°C)	n	
				by CO	by O_2
Pd/Al_2O_3	30	29.3	$(0.5\text{-}1) \cdot 10^{14}$	1	0
Pd/c	3.3	40.1	10^{12}	1	0

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

To test the possible influence of oxygen on the label content in the formed CO_2, CO oxidation was carried out by freezing CO_2 at the reactor outlet. No significant change in the value of aco occurred. This suggests the absence of a noticeable label transfer between CO_2 and the catalyst under the reaction conditions. This assumption is confirmed by the data of experiments in which the change in aco was determined for one pass of CO_2^* through the catalyst bed, which was carried out by refreezing CO_2 from a trap located in front of the reactor to a trap behind the reactor.

Table 2. Thermal desorption after adsorption of CO(ads) and reaction (re) at t=150°C, P_{CO}=2 mm Hg.

sample	CO(ads)			CO(re)			CO_2(re)	
	t_{max}, °C	I, rel. un	E_{des}, kJ/mol	t_{max}, °C	I, rel. un	E_{des}, kJ/mol	t_{max}, °C	I, rel. un
Pd/Al_2O_3	90	100	97	90	100	97	100	1000
Pd/c	70	1	91	80	1	94	150	0.8

With CO labeled with oxygen, the α_{CO2} value remains unexpectedly low even with a relatively high oxygen consumption during the reaction. Since the label content in O_2 and CO (α_{CO} = 0.25 at.%) does not change, the low α_{CO2} 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}O), or to rapid isotopic exchange of oxygen between 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 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 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 Al_2O_3 should not contain noticeable amounts of adsorbed or dissolved oxygen, which is confirmed by the absence of oxygen between O_2^* and the catalyst at T≤400 °C, as well as the absence of oxygen peaks in the thermal desorption spectrum at T≤450 °C. The introduction of the reaction mixture onto Pd/Al_2O_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 CO_2 (Table 3). The amount of this oxygen, according to the change of $\alpha_{O_2^*}$ duringisotopic 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 + $^{16}O_2$ can, in principle, reduce CO, with subsequent use of 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 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_2O_3.

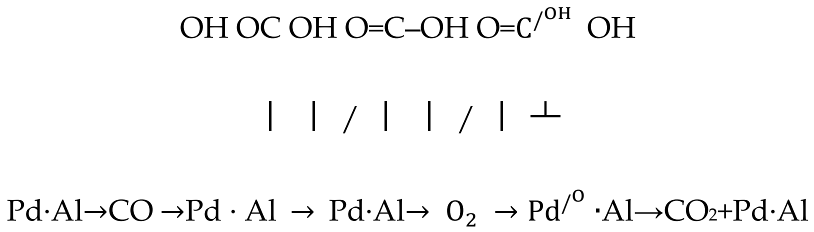
Table 3. Effective concentration of reactive OH groups.

t, ^oC	P_{CO}	P_{CO2}	$10^{-17}\cdot n_{OH}$, groups/m^3	n_{OH}, % monolayer
	mm Hg			
102	3	21	3.16	6.3
102	9.3	62	3.01	6
169	3	80	3.04	6.1

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_2O_3 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_2 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_2O_3 [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 + $^{16}O_2$ 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% ^{18}O [17–19].

The concentration of the label in CO_2 frozen out during the reaction was 36%. It is known that Al_2O_3 is characterized by the formation of hydrogen bondsbetween 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_2O_3) 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 CO_2. This circumstance removes the need to break O—H bonds during catalysis if the formation of 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 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 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 earlinerin [26] symbasis in the rates of consumption of CO and anion-radicals O_2^- on thesurface of Pd/Al_2O_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:



$$\text{OH OC OH O=C–OH O=C}/^{\text{OH}}\ \text{OH}$$

$$|\quad |\quad /\quad |\quad |\quad /\quad |\quad \perp$$

$$\text{Pd·Al}\rightarrow\text{CO}\rightarrow\text{Pd · Al}\rightarrow\text{Pd·Al}\rightarrow O_2\rightarrow\text{Pd}/^{\text{O}}\ \text{·Al}\rightarrow CO_2+\text{Pd·Al}$$

A similar mechanism of the reaction of CO oxidation with the participation of OH-groups is proposed for homogeneous catalysis by metal complexes [27]. 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 [28–31]. 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 Pd/Al_2O_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 °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 [32–36]. The decomposition of these complexes is consistent with the high activation energy.

4. Conclusions

For the Pd/ Al_2O_3 system, relative to Pd black and Al_2O_3, the effect of superadditive a dsorption capacity for carbon monoxide and specific catalytic activity in the reaction of low-temperature ($T \leq 423$ K) oxidation of CO was found. It was also discovered that the low-temperature oxidation reaction of CO on catalysts of the Pd/Al_2O_3 system can proceed via a non-trivial mechanism, which includes the participation of hydroxyl groups of the Al_2O_3 surface, coordinated by palladium, in the reaction.

It was also discovered that the low-temperature oxidation reaction of CO on catalysts of the Pd/Al_2O_3 system can proceed via a non-trivial mechanism, which includes the participation of hydroxyl groups of the Al_2O_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.

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