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Physical Chemistry

Partipication of Oxygen Hydroxyl Groups, Covered the Aluminum Oxide Surface in the Reaction of Catalytic Oxidation of Carbon Monoxide on Pd/Al_2O_3 System Catalysts

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ABSTRACT

Using oxygen enriched with the isotope $^{18}_{8}O$, the contribution of various forms of catalyst oxygen to the CO oxidation process was studied. It turned out that, contrary to expectations, the content of the isotopic label in the formed CO_2 is significantly lower than expected and at the initial stage of the reaction is close to the natural content of $^{18}_{8}O$. Taking into account that the pretreatment of the catalyst excluded the existence of any noticeable amount of adsorbed oxygen on the surface of both palladium and the support, it was concluded that CO is oxidized due to oxygen Al_2O_3, and the study of the SIMS spectra showed that oxygen is involved in the process of CO oxidation hydroxyl cover Al_2O_3.

Key Words: *Palladium, carbon monoxide, oxidation, catalysis*

1. INTRODUCTION

The most effective way to clean car exhaust gases from carbon monoxide is its post-oxidation to CO_2. The highest catalytic activity in this reaction is exhibited by the supported platinum group metals. The study of the mechanism of this reaction and the nature of the interaction of the metal with the support will make it possible to select the most efficient catalyst.

In this work, was studied the mechanism of the reaction of low-temperature oxidation of CO on catalysts, which are palladium deposited in an amount of mass 0.003 - 0.1% on the surface of $\gamma-Al_2O_3$.

The peculiarity of the catalytic properties of metals deposited on an oxide substrate, as compared with bulk metals, are usually explained by a change in the state as a result of their interaction with the support and by their high degree of dispersity [1].

2. MATERIALS AND METHODS

Supported palladium catalysts were prepared by impregnating the $\gamma - Al_2O_3$ support with a $PdCl_2$ solution, subsequent drying and reduction of Pd to the metallic state with sodium formate. The reaction was carried out in a circulating-static setup in an excess of oxygen and an initial CO concentration of $\sim 12_{vol}\%$ and a pressure of $P^0_{CO} = 0{,}4\ kPa$ in the temperature range of 360–435 K. The analysis of the reaction mixture and isotopic composition was carried out during the reaction by mass spectrometry. The standard treatment of the samples consisted in their evacuation ($P \leq 0.1$ Pa) at a temperature of 673 K. The oxygen enriched in the isotope ${}^{18}_{8}O$ ($\sim 80_{at.}\%$) used in the study as a reagent was obtained by electrolysis of water, containing ${}^{18}_{8}O$.

Secondary ion mass spectroscopy (SIMS) was used to study the nature of the reactive (I_i) recorded for m/e = 17, 19, 43, 45, 70, 72, which correspond to fragments ${}^{16}OH^+$, ${}^{18}OH^+$, $Al^{16}O^+$, $Al^{18}O^+$, $Al_2{}^{16}O^+$, $Al_2{}^{18}O$.

At T≥373K, values of catalytic activity close to stationary are established within 15–30 s. Their activity, calculated per unit mass of palladium, than that of Pd black studied under comparable conditions.

In order to study the nature of reactive oxygen species in the CO oxidation reaction on the above catalysts, oxygen enriched in the isotope ${}^{18}_{8}O$ ($\sim 80_{at.}\%$) was used as a reagent [2], also was using the method of secondary ion mass spectroscopy (SIMS).

At $T \geq 373K$, values of catalytic activity close to stationary are established within 15–30 sec. Their activity, calculated per unit mass of palladium than, that of Pd black studied under comparable conditions.

2. RESULT AND DISCUSSIONS

Considering the extremely low activity of Al_2O_3, compared to copper (CuO) and iron (Fe_2O_3) oxides in the reaction of oxygen isotope exchange [3, 4] indicates a low reactivity of aluminum oxide oxygen, the use of oxygen enriched in the ${}^{18}_{8}O$ isotope in the CO oxidation reaction led to an unexpected result. Assuming, according to [5], that CO interacts with oxygen adsorbed on the palladium surface, it was natural to expect the appearance of CO_2 with a high content of the isotope ${}^{18}_{8}O$. Nonetheless, concentration of the isotopic label (α) remains low even at the relative high consumption of oxygen during the reaction (Fig. 1).

To test the possible effect of oxygen isotopic exchange on the content of the isotopic label in the formed CO_2, CO oxidation was carried out by freezing CO_2 during the reaction. In this case, there is no significant change in the value of α, which allows us to assume that there is no noticeable transfer of the isotope label between CO_2 and the catalyst under the reaction conditions. This assumption is also confirmed by the results of experiments in which the change in the value of α in CO_2, containing the isotopic label (CO_2^*), was determined in one pass through the catalyst layer, which was carried out by refreezing CO_2^* from a trap located in front of the catalyst into a trap behind the reactor.

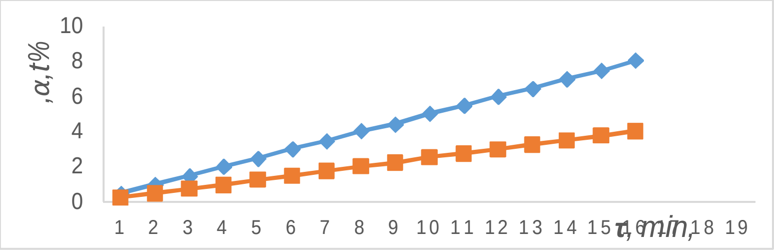

Fig.1 Change in the content of the isotope $^{18}_{8}O$ in carbon dioxide during oxidation CO with labeled oxygen: 0.1%Pd/Al_2O_3 (upper curve) and 0.04%Pd/Al_2O_3 (lower curve)

In those cases when such refreezing was carried out in a flow of a mixture of CO + $^{16}O_2$, the change in α was relatively small (Tab.1). When determining the final value of α^f, we took into account changes in α due to CO_2 formed in the reaction CO + $^{16}O_2$. This change was determined in the course of so-called blank experiments by mixing the formed CO_2 with the CO_2^*), preliminarily frozen in a trap, the amount of which corresponded to standard experimental conditions.

Table 1

Sample	T, K	P, kPa			$\alpha_{at.}$%	
		P^0_{CO}	$P^0_{O_2}$	$P^0_{CO_2}$	α^0	α^f
$\frac{Pd}{Al_2O_3}$	378	-	-	0,07	42,5	22,0
	388	0,4	2,66	0,16	42,5	40,88

Thus, under the conditions of the CO oxidation reaction, it is possible to exclude a significant effect of oxygen isotopic exchange on the content of $^{18}_{8}O$ in CO_2 formed in the reaction. Then, for the Pd/Al_2O_3 system, the low value of α observed in the reaction can be explained only 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.

The participation oxygen of studied catalysts in the CO oxidation reaction suggests the possibility of carrying out this reaction in the mode of catalyst reduction with carbon monoxide. It turned out that the CO oxidation reaction actually proceeds on these catalysts in the absence of oxygen in the gas phase, but its rate becomes noticeable only at 623–673 *K*. In this case, the formation of CO_2 is accompanied by hydrogen evolution. This fact leads to the natural conclusion that the oxygen-containing form interacting with CO is the hydroxyl groups of the support.

It is natural to assume that the oxidation of CO in the catalytic mode can be carried out with the participation of the *OH* groups of the support. This assumption is confirmed by the analysis of the SIMS spectra of samples preliminarily enriched with an isotopic label by repeated experiments on the oxidation of CO with labeled oxygen (423 *K*) under CO_2 freezing conditions. Enrichment of samples with an isotopic label under these conditions occurs as a result of the reoxidation of oxygen-containing centers with labeled oxygen (O_2^*) reacting with CO. From the SIMS spectra, the relative content of the isotope ${}^{18}_{8}O$ in various oxygen-containing fragments formed during the bombardment of both initial samples (tab. 2 a) and samples enriched with an isotope label (Tab. 2 b) with argon ions was estimated. An increased content of the isotope label was found only in OH fragments, which indicates the occurrence of the CO oxidation reaction on Pd/Al_2O_3 catalysts under the studied conditions through the interaction of CO molecules with oxygen atoms of the hydroxyl cover Al_2O_3.

Table 2

Sample	$\frac{I_{19}}{I_{17} + I_{19}}$	$\frac{I_{45}}{I_{43} + I_{45}}$	$\frac{I_{72}}{I_{70} + I_{72}}$
Pd/Al_2O_3 a)	0,58	0,21	0,014
Pd/Al_2O_3 b)	0,74	0,18	0,012

Thus, the oxidation of CO on supported palladium both in the reduction and catalysis regimes can proceed through the interaction of CO with oxygen atoms of *OH* groups, however, the temperature ranges for the implementation of these regimes differ by more than 250°C. We see the reason for this difference in the fact that in the catalysis regime there is no breaking of bonds in *OH* groups, and the formation of CO_2 and the regeneration of *OH* groups are carried out by redistribution of bonds in the intermediate complex with the participation of adsorbed oxygen. Since, in the case under consideration, CO interacts directly with OH groups and not with oxygen under the reaction conditions, CO adsorption is accompanied by the formation of carboxyl-type structures [4, 5]. The formation of such structures is apparently the stage that determines the reaction rate. In this case, the role of adsorbed oxygen is reduced to the reoxidation of palladium atoms reduced in previous events and the initiation of the decomposition of carboxyl structures with the formation of CO_2 and the regeneration of *OH* groups. The possibility of such a mechanism is consistent with a similar phenomenon of initiation of the decomposition of surface structures of the carbonate-carboxylate type by molecular oxygen [6, 7].

A similar mechanism has been proposed in the photocatalytic oxidation of CO using a supported platinum catalyst [8].

REFERENCES

1. H. Li, M. Shen, J. Wang, H.Wang, J. Wang (2020), Ind. Eng. Chem. Res., **59**, 1477.
2. Xiaoying Ye, Brian Luke, Thorkell Andresson and Josip Blonder: ^{18}O Stable Isotope Labeling in MS-based Proteomics. Briefings in functional genomics and proteomics. 2009, vol 8. no 2. 136-144;

3. A.V. Bagazeeva, V. B. Vykhodetsb, E. V. Vykhodetsc, T. E. Kurennykhb, A. Ya. Fishmand T. M. Deminaa, A. I. Medvedeva, and A. M. Murzakaeva: Oxygen Isotope Exchange in Nanosized Powders of the Al_2O_3 Oxide. THE PHYSICS OF METALS AND METALLOGRAPHY Vol. 113 No. 5 (2012), p 513-519;
4. CRAYTON J. YAPP: Oxygen isotope effects associated with the solid-state cu-FeOOH to ar-Fez03 phase transformation. (1990) Geochimica et Cosmochimico Acla Vol. 54, pp. 229-236;
5. V.A. Shwets, V.E. Shubin, V.B. Kazansky (1982), Proc. Mater. III All-Union Conf. Mechanism of Catalytic Reactions. Novosibirsk, 122.
6. P. R. Chen, M.S.Hoang, K.Y.Lai, H.S.Chen (2022), Nanomaterials, **12**, 573.
7. В.Д. Соколовский, Г.К.Боресков (1974), ДАН СССР, **214**, 1361, **216**, 599.
8. K. Czupryn, I. Kocemba, J. Rynkowski; Photocatalytic CO oxidation with water over Pt/TiO_2 catalysts (2018), React. Kinet. Mech. Cat., **124**, 187-201.

ფიზიკური ქიმია

ალუმინის ოქსიდის ზედაპირის ჰიდროქსილის ჯგუფების მონაწილეობა ნახშირბადის (II) ოქსიდის კატალიზურ ჟანგვაში Pd/Al_2O_3 კატალიზატორებზე

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თბილისი, ზ. ანჯაფარიძის 5

${}^{18}_{8}O$ იზოტოპით გამდიდრებული ჟანგბადის გამოყენებით შესწავლილ იქნა კატალიზატორის ჟანგბადის სხვადასხვა ფორმების მონაწილეობა CO-ს დაჟანგვის პროცესში. აღმოჩნდა, რომ ${}^{18}_{8}O$ იზოტოპის შემცველობა რეაქციის შედეგად მიღებულ CO_2-ში მოსალოდნელზე ბევრად დაბალი აღმოჩნდა, ხოლო რეაქციის საწყის სტადიაზე ახლოს იყო მის ბუნებრივ შემცველობასთან. კატალიზატორის წინასწარი დამუშავება გამორიცხავდა მის ზედაპირზე ადსორბირებული ჟანგბადის რამდენადმე შესამჩნევი რაოდენობის არსებობას, რაც იმ დასკვნის გაკეთების საშუალებას იძლევა, რომ CO იჟანგება Al_2O_3-ის ჟანგბადის ხარჯზე, ხოლო მეორადი იონების მასს-სპექტრომეტრიის (SIMS) მეთოდით დადგინდა, რომ CO-ს ჟანგვაში მონაწილეობს Al_2O_3-ის ზედაპირზე არსებული ჰიდროქსილის ჯგუფების ჟანგბადი.