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Mechanism of low-temperature CO oxidation on a model Pd/Fe_2O_3 catalyst

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A model Pd/Fe_2O_3 catalyst prepared by the vacuum technique has been studied in the carbon monoxide oxidation in the temperature range of 300–550 K at reagent pressures $P(CO) = 16$ Torr, $P(O_2) = 4$ Torr. It has been shown that the activity of the fresh catalysts is determined by palladium. According to the XPS data, the reduction with carbon monoxide results in the formation of Fe^{2+} (formally Fe_3O_4) and appearance of the catalytic activity in this reaction at low temperatures (350 K). High low-temperature activity of the catalyst is supposed to be connected with the reaction between oxygen adsorbed on the reduced sites of the support (Fe^{2+}) and CO adsorbed on palladium (CO_{ads}) at the metal–oxide interface.

Keywords: model catalyst, CO oxidation, X-ray photoelectron spectroscopy (XPS)

1. Introduction

As shown in a number of recent papers [1–12], catalysts prepared by the deposition of noble metals on reducible oxides (NMRO) are very effective in the CO oxidation at low temperatures. A synergetic effect is very typical for these systems, i.e., the activity of the catalyst is much higher than that of individual components. Several possible mechanisms of the superadditive activity of NMRO have been discussed in the literature. Some researchers [1–7] believe that the reaction takes place at the metal–oxide boundary with the participation of CO adsorbed on the metal and lattice oxygen of the oxide (O_L) [1–5], or oxygen adsorbed on the oxide (O_{ads}) [6,7]. In [2,7–9] the importance of the diffusion (spillover) of the adsorbed particles was emphasized: the reaction was supposed to proceed on the oxide due to the diffusion of CO_{ads} from the metal [8,9], or on the metal due to the diffusion of O_L or O_{ads} from the oxide [2,7]. In [10] the promotion of the catalytic properties of the oxide by the metal particles was discussed. In [11] the possibility of the alloy formation was discussed, and the presence of surface hydroxyl groups was believed to be the necessary requirement for the activity in the reaction. Earlier [12], high activity of the supported Pd/Fe_2O_3 sample in the CO oxidation at low temperatures was observed.

Studies [1–12] were performed on kinetic equipment on supported catalysts prepared by impregnation or coprecipitation. Certainly, the surface of such catalysts was contaminated with carbon, carbonate, hydroxyl groups, etc. The present study was devoted to the detailed investigation of the mechanism of the low-temperature CO oxidation on a model Pd/Fe_2O_3 catalyst prepared under clean conditions by the vacuum deposition of palladium on a flat iron oxide support under control of the state of the surface by XPS.

2. Experimental

2.1. Catalyst preparation and investigation by XPS

This part of the work was performed on the basis of an X-ray photoelectron spectrometer VG ESCA-3. The model system was prepared in the preparation chamber by successive vacuum evaporation of iron and palladium from two independent sources on a tantalum foil. After the deposition of iron, the sample was treated in oxygen ($P = 10$ Torr) at 650 K for 1 h for complete oxidation of the metal. Pd was evaporated onto a Fe_2O_3 film at the support temperature 300 K. Before the experiments, the catalyst was heated under vacuum for 10 h at 700 K. The photoelectron spectrum of the surface consisted of iron, oxygen and palladium lines only. The Pd/Fe atomic ratio was 0.37. To study the influence of the reaction medium on the state of the surface, the sample was heated in carbon monoxide, oxygen or the reaction mixture in the preparation chamber of the spectrometer.

2.2. Catalytic studies

The catalytic activity in the CO oxidation was studied in a separate static reactor. Precalibrated sources of iron and palladium were used for the sample preparation. The preparation regime and the amount of the metals deposited were the same as in the case of the Pd/Fe_2O_3 sample prepared under the XPS control. The reactor volume was 0.2 l. The geometric surface of the tantalum foil used as a support of the model catalyst was 20 cm^2. The sample was heated by passing an electric current through the support. Temperature was measured by a W–Re(5%)/W–Re(20%) thermocouple spot-welded to the tantalum foil. The reaction rate was calculated from the ratio of the $m/e = 44$

(CO_2) and $m/e = 28$ (CO) lines in the mass spectrum. In all the cases the conversion of the gas mixture did not exceed 10%.

3. Results

3.1. Investigation of fresh Pd/Fe_2O_3 catalyst

Figure 1 presents the temperature dependence of the CO_2 formation rate on the fresh model Pd/Fe_2O_3 catalyst in the reaction mixture containing a two-fold excess of carbon monoxide in comparison to the stoichiometric one: $P(CO) = 16$ Torr, $P(O_2) = 4$ Torr. In the Arrhenius coordinates the dependence looks like a straight line with the activation energy of 32.5 kcal/mol. Analogous data are presented for iron oxide (Fe_2O_3) and the tantalum support.

According to the XPS data, the state of palladium on the model catalyst is $E_B(\text{Pd } 3d_{5/2}) = 335.7$ eV. This is close to the values presented in the literature for the bulk metal [13]. The spectral region Fe 2p is presented in figure 2(b). Two intensive lines corresponding to the states $2p_{3/2}$ and $2p_{1/2}$ with the binding energy $E_B(\text{Fe } 2p_{3/2}) = 711.0$ eV and spin-orbital splitting 13.5 eV are observed in the spectrum. Besides, there is a satellite of low intensity in the binding energy region of 719.3 eV. The structure of the spectrum – positions of the main lines of the 2p state as well as the position and relative intensity of the satellite – are in complete agreement with XPS data for hematite [14].

The investigation of the catalytic activity at 473 K depending on the CO pressure in the reaction mixture has shown a negative first reaction order on the CO concentration. This means that carbon monoxide inhibits the reaction. The oxygen reaction order is close to 1.0 up to its stoichiometric ratio in the reaction mixture, the reaction order tending to zero in the O_2 excess.

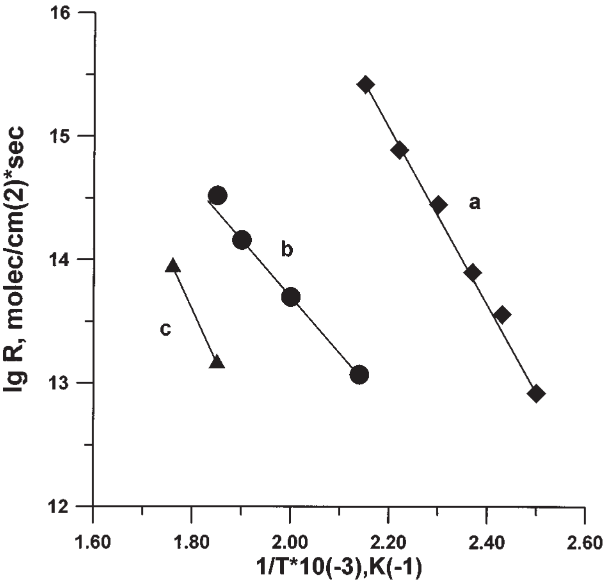

Figure 1. Temperature dependence of the carbon monoxide oxidation reaction rate at $P(CO) = 16$ Torr and $P(O_2) = 4$ Torr on model Pd/Fe_2O_3 catalyst (a), iron oxide (b), and tantalum foil (c).

3.2. Pd/Fe_2O_3 catalyst after reduction with carbon monoxide

In this series of experiments prior to the activity measurements the catalyst was subjected to a 30 min reductive treatment in the carbon monoxide atmosphere at $P(CO) = 16$ Torr and $T = 435$–515 K. The results are presented in figure 3. One can see that in this case there is a knee on the Arrhenius curve, and a new section with

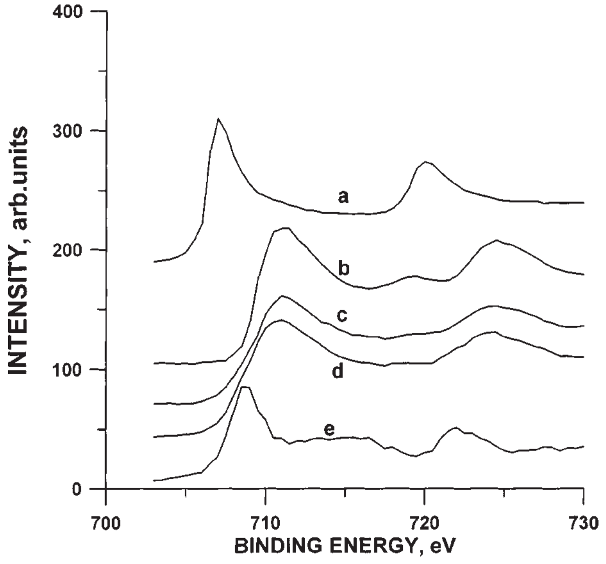

Figure 2. Fe 2p XPS spectra of iron metal (a), fresh catalyst (b), Pd/Fe_2O_3 after several cycles of the activity tests (c), Pd/Fe_2O_3 after reduction in CO at $T = 515$ K (d), and linear combination of states b and d (e).

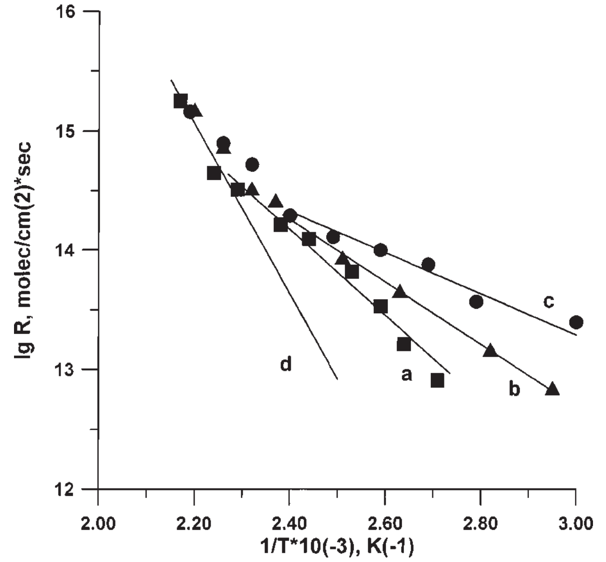

Figure 3. Temperature dependence of the CO oxidation reaction rate at $P(CO) = 16$ Torr and $P(O_2) = 4$ Torr after preliminary reduction of the catalyst in carbon monoxide ($P(CO) = 16$ Torr) for 30 min at 435 K (a), 470 K (b), and 515 K (c). The temperature dependence for fresh Pd/Fe_2O_3 is shown with line (d).

Table 1
Binding energies of Fe $2p_{3/2}$ state and positions of satellites in different states of iron in oxides.

State of iron	E_B(Fe $2p_{3/2}$) (eV)	Position of satellite	References
Fe^0	707.0	–	[this work]
	707.0	–	[16]
	706.6	–	[15]
Fe^{2+}	708.8	715.0	[this work]
	709.7	715.0	[16]
	708.8	716.0	[15]
Fe^{3+}	711.0	719.2	[this work]
	711.2	719.2	[16]
	710.2	718.2	[15]

lower activation energy and significantly higher reaction rate compared to the fresh catalyst is observed at low temperatures. This effect appears at the reduction temperature of 435 K increasing with the reduction temperature, it reaches its maximum at 515 K. It should be noted that this low-temperature activity is not stable. The reaction rate of the reduced catalyst in the isothermal regime at 385 K decreases by a factor of two in 1 h.

The XPS spectrum of the reduced catalyst differs from the spectrum of the initial Pd/Fe_2O_3. The spectral region Fe 2p of the sample reduced at 515 K is shown in figure 2(d). This temperature corresponds to the highest low-temperature activity. Changes observed in the spectrum result from the partial reduction of the oxide. Figure 2(e) presents an individual spectrum corresponding to the reduced state obtained as a linear combination of spectra in figure 2 (b) and (d). A similar structure of the spectrum has been observed for Fe^{2+} [15]. Obtained binding energies of the state Fe $2p_{3/2}$ and positions of the satellites for different states of iron as well as the literature data are listed in table 1. The relative content of Fe^{2+} in the integral spectrum (figure 2(d)) is 0.32. Formally this value is close to that typical for Fe_3O_4 [15].

It should be noted that no changes in the state of palladium and relative intensity of Pd 3d and Fe 2p lines were observed after the reduction of the catalyst. Based on the XPS data, one can exclude the possibility of the oxide reduction to metal iron or formation of a Pd–Fe alloy. The appearance of the low-temperature activity cannot result from any structural changes in the surface layer of the catalyst, formation of mixed Pd–Fe–O compounds or appearance of a promotion effect.

Evidently, the decisive role is played by the reduction of the support, the high activity being determined either by the properties of Fe_3O_4 itself, or by the cooperative action of the metal and reduced oxide.

3.3. Changes in Pd/Fe_2O_3 catalyst under the action of the reaction medium

The reaction medium also can modify Pd/Fe_2O_3, resulting in the appearance of the low-temperature activity. After several heating–cooling cycles of the initial catalyst in the reaction mixture, the growth of the activity at low temperatures was observed (figure 4(c)). A similar dependence was observed during the investigation of the catalytic properties of the reduced catalyst. For comparison, the temperature dependence of the reaction rate on the fresh (a) and reduced (b) catalysts is presented in figure 4.

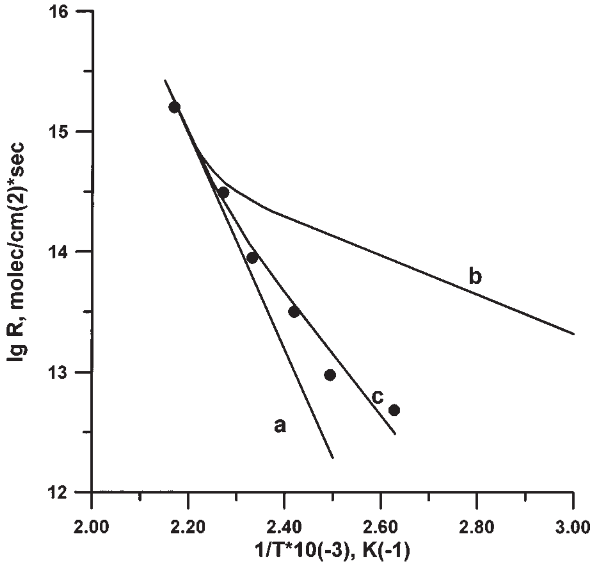

Figure 4. Temperature dependence of the CO oxidation reaction rate at $P(CO) = 16$ Torr and $P(O_2) = 4$ Torr on fresh Pd/Fe_2O_3 (a), after preliminary reduction in CO at 515 K (b), and after several cycles of the activity tests (c).

The action of the reaction mixture on the catalyst resulted in changes in the spectral region Fe 2p (figure 2(c)). The spectrum observed reflects partial reduction of iron oxide, the relative Fe^{2+} content being lower than in the sample reduced with carbon monoxide.

4. Discussion

The data presented show that there are two states of the catalyst with different activities in the carbon monoxide oxidation. The behavior of fresh Pd/Fe_2O_3 is typical for platinum metals. It is known that CO oxidation on platinum metals follows a three-way mechanism involving the carbon monoxide adsorption, dissociative adsorption of oxygen, and their reaction in the adsorbed layer (Langmuir–Hinshelwood (L–H) mechanism). At low temperatures the surface is blocked with adsorbed CO. The reaction starts only after desorption of a part of CO molecules and appearance of the surface sites for the oxygen dissociation. Hence, a negative reaction order on the CO pressure must exist. Indeed, on fresh Pd/Fe_2O_3 the CO reaction order is -1, and the O_2 reaction order is 1. This is in a good agreement with the results of the investigation of the reaction kinetics on monocrystals and supported catalysts [17,18]. As on platinum metals, the CO desorption is the rate-determining reaction stage, the measured apparent activation energy corresponds to the adsorption heat of carbon monoxide. The value obtained ($E_a = 32.5$ kcal/mol) is close to the CO adsorption heats on palladium monocrystals [17,19]. A slightly lower value ($E_a = 24.6$ kcal/mol) was found for supported Pd/SiO_2 [18].

Thus, the activity of the fresh catalyst is determined by palladium, and a measurable reaction rate is observed only at $T > 450$ K. After pretreatment in the carbon monoxide at 435–515 K (figure 2) the catalyst becomes active in the low-temperature CO oxidation. The appearance of the low-temperature activity is evidently due to the partial reduction of the support with the formation of Fe^{2+}. The XPS study has shown that the activity is maximal when the oxide is *formally* reduced to the Fe_3O_4 state. It is important to note that the individual oxide (Fe_2O_3 without Pd) is stable at these conditions. Detectable reduction of a Fe_2O_3 film with the formation of Fe^{2+} occurs only at $T > 600$ K. Therefore, it is possible to suppose that the low-temperature activity observed after the reduction of Pd/Fe_2O_3 is connected with the activity of Fe_3O_4 itself. In this case the presence of Pd on the surface is required only for the activation of CO molecules for Fe_2O_3 reduction to Fe_3O_4 under reaction conditions.

To check if Fe_3O_4 is an effective catalyst itself, we studied the activity of an iron oxide film reduced in CO at 635 K [21]. The XPS data prove the formation of Fe_3O_4 under these conditions. However, the activity of Fe_3O_4 appeared to be not very different from that of Fe_2O_3: detectable rates of the CO oxidation were measured only at $T > 550$ K. Hence, it seems impossible to explain the high low-temperature activity of the Pd/Fe_2O_3 catalyst by the activity of Fe_3O_4.

Thus, neither palladium, nor iron oxides (Fe_2O_3 or Fe_3O_4) are able to catalyze the CO oxidation at low temperatures. According to XPS, no intermediate compounds, for example, iron metal, Pd–Fe alloys or mixed Pd–Fe–O compounds are formed. Therefore, one has to assume that the high low-temperature activity of the Pd/Fe_2O_3 catalyst is due to the cooperative participation of Pd sites and sites on reduced iron oxide (Fe^{2+}), which selectively adsorb the components of the reaction mixture.

On the sites of the first type (Pd) the sticking coefficient of carbon monoxide s(CO) is higher than that of oxygen $s(O_2)$, therefore the surface is covered with CO_{ads}. According to Sadykov's data [22], the rate of the O_2 adsorption on Fe_3O_4 exceeds the rate of the CO oxidation by an order of magnitude. Consequently, it is possible to assume that on the sites of the second type – reduced iron oxide (Fe^{2+}) – $s(O_2) > s(CO)$, and the surface is covered with O_{ads}. The mathematical modeling [23,24] of such discrete-inhomogeneous systems with the surface consisting of sites of two types with $s(O_2) < s(CO)$ on the sites of the first type and $s(O_2) > s(CO)$ on the sites of the second type has shown that the sites of the first type are covered with CO_{ads}, the sites of the second type are covered with O_{ads}, and the beginning of the reaction at the CO_{ads}/O_{ads} boundary or CO_{ads} spillover results in a sharp increase of the reaction rate on the whole complex surface at low temperatures.

The question is which type of oxygen – adsorbed O_{ads} or lattice O_L – participates in the reaction. In [1–5] lattice oxygen was supposed to take part in the reaction. Naturally, the situation can vary for different oxides. This is determined by the difference in the bond energy, reactivity and rate of the diffusion exchange between O_{ads} and O_L. For Fe_2O_3, a thermodynamic consideration of reaction (1) with participation of O_L and CO_{ads} on palladium shows that this reaction is endothermic ($\Delta H = +24.4$ kcal/mol):

$$3Fe_2O_3 + CO_{ads} \rightleftharpoons 2Fe_3O_4 + CO_2 \tag{1}$$

The calculation was performed using the heat of the CO adsorption on Pd equal to 32.5 kcal/mol and standard formation enthalpies of individual compounds [25]. This means that the activation energy of the reaction between O_L and CO_{ads} should exceed 25 kcal/mol, and the rate of this reaction at $T = 350$ K should be very low.

One can suppose that the bond energy of oxygen adsorbed on the oxide is lower than that of the lattice oxygen. Unfortunately, no data on the heat of the oxygen adsorption on Fe_3O_4 is available in the literature. If the adsorption energy does not exceed $\sim$60 kcal/mol, reaction (2) with participation of adsorbed oxygen is exothermic:

$$O_{ads} + CO_{ads} \rightleftharpoons CO_2 \tag{2}$$

This proposed value corresponds to the oxygen adsorption energies on platinum metals, on which the reaction in the adsorbed layer proceeds at a high rate at room temperature [19]. In such case effective realization of reaction (2) with participation of O_{ads} on Fe^{2+} sites and CO_{ads} on palladium at low temperatures seems to be quite possible.

The reoxidation of iron sites $Fe^{2+} \rightarrow Fe^{3+}$ takes place simultaneously with the CO oxidation in reaction (2) but with a significantly lower rate. This results in a decrease of the catalyst activity with time. On the other hand, reduction of Fe^{3+} to Fe^{2+} under the action of the reaction medium (reaction (1)) results in a slow increase of the activity of inactive fresh Pd/Fe_2O_3 catalyst. Thus, depending on the $P(CO)/P(O_2)$ ratio, total pressure and temperature, the reaction medium determines the degree of the oxide surface reduction (Fe^{2+}/Fe^{3+} ratio) and, hence, the value of the low-temperature catalytic activity.

So, the most probable mechanism of the high low-temperature activity of Pd/Fe_2O_3 is connected with the reaction of O_{ads} adsorbed on reduced sites of the oxide (Fe^{2+}) with CO_{ads} on palladium at the interface metal–oxide boundary with a possible diffusion (spillover) of adparticles through the boundary to the other phase. The reduction of Fe_2O_3 to formal Fe_3O_4 results in the increase of the catalytic activity at $T = 300$ K by four orders of magnitude. Gradual changes in the catalytic activity with time – its increase or decrease depending on the catalyst pretreatment – are caused by the alteration of the Fe^{2+}/Fe^{3+} ratio under the action of the reaction medium.

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