

# Reaction of CO Oxidation on Platinum, Rhodium, a Platinum–Rhodium Alloy, and a Heterophase Bimetallic Platinum/Rhodium Surface

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**Abstract**—The reaction of CO oxidation on thin metal films of platinum, rhodium, and their alloy and on a heterophase bimetallic Pt/Rh surface that consisted of platinum particles of size 10–20 nm on the surface of rhodium was studied in the region of low reactant pressures (lower than  $2 \times 10^{-5}$  mbar). At low temperatures ( $T < 200^\circ\text{C}$ ), the activity of samples increased in the order  $\text{Rh} > \text{Pt/Rh} > \text{Pt–Rh alloy} > \text{Pt}$ . Above  $200^\circ\text{C}$ , the rate of reaction on the heterophase Pt/Rh surface was almost twice as high as the sum of the rates of reaction on the individual metals; this fact is indicative of a synergistic effect. The nature of this effect is considered.

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## INTRODUCTION

The phenomenon of synergism, that is, a nonadditive increase in catalytic activity upon mixing various catalyst components, has long been known in heterogeneous catalysis. The process of hydrofining on bimetallic sulfide catalysts is a classic example of the commercial use of this effect. The addition of cobalt or nickel, which practically does not exhibit intrinsic activity in the reactions of C–S bond hydrogenolysis, dramatically increases the activity of molybdenum or tungsten, respectively, in this process [1]. Another example of the use of synergism is the reforming of hydrocarbons on supported bifunctional Pt/Al<sub>2</sub>O<sub>3</sub> catalysts [2].

These obvious advantages of multicomponent catalysts resulted in attempts to develop new types of catalytic systems that exhibit a synergistic effect. Among these systems are current catalysts for automobile exhaust emission control; these catalysts are prepared based on various combinations of platinum, palladium, and rhodium [3]. Oh and Carpenter [4] were the first to find a synergistic effect in the reaction of CO oxidation on supported Pt–Rh/Al<sub>2</sub>O<sub>3</sub> catalysts performed in an excess of oxygen. The catalyst, which was prepared by successively impregnating aluminum oxide with the solutions of platinum and rhodium salts, was found to be much more active than a mechanical mixture of two individual catalysts. Cai et al. [5] obtained an analogous result; they also found that Pt/Rh catalysts prepared by successive impregnation exhibited a synergistic effect in the reaction of CO oxidation. The enhanced activity of the bimetallic catalyst was explained by the selective adsorption of reactants at different surface sites (oxygen and CO at rhodium and platinum, respectively) and a reaction between them.

On the other hand, data surveyed by Nieuwenhuys [3] do not support the occurrence of a synergistic effect in the above system: only a monotonic change in catalytic properties was observed on gradually going from monometallic platinum to monometallic rhodium. These discrepancies were explained by the different natures of the samples and nonidentical experimental conditions. An additional reason could consist in different catalyst preparation procedures used in the cited studies [3–5]. In the studies described by Nieuwenhuys [3], the simultaneous impregnation of aluminum oxide with the solutions of platinum and rhodium salts was used for the preparation of bimetallic catalysts. It is believed that a statistical distribution of platinum and rhodium with the formation of an alloy occurred in this case. Note that Oh and Carpenter [4] did not observe a synergistic effect if they used simultaneous impregnation to prepare a bimetallic catalyst.

However, it is likely that the catalyst acquired another structure with the use of successive impregnation; in this case, the active component consisted of isolated Pt and Rh particles.

To test this hypothesis, in this work, we performed the reaction of CO oxidation on continuous polycrystalline films of Pt and Rh, an alloy of these metals, and a heterophase bimetallic Pt–Rh surface at a reaction mixture pressure of no higher than  $2 \times 10^{-5}$  mbar. The high-vacuum conditions allowed us to exclude the oxidation of the catalyst surface from our experiments; the same cannot be said of studies [4, 5]. The heterophase surface can be considered a physical model of a catalyst prepared by successive impregnation, whereas the alloy surface can be considered a model of a catalyst prepared by simultaneous impregnation.

## EXPERIMENTAL

The experiments were performed using a VG ESCA-3 X-ray photoelectron spectrometer. The catalyst samples were continuous films of metals supported onto tantalum foil by vacuum sputtering. Before sputtering, the Ta foil was coated with an ultrafine film of  $\text{Al}_2\text{O}_3$  in order to exclude the possibility of mutual diffusion of the support material and the catalyst. The composition of the samples was monitored using XPS at various stages of catalyst preparation and characterization. The alloy containing 56 at % Pt and 44 at % Rh was prepared by successively sputtering platinum and rhodium from two independent sources. Before the experiments, an alloy sample was heated at  $800^\circ\text{C}$  in a vacuum for 10 min to establish an equilibrium composition. Esch et al. [6] found that the thin films of rhodium and platinum form an alloy by mixing at  $T > 400^\circ\text{C}$ .

The procedure for preparing a heterophase Pt/Rh surface involved the following stages:

(a) the vacuum sputtering of a continuous film of rhodium onto a support;

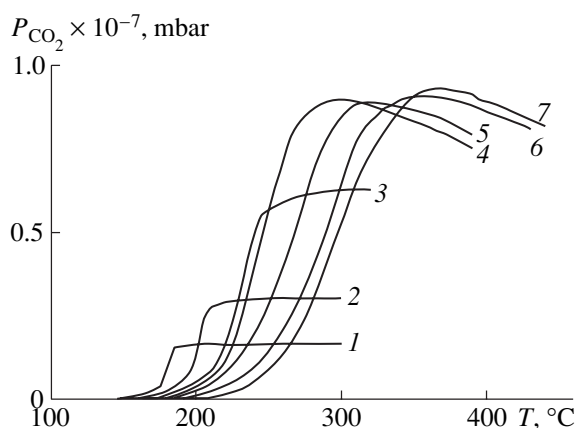
(b) the complete oxidation of the metal to  $\text{Rh}_2\text{O}_3$  by the treatment of the film in an atmosphere of oxygen for 30 min at  $P = 10$  mbar and  $T = 400^\circ\text{C}$ ;

(c) the vacuum sputtering of platinum onto the oxidized rhodium surface to reach the ratio  $\text{Pt}(4f_{7/2})/\text{Rh}(3d_{5/2}) = 0.38$  between lines in the photoelectron spectrum;

(d) the reduction of the resulting surface in an atmosphere of hydrogen at  $P = 10^{-6}$  mbar and  $T = 300^\circ\text{C}$ .

The study of a sample prepared in accordance with this procedure by scanning tunnel microscopy (STM) demonstrated that the sample consisted of platinum particles of size 10–20 nm arranged on a flat surface of rhodium. In this case, the surface fraction occupied by Pt particles was about 50%. The heterophase surface was stable to  $350^\circ\text{C}$ , whereas the metal constituents formed an alloy at higher temperatures. This was evidenced by a constant ratio between the photoelectron lines of Pt and Rh on the condition that the sample temperature was no higher than  $350^\circ\text{C}$  in the course of thermal treatments. At higher temperatures, the Pt4f line intensity monotonically decreased because of the mutual diffusion of metal atoms and the formation of an alloy. The conditions of sample preparation and the studies of the structure and stability boundaries of this sample were described in detail elsewhere [7]. In all of the subsequent experiments where the rate of reaction on the heterophase surface was studied, the temperature of the sample surface was no higher than  $350^\circ\text{C}$ .

For all of the samples, the temperature dependence of the rate of CO oxidation was obtained at the fixed oxygen pressure  $P_{\text{O}_2} = 10^{-6}$  mbar and various CO pressures. An ANAVAC quadrupole mass spectrometer, which was precalibrated against  $\text{O}_2$ , CO, and  $\text{CO}_2$  with the use of an ion gage, was used for measuring the rate



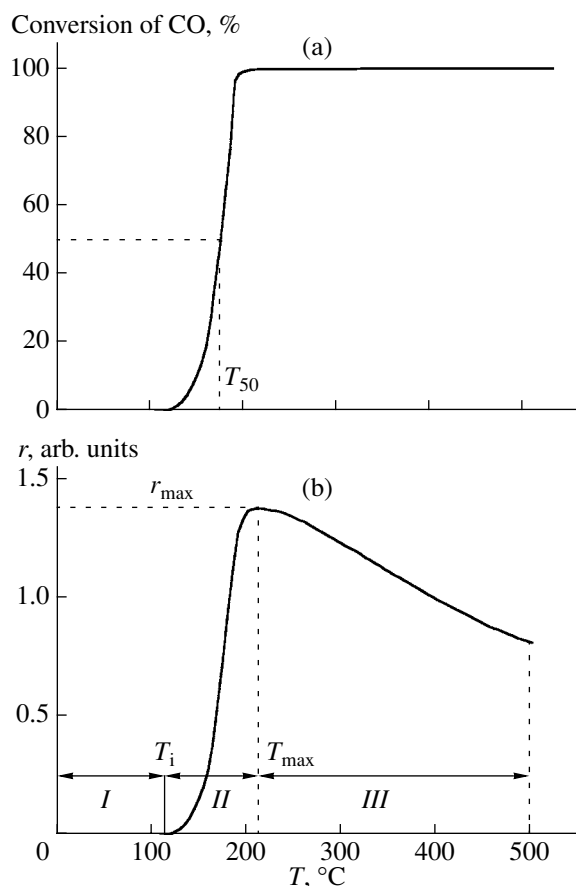
**Fig. 1.** Temperature dependence of the pressure of  $\text{CO}_2$  formed on Pt (the rate of CO oxidation) at  $P_{\text{O}_2} = 10^{-6}$  mbar and  $P_{\text{CO}}$ , mbar: (1)  $0.07 \times 10^{-6}$ , (2)  $0.17 \times 10^{-6}$ , (3)  $0.35 \times 10^{-6}$ , (4)  $0.47 \times 10^{-6}$ , (5)  $0.96 \times 10^{-6}$ , (6)  $3.6 \times 10^{-6}$ , and (7)  $8.6 \times 10^{-6}$  (according to published data [8]).

of reaction. The vacuum chamber of the mass spectrometer served as a differential flow reactor. The rate of reaction was proportional to the partial pressure of  $\text{CO}_2$ . The rate of sample heating, which was equal to 1 K/s in all of the experiments, provided steady-state conditions. The temperature was measured using a Chromel–Alumel thermocouple, which was point-welded to the backside of tantalum foil. In all cases, substrates with the same surface area of  $0.7 \text{ cm}^2$  were used for a correct comparison between the activities of different samples. The conversion of reaction mixture components was no higher than 20%.

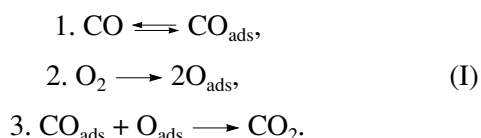
## RESULTS AND DISCUSSION

Figure 1 shows a typical series of curves for the temperature dependence of the pressure of  $\text{CO}_2$  (which is proportional to the rate of CO oxidation) formed on a platinum sample at a fixed  $\text{O}_2$  pressure of  $10^{-6}$  mbar and various CO pressures. As can be seen in Fig. 1, these curves exhibit three main portions. In the region of low temperatures, the rate of reaction was low (below the limiting sensitivity of the instrumentation used). As the temperature was increased to a critical level,  $\text{CO}_2$  appeared in the gas phase; the rate of reaction rapidly increased with heating to reach a maximum value. Next, the rate of reaction began to decrease smoothly. Analogous curves were also obtained for all of the other samples.

This shape of the pressure–temperature curves, which is characteristic of platinum-group metals, depends on the adsorption mechanism of CO oxidation (Langmuir–Hinshelwood mechanism). This mechanism involves the steps of the molecular adsorption and desorption of CO, the dissociative adsorption of  $\text{O}_2$ , and the interaction between adsorbed species on the surface [9]:



**Fig. 2.** Schematic diagrams of the temperature dependence of (a) the conversion of CO and (b) the rate of CO oxidation on platinum-group metals in (a) flow and (b) differential reactors.



At low temperatures, the surface of metals is covered with adsorbed CO molecules, which block surface sites accessible to the adsorption of  $\text{O}_2$ . Therefore, the rate of reaction is low. As the temperature is increased, the desorption of  $\text{CO}_{\text{ads}}$  occurs and surface sites are liberated for the adsorption of  $\text{O}_2$ . Under these conditions, the desorption of carbon monoxide is a rate-limiting step of the reaction, whereas the rate of oxidation ( $\text{CO}_2$  formation) is proportional to  $P_{\text{O}_2}$  and inversely proportional to  $P_{\text{CO}}$  ( $r \sim P_{\text{O}_2}/P_{\text{CO}}$ ); that is, carbon monoxide inhibits the reaction. As the temperature is further increased, when the rate of reaction rapidly increases to reach a maximum value, the composition of the adsorption layer is changed:  $\text{O}_{\text{ads}}$  rather than  $\text{CO}_{\text{ads}}$  becomes predominant [10]. The subsequent smooth decrease of the rate of reaction is usually related to the blocking effect of adsorbed oxygen. At high temperatures, the

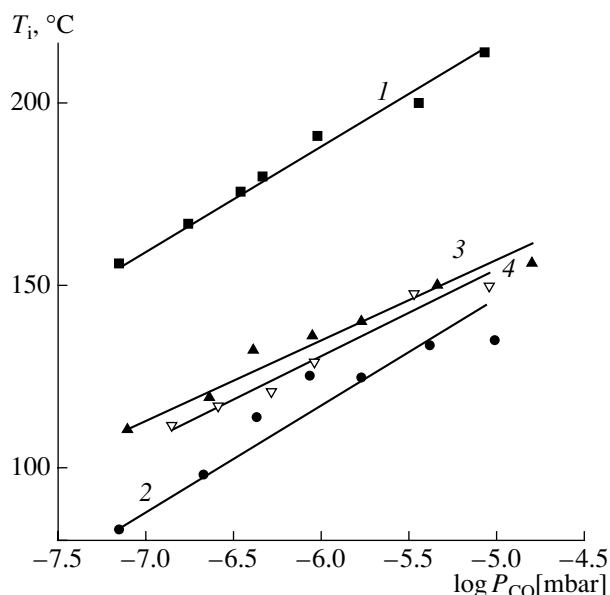
reaction is of zero order with respect to an excess reactant and of nearly first order with respect to the second reactant [9].

Bearing in mind that the oxidation of CO occurs by the Langmuir–Hinshelwood mechanism, the temperature dependence of CO conversion (referred to as combustion curves) is used in industry for testing automobile-exhaust emission control catalysts. Figure 2a shows a typical combustion curve for the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst. It can easily be seen that its shape is analogous to the shape of the temperature dependence of the rate of CO oxidation obtained in this work when the reaction was performed in the chamber of the photoelectron spectrometer (Fig. 2b). The conversion of CO was insignificant at low temperatures; however, it rapidly increased, as the temperature was increased above a critical value, and reached 100%. This fact can easily be explained taking into account that  $\text{CO}_2$  is the only product of CO oxidation. A catalyst on which 100% CO conversion is reached at a lower temperature is considered the best catalyst. For quantitative comparison, it is conventional to use a temperature at which conversion is 50% ( $T_{50}$ ).

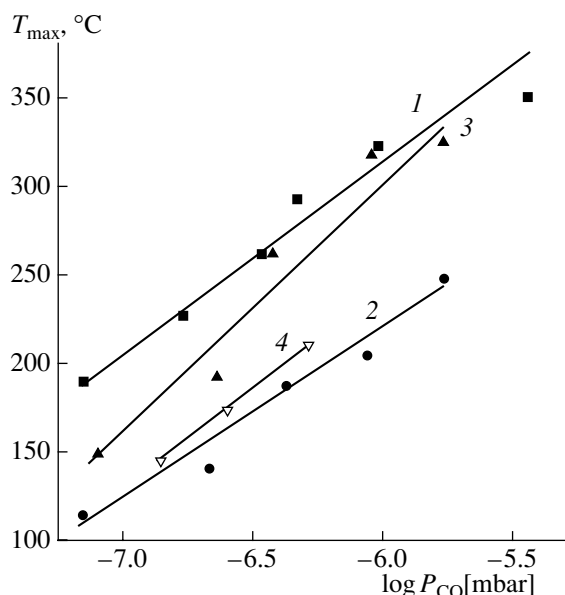
Evidently, in our experiments where conversion was no higher than 20%, other quantities should be used for a comparative analysis of various catalysts. These quantities were chosen based on the shape analysis of the temperature dependence of the rate of reaction, which can be subdivided into three different regions I, II, and III (Fig. 2b). One of these quantities is the temperature at which  $\text{CO}_2$  appeared in a gas phase. We designated it as the ignition temperature ( $T_i$ ) tentatively assuming that  $T_i$  corresponds to an increase in the pressure of  $\text{CO}_2$  in a gas phase to  $10^{-9}$  mbar. The other two quantities refer to the most active state of a test sample under particular experimental conditions: these are the temperature ( $T_{\text{max}}$ ) at which a maximum rate is reached and the maximum rate of reaction ( $r_{\text{max}}$ ) at  $T_{\text{max}}$ .

Figure 3 shows a series of curves for the dependence of  $T_i$  on the partial pressure of CO at  $P_{\text{O}_2} = 10^{-6}$  mbar for platinum, rhodium, a Pt–Rh alloy, and the heterophase Pt/Rh surface (the values of  $P_{\text{CO}}$  are given on a logarithmic scale), and Fig. 4 shows analogous curves for  $T_{\text{max}}$ .

In all of the test samples, the shape of the  $T_i$ – $\log P_{\text{CO}}$  curves is nearly linear. In this case, an increase in  $P_{\text{CO}}$  in the reaction mixture by two orders of magnitude was accompanied by an increase in  $T_i$  by approximately  $60^\circ\text{C}$  regardless of the nature of the sample. The temperature  $T_i$  increased in the order  $\text{Rh} > \text{Pt/Rh} > \text{Pt–Rh alloy} > \text{Pt}$  over the entire range of CO pressures. Differences in the ignition temperatures of reaction on rhodium, the heterophase surface, and the alloy were as small as  $10$ – $20^\circ\text{C}$ . Platinum was least active under conditions of low-temperature CO oxidation: the difference between the values of  $T_i$  on platinum and rhodium was  $70^\circ\text{C}$ .



**Fig. 3.** Dependence of the ignition temperature on the pressure of CO in the reaction mixture at  $P_{O_2} = 10^{-6}$  mbar on (1) Pt, (2) Rh, (3) the Pt-Rh alloy, and (4) the heterophase Pt/Rh surface.



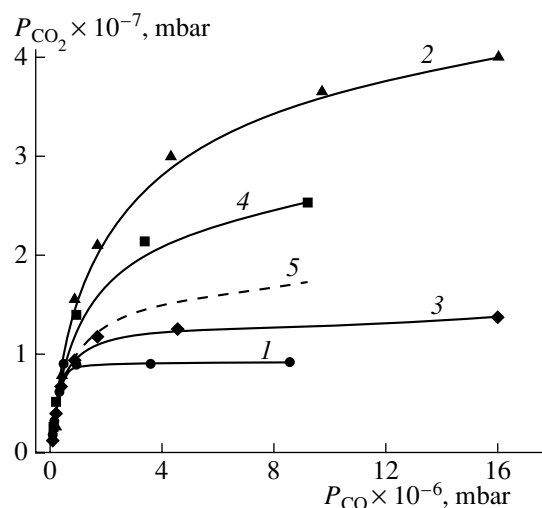
**Fig. 4.** Dependence of the temperature of the maximum rate of reaction on the pressure of CO in the reaction mixture at  $P_{O_2} = 10^{-6}$  mbar on (1) Pt, (2) Rh, (3) the Pt-Rh alloy, and (4) the heterophase Pt/Rh surface.

Generally, the dependence of  $T_{max}$  on  $P_{CO}$  (Fig. 4) was analogous to the dependence of  $T_i$ . An increase in the pressure of CO in the reaction mixture was also accompanied by an increase in the temperature of the maximum rate of reaction. The lowest  $T_{max}$  was observed on rhodium, and the highest  $T_{max}$  was observed on platinum, whereas intermediate values were observed on the heterophase surface and the Pt-Rh alloy.

In terms of catalytic activity, the Pt-Rh alloy occupied an intermediate position between the individual metals at any  $P_{CO}/P_{O_2}$  ratios, whereas the activity depended on experimental conditions. At low temperatures, differences between the rates of reaction on the alloy and rhodium were small. As can be seen in Fig. 3, the difference between  $T_i$  for these samples was about 15°C. As the temperature was increased, the activity of the alloy approached the activity of platinum. Thus, the values of  $T_{max}$  for the alloy and individual metals at low CO pressures differed approximately equally; however, at high  $P_{CO}$ , the temperatures  $T_{max}$  for the alloy and platinum were practically equal (Fig. 4). In an excess of CO in the reaction mixture, the values of  $r_{max}$  on platinum and the alloy were also close to each other.

Figure 5 shows the dependence of  $P_{CO_2}$  on the pressure of CO at the temperatures of maximum reaction rates. As can be seen in Fig. 5, the run of the curves was the same in all of the samples at  $P_{CO} < 0.5 \times 10^{-6}$  mbar. In this case, the rate of reaction was proportional to the pressure of carbon monoxide in the reaction mixture,

that is,  $r_{max} \sim P_{CO}$ . As the pressure of CO was increased, the rate of reaction (or  $P_{CO_2}$ ) gradually reached a constant level. In an excess of CO, the activity of samples at  $T_{max}$  changed in the order Rh > Pt/Rh > Pt-Rh alloy > Pt. The maximum rate on rhodium was higher than the reaction rate on platinum by a factor of ~5. Thus, all of



**Fig. 5.** Pressure of CO<sub>2</sub> formed at the temperatures of maximum rates of reaction on (1) Pt, (2) Rh, (3) the Pt-Rh alloy, or (4) the heterophase Pt/Rh surface as a function of CO pressure in the reaction mixture at  $P_{O_2} = 10^{-6}$  mbar. Dashed curve 5 refers to a calculated function plotted using Eq. (1).

the above data suggest that rhodium metal is the most efficient catalyst for the low-temperature oxidation of CO.

The differences observed in the activity of test samples can be explained based on the Langmuir–Hinshelwood adsorption mechanism (scheme (I)) with consideration for reaction kinetics on various platinum-group metals. The manifestation of low-temperature activity was usually associated with a decrease in the inhibiting effect of CO. Siera et al. [11] found that the temperature behaviors of the rates of CO oxidation on different crystallographic faces of a single crystal of the  $\text{Pt}_{0.25}\text{Rh}_{0.75}$  alloy were essentially different. The lowest values of  $T_i$  and  $T_{\max}$  were observed on the closely packed (111) and (100) faces, which are characterized by a comparatively low heat of CO adsorption. Siera et al. [11] explained the higher values of  $T_i$  and  $T_{\max}$  on the high-index (410) and (210) faces by the appearance of strongly bound  $\text{CO}_{\text{ads}}$  on steps. The low heat of adsorption of CO on Au was considered the main reason for the high activity of supported gold-containing catalysts in the reaction of carbon monoxide oxidation at low temperatures [3]. The effect of the heat of adsorption of  $\text{CO}_{\text{ads}}$  on the shape of the temperature dependence of the rate of reaction was supported by theoretical calculations (for example, see [12]).

However, data obtained in a study of the single crystals and polycrystalline samples of platinum and rhodium [9] indicate that the heats of adsorption of CO on both of the metals are similar. This conclusion was also supported by our results. According to calculations based on an analysis of the temperature dependence of the rate of oxidation near  $T_i$  (Fig. 2b), the activation energy of the reaction is  $E_a = 22 \pm 3$  kcal/mol in all of the samples at any  $P_{\text{CO}}/P_{\text{O}_2}$  ratios. This value is consistent with  $E_a$  on a Rh(111) single crystal [10]. Because the desorption of  $\text{CO}_{\text{ads}}$  is a rate-limiting step of reaction at low temperatures, the value of  $E_a$  is equal to the heat of CO adsorption.

Note that the reaction activation energy ( $E_a$ ) found in this work is much lower than the activation energy of CO desorption ( $E_{\text{CO}}$ ) found in the course of thermal-desorption experiments [9]. In our opinion, the reason for the above difference consists in different surface coverage of metals with carbon monoxide ( $\theta_{\text{CO}}$ ). The value of  $E_{\text{CO}}$  was calculated on the condition that  $\theta_{\text{CO}} \rightarrow 0$  [9], whereas the catalyst surface was really covered with a saturated layer of  $\text{CO}_{\text{ads}}$  at temperatures close to  $T_i$  [10]. It is well known that  $E_{\text{CO}}$  dramatically decreases as the surface coverage approaches a maximum because of lateral interactions between molecules in the adsorbed layer, which are accompanied by a decrease in  $E_a$  [9].

The surface reaction between  $\text{CO}_{\text{ads}}$  and  $\text{O}_{\text{ads}}$  (step 3 in scheme (I)) occurs very effectively on all of the platinum-group metals, and this fact cannot explain the observed differences in the behaviors of platinum and

rhodium. It only remains for us to analyze the step of dissociative oxygen adsorption. It is well known that the rates of  $\text{O}_2$  adsorption on polycrystalline rhodium and platinum samples differ several times. According to published data, the initial sticking coefficient of oxygen ( $s_0$ ) is 0.2 on Pt or 1.0 on Rh [13, 14].

Under conditions of the competitive adsorption of CO and  $\text{O}_2$  on free adsorption sites, a greater value of  $s_0(\text{O}_2)$  results in the more effective formation of both  $\text{O}_{\text{ads}}$  and new free sites on Rh because of the occurrence of the subsequent reaction between  $\text{CO}_{\text{ads}}$  and adsorbed oxygen atoms. As a result,  $T_i$  and  $T_{\max}$  on rhodium are much lower than the corresponding values on platinum (Figs. 3, 4).

Because of the more efficient adsorption of  $\text{O}_2$  on rhodium, the reaction of CO oxidation at low temperatures will predominantly occur at rhodium sites. This fact explains the similarity of the values of  $T_i$  on the Pt–Rh alloy and on Rh. Two adsorption sites, which consist of several metal atoms, are required for the dissociative adsorption of  $\text{O}_2$ . The fraction of these sites composed of only Rh atoms is small. At temperatures higher than  $T_i$ , mixed sites containing one or more Pt atoms also exhibit catalytic activity. It is believed that the rate of  $\text{O}_2$  adsorption at these sites will progressively decrease with increasing numbers of Pt atoms and  $s_0$  will gradually reach a value of 0.2. Because mixed sites dominate on the alloy surface, the alloy begins to behave similarly to platinum at temperatures close to  $T_{\max}$ .

Different rates of oxygen adsorption can also explain the run of  $P_{\text{CO}_2}$ – $P_{\text{CO}}$  curves (Fig. 5). At low CO pressures in the reaction mixture, when the adsorption of oxygen at freed sites was noticeably higher than the adsorption of CO, the rate of reaction weakly depended on the rate of  $\text{O}_2$  adsorption and, consequently, on the nature of the metal. Under these conditions,  $r_{\max} \sim P_{\text{CO}}$ . Because of this, at  $P_{\text{CO}} < 5 \times 10^{-7}$  mbar, the corresponding curves for Pt and Rh coincided. At high CO pressures, the rate of reaction was limited by the supply of oxygen to the active center. Consequently, at equal  $P_{\text{O}_2}$ , the following condition should be fulfilled:  $r_{\max}(\text{Rh})/r_{\max}(\text{Pt}) = s_0(\text{Rh})/s_0(\text{Pt})$ . Thus, the experimentally observed fivefold increase in the rate of reaction on rhodium with respect to the rate of this reaction on platinum is a consequence of different values of  $s_0$  for  $\text{O}_2$ .

As mentioned above, the rate of CO oxidation depends on the surface area of the sample. Therefore, comparative experiments were performed in samples with equal surface areas. With consideration for this circumstance, we can state that the activity of rhodium is higher than that of platinum. Monometallic and bimetallic samples are more difficult to compare. For example, a higher rate of CO oxidation on Rh, as compared with that on a bimetallic sample (Fig. 5), can be simply a consequence of a higher concentration of rhodium atoms on the surface of a monometallic sam-

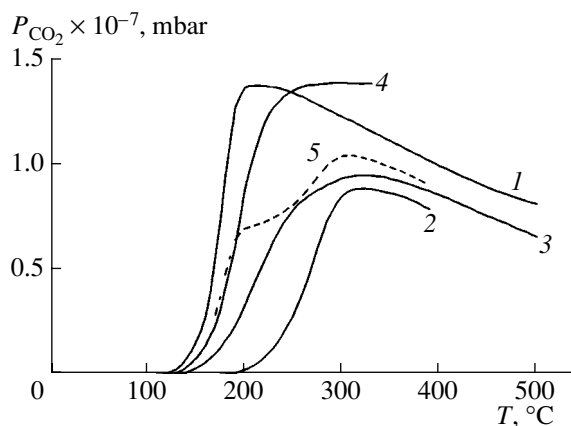
ple. To solve this problem, we developed a procedure for calculating the rate of CO oxidation on bimetallic samples. This procedure was based on the assumption that the reaction occurs independently at platinum and rhodium surface sites:

$$r_{\text{theor}} = 0.5r_{\text{Pt}} + 0.5r_{\text{Rh}}, \quad (1)$$

where  $r_{\text{Pt}}$  and  $r_{\text{Rh}}$  are the experimental rates of reaction on the corresponding individual metals. The coefficients 0.5 reflect the fact that the surface concentrations of Pt and Rh were approximately equal, as found using XPS and STM. The atomic concentration of either metal in a bimetallic sample was half the concentration of this metal on the corresponding monometallic surface. As can be seen in Fig. 5, the curve calculated from Eq. (1) occupies an intermediate position: the maximum activity of the heterophase Pt/Rh surface in the reaction of CO oxidation is higher and that of the Pt–Rh alloy is lower than the activity of the model bimetallic surface. This result suggests that, as applied to the heterophase surface, we can state a nonadditive increase in the rate of reaction. A synergistic effect was absent from the alloy; moreover, a decrease in the catalytic activity was observed. In our opinion, this supports the above hypothesis that the statistically homogeneous distribution of platinum and rhodium atoms (the alloy in this work and the Pt–Rh/Al<sub>2</sub>O<sub>3</sub> catalyst prepared previously [3, 4] by simultaneous impregnation) does not facilitate the appearance of a synergistic effect. Contrastingly, such an effect manifested itself on a bimetallic surface, in which platinum particles were supported onto the surface of rhodium (heterophase surface) or mixed with rhodium particles (the Pt–Rh/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by successive impregnation [4]).

To test the occurrence of a synergistic effect in the course of reaction on the heterophase surface, we compared the temperature dependence of the rates of CO oxidation on the Pt–Rh alloy, the heterophase Pt/Rh surface, and a bimetallic sample whose surface consisted of independent platinum and rhodium sites with half as large surface areas as that of individual monometallic samples. Figure 6 shows the corresponding curves. The curve for the bimetallic system was calculated in accordance with Eq. (1) on the assumption that the amounts of platinum and rhodium surface sites were equal in all three cases. All of the experimental curves, including curves for monometallic samples, were obtained under identical conditions with the use of equimolar mixtures of CO and O<sub>2</sub> (the pressure of each particular component was  $\sim 10^{-6}$  mbar).

As can be seen, rhodium (curve 1) exhibited a much higher activity than that of platinum (curve 2). Note that a high rate of reaction on rhodium was reached even at relatively low temperatures. Thus, at 200°C, the activity of rhodium reached a maximum, whereas the activity of platinum remained near-zero. The Pt–Rh alloy (curve 3) occupied an intermediate position; in terms of activity, this alloy was close to rhodium or platinum at



**Fig. 6.** The temperature dependence of the pressure of CO<sub>2</sub> formed on (1) Rh, (2) Pt, (3) the Pt–Rh alloy, or (4) the heterophase Pt/Rh surface at  $P_{\text{CO}} = P_{\text{O}_2} = 10^{-6}$  mbar. Dashed curve 5 refers to the calculated function for the heterophase surface.

low or high temperatures, respectively. The temperature dependence of the rate of reaction on the heterophase surface corresponded to curve 4. Calculated curve 5 exhibited an inflection at 200°C, when the highest activity of rhodium was reached, and a maximum, which coincided with  $T_{\text{max}}$  on platinum.

At  $T < 200^\circ\text{C}$ , curves 4 and 5 were practically coincident. At higher temperatures, the rate of reaction on the heterophase Pt/Rh surface was much higher than the value expected from calculations based on the assumption that the reaction occurred independently on Pt and Rh. We explain this fact by the structure of the adsorption layer formed in the course of the reaction. At  $T_i$ , the reaction on the Pt/Rh sample began at rhodium particles and the rate of reaction reached a maximum at  $T = 200^\circ\text{C}$ , which corresponds to  $T_{\text{max}}$  on Rh (Fig. 6, curve 1). In this case, rhodium particles were covered with a layer of O<sub>ads</sub>. The rate of reaction on platinum at the specified temperature was low (Fig. 6, curve 2), and platinum particles were covered with a layer of CO<sub>ads</sub>. Above 200°C, the reaction on the Pt/Rh sample occurred with the participation of CO<sub>ads</sub> on platinum and O<sub>ads</sub> on rhodium. Thus, the synergistic effect observed in this case was related to the involvement of Pt particles, which served as the donor of a reactant (CO<sub>ads</sub>), in the reaction.

Synergism in the given system was also observed in studies of CO oxidation on supported catalysts [4, 5]. In some cases, bimetallic samples were more active at low temperatures than monometallic catalysts. In our experiments, a synergistic effect manifested itself at relatively high temperatures. Experimental conditions may be responsible for this difference. Activity in the low-temperature region was observed at high pressures of the reaction mixture with an excess of oxygen. Under these conditions, a considerable portion of the active catalyst component can be oxidized with the for-

mation of oxides, primarily  $\text{Rh}_2\text{O}_3$ , which are inactive in the reaction [5]. It is believed that bimetallic samples are more stable to oxidation, and this is the reason for their higher activity at low temperatures, as compared with monometallic samples. We cannot exclude that, at relatively low temperatures, rhodium oxide can serve as a source of lattice or adsorbed oxygen, which interacts with  $\text{CO}_{\text{ads}}$  on platinum. Such a reaction scheme was used to explain the low-temperature activity of the  $\text{Rh}/\text{CeO}_2$  [15] and  $\text{Pd}/\text{Fe}_2\text{O}_3$  [16] model catalysts, as well as the  $\text{Pd-Rh}/\text{SiO}_2$  bimetallic supported catalyst [17]. In our experiments, the formation of oxides was excluded because of the low oxygen pressure ( $10^{-6}$  mbar).

Thus, we can conclude that the conditions of catalysis are responsible for synergism in the bimetallic system. At high reactant pressures, the oxide factor, which facilitates the appearance of low-temperature activity, plays a crucial role. At low pressures, the adsorption factor, which consists in the selective adsorption of reaction mixture components on different phases (carbon monoxide on Pt and oxygen on Rh) and the occurrence of the reaction  $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$  at the interface, comes into play on the heterophase surface.

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