

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 2×10^{-5} mbar). At low temperatures ($T < 200^\circ\text{C}$), the activity of samples increased in the order Rh > Pt/Rh > Pt–Rh alloy > Pt. Above 200°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/Al₂O₃ 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/Al₂O₃ 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 2×10^{-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 Al_2O_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°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:

- the vacuum sputtering of a continuous film of rhodium onto a support;
- the complete oxidation of the metal to Rh_2O_3 by the treatment of the film in an atmosphere of oxygen for 30 min at $P = 10$ mbar and $T = 400^\circ\text{C}$;
- 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;
- 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°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°C in the course of thermal treatments. At higher temperatures, the $\text{Pt}4f$ 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°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 O_2 , CO, and CO_2 with the use of an ion gage, was used for measuring the rate

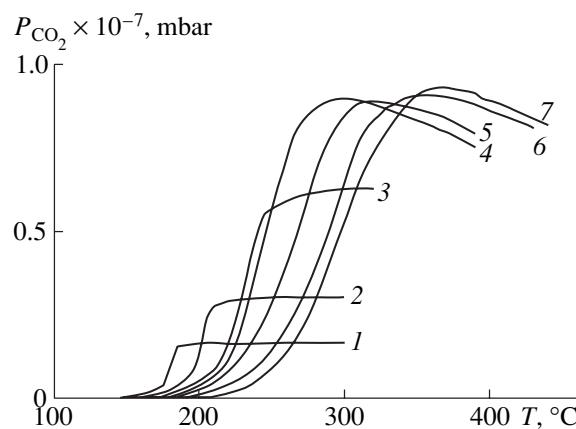


Fig. 1. Temperature dependence of the pressure of CO_2 formed on Pt (the rate of CO oxidation) at $P_{\text{O}_2} = 10^{-6}$ mbar and P_{CO} , mbar: (1) 0.07×10^{-6} , (2) 0.17×10^{-6} , (3) 0.35×10^{-6} , (4) 0.47×10^{-6} , (5) 0.96×10^{-6} , (6) 3.6×10^{-6} , and (7) 8.6×10^{-6} (according to published 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 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 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 CO_2 (which is proportional to the rate of CO oxidation) formed on a platinum sample at a fixed 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, 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 O_2 , and the interaction between adsorbed species on the surface [9]:

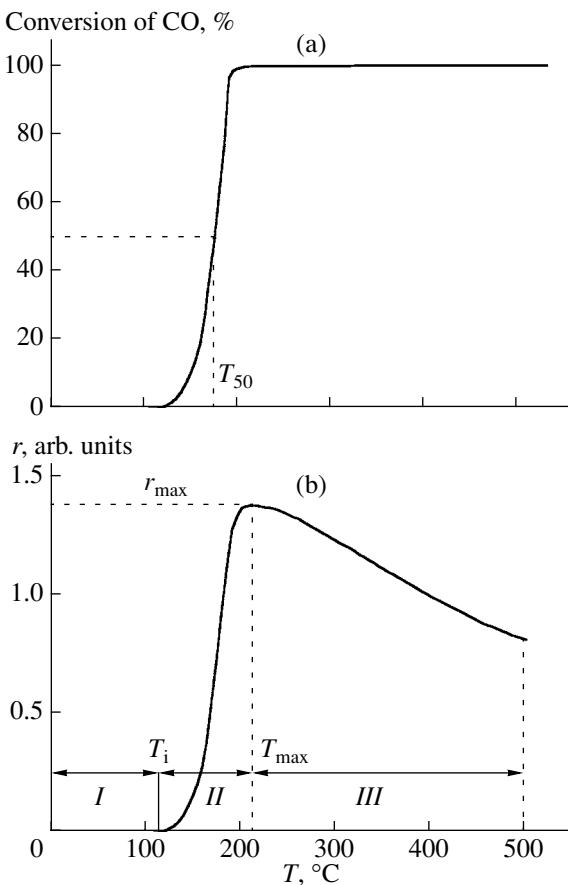
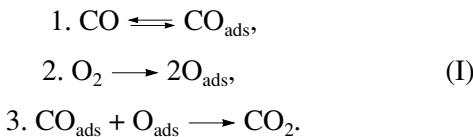


Fig. 2. Schematic diagrams of the temperature dependence of (a) the conversion of CO and (b) the rate of CO oxidation on platinum-group metals in (a) flow and (b) differential reactors.



At low temperatures, the surface of metals is covered with adsorbed CO molecules, which block surface sites accessible to the adsorption of O₂. Therefore, the rate of reaction is low. As the temperature is increased, the desorption of CO_{ads} occurs and surface sites are liberated for the adsorption of O₂. Under these conditions, the desorption of carbon monoxide is a rate-limiting step of the reaction, whereas the rate of oxidation (CO₂ formation) is proportional to P_{O₂} and inversely proportional to P_{CO} ($r \sim P_{O_2}/P_{CO}$); 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: O_{ads} rather than CO_{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 Pt/Al₂O₃ 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 CO₂ 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 CO₂ 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 CO₂ 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_{max}) at which a maximum rate is reached and the maximum rate of reaction (r_{max}) at T_{max} .

Figure 3 shows a series of curves for the dependence of T_i on the partial pressure of CO at $P_{O_2} = 10^{-6}$ mbar for platinum, rhodium, a Pt–Rh alloy, and the heterophase Pt/Rh surface (the values of P_{CO} are given on a logarithmic scale), and Fig. 4 shows analogous curves for T_{max} .

In all of the test samples, the shape of the $T_i - \log P_{CO}$ curves is nearly linear. In this case, an increase in P_{CO} in the reaction mixture by two orders of magnitude was accompanied by an increase in T_i by approximately 60°C regardless of the nature of the sample. The temperature T_i increased in the order Rh > Pt/Rh > Pt–Rh alloy > 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°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°C.

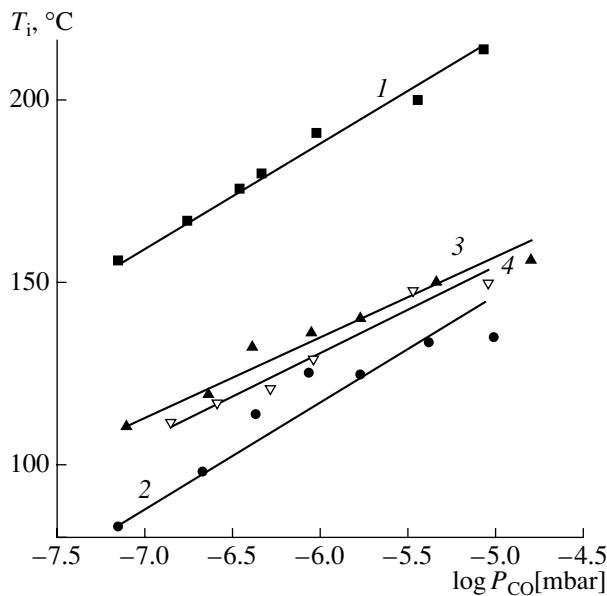


Fig. 3. Dependence of the ignition temperature on the pressure of CO in the reaction mixture at $P_{O_2} = 10^{-6}$ mbar on (1) Pt, (2) Rh, (3) the Pt–Rh alloy, and (4) the heterophase Pt/Rh surface.

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,

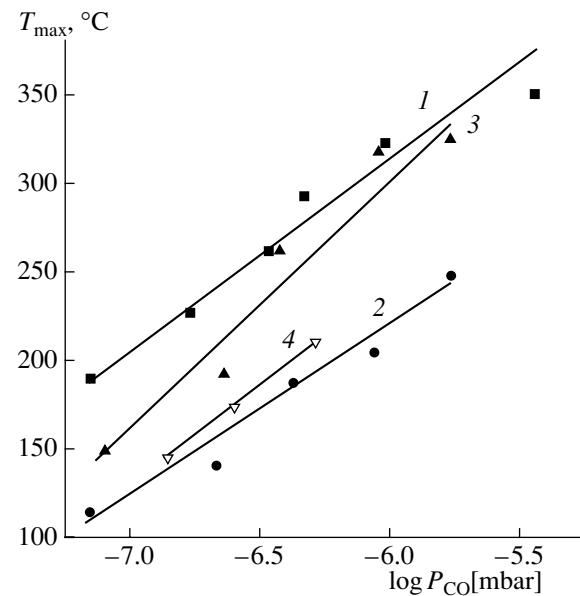


Fig. 4. Dependence of the temperature of the maximum rate of reaction on the pressure of CO in the reaction mixture at $P_{O_2} = 10^{-6}$ mbar on (1) Pt, (2) Rh, (3) the Pt–Rh alloy, and (4) the heterophase Pt/Rh surface.

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

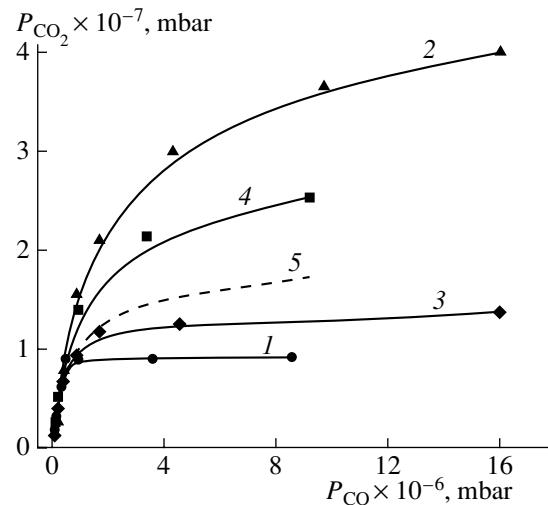


Fig. 5. Pressure of CO_2 formed at the temperatures of maximum rates of reaction on (1) Pt, (2) Rh, (3) the Pt–Rh alloy, or (4) the heterophase Pt/Rh surface as a function of CO pressure in the reaction mixture at $P_{O_2} = 10^{-6}$ mbar. Dashed curve 5 refers to a calculated function plotted using 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 CO_{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 CO_{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 CO_{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_{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 (θ_{CO}). The value of E_{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 CO_{ads} at temperatures close to T_i [10]. It is well known that E_{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 CO_{ads} and O_{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 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 O_2 on free adsorption sites, a greater value of $s_0(\text{O}_2)$ results in the more effective formation of both O_{ads} and new free sites on Rh because of the occurrence of the subsequent reaction between CO_{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 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 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 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_{CO_2} – P_{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 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_{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 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_{Pt} and r_{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/Al₂O₃ 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/Al₂O₃ 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 O₂ (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

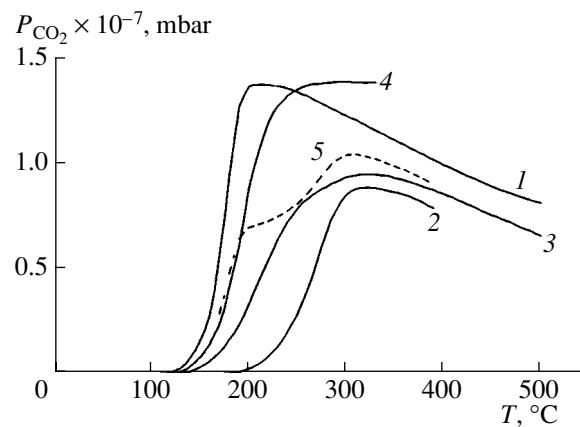


Fig. 6. The temperature dependence of the pressure of CO₂ formed on (1) Rh, (2) Pt, (3) the Pt–Rh alloy, or (4) the heterophase Pt/Rh surface at $P_{\text{CO}} = P_{\text{O}_2} = 10^{-6}$ mbar. Dashed curve 5 refers to the calculated function for the heterophase surface.

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_{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_{max} on Rh (Fig. 6, curve 1). In this case, rhodium particles were covered with a layer of O_{ads}. 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_{ads}. Above 200°C, the reaction on the Pt/Rh sample occurred with the participation of CO_{ads} on platinum and O_{ads} 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_{ads}), 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 Rh_2O_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 CO_{ads} on platinum. Such a reaction scheme was used to explain the low-temperature activity of the Rh/CeO_2 [15] and $\text{Pd}/\text{Fe}_2\text{O}_3$ [16] model catalysts, as well as the $\text{Pd}-\text{Rh}/\text{SiO}_2$ 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.

REFERENCES

1. Topsøe, H., in *Surface Properties and Catalysis by Non-Metals*, Bonelle, J.P., Ed., New York: Reidel, 1983.
2. *Encyclopedia of Catalysis*, Horvath, I.T., Ed., Chichester: Wiley, 2003, vol. 6.
3. Nieuwenhuys, B.E., *Adv. Catal.*, 2000, vol. 44, p. 259.
4. Oh, S.H. and Carpenter, J.E., *J. Catal.*, 1986, vol. 98, p. 178.
5. Cai, Y., Stenger, H.G., and Lyman, C.E., *J. Catal.*, 1996, vol. 161, p. 123.
6. Esch, F., Gunter, S., Schutz, E., Schaak, A., Kevrekidis, I.G., Marsi, M., Kiskinova, M., and Imbihl, R., *Catal. Lett.*, 1998, vol. 52, p. 85.
7. Kalinkin, A.V., Pashis, A.V., and Kvon, R.I., *React. Kinet. Catal. Lett.*, 2001, vol. 72, p. 163.
8. Kalinkin, A.V., Pashis, A.V., and Bukhtiyarov, V., *React. Kinet. Catal. Lett.*, 2002, vol. 77, p. 255.
9. Engel, T. and Ertl, G., *Adv. Catal.*, 1983, vol. 28, p. 1.
10. Schwartz, S.B., Schmidt, L.D., and Fisher, G.B., *J. Phys. Chem.*, 1986, vol. 90, p. 6194.
11. Siera, J., Rutten, F., and Nieuwenhuys, B.E., *Catal. Today*, 1991, vol. 10, p. 353.
12. Elokhin, V.I., *Cand. Sci. (Chem.) Dissertation*, Novosibirsk: Inst. of Catalysis, 1981.
13. Helms, C.R., Bonzel, H.P., and Kelemen, S., *J. Chem. Phys.*, 1976, vol. 65, p. 1173.
14. Daniel, W.M., Kim, Y., Peebles, H.C., and White, J.M., *Surf. Sci.*, 1981, vol. 111, p. 189.
15. Zafiris, G.S. and Gorte, R.J., *J. Catal.*, 1993, vol. 143, p. 86.
16. Kalinkin, A.V., Savchenko, V.I., and Pashis, A.V., *Catal. Lett.*, 1999, vol. 59, p. 115.
17. Araya, P. and Diaz, V., *J. Chem. Soc., Faraday Trans.*, 1997, vol. 93, p. 3887.