Kinetics and Catalysis, Vol. 44, No. 5, 2003, pp. 669–676. Translated from Kinetika i Kataliz, Vol. 44, No. 5, 2003, pp. 731–738.
Original Russian Text Copyright © 2003 by Yatsimirsky, Boldyreva.

CATALYTIC REACTION MECHANISMS

Catalytic Oxidation of Small Molecules in a Gas Phase in the Presence of Heterogenized Platinum and Palladium Complexes with Chemically Different Ligands

V. K. Yatsimirsky and O. Yu. Boldyreva
Shevchenko National University, Kiev, 01033 Ukraine

Received November 22, 2002

Abstract—This work is devoted to the study of catalytic properties of the metal complexes of platinum and palladium with acetylacetone and *N*-allyl-*N*'-propylthiourea heterogenized on the surface of silica in the oxidation reactions of H_2 and CO in a gas phase. We found that the acetylacetonate complexes were not degraded under catalytic reaction conditions, whereas the metal complexes with *N*-allyl-*N*'-propylthiourea exhibited a high activity only after partial degradation of the ligand. We demonstrated that the catalytic activity of the grafted metal complexes was higher than that of traditional supported platinum and palladium catalysts with the same metal content. Taking into account the structure of active centers in Pt and Pd complexes grafted on SiO_2 and the interaction of these centers with reactants, we proposed a detailed mechanism for the catalytic action, which adequately describes the entire set of experimental data.

INTRODUCTION

Heterogenized transition metal complexes are a special class of catalytic systems, which combine the advantages of heterogeneous and homogeneous catalysts. The activity of these systems is often much higher than the activity of homogeneous analogs. These catalysts are primarily used for liquid-phase processes, whereas they are poorly studied as catalysts for gas-phase reactions [1–3]. A study of catalytic reactions on grafted metal complexes opens up opportunities for producing highly active catalysts with the active centers of a specified type. The reactions of hydrogen and carbon monoxide oxidation are promising for these studies; the kinetics of these reactions can be used in the studies of oxidation reactions that are more complex. In actual practice, the catalytic oxidation of hydrogen is used in cryogenic techniques for the removal of hydrogen and oxygen traces from inert gases and in the development of fuel cells and sensor systems, whereas the oxidation of carbon monoxide is one of the most important reactions of environmental catalysis.

In this paper, we report on the results of studies of platinum and palladium complexes with chemically different ligands (β-acetylacetone and *N*-allyl-*N*'-propylthiourea) grafted on the surface of silica in the gas-phase reactions of hydrogen and carbon monoxide oxidation.

The heterogenized platinum and palladium complexes with acetylacetone were prepared by chemical assembling as described elsewhere [4]; the metal complexes with *N*-allyl-*N*'-propylthiourea were prepared by Skopenko *et al.* [5]. In the preparation of the metal complexes with acetylacetone, Silochrome 120 (S_{sp} = 112 m^2/g) was used as a support, whereas Silochrome 80 (S_{sp} = 82 m^2/g) was used in the immobilization of the complexes with *N*-allyl-*N*'-propylthiourea.

According to atomic absorption spectroscopic data, metal concentrations were 0.024, 0.064, and 0.64 wt % in the acetylacetonate complexes or 0.02 and 0.4% in the complexes with the thiourea ligand. The catalyst surfaces were studied by diffuse-reflectance IR Fourier transform spectroscopy on a Nicollete Magna IR-1500 FTIR spectrometer. The XPS spectra of samples were obtained on a Kratos 800 XPS spectrometer with AlK_α radiation ($h\nu$ = 1486.6 eV).

To compare the catalytic activity of grafted Pt and Pd complexes with the activity of traditional supported catalysts, we prepared Pt/SiO_2 and Pd/SiO_2 samples by impregnating a support with H_2PtCl_6 and $PdCl_2$ solutions followed by reduction with hydrazine hydrate.

1. HYDROGEN OXIDATION REACTION ON HETEROGENIZED PLATINUM AND PALLADIUM COMPLEXES WITH ACETYLACETONE

The catalytic activity of samples was measured under flow conditions at atmospheric pressure; the gas flow rate was 0.1 l/s. The reaction components were analyzed by chromatography (an LKhM 8-MD chromatograph with a thermal-conductivity detector).

Figure 1 demonstrates the results of studies of the catalytic properties of platinum and palladium complexes with acetylacetone heterogenized on SiO_2 in the reaction of hydrogen oxidation (curves *1*, *1*', *2*, and *2*'). High conversions of hydrogen and counterclockwise hysteresis with respect to temperature were observed in mixtures with an excess of oxygen. The catalytic activ-

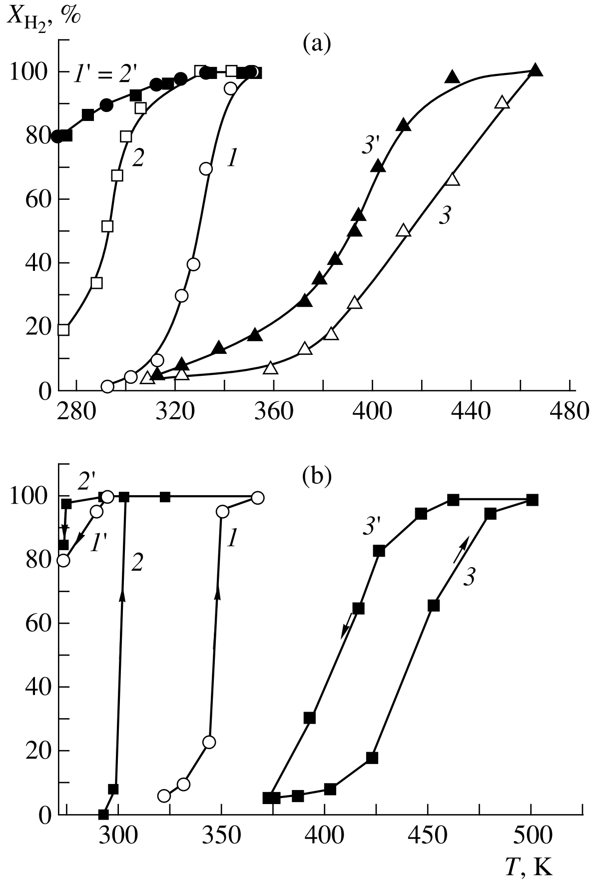


Fig. 1. The temperature dependence of the conversion of hydrogen on heterogenized (a) platinum and (b) palladium acetylacetonates (0.024 wt % metal) (1.75% H_2 and 38.5% O_2 in argon): (*1*–*3*) increasing temperature and (*1'*–*3'*) decreasing temperature; *1*, *1'* and *2*, *2'* correspond to the first and second reaction cycles, respectively; *3*, *3'* correspond to the activity of the supported catalysts 0.024% Pt/SiO_2 and 0.024% Pd/SiO_2, respectively.

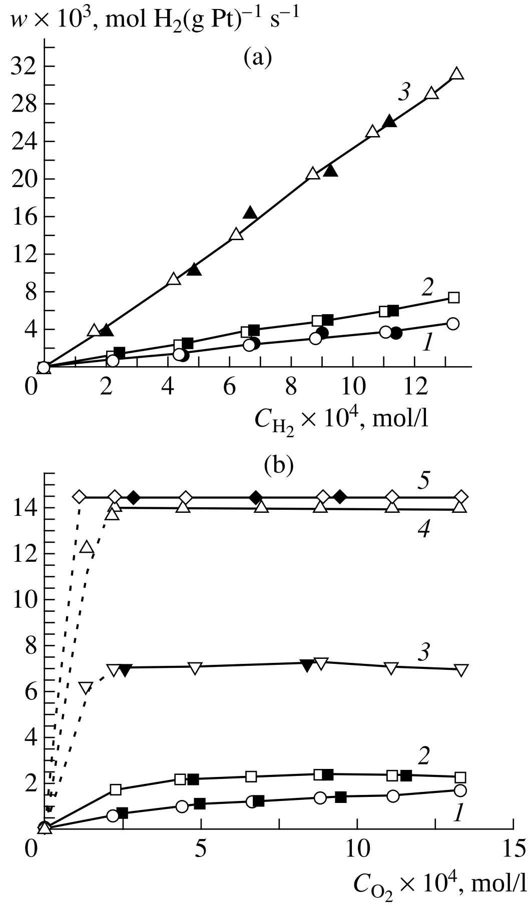


Fig. 2. Reaction rates of hydrogen oxidation on the heterogenized complexes of platinum with acetylacetone (0.024% Pt) as functions of (a) H_2 ($C_{O_2} = 8.9 \times 10^{-3}$ mol/l = const) and (b) O_2 ($C_{H_2} = 6.7 \times 10^{-4}$ mol/l = const) concentrations at the following temperatures (K): (a) (*1*) 313, (*2*) 323, and (*3*) 343; (b) (*1*) 308, (*2*) 318, (*3*) 308 (after operation of the catalyst in a highly active state), (*4*) 338, and (*5*) 343 (open and closed circles correspond to increasing and decreasing hydrogen concentrations, respectively).

ity increased in the second reaction cycle. The active state of a sample was retained for 5–7 days in air at room temperature; that is, the catalyst exhibited a surface memory effect with respect to the previously performed reaction.

The hysteresis of the rate of catalytic reaction (Fig. 1, curves *3*, *3'*) with respect to temperature was also typical of the supported catalysts. At the same time, the surface memory effect was not observed in these samples; their activity was stable upon performing several reaction cycles.

Even without pretreatment with a reaction mixture, the catalytic activity of the metal complex samples (Fig. 1, curves *1*, *1'*) was higher than that of the supported catalysts (0.024 wt % Pt(Pd)/SiO_2), which were prepared by the conventional impregnation method (curves *3*, *3'*). An increase in the metal content of heterogenized complexes resulted in a considerable increase in the catalytic activity: the temperatures of the complete conversion of hydrogen were equal to 353, 333, and 293 K for complexes with 0.024, 0.064, and 0.64% Pt contents, respectively.

According to the kinetic data obtained in a gradientless reactor for hydrogen oxidation on grafted platinum acetylacetonates, the order of reaction with respect to hydrogen was equal to unity, whereas the order of reaction with respect to oxygen varied from unity to zero (Fig. 2). The surface memory effect also manifested itself in the dependence of the rate of reaction on reactant concentrations (Fig. 2b, curve *3*). Analogous functions were also observed with Pd acetylacetonate grafted onto SiO_2.

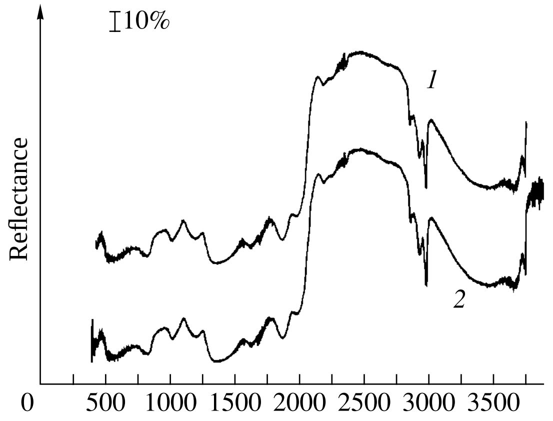


Fig. 3. IR spectra of the grafted acetylacetonate complex of Pt (0.64% metal) (*1*) before and (*2*) after performing the catalytic reaction of hydrogen oxidation.

The above kinetic data can be explained using the following reaction scheme:

$$\begin{aligned} &1.\ Z + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ZO_2,\\ &2.\ ZO_2 + H_2 \xrightarrow[{[Z(O_2H_2)^*]}]{k_2} ZO + H_2O, \qquad (I)\\ &3.\ ZO + H_2 \xrightarrow[{[ZOH_2]^*}]{k_3} Z + H_2O, \end{aligned}$$

where Z is an active center.

From this kinetic scheme, we obtain the following equation for the reaction rate:

$$w = \frac{2k_1k_2C_{O_2}C_{H_2}}{k_1C_{O_2}\left(1 + \frac{k_2}{k_3}\right) + k_2C_{H_2} + k_{-1}}. \qquad (1)$$

At small values of k_2, Eq. (1) is simplified to

$$w = \frac{2k_1k_2C_{H_2}C_{O_2}}{k_1C_{O_2} + k_{-1}}. \qquad (2)$$

It follows from Eq. (2) that the reaction is of first order with respect to hydrogen and of variable (from 1 to 0) order with respect to oxygen; this is consistent with experimental data.

The mechanism of reactant activation on the given catalysts is described below.

The IR spectrum of an grafted platinum metal complex (Fig. 3, spectrum *1*) exhibited bands due to the stretching vibrations of carbonyl (1700 cm^{-1}), methylene (2858 and 2980 cm^{-1}), and methyl (2930 cm^{-1}) groups. The IR spectrum of the spent catalyst (Fig. 3, spectrum *2*) was identical to the spectrum before catalysis (Fig. 3, spectrum *1*); that is, the exposure to a reaction mixture at a relatively high temperature did not result in the degradation of the acetylacetonate ligand in the complex. Note that the frequency of the stretching vibrations of carbonyl groups in the grafted complex (1700 cm^{-1}) was somewhat lower than that in the chemically grafted acetylacetone in the absence of platinum (1720 cm^{-1}) [4]. This fact is indicative of the interaction of the ligand with the transition metal on surface complexation with the participation of platinum atoms and carbonyl groups.

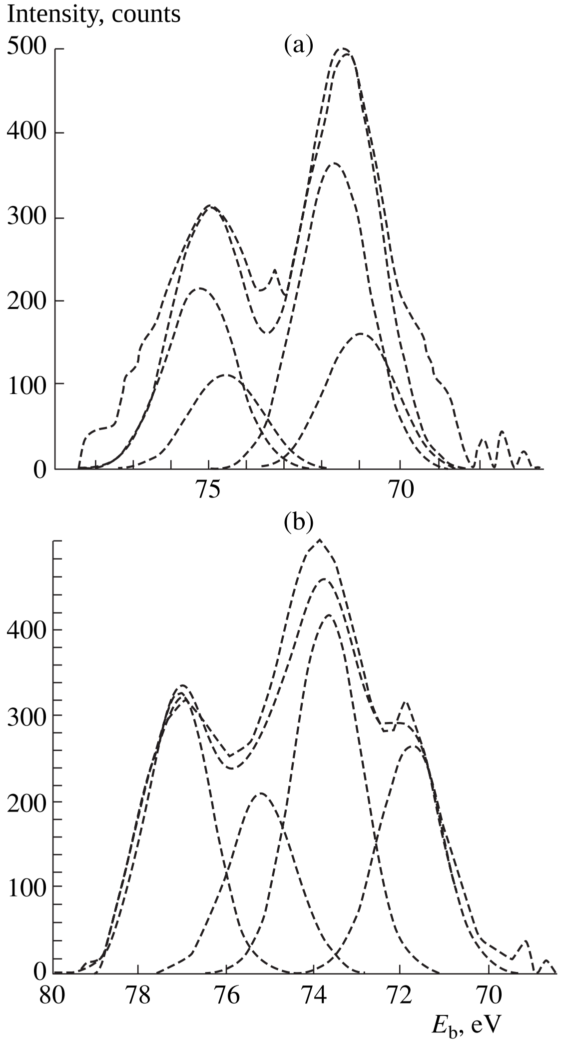
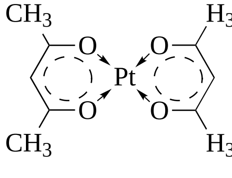
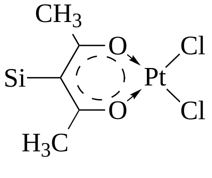


Fig. 4. XPS spectra of the platinum complex with acetylacetone grafted on the surface of SiO_2 (a) before and (b) after the reaction of hydrogen oxidation.

The Pt4$f_{7/2}$ XPS core-level spectra exhibited binding energies (E_b) of 71.0 and 71.6 eV (Fig. 4a). The former value is characteristic of platinum complexes with triphenylphosphine-like organic ligands $Pt(PPh_3)_4$, whereas the latter is characteristic of complexes like $Pt(PPh_3)_2Cl_2$ [6]. It is reasonable to believe that the above values of E_b belong to the following structures:



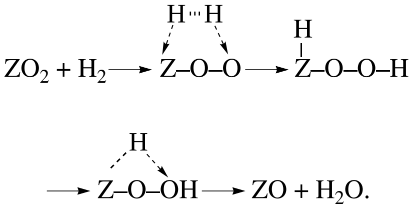
A



B

As the temperature increased, one of the ligands (acetylacetone) of compound **A** was eliminated to give a labile coordinatively unsaturated species.

Molecular oxygen was primarily added at free coordination sites (the formation of ZO_2 in accordance with scheme (I), step *1*). Because of its sufficient electronegativity, the coordinated oxygen was converted into the superoxide ion O_2^-; correspondingly, the central metal atom (ion) underwent oxidation, losing an electron. This provides additional coordination capabilities to platinum and, in turn, facilitates the addition of the second reactant (hydrogen) to the catalyst. The activation and subsequent reaction of molecular hydrogen with coordinated oxygen resulted in the formation of an intermediate complex with the empirical formula $Z(O_2H_2)^*$, which relatively easily eliminated a water molecule (step 2, where ZO_2 is transformed into ZO). It is most likely that the $Z(O_2H_2)^*$ complex is an intermediate hydroperoxide species, the formation and degradation of which occurred in accordance with the following reaction scheme:



$$ZO_2 + H_2 \longrightarrow Z\text{–O–O} \longrightarrow Z\text{–O–O–H} \longrightarrow Z\text{–O–OH} \longrightarrow ZO + H_2O.$$

The XPS spectra after catalytic tests (Fig. 4b) exhibited the E_b of Pt4$f_{7/2}$ equal to 73.7 eV. This value is close to E_b in PtO [6] and it corresponds to ZO in the kinetic scheme. Moreover, the value E_b = 71.8 eV was present, which corresponds to ZO_2. The initial state of *Z* (structure **A**) disappeared after catalyst operation in a reaction mixture containing an excess of oxygen.

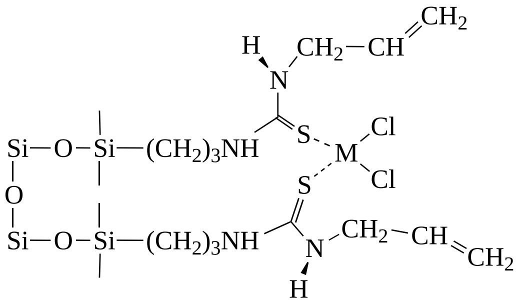
Note that the value of E_b = 71.0 eV is close to the binding energy of platinum metal; however, as demonstrated above, platinum metal supported on SiO_2 exhibited a much lower activity than that of grafted complexes. Moreover, according to data obtained by electronic spectroscopy [4], the diffusion-reflectance spectrum of an grafted platinum complex exhibited absorption bands corresponding to the acetylacetone ligand (193 and 217 nm), bands at 388 and 344 nm, which are characteristic of the *d*–*d* transitions of Pt(II), and a ligand–metal charge-transfer band at 280 nm. The low value of E_b for Pt in the acetylacetonate complex is mainly due to the covalent character of the metal–ligand bond and a low electronegativity of acetylacetonate ligands.

The appearance of chlorine, which is more electronegative, in the acetylacetonate–chloride complex (structure **B**) resulted in an increase in the binding energy up to 71.6 eV; this value is lower than E_b = 75.2 eV for the purely chloride complex of platinum [6]. Note that, if compound **B** is considered as a parent compound for the formation of catalytically active structures, it is reasonable to assume that chloride ions are gradually replaced by OH^- groups under the action of a reaction mixture to result in the formation of structures similar to those described above. The conversion of **B** into ZO can be considered as the reaction of high-temperature hydrolysis (with the subsequent elimination of a water molecule). Note that, according to XPS and mass-spectrometric data, the amount of chlorine in the catalyst formed was lower than the amount of platinum by one order of magnitude.

The pretreatment of a heterogenized metal complex in an atmosphere of pure hydrogen at 423 K resulted in a considerable decrease in the catalytic activity due to the blocking of vacant coordination sites by the hydride ions formed in the reaction of H_2 with the catalyst. The pretreatment of a heterogenized complex in pure oxygen also resulted in a decrease in the catalytic activity because of the blocking of coordination sites by atomic oxygen. As distinct from the blocking effects of individual reactants, the exposure of the catalyst to a reaction mixture did not result in the blocking of active centers because of a reaction between initial components.

2. HYDROGEN OXIDATION REACTION ON HETEROGENIZED PLATINUM AND PALLADIUM COMPLEXES WITH *N*-ALLYL-*N*'-PROPYLTHIOUREA

According to IR spectra and published data [5], the grafted Pt and Pd complexes with *N*-allyl-*N*'-propylthiourea exhibit the following structure:



The studies performed by XPS demonstrated that the binding energy of Pt4$f_{7/2}$ in the heterogenized metal complex is 72.8 eV. This value is close to E_b = 72 eV for $Pt(PBu_3)_2Cl_2$, 72.1 eV for $Pt(PPh_3)_2Cl_2$, and 72.8 eV for K_2PtCl_4; that is, it suggests that platinum occurs in the Pt(II) state [6].

The heterogenized complexes of platinum and palladium with *N*-allyl-*N*'-propylthiourea exhibited high catalytic activity (Fig. 5) only after heating them in a reaction mixture with an excess of oxygen at 555–573 K, which was accompanied by partial degradation of the ligand. Absorption bands corresponding to the bending (1556 cm^{-1}) and stretching (3085 cm^{-1}) vibrations of NH-bonds in the ligand disappeared from the IR spectra of the test samples after high-temperature treatment in a reaction mixture. The DTA curve exhib-

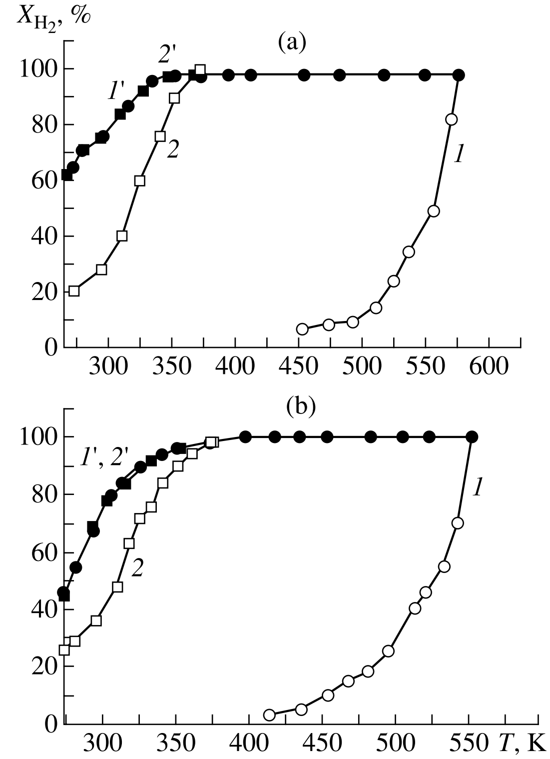


Fig. 5. The temperature dependence of the conversion of hydrogen on heterogenized (a) platinum and (b) palladium complexes with *N*-allyl-*N*'-propylthiourea (0.02 wt % metal; C_{H_2} = 1.5% and C_{O_2} = 38.5% in argon): (*1*, *2*) increasing temperature and (*1*', *2*') decreasing temperature; *2*, *2*' after heating in the reaction mixture with an excess of O_2 at 555–573 K.

ited an endo effect at 515 K, which corresponds to the thermal transformation of the ligand with the release of H_2S. This evidences the occurrence of the following reaction:

$$\text{R–NH–CS–NH–R}' \longrightarrow H_2S + \text{R–N=C=N–R}'.$$

Thus, the partial degradation of grafted complexes affected the character of binding platinum and palladium. In place of strong bridge bonds via sulfur, the transition metals coordinate to organic ligands via nitrogen.

According to thermographic analysis data, the organic ligand was completely decomposed at a temperature higher than 643 K, which is much higher than the temperature of catalytic measurements. Therefore, it is believed that the oxidation of H_2 on the heterogenized complexes of platinum and palladium with *N*-allyl-*N*'-propylthiourea occurred at active centers that were formed in the reaction mixture upon partial degradation of the ligand. This increased the coordinative unsaturation of the metal ion and enhanced the catalytic activity.

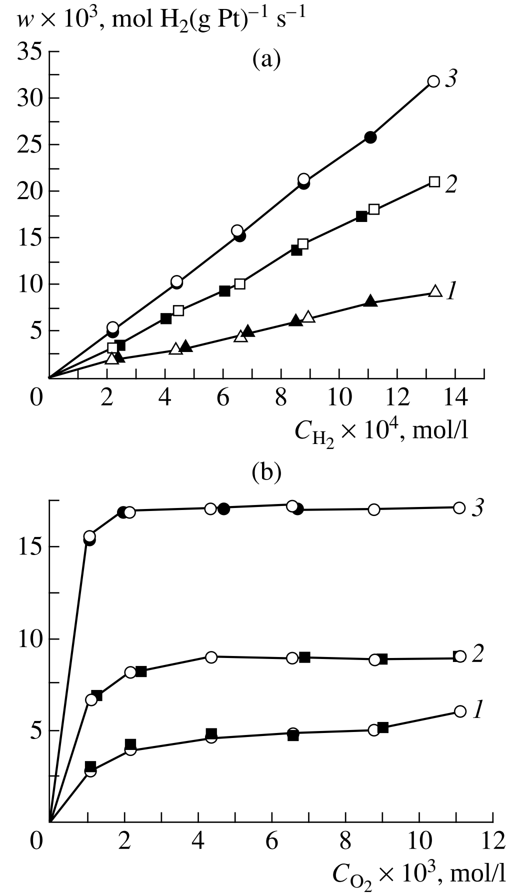


Fig. 6. Reaction rates of hydrogen oxidation on the heterogenized complexes of platinum with *N*-allyl-*N*'-propylthiourea (0.02% Pt) as functions of (a) H_2 (C_{O_2} = 8.9 × 10^{-3} mol/l = const) and (b) O_2 (C_{H_2} = 6.7 × 10^{-4} mol/l = const) concentrations at the following temperatures (K): (*1*) 313, (*2*) 333, and (*3*) 373.

The rate laws of the reactions of hydrogen oxidation on grafted Pt and Pd complexes with *N*-allyl-*N*'-propylthiourea, as well as on the heterogenized platinum and palladium acetylacetonates, were first order with respect to hydrogen and variable order (from 1 to 0) with respect to oxygen (Fig. 6) [7].

The reaction mechanism proposed for hydrogen oxidation on the complexes of Pt and Pd with acetylacetone grafted on SiO_2 can also be used for the metal complexes with the thiourea ligand.

3. CARBON MONOXIDE OXIDATION REACTION ON HETEROGENIZED PLATINUM AND PALLADIUM COMPLEXES WITH ACETYLACETONE AND *N*-ALLYL-*N*'-PROPYLTHIOUREA

The catalytic activity of the heterogenized complexes of platinum and palladium with acetylacetone in

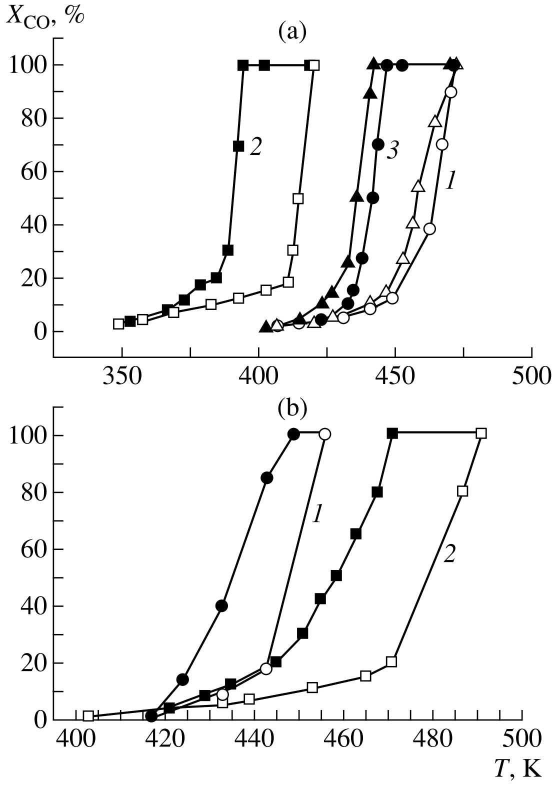


Fig. 7. The temperature dependence of the conversion of CO on (a) (*1*, *2*) heterogenized platinum acetylacetonate complexes or (*3*) the supported Pt/SiO$_2$ catalyst (*1*, 0.64, *2*, 0.064, and *3*, 0.64 wt % Pt; C_{CO} = 1%; C_{O_2} = 20%) and (b) (*1*) the heterogenized complex of Pt with *N*-allyl-*N*'-propylthiourea or (*2*) the supported Pt/SiO$_2$ catalyst (platinum content of 0.4 wt %; C_{CO} = 1%; C_{O_2} = 20%) (open and closed circles correspond to increasing and decreasing hydrogen concentrations, respectively).

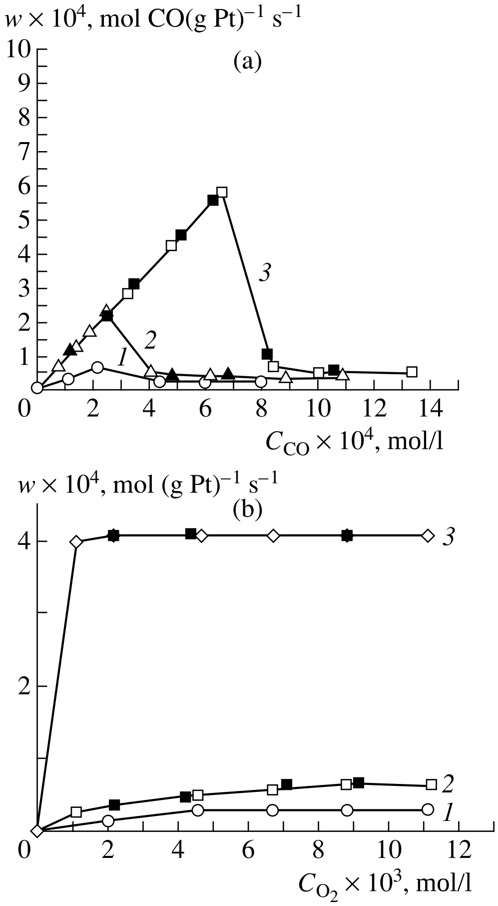


Fig. 8. Reaction rates of carbon monoxide oxidation on the heterogenized complex of platinum with acetylacetone as functions of (a) CO (C_{O_2} = 8.9 × 10^{-3} mol/l) and (b) O$_2$ (C_{CO} = 4.46 × 10^{-4} mol/l) concentrations at (*1*) 393, (*2*) 413, and (*3*) 423 K (open and closed circles correspond to increasing and decreasing concentrations, respectively).

the reaction of carbon monoxide oxidation was higher than that of traditional supported catalysts (Fig. 7).

Figure 8 demonstrates the rates of reaction as functions of carbon monoxide and hydrogen concentrations at a constant concentration of the second component for grafted Pt complexes with acetylacetone.

The curves of $w = f(C_{CO})$ (Fig. 8a) exhibit a maximum; that is, the order of reaction with respect to CO varied from 1 to –1 (curve *1*). As the temperature was increased, this maximum became better pronounced and shifted to higher concentrations of CO (curves *2*, *3*).

The rates of reaction as functions of O$_2$ concentration have the shape of saturation curves; that is, the order of reaction with respect to oxygen changed from 1 to 0 (Fig. 8b). Analogous relationships between the rate of reaction and CO and O$_2$ concentrations were also observed with the grafted complex of palladium with acetylacetone [8]. Note that heterogenized complex catalysts are characterized by memory with respect to only a highly active state. The concentration dependence of the rate of reaction did not exhibit nonstationary phenomena, which were characteristic of supported Pt and Pd.

The reaction mechanism of CO oxidation on grafted Pt and Pd complexes can be described by the following scheme:

$$\begin{aligned}
&1.\ Z + O_2 \xrightarrow{k_1} ZO_2,\\
&2.\ ZO_2 + CO \xrightarrow[{[ZO_2CO^*]}]{k_2} ZO + CO_2,\\
&3.\ ZO + CO \xrightarrow[{[ZOCO^*]}]{k_3} Z + CO_2,\\
&4.\ Z + CO \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} ZCO.
\end{aligned} \tag{II}$$

This scheme resulted in the following rate equation:

$$w = \frac{2k_1k_2C_{CO}C_{O_2}}{k_1C_{O_2}\left(1 + \dfrac{k_2}{k_3}\right) + k_2C_{CO}(1 + K_4C_{CO})}, \tag{3}$$

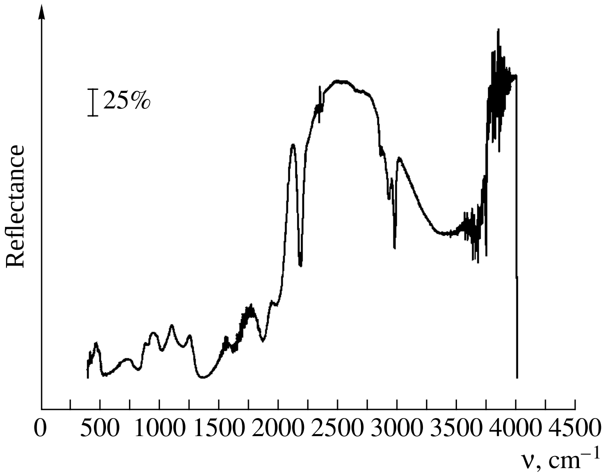


Fig. 9. IR spectrum of the platinum complex with acetylacetone grafted on the surface of SiO_2 (0.64 wt % Pt) after performing the reaction of CO oxidation.

where $K_4 = k_4/k_{-4}$.

Equation (3) is fully consistent with experimental data.

According to XPS data, in the oxidation of CO in a mixture with an excess of oxygen on grafted platinum acetylacetonate, the oxidation of platinum took place (E_b = 73.1 eV for Pt4$f_{7/2}$), as observed in the reaction of hydrogen oxidation. That is, active centers were formed on the treatment of grafted acetylacetonate complexes with a reaction mixture. This mechanism does not describe the reaction kinetics on supported Pt and Pd catalysts, which are characterized by the occurrence of nonstationary phenomena.

The IR spectra of the heterogenized complex of platinum with acetylacetone after performing the reaction of CO oxidation exhibited an intense band at 2175 cm^{-1} (Fig. 9). It is well known [9–12] that this band is characteristic of linear CO species with the formation of a coordination bond with an electron-donor center. This provides support for the occurrence of intermediate carboxylate (carbonate) compounds at the active centers of platinum complexes after performing the reaction of CO oxidation; thus, the surface memory effect can be explained. The mechanism of the activation of reactant molecules was the same for the grafted metal complexes of palladium with acetylacetone.

The rate laws of the reactions of CO oxidation on the grafted complexes of platinum and palladium with *N*-allyl-*N'*-propylthiourea (Fig. 10) are similar to the dependence of the reaction rates on reactant concentrations for grafted complexes with acetylacetone, and they are characterized by the absence of nonstationary phenomena [13]. The reaction mechanism proposed for the heterogenized acetylacetonate complexes of Pt and Pd can be used for describing the kinetics of CO oxidation on the metal complexes of platinum and palladium with *N*-allyl-*N'*-propylthiourea.

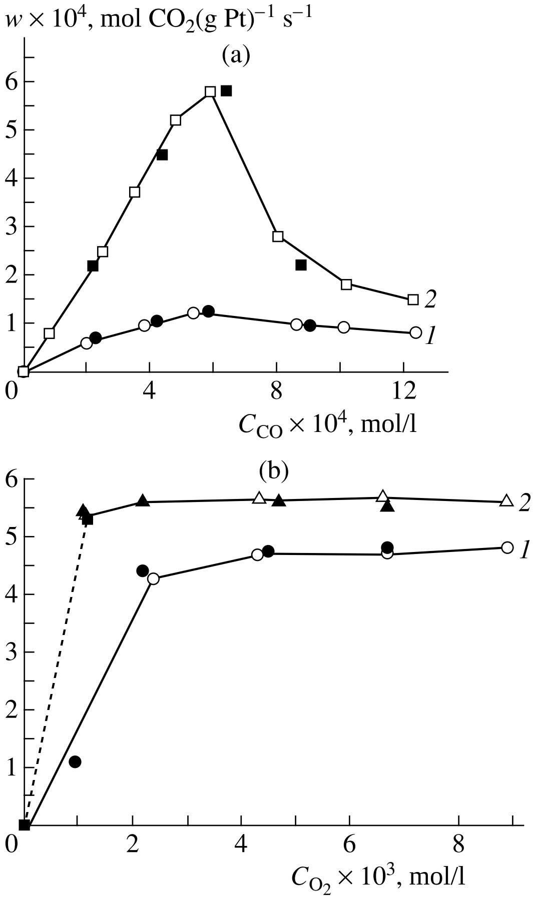


Fig. 10. Reaction rates of CO oxidation on the heterogenized complex of platinum with *N*-allyl-*N'*-propylthiourea as functions of (a) CO (C_{O_2} = 8.9 × 10^{-3} mol/l; (*1*) 423 or (*2*) 438 K) and (b) O_2 (C_{CO} = 4.46 × 10^{-4} mol/l; (*1*) 438 or (*2*) 453 K) concentrations (open and closed circles correspond to increasing and decreasing concentrations, respectively).

It is believed that active centers are formed on the gradual replacement of Cl$^-$ ions by OH$^-$ groups because of high-temperature hydrolysis (due to H_2O impurities that occurred in the reaction mixture and on the catalyst surface) followed by the elimination of water molecules to form intermediate structures.

Based on the experimental data, we can conclude that the difference between the reaction kinetics of CO oxidation on supported Pt and Pd catalysts and the grafted metal complexes can be explained by different characters of the chemisorption of CO. On the grafted catalysts containing active centers (monoatomic with respect to platinum or palladium as complexes of these metals), carbon monoxide can undergo chemisorption only in a weakly bound linear form. This form is favorable for the catalytic oxidation of CO; this was found previously using Pd–Ag catalysts as an example [14]. At the same time, chemisorbed bridging multicenter CO species, which are more strongly bound to the catalyst surface, also occurred on metal, including supported platinum and palladium catalysts. This fact is responsible for the weak reversibility of the unimolecular step of CO chemisorption (step 4 in scheme (II)) resulting in the appearance of nonstationary phenomena in the concentration dependence of the reaction rate on these catalysts.

ACKNOWLEDGMENTS

This work was supported by INTAS (grant no. 00-291).

REFERENCES

1. Lisichkin, G.V. and Yuffa, A.Ya., *Geterogennye metallokompleksnye katalizatory* (Heterogeneous Metal Complex Catalysts), Moscow: Khimiya, 1981.
2. Ermakov, Yu.I., Zakharov, V.A., and Kuznetsov, B.N., *Zakreplennye kompleksy na okisnykh nositelyakh v katalize* (The Fixation of Complexes on Oxide Carriers in Catalysis), Novosibirsk: Nauka, 1980.
3. Hartley, F.R., *Supported Metal Complexes: A New Generation of Catalysts*, Boston: Reidel, 1985.
4. Oleksenko, L.P., Belyakova, L.A., Yatsimirskii, V.K., Boldyreva, O.Yu., and Lyashenko, D.Yu., *Teor. Eksp. Khim.*, 1998, vol. 34, no. 3, p. 170.
5. Skopenko, V.V., Trofimchuk, A.K., and Yanovskaya, E.S., *Ukr. Khim. Zh.*, 1993, vol. 59, no. 5, p. 549.
6. Nefedov, V.I. *Rentgenoelektronnaya spektroskopiya khimicheskikh soedinenii* (X-ray Electron Spectroscopy of Chemical Compounds), Moscow: Khimiya, 1984.
7. Yatsimirskii, V.K. and Boldyreva, O.Yu., *Teor. Eksp. Khim.*, 2002, vol. 38, no. 1, p. 45.
8. Yatsimirskii, V.K., Boldyreva, O.Yu., and Oleksenko, L.P., *Teor. Eksp. Khim.*, 2001, vol. 37, no. 6, p. 357.
9. Little, L.H., *Infrared Spectra of Adsorbed Molecules*, London: Academic, 1966.
10. Fernandez-Garcia, M., Martinez-Arias, A., and Anderson, J.A., *Stud. Surf. Sci. Catal.*, 2000, vol. 130, p. 1325.
11. Almaric, D., Hermann, J.-M., and Bozon-Veruraz, F., *Stud. Surf. Sci. Catal.*, 2000, vol. 130, p. 1307.
12. Kiperman, S.L. and Gaidai, N.A., *Kinet. Katal.*, 1999, vol. 40, no. 5, p. 705.
13. Yatsimirskii, V.K., Boldyreva, O.Yu., and Oleksenko, L.P., *Ukr. Khim. Zh.*, 2002, vol. 68, no. 1, p. 22.
14. Yatsimirskii, V.K. and Boldyreva, N.A., Abstracts of Papers, *V Vsesoyuznaya konferentsiya po mekhanizmam kataliticheskikh reaktsii* (V All-Union Conf. on the Mechanisms of Catalytic Reactions), Moscow, 1990, p. 117.