Kinetics and Catalysis, Vol. 45, No. 4, 2004, pp. 598–606. Translated from Kinetika i Kataliz, Vol. 45, No. 4, 2004, pp. 632–641.

CATALYTIC REACTION MECHANISMS

The Study of Nitric Oxide Adsorption and the Mechanism of Surface "Explosions" in the Reaction of CO + NO on Pt(100) and Pd(110) Single Crystal Surfaces

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Received January 21, 2003

Abstract—High resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) were used to study NO adsorption and the reactivity of CO_{ads} and NO_{ads} molecules on Pd(110) and Pt(100) single crystal surfaces. Compared to the Pt(100)-(1 × 1) surface, the unreconstructed Pt(100)-hex surface is chemically inert toward NO dissociation into N_{ads} and O_{ads} atoms. When a mixed adsorbed $CO_{ads} + NO_{ads}$ layer is heated, a so-called surface "explosion" is observed when the reaction products (N_2, CO_2, and N_2O) synchronously desorb in the form of sharp peaks with a half-width of 7–20 K. The shape specificity of TPR spectra suggests that the "vacancy" mechanism consists of the autocatalytic character of the reaction initiated by the formation an initial concentration of active sites due to partial desorption of molecules from the $CO_{ads} + NO_{ads}$ layer upon heating to high temperatures. Kinetic experiments carried out on the Pd(110) surface at a constant reaction pressure and a linear increase in the temperature confirm the explosive mechanism of the reaction NO + CO.

INTRODUCTION

Mechanistic studies of the reactions CO + O_2 and NO + CO on platinum group metal (Pt, Pd) single crystal surfaces are still of interest in connection with the possibility of obtaining new experimental data that might shed light on the mechanism of oscillations, chemical waves, and the so-called surface "explosions" [1–3]. It is known that oscillations of the reaction rate of CO oxidation on platinum are associated with the reversible phase transition of the surface Pt(100)-hex $\rightleftharpoons$ 1 × 1. Because on the Pd single crystal surfaces reversible phase transitions do not occur, oscillations are thought to be due to the penetration of oxygen atoms in the subsurface layer of the metal. For the NO + CO reaction on the Pt(100) surface, the vacancy-site mechanism is proposed to describe oscillations [4]. The appearance of extremely narrow peaks of CO_2 and N_2 with a half-width of ~5 K in the reaction $NO_{ads} + CO_{ads}$ on the Pt(100) surface during heating to $T \sim 400$ K was assigned to the surface explosion [4]. The explosive nature of the formation of CO_2 molecules has also been observed on the Pd(320) and Pd(100) single crystal surfaces [5, 6]. The limiting step in the reaction NO_{ads} + CO_{ads} on Pt and Pd is assumed to be the dissociative adsorption of NO. At temperatures of ~400 K, adsorbed oxygen atoms formed in the course of NO dissociation readily react with the CO_{ads} layer to form CO_2. The recombination of nitrogen atoms on the clean surface is accompanied by N_2 desorption. In the course of surface explosions, autocatalytic formation of free sites that are necessary for the NO_{ads} dissociation occurs, and this fact forms the basis of the vacancy mechanism of oscillations [4].

Possible products of the reaction NO + CO are nitrogen, carbon dioxide, and nitrous oxide [7]. The route of reaction is determined by the nature of a metal, reaction conditions (P_i, T), and the state of adsorbed NO (molecular or dissociated). At 300 K, NO adsorption in the molecular state was found for the surfaces Pd(111), Pd(100), Pd(112), Pt(111), Pt(210), and Pt(110)-hex; adsorption in the molecular state with dissociation into N_{ads} and O_{ads} atoms was found for the surfaces Pt(410) and Pt(100)-(1 × 1) [8]. In the literature, the high specificity of various platinum surfaces has been determined in NO dissociation. The highest activity in dissociation is seen for the surfaces (410), (210), (100); the surfaces (111) are the least active and NO adsorbs on it only in the molecular form [8]. It has been found that the formation of the adsorbed oxygen layer via N–O bond dissociation suppresses further NO molecule dissociation.

The goal of this work is to study adsorption and catalytic activity of the Pt(100)-(1 × 1), Pt(100)-hex, and Pd(110) surfaces and elucidate the mechanism for the effect of a preadsorbed oxygen layer on the reaction $NO_{ads} + CO_{ads}$ in the mixed adsorbed layer. These studies are a necessary step toward solving the problem of low-temperature NO conversion into N_2 in the reaction NO + CO on platinum-group metals. The first task here is a search for conditions of nitrogen atom N_{ads} formation during NO dissociation and the ease of their recombination to N_2 molecules at $T \approx 300$ K. We used high resolution electron energy loss spectroscopy

(HREELS), temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR).

EXPERIMENTAL

Experimental studies were carried out in a vacuum chamber of a VG ADES 400 electron spectrometer equipped with a monochromatic EMU 50 electron gun and a semispherical electrostatic-type energy analyzer. The base pressure in the chamber was ~3 × 10^{-11} Torr. HREEL spectra were recorded in the specular direction at an electron energy of ~2.5 eV and an incident angle of ~35° with a resolution of ~70–90 cm^{-1}. TPR and TPD spectra were obtained using a VG QXK 400 quadrupole mass spectrometer in the regime of linear heating at a ramp of 2–6°C/s with simultaneous recording of ten different masses.

Pt(100)-hex and Pd(110) single crystals were cleaned by Ar^+ ion etching with further annealing in oxygen and a vacuum [9]. The nonreconstructed Pt(100)-(1 × 1) surface was prepared by the titration reaction of the preadsorbed NO_{ads} layer with hydrogen and further removal of the H_{ads} layer in a vacuum according to the procedure described in [10]. The clean surface was characterized by the (1 × 1) diffraction pattern for Pt(100)-(1 × 1) and Pd(110) single crystal surfaces and by the (5 × 20) diffraction pattern for the Pt(100)-hex surface. Temperature was measured using a chromel–alumel thermocouple welded to the edge of a crystal. In the experiments we used nitric oxide ^{15}NO.

RESULTS AND DISCUSSION

Vibrational Electron Spectroscopy: NO/Pt(100)

To elucidate the role of reversible phase transition Pt(100)-hex $\rightleftarrows$ 1 × 1 in oscillations in the reaction CO + NO, we studied the nature of adsorbed NO on the (1 × 1) and hex surfaces by HREELS. At the initial stage at $\theta_{NO} = 0.2$ ML (1 ML = 1 monolayer = 1.28 × 10^{15} cm^{-2}) NO_{ads} islands are formed due to NO adsorption on the clean hex surface [11]. HREELS data for the formation of saturated NO layer suggest the appearance of two molecular NO states: $NO_{1\times1}$ on the (1 × 1) surface and NO_{def} on defects. The stretching vibrations are ν(NO) = 1620 cm^{-1} and ν(Pt–NO) = 370 cm^{-1} for $NO_{1\times1}$ and ν(NO) = 1775 cm^{-1} for NO_{def}. The formation of defects is due to the phase transition hex $\longrightarrow$ 1 × 1 (Fig. 1a). Figure 1b shows spectra that characterize NO adsorption on Pt(100)-1 × 1. At saturation NO coverage (NO = 0.5 ML), the molecular NO is characterized by the bands ν(NO) = 1620 cm^{-1} and ν(Pt–NO) = 370 cm^{-1}. The spectra also show the band of a stretching vibration ν(Pt–O) = 540 cm^{-1} from O_{ads} atoms formed via the dissociation of NO_{ads} molecules [12]. The corresponding vibration of N_{ads} expected at 300–600 cm^{-1} is not resolved in the spectrum because of the overlap with the frequencies ν(Pt–O) and ν(Pt–NO). For instance, on the Pt(111) surface, the ν(Pt–N) vibration corresponds to a frequency at 480 cm^{-1} [13].

It is known that NO adsorption on the Pt(100)-1 × 1 surface at 300 K is statistical. At the initial stage of NO adsorption, it dissociates into N_{ads} and O_{ads}. As the surface coverage increases, adsorption becomes molecular [12]. The saturation coverage is $\theta_{NO} \approx 0.4$–0.5 ML [14]. Unlike the (1 × 1)-hex surface, on the hex surface NO adsorption at 300 K is accompanied by the backward reconstruction of the Pt(100)-hex surface with the formation of $NO_{1\times1}$ islands [11]. Adsorption-induced phase transition hex $\longrightarrow$ 1 × 1 leads to the formation of structural defects in the islands like small clusters due to squeezing platinum atoms out of the upper layer because of the higher atomic density of the hex phase (>20%). The surface coverage of NO on the hex surface is $\theta_{NO} \approx 0.4$–0.5 ML [14].

Vibrational Electron Spectroscopy: CO/Pt(100)

The sequence of vibrational spectra that characterizes the molecular CO adsorption state on Pt(100)-hex at 300 K is shown in Fig. 1c. It is known that CO adsorption on the hex surface at coverages below critical ($\theta \le 0.1$ ML) occurs with $CO_{1\times1}$ island formation [15]. At an exposure of 0.2–3.6 L (1 L = 10^{-6} Torr s) CO molecules are at the terminal state CO_{term} characterized by the bands ν(CO) = 2100 cm^{-1} and ν(Pt–CO) = 480 cm^{-1} [15]. The formation of structural defects due to the phase transition hex $\longrightarrow$ 1 × 1 occurs upon an exposure of 0.2 L as follows from the appearance of bridging CO state with a band at ~1890 cm^{-1} [15]. The growth of $CO_{1\times1}$ islands with an increase in the exposure is accompanied by a simultaneous growth of the intensity of the CO_{bridge} and CO_{term} bands. Upon an exposure of 3.6 L, the apparent shift of the band by 6 cm^{-1} is due to the dipole–dipole interaction between CO_{ads} molecules inside the adsorption island. The rate of hex $\longrightarrow$ 1 × 1 phase transition is characterized by the power law with respect to the partial pressure of CO. It was expectable that there would be a substantial difference in the positions of bands in CO adsorption on the unreconstructed (1 × 1) and hex surfaces because the heat of CO adsorption on the (1 × 1) surface is higher [16]. However, our spectral data [17] show that the adsorbed CO layer on Pt(100)-(1×1) consists of terminal (ν(CO) = 2125 cm^{-1}) and bridging ($\nu(CO_{bridge})$ = 1920 cm^{-1}) states of CO. This fact points to the similar nature of the structural defects formed in the course of the preparation of the clean (1 × 1) surface according to the procedure described in [10]. CO adsorption on the Pt(100)-(1 × 1) surface at 300 K occurs in a statistical manner with surface coverage up to $\theta_{CO} \approx 0.75$ ML [15].

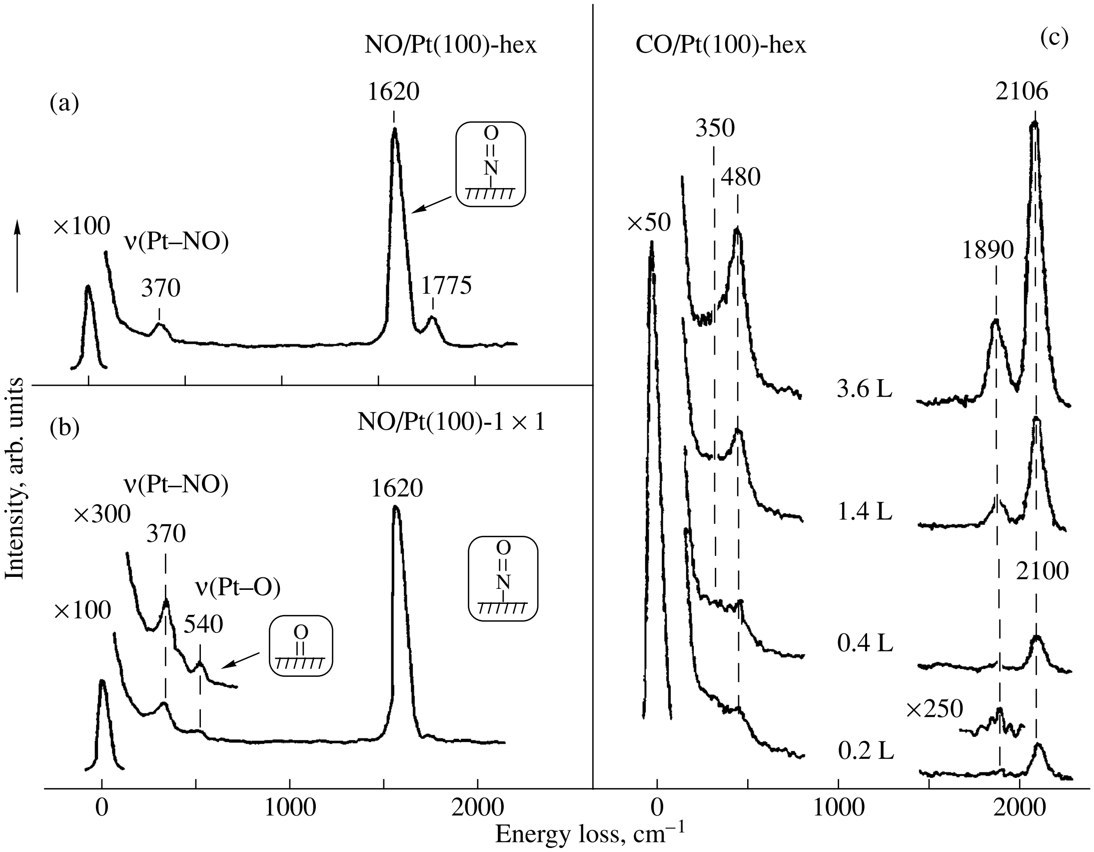

Fig. 1. HREEL spectra obtained in the adsorption of (a, b) NO and (c) CO at 300 K: (a) Pt(100)-hex, exposure 5.0 L (NO); (b) Pt(100)-(1×1), exposure 0.3 L (NO); (c) Pt(100)-hex, exposure 0.2–3.6 L (CO).

Temperature-Programmed Reaction on Pt(100)

Figure 2 shows the TPR spectra of NO + CO on Pt(100)-hex. The nature of the spectra suggest the mechanism of the surface explosion, which expresses itself as anomalously narrow desorption peaks of the products N_2 and CO_2 [4]. According to spectral data, adsorption of NO and CO molecules on Pt(100)-hex at $T < 400$ K occurs without dissociation into N_{ads} and O_{ads} atoms. Adsorption is accompanied by the phase transition hex $\longrightarrow$ 1 × 1 resulting in the formation of the islands of unreconstructed surface covered by the mixed NO_{ads} + CO_{ads} layer. The reaction in the $NO_{1\times1}$ + $CO_{1\times1}$ islands is initiated by the partial desorption of the NO_{ads} layer upon heating to $T \sim 350$ K, which is accompanied by the appearance of vacancies on the metal surface (free adsorption sites) that are necessary for the dissociation of nitric oxide into N_{ads} and O_{ads} atoms. Then, the reaction occurs in the autocatalytic regime of surface explosion characterized by narrow peaks of desorption of N_2 and CO_2 molecules at 395 K.

On the unreconstructed surface of the Pt(100)-(1 × 1) surface, reaction in the NO_{ads} + CO_{ads} layer occurs in a different manner (Fig. 3). In the successive filling of the (1 × 1) surface, the reaction between CO_{ads} and NO_{ads} occurs at lower temperatures and leads to the formation of N_2 and CO_2 in the form of individual peaks at $T_{des} \sim 350$ K.

Preliminary activation of the NO_{ads} layer at 270 K is accompanied by the formation of additional peaks in the reaction products: the low-temperature peak of CO_2 at $T_{des} \sim 270$ K and the high-temperature peak of N_2 at $T_{des} \sim 435$ K (Fig. 4). According to spectral data (Fig. 1b), the dissociative adsorption of NO on Pt(100)-(1 × 1) occurs with the formation of the O_{ads} that readily reacts with CO_{ads} at T ~ 250 K [17]. This fact explains the appearance of the low-temperature peak of CO_2 at 270 K. The formation of the high-temperature peak of N_2 at 435 K is probably due to the recombination of strongly bound N_{ads} atoms adsorbed on the (1 × 1) surface defects. It is known that on the clean Pt(100) surface the layer of atomic N_{ads} is stable at 300 K. Nitrogen atoms recombine at high temperatures and form N_2 presented by two peaks at 390 and 450 K [18]. Earlier, we observed the high-temperature formation of N_2 at 490 K as the dissociation of NO molecules on the defects of the Pt(111) surface [19].

Temperature-Programmed Desorption on Pd(110)

TPD spectra at different exposures to NO at T_{ads} = 100 K are shown in Fig. 5. At low exposures (0.2–1.0 L),

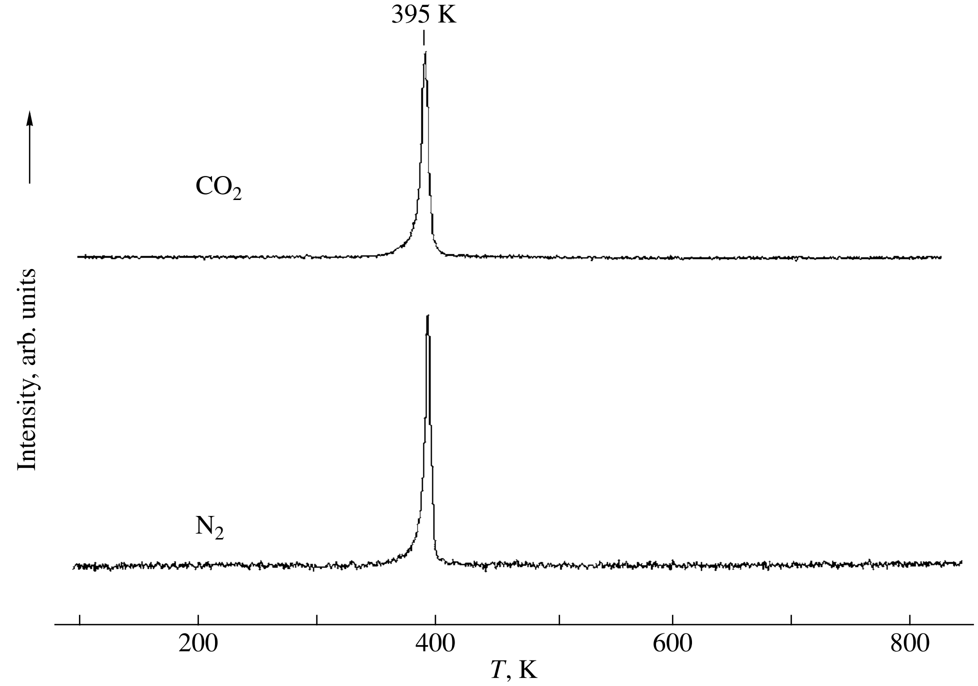

Fig. 2. Synchronous formation of CO_2 and N_2 on Pt(100)-hex as a result of surface explosions of the mixed layer formed by the consecutive adsorption of NO (0.3 L) and CO (0.3 L) at 120 K.

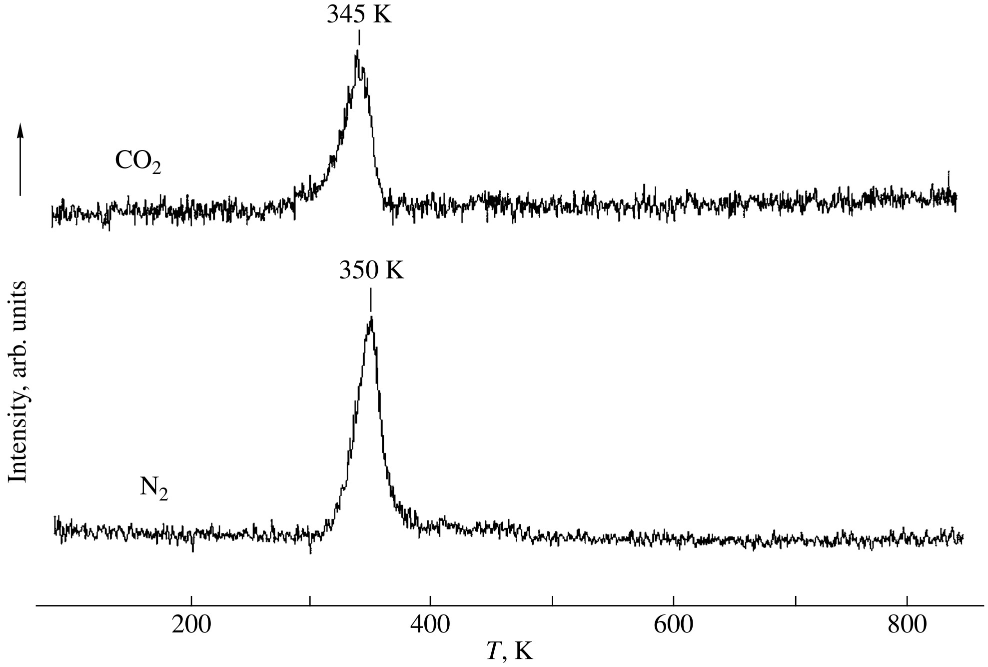

Fig. 3. Synchronous formation of CO_2 and N_2 on Pt(100)-(1×1) for the mixed layer formed by the consecutive adsorption of NO (0.3 L) and CO (0.3 L) at 120 K.

the desorption spectrum is characterized by the NO peak at 490 K and the peaks of dissociation products: N_2 (495 K), N_2O (495 K), and O_2 (815 K), which are in agreement with data reported in [20]. An increase in the exposure to 2.0 L leads to the appearance of additional low-temperature states of NO adsorption which are characterized by the desorption peaks at 345, 265, and ~200 K. The studies of NO adsorption on palladium

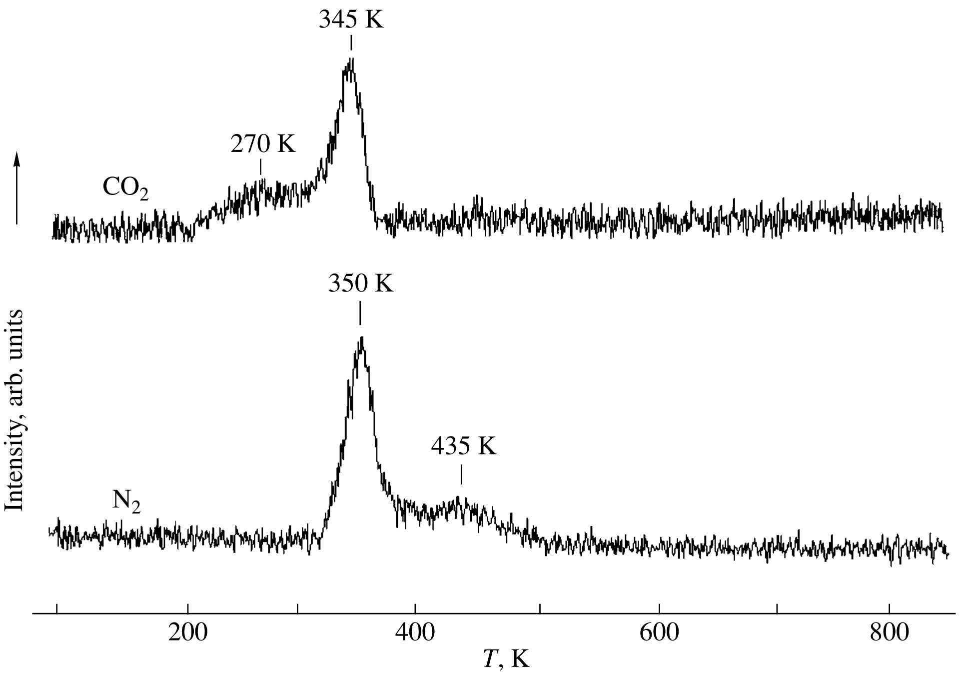

Fig. 4. Synchronous formation of CO_2 and N_2 on Pt(100)-(1 × 1) for the mixed layer formed by the consecutive adsorption of NO (0.3 L, 270 K) and CO (0.3 L, 120 K).

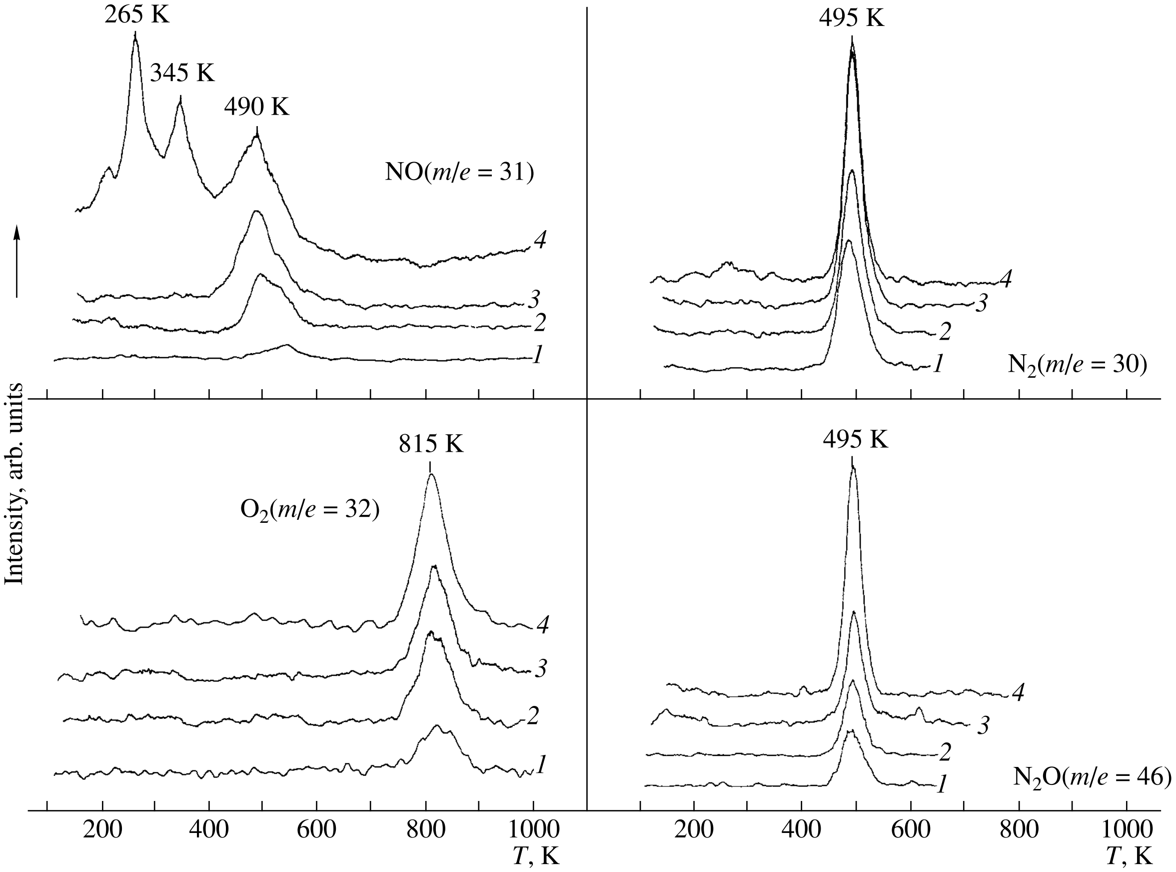

Fig. 5. TPD spectra for NO, N_2, N_2O, and O_2 upon ^{15}NO adsorption on Pd(110) at 100 K at exposures equal to (*1*) 0.2, (*2*) 0.4, (*3*) 1.0, and (*4*) 2.0 L.

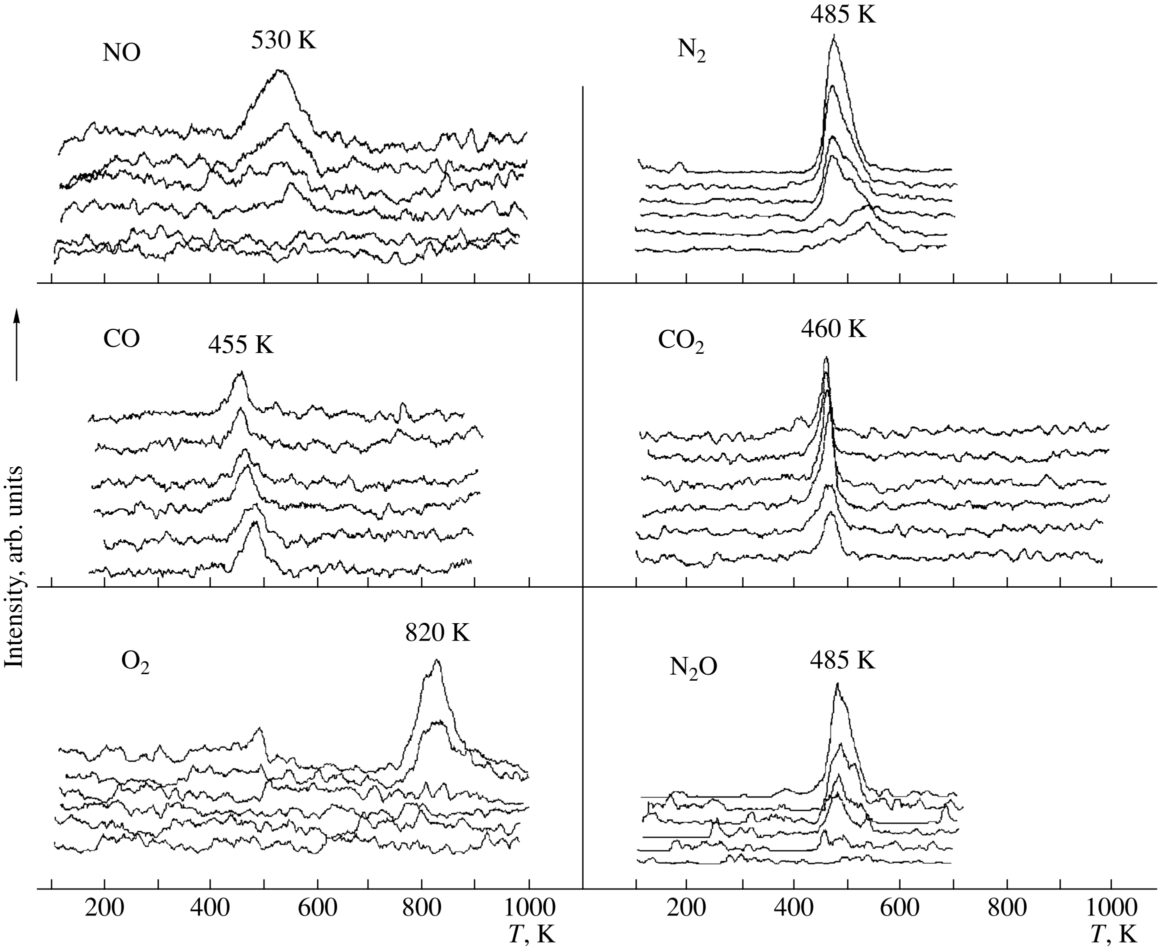

Fig. 6. Formation of reaction products N_2, CO_2, N_2O, and O_2 on Pd(110) for the mixed layer formed by adsorption of CO molecules at 100 K (0.1 L) and additional adsorption of ^{15}NO at exposures equal to 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 L (bottom-up increase in the exposure). Heating ramp is 6°C/s.

single crystal surfaces (100), (111), (110), (112), and (320) [5, 24] showed that the NO_{ads} layer is molecular at $T < 300$ K and these molecules dissociate at $T \geq 300$ K [22]. It has also been found that N_{ads} and O_{ads} atoms readily diffuse into the subsurface layer of palladium at $T \sim 300$ K and reverse if the temperature is increased. It has been shown that the dissolution of O_{ads} atoms in the subsurface layer of Pd is due to the low activation barrier for the process $O_{ads} \longrightarrow O_{dissolv}$ [2]. The surfaces of palladium can be arranged in a series according to their reactivity toward N–O bond cleavage: Pd(100) > $Pd_{polycryst}$ > Pd(111) > Pd(110) [22].

Temperature-Programmed Reaction on Pd(110)

Spectra shown in Fig. 6 point to the explosive character of the reaction of $^{15}NO_{ads}$ (0.05–0.30 L) and CO_{ads} (0.10 L) adsorbed on the Pd(110) surface at 100 K. The formation of CO_2 occurs at 460 K. The formation of N_2 and N_2O occurs synchronously at $T \sim 485$ K. Oxygen and unreacted NO and CO molecules desorb from the surface in the same range of temperatures as from the clean surface (Fig. 5). The results obtained are close to the characteristics of the surface explosion on the Pd(100) surface observed at 470–485 K [6]. The desorption peaks of N_2 (483 K) and CO_2 (471 K) at Pd(100) and Pd(110) practically coincide, which suggests that this reaction is structure-insensitive. However, compared to Pt(100), the reactivities of NO_{ads} and CO_{ads} molecules on Pd(110) were much lower, as becomes clear from comparing the spectra of Figs. 6 and 2–4. On the Pd(110) surface, the reaction products N_2 (485 K) and CO_2 (460 K) are formed at ~100 K higher temperatures compared to Pt(100).

The effect of the layer of atomic oxygen O_{ads} on the reaction (CO_{ads} + NO_{ads})/Pd(110) is illustrated in Fig. 7. TPR spectra were recorded after consecutive adsorption of molecules $^{18}O_2$ (0.2 L) + ^{15}NO (1.0 L) at 100 K on the clean metal surface and further adsorption of CO (0.1–0.5 L). The oxygen layer was initially heated to 200 K to remove molecular O_{2ads}. Figure 7 shows CO_2

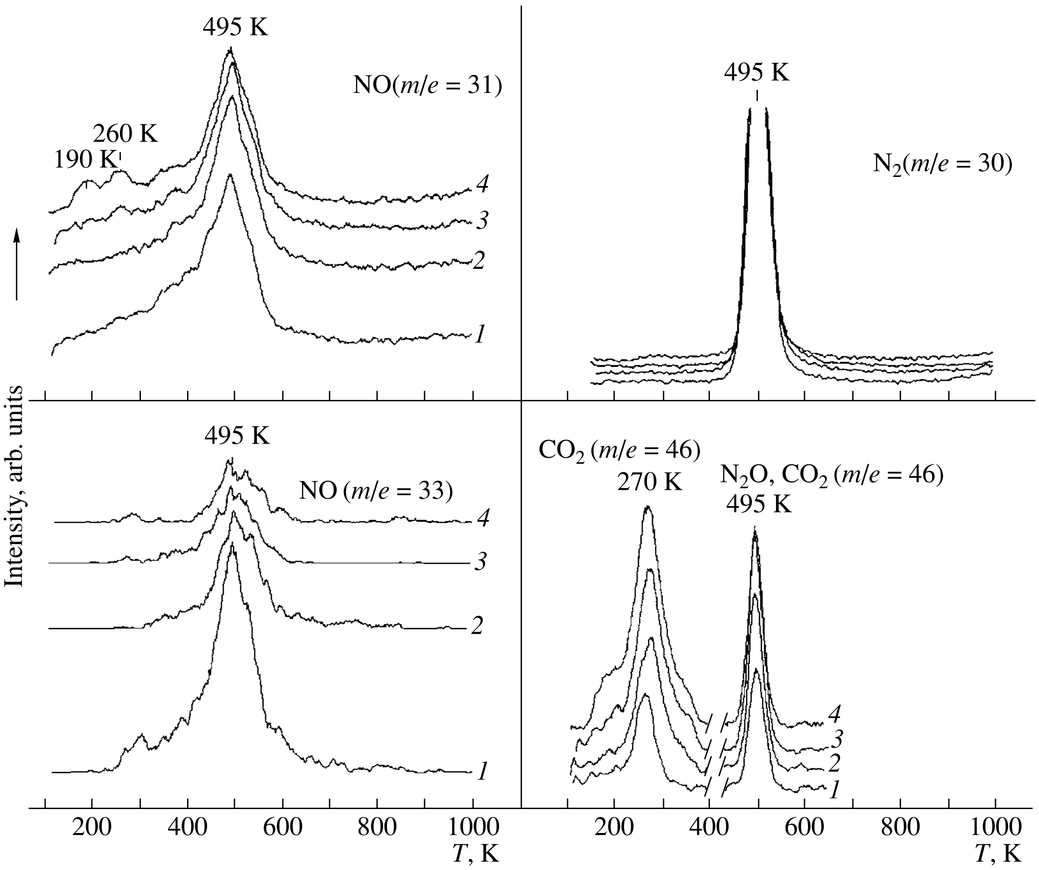

Fig. 7. Effect of atomic oxygen layer O_{ads} on the formation of reaction products N_2, CO_2, and N_2O on Pd(110) for the mixed layer formed by the consecutive adsorption of O_2 (0.1 L, 200 K) and ^{15}NO (100 K) with additional CO adsorption at 100 K and exposures (*1*) 0.1, (*2*) 0.2, (*3*) 0.3, (*4*) 0.5. Heating ramp is 6°C/s.

peaks at 270 and 495 K in contrast to TPR spectra in Fig. 6. The low-temperature peak of CO_2 probably results from the existence of two parallel reaction routes:

$$CO_{ads} + {}^{18}O_{ads} \longrightarrow C^{16}O^{18}O_{gas}\ (m/e = 46) + 2^* \qquad (1)$$

(where * is the active site of the surface);

$$2)\ CO_{ads} + {}^{15}N^{18}O_{ads} \longrightarrow C^{16}O^{18}O_{gas}\ (m/e = 46) + {}^{15}N_{ads} + {}^*. \qquad (2)$$

The possibility of the second reaction on palladium was suggested in [23]. The formation of nitric oxide with the isotopic composition $^{15}N^{18}O_{ads}$ is due to the isotope exchange reaction $^{15}N^{16}O_{ads} + {}^{18}O_{ads} \longrightarrow {}^{15}N^{18}O_{ads} + {}^{16}O_{ads}$ and is characterized by the desorption peak $^{15}N^{18}O_{ads}$ with $T = 495$ K (Fig. 7). In the presence of the oxygen layer, the high-temperature formation of molecules CO_2, N_2, and N_2O occurs in a synchronous manner in the form of narrow peaks at $T_{des} \sim 495$ K pointing to the explosive mechanism of the reaction.

Hysteresis: Pd(110)

Figure 8 illustrates the hysteretic character of a change in the rate of formation of reaction products in the course of slow heating and cooling of the Pd(110) sample in the reaction mixture NO + CO at a constant partial pressure of reactants. It is seen that with an increase in temperature the rate of N_2 formation is characterized by two temperature maximums at 495 and 545 K, whereas when the temperature is decreased there is only one temperature maximum (at 530 K). Let us analyze this hysteresis using the vacancy-site mechanism proposed to explain the surface explosions observed in the reactions NO + CO and NO + H_2 on Pt(100) [1–4, 6]. The reaction mechanism is described as a sequence of the following steps:

$$1)\ CO + {}^* \rightleftharpoons CO_{ads},$$

$$2)\ NO + {}^* \rightleftharpoons NO_{ads},$$

$$3)\ NO_{ads} + {}^* \longrightarrow N_{ads} + O_{ads},$$

$$4)\ 2N_{ads} \longrightarrow N_2 + 2^*,$$

$$5)\ CO_{ads} + O_{ads} \longrightarrow CO_2 + 2^*,$$

$$6)\ NO_{ads} + N_{ads} \longrightarrow N_2O + 2^*.$$

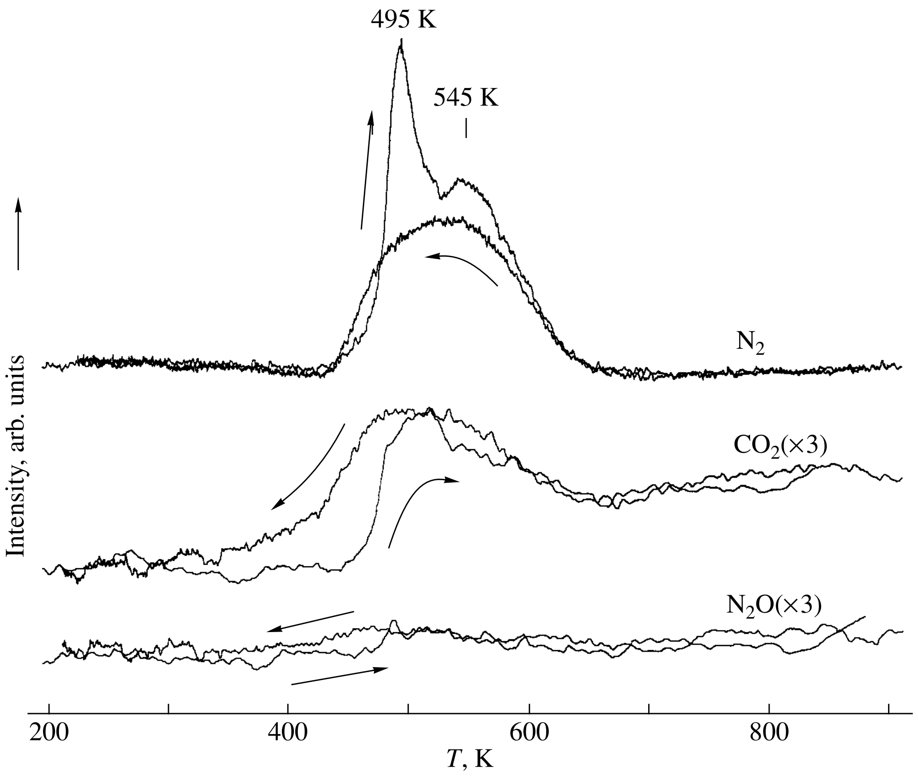

Fig. 8. Hysteresis of the rate of formation of molecules N_2, CO_2, and N_2O in the reaction NO + CO on Pd(110) (P(CO) = 7.6×10^{-8} Torr, P(NO) = 3.8×10^{-8} Torr. Heating and cooling ramp is 2°C/s.

On the Pd(110) surface at $T < 430$ K, the rate of reaction product formation in the saturated adsorption layer of reactants is insignificant. At $T > 430$ K desorption of some NO_{ads} and CO_{ads} molecules is accompanied by the formation of vacant sites that are necessary for the dissociation of nitric oxide. The rate-limiting step is the reaction of NO_{ads} dissociation (step 3) with the coverages of highly reactive O_{ads} and N_{ads} atoms leading to the formation of N_2, CO_2, and N_2O in subsequent steps (4–6). This process initiates a drastic increase in the rate of formation of N_2 and CO_2 (the forward branch of hysteresis), which is typical of the reaction NO_{ads} + CO_{ads} in the regime of surface explosion (see Fig. 6). The second maximum in the formation of nitrogen molecules is probably due to the recombination of strongly bound N_{ads} (T_{des} ~ 550 K), which is accumulated on the surface due to the low contribution of nitrogen atoms to the reaction that produces N_2O molecules (step 6). The backward branch of hysteresis in the range T ~ 380–430 K is characterized by the high catalytic activity in the formation of CO_2. This is associated with the high concentration of O_{ads} atoms formed by the dissociation of NO_{ads} molecules at high temperatures.

The results of this work led us to determine the following main features of the reaction NO + CO on Pt(100) and Pd(110) surfaces: (1) the interaction NO_{ads} + CO_{ads} is autocatalytic with explosion-like formation of products CO_2 and N_2 in the form of synchronous peaks; (2) the reaction occurs via the Langmuir–Hinshelwood mechanism with the formation of CO_2 and N_2 only under conditions for formation of vacant adsorption sites in a high concentration; these are necessary for the dissociative adsorption of NO; (3) the vacancy model is proposed to describe hysteresis on the Pd(110) surface; (4) in the reaction NO_{ads} + CO_{ads}, the activity of the Pt(100) surface is much higher than those of the Pd(110) and Pd(100) surfaces.

One might expect that the formation of $NO_{1 \times 1}$ and $CO_{1 \times 1}$ islands with a high local density ($\theta \sim 0.5$) in the mixed adsorption layer on the Pt(100)-hex surface would make it possible to initiate the bimolecular disproportionation reaction $NO_{ads} + CO_{ads} \longrightarrow N_{ads} + CO_{2gas} + *$ that frees active sites for further dissociation of NO_{ads} molecules. However, the results obtained for the Pt(100)-hex surface did not confirm this hypothesis. On the Pd(110) surface, the mechanism of CO_2 molecule formation at low temperatures in the reaction $CO_{ads} + {}^{15}N^{18}O_{ads} \longrightarrow C^{16}O^{18}O_{gas}$ ($m/e = 46$) $+ {}^{15}N_{ads} + *$ can be interpreted in the framework of the “molecular catalysis” mechanism with the participation of molecular forms of reactant adsorption, but this should be further confirmed by other studies.

Kinetic experiments carried out at a constant pressure of the reaction mixture and with a linear increase in the temperature confirm the explosive character of the reaction NO + CO. Pd(110) shows the maximum catalytic activity in the temperature range 450–650 K.

CONCLUSIONS

The study of critical phenomena, including phase transitions, hysteresis, oscillations, surface explosions, etc., is very interesting for understanding the factors affecting the kinetics of heterogeneous catalytic reactions. Despite tremendous complexity in the experimental studies of critical phenomena due to their high sensitivity to external influence, it has become possible to study the mechanism of these phenomena in detail for the reaction NO + CO on platinum-group metals. On the Pt(100)-hex surface, the rate-limiting step is the step of activated dissociation of NO molecules at $T > 400$ K. HREELS studies show that the unreconstructed Pt(100)-hex surface is chemically inactive toward NO_{ads} dissociation compared to the active Pt(100)-(1 × 1) and Pd(110) surfaces. The layer of atomic oxygen O_{ads} is highly reactive and readily transforms into CO_2 in the reaction with CO. The initiating role of the phase transition Pt(100)-hex $\longrightarrow$ (1 × 1) is likely to consist in the formation of vacant sites, which are necessary for NO dissociation. On the Pt(100) and Pd(110) surfaces, experimental results on the coadsorption of CO and NO point to the explosive character of the reaction. The half-width of the TPR peaks of the reaction products (CO_2, N_2, and N_2O) is 7–20 K. The TPR spectra suggests the vacancy-site mechanism of the reaction, consisting in the formation of an initial concentration of active sites due to the partial desorption of CO_{ads} or NO_{ads} molecules. This step initiates autocatalytic formation of active site concentration leading to the synchronous formation of N_2 and CO_2 molecules. Under conditions of constant composition of the reaction medium, the transition of palladium from the low-active state to the highly active catalytic state can be explained from the standpoint of the vacancy-site mechanism of the reaction. In the forward branch of hysteresis, the active state of the surface is initiated by the partial desorption of adsorbed NO and CO molecules with the formation of vacant sites, which are necessary for NO_{ads} dissociation. The further reaction of carbon monoxide with oxygen atoms is accompanied by the autocatalytic (explosion-like) vacant site formation. The backward branch of hysteresis at $T \sim 380$–430 K, which is characterized by the high catalytic activity toward CO_2 and N_2 formation, is due to the fast dissociation of NO_{ads} molecules on the vacant sites and due to the high rate of recombination of N_{ads} atoms to form N_2.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant nos. 02-03-32568 and 02-03-06246) and the Dutch Science Society (grant no. 047-015-002).

REFERENCES

1. Ertl, G., *Adv. Catal.*, 1990, vol. 37, p. 213.
2. Imbihl, R. and Ertl, G., *Chem. Rev.*, 1995, vol. 95, no. 3, p. 697.
3. Slinko, M.M. and Jaeger, N.I., *Stud. Surf. Sci. Catal.,* 1994, vol. 86.
4. Fink, Th., Dath, J.-P., Basset, M.R., Imbihl, R., and Ertl, G., *Surf. Sci.*, 1991, vol. 245, no. 1, p. 96.
5. Hirsimäki, M., Suhonen, S., Pere, J., Valden, M., and Pessa, M., *Surf. Sci.*, 1998, vols. 402–404, p. 187.
6. Daté, M., Okuyama, H., Takagi, N., Nishijima, M., and Aruga, T., *Surf. Sci.*, 1996, vol. 350, no. 1, p. 79.
7. Nieuwenhuys, B.E., *Adv. Catal.*, 2000, vol. 44, p. 259.
8. Banholzer, W.F., Park, Y.U., Mak, K.M., and Masel, R., *Surf. Sci.*, 1983, vol. 128, no. 1, p. 179.
9. Gorodetskii, V.V., Matveev, A.V., Cobden, P.D., and Nieuwenhuys, B.E., *J. Mol. Catal., A: Chem.*, 2000, vol. 158, no. 1, p. 155.
10. Zemlyanov, D.Yu., Smirnov, M.Yu., and Gorodetskii, V.V., *Catal. Lett.*, 1997, vol. 43, p. 181.
11. Ritter, E., Behm, R.J., Potschke, G., and Wintterlin, J., *Surf. Sci.*, 1987, vol. 181, nos. 1/2, p. 403.
12. Zemlyanov, D.Yu., Smirnov, M.Yu., Gorodetskii, V.V., and Block, J.H., *Surf. Sci.*, 1995, vol. 329, nos. 1/2, p. 61.
13. Smirnov, M.Yu., Gorodetskii, V.V., and Block, J.H., *J. Mol. Catal., A: Chem.*, 1966, vol. 107, nos. 1–3, p. 359.
14. Bonzel, H.P., Broden, G., and Pirug, G., *J. Catal.*, 1978, vol. 53, no. 1, p. 96.
15. Martin, R., Gardner, P., and Bradshaw, A.W., *Surf. Sci.,* 1995, vol. 342, no. 1, p. 69.
16. Thiel, P.A., Behm, R.J., Norton, P.R., and Ertl, G., *Surf. Sci.*, 1982, vol. 121, no. 2, p. L553.
17. Gorodetskii, V.V. and Drachsel, W., *Appl. Catal., A.*, 1999, vol. 188, p. 267.
18. Schwaha, K. and Bechtold, E., *Surf. Sci.*, 1977, vol. 66, no. 2, p. 383.
19. Smirnov, M.Yu. and Gorodetskii, V.V., *Poverkhnost.*, 1989, vol. 9, p. 68.
20. Scharpe, R.G. and Bowker, M., *Surf. Sci.*, 1996, vol. 360, nos. 1–3, p. 21.
21. Ramsier, R.D., Gao, Q., Neergaard Waltenburg, H., and Yates, J.T., Jr., *J. Chem. Phys.*, 1994, vol. 100, no. 9, p. 6837.
22. Sugai, S., Watanabe, H., Kioka, T., Miki, H., and Kawasaki, K., *Surf. Sci.*, 1991, vol. 259, nos. 1/2, p. 109.
23. Klein, R.L., Schwartz, S., and Schmidt, L.D., *J. Phys. Chem.*, 1985, vol. 89, no. 3, p. 4908.