

Influence of Oxygen Adsorption on Surface Explosion Phenomena in the NO + CO/Pd(110) System

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Abstract

In the present work adsorption of NO and coadsorption of NO, CO and O₂ has been investigated by means of thermal desorption spectroscopy (TDS) and temperature programmed reaction (TPR). Influence of adsorbed oxygen on morphology of Pd-nanoparticles as well as Pd(110) plane was studied by the theoretical method of interacting bonds (MIB). It has been shown that adsorption of atomic oxygen induces the morphology changes of Pd-nanocrystals and Pd(110) plane. By analysis of TPR spectra of desorbing N₂ and CO₂ for different NO_{ads} + CO_{ads} coverages, we suggest an autocatalytic reaction in an “explosive” way. The addition of oxygen was found to inhibit the process of NO dissociation. Exposure of NO and CO on oxygen preadsorbed layer results in appearing of low-temperature peak of CO₂ in TPR spectra at 265 K.

INTRODUCTION

The NO + CO reaction on Pt and Pd surfaces is of practical importance due to the key role of NO_x emission in air pollution and interest due to the dynamic behavior, especially in connection with new experimental data, allowing to throw light upon the nature of sustained kinetic oscillations [1]. In contrast to the CO + O₂ reaction on a Pt(100) surface, the adsorbate-induced Pt(100) 1×1 ⇌ hex phase transition is not considered to be essential for the NO + CO oscillation mechanism [2]. Under heating of Pt(100) surface at the coadsorbed NO_{ads} and CO_{ads} layer up to $T \sim 400$ K, the reaction product forms in an “explosive” way giving rise to extremely narrow desorption peaks (FWHM ~ 5 K) CO₂ and N₂. This surface “explosion” is due to an autocatalytic increase of vacant sites for NO dissociation being as a main driving force for kinetic oscillations under steady-state conditions. Some studies of CO + NO reaction over palladium surfaces have shown that the decomposition of nitric oxide to N₂ molecules is the rate limiting step followed by rapid CO_{ads} + O_{ads} reaction to yield

CO₂. It has been shown that the bimolecular reaction step (NO_{ads} + CO_{ads} → N_{ads} + CO₂) can be a limiting stage in CO + NO reaction at higher pressures [3].

The purposes of the present work were (i) to investigate the coadsorption of ¹⁵NO and CO on Pd(110) surface; (ii) to find out the influence of oxygen adsorption on the structure of Pd(110) plane and Pd nanocrystals theoretically, by the method of interacting bonds; (iii) experimentally, by temperature-programmed reaction spectroscopy, to examine the effect of coadsorbed oxygen (O_{ads} and O_{ss}) on both the NO_{ads} + CO_{ads} reaction and adsorption of NO.

EXPERIMENTAL

The TDS and TPR experimental device used on the single crystal Pd(110) surface is described in detail in ref. [4]. The UHV chamber is equipped with VG QXK 400 quadrupole mass spectrometer, sputtering ion gun and a molecular beam doser. The TD spectra were obtained with a heating rate of 6 K s⁻¹. Steady-state

rates for the catalytic NO + CO reaction on Pd(110) surfaces have been measured with the gas flow controlled by mass spectrometer. Using a semiempirical method of interacting bonds the heat of oxygen adsorption has been estimated in a dissociative form on the Pd(110) and Pd nanocrystals [5].

RESULTS

NO dissociation

TD spectra of ^{15}NO adsorbed on Pd(110) surface at 100 K have one desorption peak at 490 K, when the surface coverage is low at ^{15}NO exposure (0.2–1.0 L, $1\text{L} = 10^{-6}\text{ Torr s}$) (Fig. 1). If the NO coverage increases up to 2 L, additional desorption peaks at 345, 265

and around $\sim 200\text{ K}$ will appear. During these experiments single desorption peaks N_2 (495 K), N_2O (495 K) and O_2 (815 K) were observed as a result of NO decomposition according to [6].

The adsorption of NO on palladium surfaces has been studied for the (100), (111), (110), (112) and (320) surfaces [7–9]. It is reported that molecular NO states desorb at low temperature ($T < 300\text{ K}$) and then NO_{ads} molecules dissociate partially at room temperature [10, 11]. It is concluded that the produced N and O atoms diffuse into the metal at 300 K and diffuse back to the surface at increasing temperature. The diffusion of O_{ads} atoms into Pd is well known to be a result of presence of a small energy barrier for $\text{O}_{\text{ads}} \rightarrow \text{O}_{\text{sub}}$ process [2]. The order of activity for the N–O bond break-

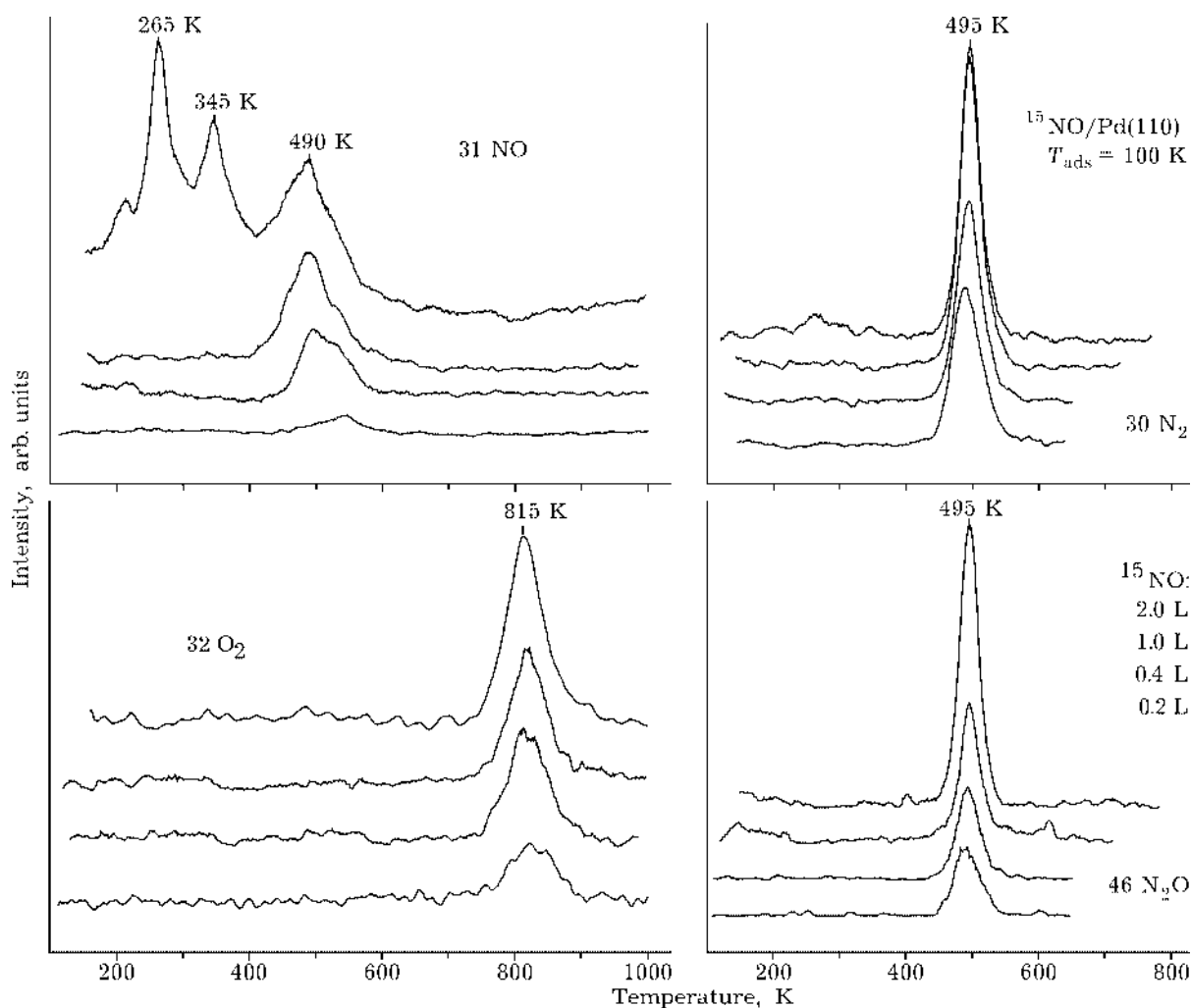


Fig. 1. TD spectra of NO (31), N_2 (30), N_2O (46) and O_2 (32) after exposure the Pd(110) surface to various doses of NO at 100 K.

ing is as follows [10]: Pd (100) > Pd_{poly} > Pd(111) ≥ Pd(110).

NO + CO reaction

Figure 2 shows series of spectra produced when the Pd(110) surface is exposed to 0.1 L of CO followed by 0.05–0.3 L of ¹⁵NO. Comparison of these spectra with those in Fig. 1 shows that the N₂ and N₂O peaks (485 K) look different from the peaks (495 K) seen at the surface exposure to pure NO. Oxygen desorbs as a peak centered at 820 K. The products, N₂ and CO₂, desorb in simultaneous peaks with in the temperature interval 455–485 K. Thus, it is indicative of a so-called “surface explosion” [12]. Recent studies of the CO + NO reaction have

reported an explosive CO₂ production over Pd(100) surface which does not reconstruct [13, 14]. The behaviour of the N₂ and CO₂ desorption peaks for (NO + CO)/Pd(100) does not differ from that for (NO + CO)/Pd(110). The peak temperatures of N₂ (483 K) and CO₂ (471 K) for Pd(100) are close to those for Pd(110).

Method of interacting bonds

Effect of the metal particle size on catalytic properties has been studied by the semi-empirical method of interacting bonds (MIB) [5] by calculating the heats of oxygen adsorption in a dissociative form on the Pd(110) and Pd nanocrystals. This technique permits to study the influence of the oxygen atoms (O_{ads}) on

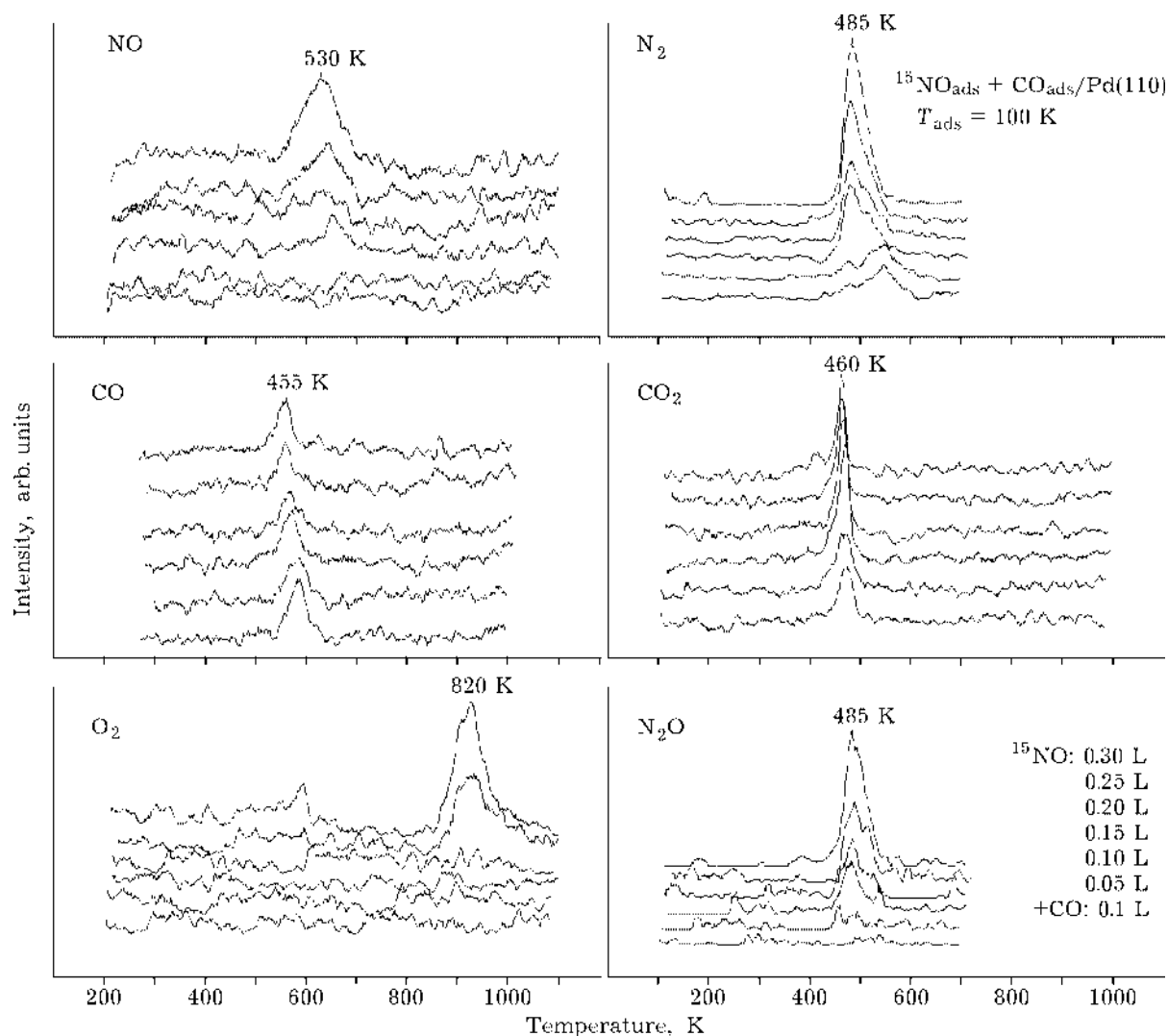


Fig. 2. TPR spectra for Pd(110) precovered with CO and exposed to ¹⁵NO at 100 K. The heating rate is 6 K s⁻¹.

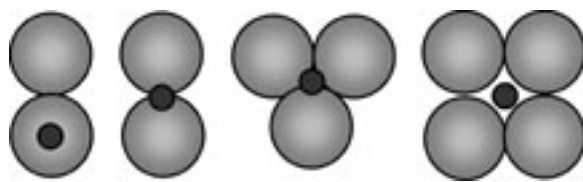


Fig. 3. On-top, bridge and hollow sites location of O_{ads} on the (111), (110) and (100) surfaces.

TABLE 1

Calculated heats of oxygen adsorption ΔH , kcal/mol

On-top	Bridge	Hollow	Hollow	Cluster
-2.5	18	29	35	Octahedron
-4.5	15	26		Icosahedron

the stability of palladium nanoparticles and Pd(110) single crystal surface reconstruction. The simulation has shown that the most energy favorable states for palladium are the multiple bonded states of atomic O_{ads} in the structures Pd_3-O_{ads} and Pd_4-O_{ads} as shown in Fig. 3. The adsorption heat of oxygen in multiple bonded states Pd_4-O_{ads} (hollow) is much higher in comparison with Pd_2-O_{ads} (bridged) state: this species is likely to exist in the initial steps of adsorption as an intermediate state which converts into the more multiple bonded forms (Table 1).

Using MIB, for the first time the morphological convertibility of palladium nanoclusters under the influence of the O_{ads} adlayer has been revealed. In accordance with simulations the most stable cluster configuration for the 13-atomic cluster is the regular icosahedron. But adsorption of 9 oxygen atoms in the Pd_3-O_{ads} and Pd_4-O_{ads} states is accompanied by the structure

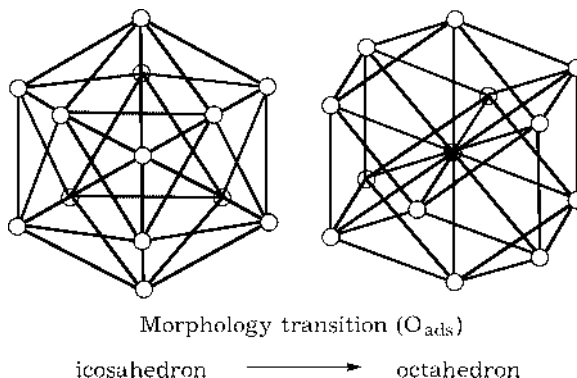


Fig. 4. The equilibrium configurations of the icosahedron and cuboctahedron clusters.

transition and by transformation of the icosahedron into the cuboctahedron as shown in Fig. 4. That is of special interest in oxidative catalysis because of the morphological stability of nanoclusters in oxygen presence. The six-oriented metal cluster has been shown to be the most stable for the 20-atomic cluster in toroidal structure. The adsorption of 17 oxygen atoms leads to the reconstruction of the six-oriented 20-atomic cluster into the four-oriented one. Taking into account the interactions of the palladium atoms situated in the second and third cluster layers with the upper layer of the metal atoms, the drastic decrease of the oxygen atoms concentration has been observed (up to 6 O_{ads} atoms) resulting in the reconstruction of the 20-atomic cluster into the four-oriented one. The same result was obtained for Pd(110) plane: adsorption of 0.5 ML (1 ML = $9.4 \cdot 10^{14}$ atom/cm²) of oxygen results to reconstruction: (1×1) → (1×2) of “missing-row” structure (Fig. 5) with agreement of well known results [2].

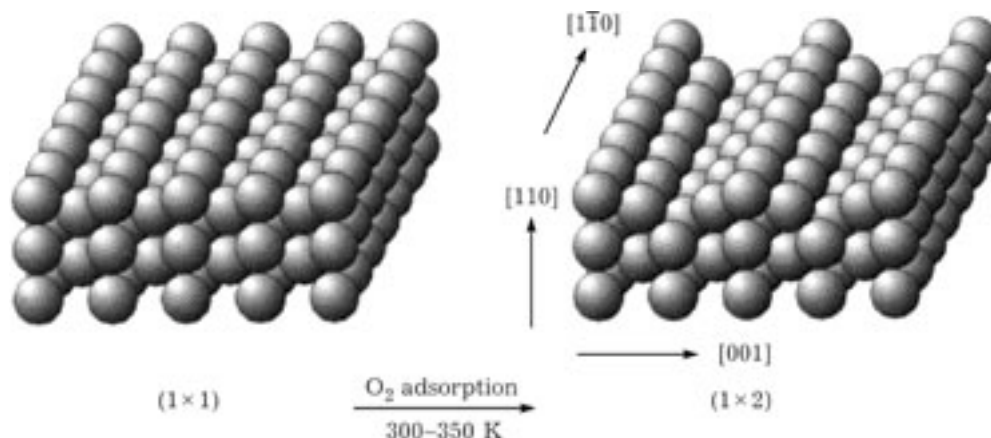


Fig. 5. Reconstruction of the Pd(110)-(1×1) surface into the (1×2) “missing-row” structure.

$O_{ads} + NO$ coadsorption

Experimentally an effect of oxygen preadsorption has been studied at an initial coverage of oxygen and NO applying both adsorption sequences. Desorption/decomposition processes occurring upon heating of NO layer on clean Pd(110) and O/Pd(110) surfaces can be deduced from Fig. 6, *a*–*b*. As an example in Fig. 6, *b* TD spectra are shown the increase of amount of molecular NO_{ads} states after exposing of O/Pd(110) surface to nitric oxide. Preheating up to 200 K was made for removing of molecular oxygen species from the surface. Two NO desorption peaks are observed at 450 and 290 K and a shoulder occurs at around 200 K. Intensity of N_2 and N_2O peaks in the temperature range where dissociation occurs is

strongly decreased. It has been suggested that the probability of NO dissociation is decreased for oxygen-covered Pd surfaces in comparison to the clean palladium surfaces. Similar results have been observed on the Pd(331) single crystal: small amounts of oxygen block the step sites and inhibit NO dissociation [11].

 $O_{ads} + NO + CO$ coadsorption

Preadsorption of oxygen and nitric oxide on Pd(110) surface has a dramatic effect on the $CO_{ads} + O_{ads}$ reaction at low coverages. Figure 7 shows TPR spectra obtained after $^{18}O_2$ (0.2 L) + ^{15}NO (1 L) exposure on the clean surface, followed by exposure to CO (0.1–0.5 L). Figure 8 shows TPR spectra obtained after $^{18}O_2$ (0.2 L)

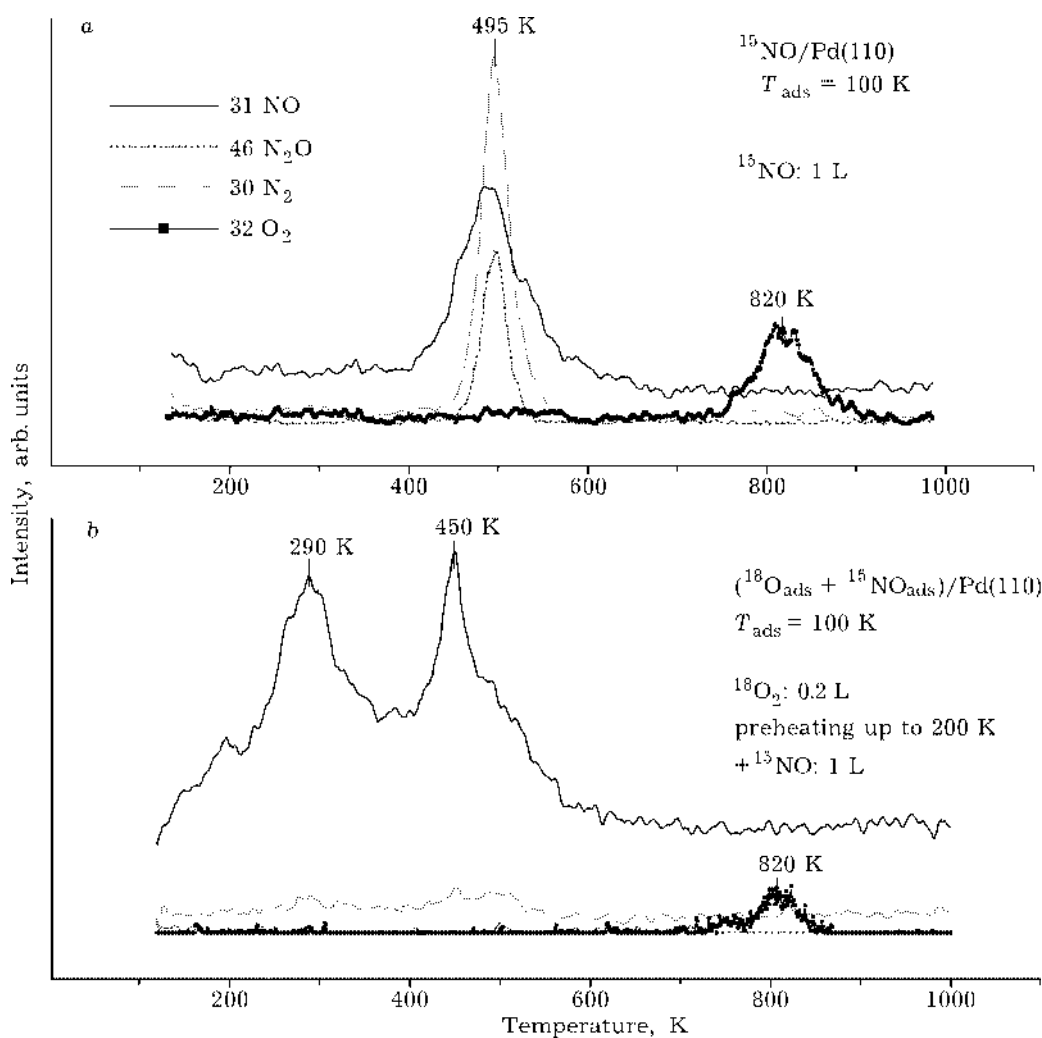


Fig. 6. TD spectra after exposure clean Pd(110) surface to NO at 100 K (a) and of mixed O/NO layers at fixed oxygen 0.2 L preexposure surface (b).

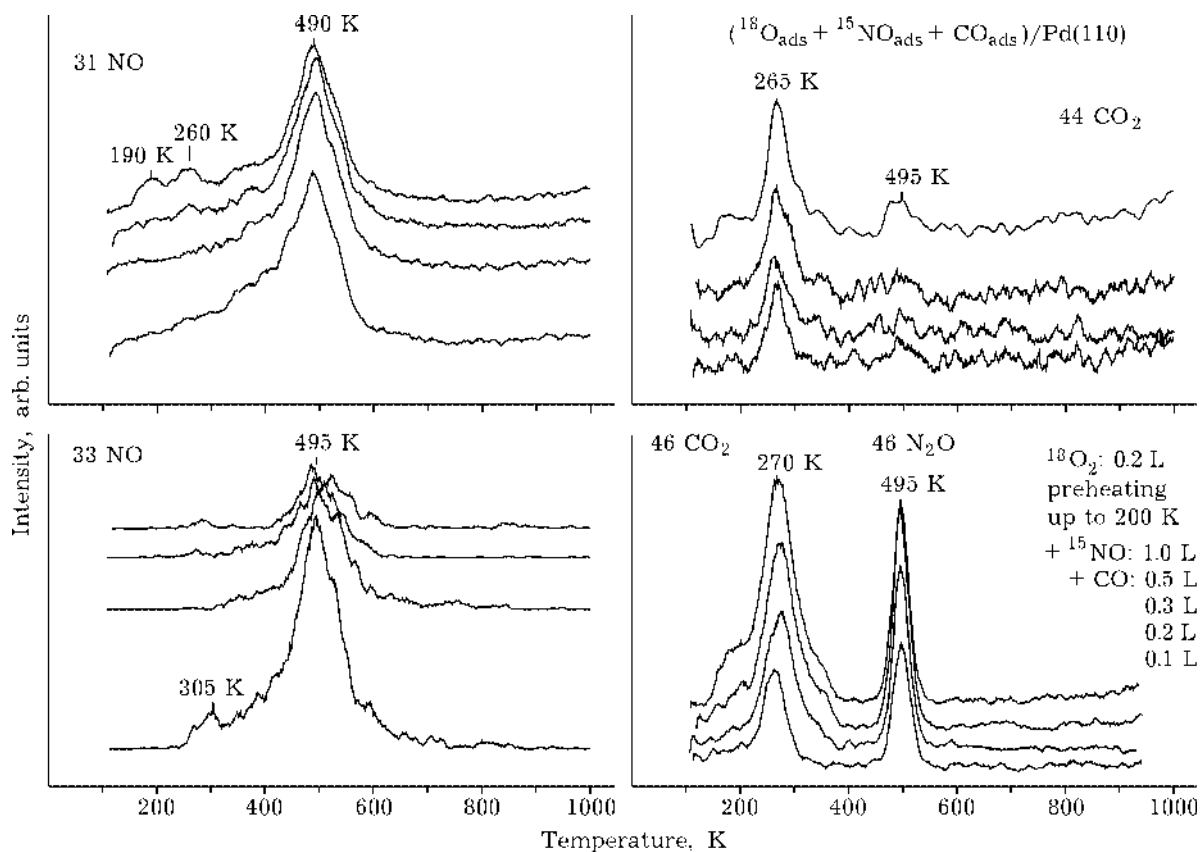
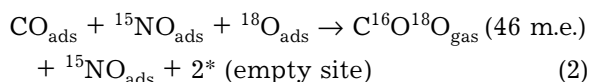
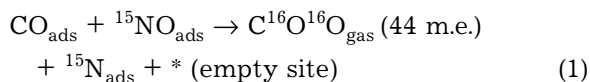


Fig. 7. TPR spectra after exposure of mixed O/NO layers at fixed oxygen 0.2 L and nitric oxide 1 L preexposure Pd(110) surface to CO at 100 K. Peak at 270 K in 46 mass spectra corresponds to CO₂, peak at 495 K – to N₂O.

+ ¹⁵NO (0.1–1 L) exposure on the clean surface, followed by exposure to 0.1 L CO. Comparing the spectra in Figs. 2, 7 and 8, we see new CO₂ peak at 265 K. The low temperature production of carbon dioxide molecules is due to the reactions:



In summary the low temperature CO_{ads} + ¹⁵NO_{ads} interaction on a precovered layer of atomic oxygen on the Pd(110) surface shows a possibility of realization of bimolecular reaction mechanism.

DISCUSSION

Several mechanisms have been proposed in the literature for the “surface explosion” over

platinum metals [13–15]. The 1×1 ↔ hex structural phase transition is proposed on (NO + CO)/Pt(100) [15]. Since no structural phase transition was observed over Pd(100) single crystal surface, a “vacancy model” mechanism has been proposed [14, 15].

It has been shown that the NO_{ads} dissociation on the Pd(100) and Pd(110) surfaces requires the adjacent vacant adsorption sites. A clean-off reaction between CO_{ads} and O_{ads} results in the CO_{2gas} formation; then a recombination of two N_{ads} atoms leading to the N₂ formation occurs accompanied by the release of the vacant adsorption sites, necessary for the dissociation of further NO_{ads} molecules and for the CO adsorption. It can be seen on Fig. 2, that formation of N₂ and N₂O begins with desorption of CO – during the desorption of CO new vacant sites appear and it induces the dissociation of NO. This behavior as well as narrow peak of CO₂ in TPR spectra points at the “explosive” reaction mechanism, which is described as follows:

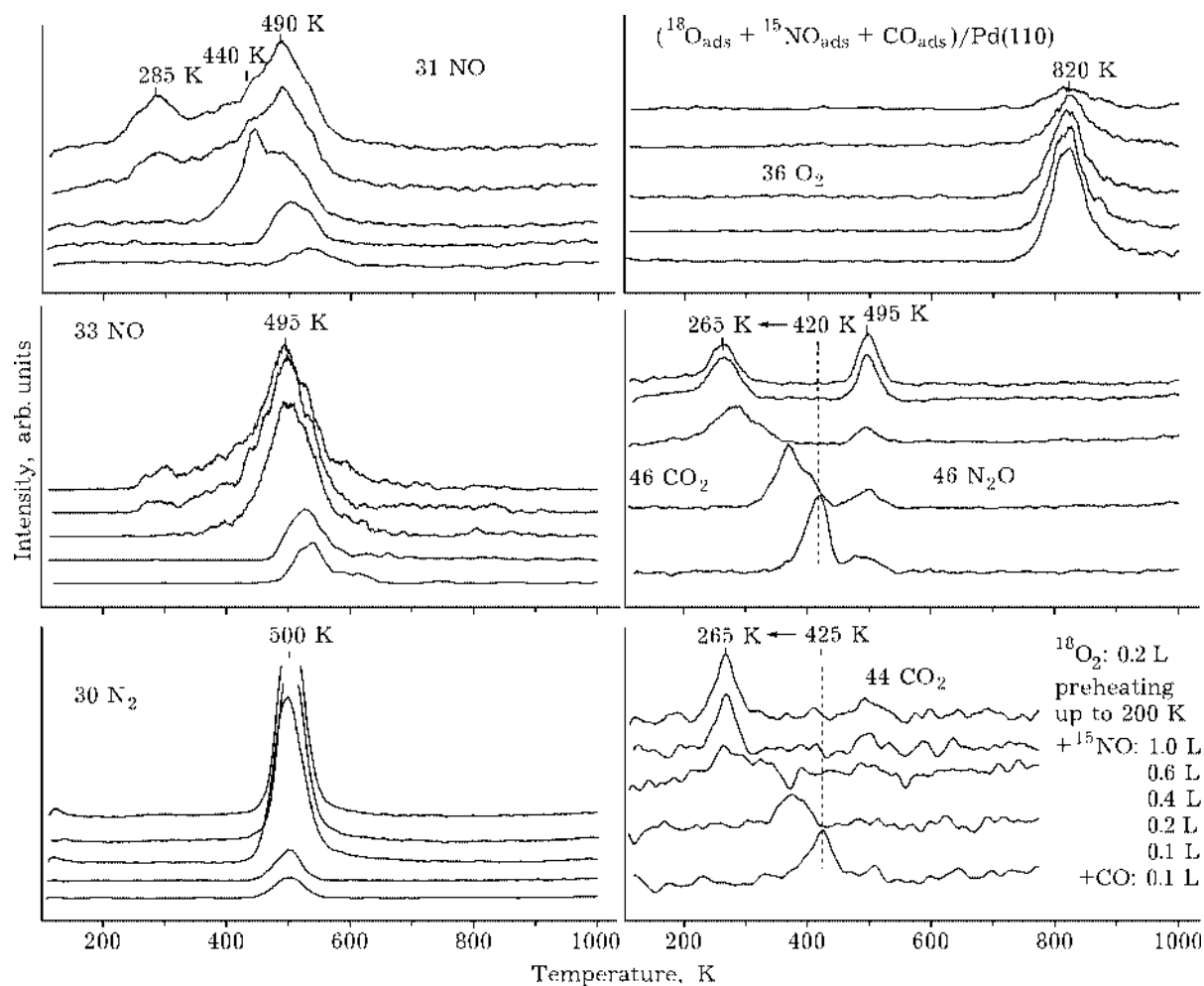
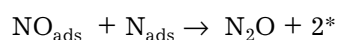
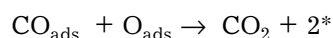
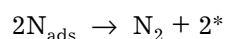
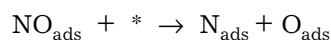
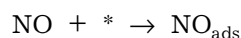
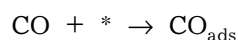


Fig. 8. TPR spectra after exposure of mixed O/NO layers at fixed oxygen 0.2 L and nitric oxide preexposure Pd(110) surface to 0.1 L CO at 100 K. Shifting peaks at 420–270 K in 46 mass spectra corresponds to CO₂, peaks at 495 K – to N₂O.



Preadsorption of oxygen on Pd(110) surface decreases the probability of NO dissociation. From another side, it can be seen from Fig. 8, in system O_{ads} + CO_{ads} + NO_{ads}, NO_{ads} increases the rate of CO_{ads} + O_{ads} reaction.

The unreconstructed Pt(100)-(1×1) surface shows a high activity in the NO_{ads} + CO_{ads} reaction accompanied by N₂ and CO₂ peaks formation (350 K). The reconstructed Pt(100)-hex surface appears to be less active under the same

conditions (395 K). The Pd(110) surface shows a low activity (460–482 K). The 1×1 ↔ hex phase transition is related with the “surface explosion” on (NO_{ads} + CO_{ads})/Pt(100). Since no reversible structural phase transition was observed on the Pd(110) surface, the low activity of palladium is considered to reflect the different bonding energy of oxygen and nitrogen adatoms for Pt and Pd surfaces.

CONCLUSION

We have studied the reaction between ¹⁵NO_{ads} and CO_{ads} molecules on the Pd(110) single crystal surface by temperature-programmed reaction spectroscopy. The effect of the metal particle size on catalytic properties has been studied using the semiempirical method of

interacting bonds by calculating the heats of adsorption of O₂ and NO in a dissociative form on the Pd(110) and Pd nanocrystals. The addition of oxygen was found to inhibit the process of NO dissociation. Exposure of NO and CO on oxygen preadsorbed layer results in appearing of low-temperature peak of CO₂ in TPR spectra at 265 K, which can be explained by increasing of CO_{ads} + O_{ads} rate in presence of NO_{ads}.

Acknowledgement

This work is supported in part by RFBR Grant No. 02-03-32568, 02-03-06246, INTAS Grant No. 99-01882 and Zamaraev International Charitable Scientific Foundation.

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