Catalysis Letters 28 (1994) 153–160

HREELS/TDS study of NO reaction with hydrogen on Pt(100) surface

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Received 6 December 1993; accepted 30 June 1994

NO adsorption on a Pt(100)-(hex) surface and NO_{ads} reaction with hydrogen at 300 K have been studied by HREELS, LEED, TDS and isothermal desorption. NO adsorbs in molecular form, its molecules gathering in islands with a high local coverage. Surface reconstruction into a (1 × 1) phase proceeds within the boundaries of islands. Reaction $NO + H_2$ is performed via NO_{ads} previous heating in vacuum at $T_h = 375–425$ K. Kinetics of NO_{ads} titration appears to be autocatalytic. Nitrogen is the major reaction product.

Keywords: platinum; $NO + H_2$ reaction; autocatalysis; surface reconstruction

1. Introduction

The mechanisms of NO adsorption and hydrogen or CO reduction attract considerable attention with regard to the fundamentals of heterogeneous catalysis by metals. The ability of NO to dissociate is known to depend on both chemical properties and structure of the metal surface [1]. With this regard, NO reactions on Pt(100) are of evident interest since this face can exist as two structural phases [2]. The well-annealed and clean Pt(100) surface prepared by conventional methods under UHV-conditions is reconstructed and characterized by pseudo-hexagonal (hex) or (5 × 20) phase. A clean un-reconstructed (1 × 1) surface obtained by a special procedure [2] remains stable up to 390 K but turns irreversibly to the (hex) phase under heating at $T > 390$ K. The (hex) phase and the (1 × 1) phase show pronounced adsorption abilities. Meanwhile, NO_{ads} dissociation is observed on Pt(100)-(1 × 1) only [2,3].

The surface reconstruction of Pt(100) is agreed to be somewhat responsible for the kinetic peculiarities of $NO + H_2$ and $NO + CO$ reactions such as reaction rate oscillations [4–6]. Thermal desorption from the mixed adlayers $NO_{ads} + CO_{ads}$ and $NO_{ads} + H_{ads}$ produces extremely sharp peaks of CO_2 and N_2. This phenomenon is known as "surface explosion" associated with autocatalytic behaviour of reaction systems [7–9].

In this work an autocatalytic reaction NO + H_2 is studied when NO_{ads} is titrated by hydrogen. The study is carried out by HREELS, LEED, TDS and isothermal desorption methods.

2. Experimental

Experiments have been conducted in a VG ADES-400 spectrometer (residual pressure $<5 \times 10^{-10}$ Torr). A monochromatic electron gun EMU-50 and 150°-hemispheric analyzer were used for HREELS. In-specular loss spectra were measured using electron beams with a kinetic energy of ca. 2.5 eV, an incident current of ca. 5×10^{-11} A and at an incident angle of ca. 45° with respect to the surface normal. Intensity and resolution for elastic peak made up 10^5 cps and 6.5 meV (50 cm^{-1}), respectively. TD spectra were obtained using a quadrupole mass-spectrometer VG QXK-400 at a heating rate of ca. 12.5 K/s. A 4-grid LEED system from VG was used to give diffraction patterns.

A platinum crystal was (100)-oriented within 0.5°. The crystal was spot-welded between two tungsten wires; it can be heated up to 1200 K by the current passing through the wires. Temperature was measured by the Cr/Al thermocouple spot-welded to the crystal edge. A signal from the thermocouple was used as a feedback input for the heating control unit. Cleaning included annealing in oxygen, vacuum and Ar^+-etching. The surface cleanliness was tested by HREELS, TDS and LEED. H_2, D_2 and nitric oxide labeled with ^{15}N were used.

3. Results

A saturated NO_{ads} layer was prepared by NO adsorption on the Pt(100)-(hex) surface at room temperature and exposure of ca. 5.4 L (1 L = 10^{-6} Torr s). It was found [3,10,11] that two molecular NO states exhibit the bands of ν(NO) stretchings at 1620 and 1760 cm^{-1} (fig. 1A). These spectra also show the low frequency mode at 370 cm^{-1} that results from the Pt–N–O bending vibration [3]. According to LEED, the NO adsorption removes the surface reconstruction. However, integral order beams in the (1×1) are broad and fractional order beams provided by the (5×20) pattern fade strongly but are still visible. Thus some residual reconstruction within the areas unoccupied by NO_{ads} islands remains after adsorption up to the surface saturation. TD spectra for the saturated layer show NO (370–500 K), N_2 (400–500 K) and O_2 (690 K) desorptions similar to those described in refs. [10,12]. N_2 and O_2 are produced in the ratio of 1 : 1. According to ref. [13], NO_{ads} coverage in the saturated adlayer is equal to 0.38 ML (1 ML = 1 monolayer = 1.28×10^{15} cm^{-2}).

NO_{ads} desorption starts at 375 K. At this temperature, the intensity of the band at 1760 cm^{-1} decreases (fig. 1B). Some NO_{ads} dissociation is observed provided

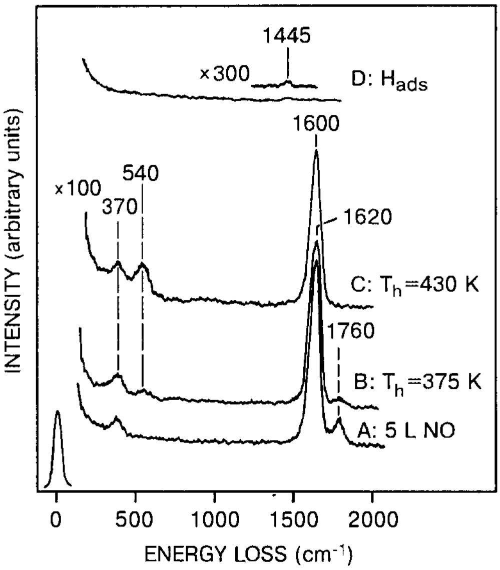

Fig. 1. HREELS spectra of the Pt(100)-(hex) surface saturated by NO at 300 K (A) and followed by heating in vacuum at 375 K (B) and 430 K (C). Spectrum D is given by the H_{ads}/Pt(100)-(1 × 1) resulted from the NO_{ads} titration by hydrogen.

for a ν(Pt–O) band at 540 cm^{-1} [3,11]. When the temperature attains 430 K, the ν(NO) of the major band shifts to 1600 cm^{-1} (fig. 1C). The intensity of the band at 540 cm^{-1} increases.

For reaction NO + H_2 to proceed the saturated NO_{ads} should be previously heated at $T > 375$ K. Under this condition a portion of NO_{ads} molecules escapes from the surface. After NO is re-cooled to room temperature, a subsequent addition of hydrogen results in a decrease of NO_{ads} coverage. Fig. 2 shows a set of ^{15}NO, $^{15}N_2$ and H_2 TD spectra obtained in the course of NO_{ads} titration. Obviously, when hydrogen exposure exceeds 3.5 L a slow stage turns to a fast stage characterized by a complete NO_{ads} removal followed by the hydrogen adsorption. The H_{ads} coverage by 30-fold exceeds that obtained by the saturation of the clean Pt(100)-(hex) surface by hydrogen at 300 K. Such a high coverage is typical for the un-reconstructed (1 × 1) phase [14]. Indeed, when reaction completes, LEED gives a sharp (1 × 1) pattern revealing no (hex) phase. The loss spectrum of H_{ads} exhibits a band at 1445 cm^{-1} (fig. 1D).

Similar TD spectra are observed in the course of NO_{ads} titration by deuterium. D_2 exposure needed for the same conversion differs from H_2 exposure by a factor $\sqrt{2}$. This agrees well with the ratio of incident numbers, $n_{H_2} : n_{D_2}$, determined at the same exposure.

Fig. 3 shows the kinetics of NO_{ads} titration at 300 K by deuterium, obtained from TD data, corresponding to three different pre-heating temperatures $T = 375$, 400 and 425 K. Coverage θ_{NO} is determined from the $^{15}N_2$ and ^{15}NO TD peak

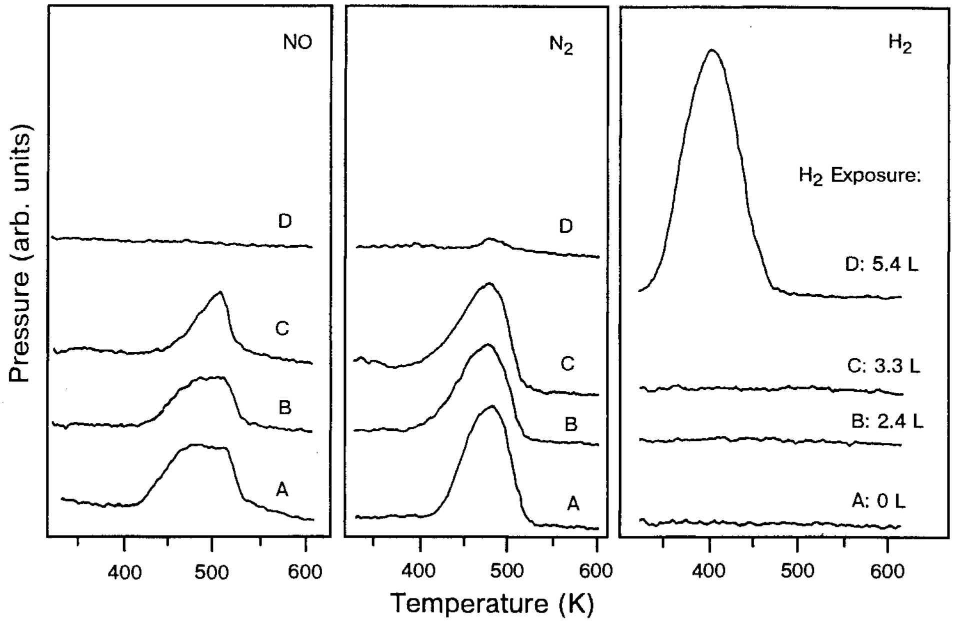

Fig. 2. ^{15}NO ($m/e = 31$), $^{15}N_2$ ($m/e = 30$) and H_2 ($m/e = 2$) desorption spectra at NO_{ads} titration by hydrogen at 300 K. The initial NO_{ads} layer is prepared by the saturation of the Pt(100)-(hex) surface at 300 K and NO exposure of 5.4 L followed by heating in vacuum at $T = 375$ K for 1 min. The heating rate is 12.5 K/s.

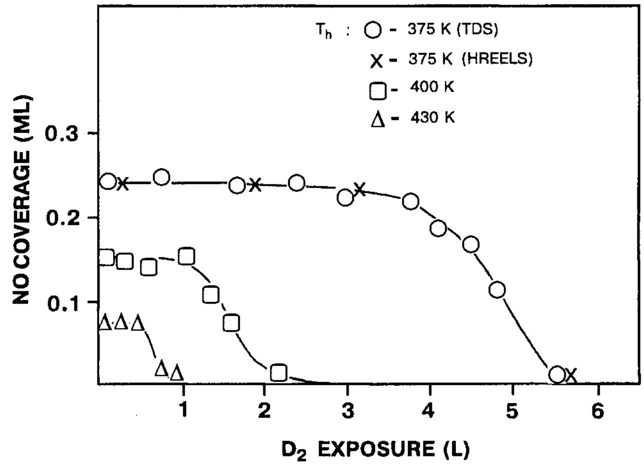

Fig. 3. The kinetic curves for NO_{ads} titration by deuterium at 300 K. The initial NO layers are prepared by the saturation of the Pt(100)-(hex) surface with NO at 300 K followed by heating in vacuum at $T_h = 375$, 400 and 425 K. Coverages, θ_{NO}, are determined from the NO and N_2 TD-peak areas (see the text). The HREELS-data are presented in arbitrary units.

areas with regard to stoichiometry, $\theta_{NO} \approx S_{NO} + 2S_{N_2}$, the saturation coverage at 300 K is $\theta_{NO} = 0.38$ ML [13]. Kinetic curves exhibit a nearly constant NO_{ads} coverage at the early stage followed by a steep decline to the point of disappearance, suggesting an autocatalytic reaction mechanism. Inflection point shifts to lower exposures with T_h raise. The shape of kinetic curves is confirmed by HREELS-data obtained in the course of NO_{ads} titration for $T_h = 375$ K. Fig. 3 depicts the intensities of the ν(NO) band at 1620 cm^{-1} expressed in arbitrary units. D_{ads} layers formed after reaction completion had the same coverages for all three T_h. Gas phase analysis by mass-spectrometry, performed during NO_{ads} titration by hydrogen (deuterium) at 300 K, shows nitrogen to be the main reaction product. Fig. 4 shows $^{15}N_2$ at NO_{ads} titration by deuterium when NO_{ads} is prepared by the saturated adlayer heating at $T_h = 375$ K. The kinetics of nitrogen evolution has a maximum in point in time, $t \neq 0$, confirming the autocatalytic reaction mechanism.

4. Discussion

According to refs. [2,3,10,11] NO adsorbs molecularly on the Pt(100)-(hex) at 300 K. NO molecules gather in islands up to a high local concentration approximate to that of saturated adlayer on the un-reconstructed surface. The surface back reconstruction into (1 × 1) phase occurs within the areas occupied by NO islands [9,15]. The ν(NO) band at 1620 cm^{-1} is assigned to the molecules adsorbed inside the islands. The band at 1760 cm^{-1} may be attributed to NO_{ads} located outside the islands on the defect sites created during the surface reconstruction [10]. It was found that these molecules occupy the island boundary [17].

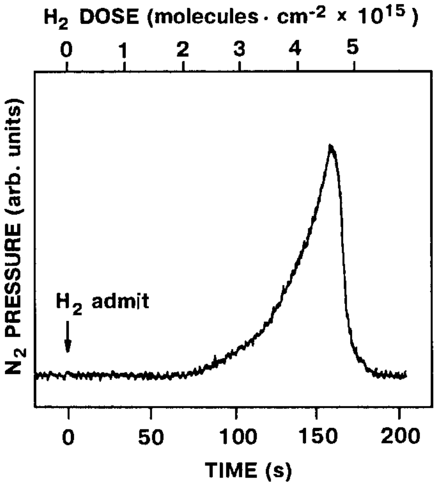

Fig. 4. $^{15}N_2$ evolution in the course of isothermal reaction $NO_{ads} + H_2$ at $T = 300$ K and $P_{H_2} = 4 \times 10^{-8}$ Torr. The initial NO_{ads} layer is prepared by the saturation of the Pt(100)-(hex) with NO followed by the heating in vacuum at 375 K for 1 min.

The saturated NO_{ads} layer prepared on Pt(100)-(hex) is shown schematically in fig. 5A. It is inert to hydrogen because the high NO coverage prevents the dissociative adsorption of H_2 inside the islands. Adlayer heating before the hydrogen admission results in the desorption of some NO molecules and partial NO_{ads} dissociation. Heating is believed to leave an average size of islands disposed on the (1 × 1) areas unchanged (fig. 5B). Hence, in causing the heating at 425 K a decrease of total NO coverage lowers the local coverage θ_{NO}^{lok} inside the islands. It agrees in general with the ν(NO) shift to a lower frequency (fig. 1) that has been found to be caused by a decrease of dipole–dipole interaction between the adsorbed

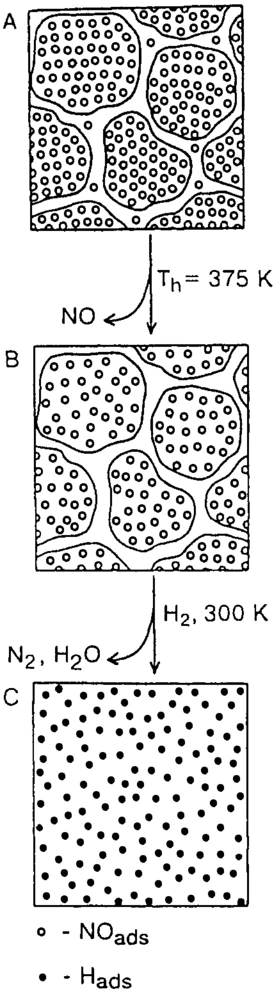

Fig. 5. A schematic view of NO_{ads} layer prepared by the saturation of the Pt(100)-(hex) with NO at 300 K (A) and followed by its heating in vacuum at 375 K (B). C depicts the hydrogen adlayer resulting from B after its reaction with H_2 at 300 K.

molecules [10,16]. Thus, vacant (1 × 1) adsites appear inside the islands. This opens the possibility for (i) dissociative adsorption of hydrogen, and (ii) NO_{ads} dissociation. NO was shown [3] to adsorb dissociatively on the un-reconstructed Pt(100) surface at 300 K and low NO_{ads} coverages. In the reaction course the concentration of vacant adsites on the (1 × 1) areas increases thus accelerating the process. $NO_{ads} + H_2$ reaction proceeds via the autocatalytic mechanism which resembles that proposed in ref. [8] for reaction $NO_{ads} + CO_{ads}$ accomplished during the thermal desorption from the mixed coadsorbed layer.

Reaction is completed by the formation of H_{ads}/Pt(100)-(1 × 1). At this final stage the dim LEED pattern containing the broad integral order beams and residuals from the fractional order beams changes abruptly to the sharp (1 × 1) pattern. The more complete conversion of the (hex) phase into the (1 × 1) phase seems to occur. Indeed, fig. 5C shows the uniform H_{ads} layer and no islands. Note, that H_{ads} layers at saturation are identical and do not depend on the pre-heating temperature T_h (fig. 3). This is consistent with the assumption that NO_{ads} heating at 375–425 K leaves the average island size unchanged. We should have observed the increase of the (hex) phase if the island size had decreased with the increase of T_h. As a consequence, considering that hydrogen weakly adsorbs on the (hex) surface, we should expect coverage θ_H after reaction to fall with the rise of T_h, which is not true. Really, the T_h increase makes NO_{ads} reactivity towards hydrogen increase (see fig. 3) due to the growing initial concentration of vacant adsites with structure (1 × 1).

In conclusion, the titration by hydrogen of NO_{ads} prepared by NO adsorption on the reconstructed Pt(100)-(hex) surface can proceed even at room temperature. A necessary condition is the access to vacant (1 × 1) adsites produced in the initial NO_{ads} layer by its previous heating in vacuum at $T \geqslant 375$ K. At first, reaction occurs with a negligible rate, then accelerates. This tells for the autocatalytic reaction mechanism. The position of the inflection point on the kinetic curve is determined by the initial concentration of vacant adsites, which is closely related to T_h. When reaction is completed the hydrogen adlayer on the un-reconstructed surface, H_{ads}/Pt(100)-(1 × 1), forms at any T_h ranging from 375 to 425 K.

Acknowledgement

This work was supported by the Russian Foundation of Fundamental Studies (Project 93-03-4793) and the International Science Foundation (Grant No. Ch3-6754-0935). We would like to thank Professor J.H. Block (Fritz-Haber-Institute der Max-Planck-Gesellschaft, Berlin) for supplying the Pt crystal.

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