Kinetic isotope effect in the reaction of NO_{ads} and CO_{ads} on the Pt(100) surface

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Received 21 February 1997; accepted 2 May 1997

The reaction of CO with ^{15}NO and ^{14}NO mixtures in a co-adsorption layer on the Pt(100)-(hex) surface was studied by TPR. The kinetic isotope effect (KIE) manifests itself in the variation of the temperature of the maximum of the N_2 desorption peak depending on the isotopic composition: $T_{max}(^{14}N_2) < T_{max}(^{14}N^{15}N) \approx T_{max}(^{15}N_2)$. The KIE observed is consistent with the assumption that the NO_{ads} dissociation is the rate-determining step of the reaction.

Keywords: Pt(100), surface explosion, kinetic isotope effect, TPR, NO, CO

1. Introduction

1.1. *The mechanism of the reaction of NO with CO on the Pt(100) surface*

The catalytic reaction between NO and CO on a Pt(100) surface proceeding in a co-adsorption layer under thermal desorption conditions (temperature-programmed reaction – TPR), leads to a so-called "surface explosion", revealing itself in the extremely narrow desorption peaks of the reaction products – N_2 and CO_2. The full width at half maximum (FWHM) of the TPR peaks lies in the range of 2–15 K [1–4]. The model developed for the explanation of the surface explosion in ref. [3] is based on the fact that the adsorption of carbon monoxide and nitric oxide on a reconstructed Pt(100)-(hex) surface lifts the (hex) reconstruction resulting in the formation of islands of an unreconstructed (1×1) surface phase covered with adsorbed molecules [5–7]. The local coverage of adsorbed molecules within the islands is assumed to be 0.5 ML, whereas the surrounding (hex) phase is nearly free of adsorbed molecules. ($1\ \mathrm{ML} \equiv 1$ monolayer is taken as the number of platinum atoms in the topmost layer on the Pt(100)-(1×1) surface, $1.28 \times 10^{15}\ \mathrm{cm}^{-2}$.) It is suggested that the (1×1) islands containing the mixture of CO_{ads} and NO_{ads} molecules are formed during a concurrent or subsequent adsorption of nitric oxide and carbon monoxide. Fink et al. [3] proposed the following reaction mechanism:

$$NO_g + * \rightarrow NO_{ads}$$

$$NO_{ads} + * \rightarrow N_{ads} + O_{ads}$$

$$CO_{ads} + O_{ads} \rightarrow CO_{2\,g} + 2*$$

$$N_{ads} + N_{ads} \rightarrow N_2 + 2* \qquad (1)$$

where $*$ denotes a vacant adsorption site within the (1×1) island. The NO_{ads} dissociation, which is assumed to be the rate-determining step in the mechanism, can occur exclusively in the presence of vacant adsites. The requisite vacant sites are released by the desorption of NO [3]. The production of CO_2 and N_2 occurs immediately after the dissociation of NO_{ads}. Thus the vacant adsites involved in the rate-determining step are the product of the total reaction:

$$NO_{ads} + CO_{ads} \rightarrow \tfrac{1}{2}N_{2\,g} + CO_{2\,g} + 2*$$

Obviously the reaction rate accelerates with ongoing time causing the development of the surface explosion.

The model proposed in ref. [3] for describing the surface explosion is based on the TPR data. However, the assumptions that the NO_{ads} dissociation is the rate-determining step, was not proved by an experiment directly. On the basis of this result other mechanisms cannot be ruled out, for example a mechanism including the formation of N_2 through the reaction $NO + N \rightarrow N_2$. In early studies of the Rh surface several different groups [8–11] proposed the elementary step:

$$NO_{ads} + N_{ads} \rightarrow O_{ads} + N_2 \qquad (2)$$

based on temperature-programmed desorption (TPD) data from adsorbed NO. Thus it is evident that mechanism (1) needs additional experimental proofs.

1.2. *The kinetic isotope effect in the NO + CO reaction: theoretical estimation*

If NO_{ads} dissociation is the rate-determining step of

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the reaction, the substitution of ^{14}NO by ^{15}NO should result in a kinetic isotope effect (KIE). The KIE may be estimated quantitatively basing on the theory of absolute reaction rate, supposing that in the course of the NO_{ads} dissociation elementary step, the N–O stretching vibration turns into the translation along the reaction coordinate. The stretching ν(NO) frequency of $^{15}NO_{ads}$ is equal to $\nu_{15} = 1570\ \mathrm{cm}^{-1}$ without intermolecular interaction the adsorption layer (for the case of low NO_{ads} coverage) [7,12]. The stretching frequency of $^{14}NO_{ads}$ is $\nu_{14} \approx (\mu_{15}/\mu_{14})^{1/2}\nu_{15} = 1600\ \mathrm{cm}^{-1}$, where μ_{14} and μ_{15} are the reduced masses of ^{14}NO and ^{15}NO, respectively. Assuming that both the pre-exponential factors for the ^{14}NO and ^{15}NO dissociation steps are equal to k_0, the kinetic constants are

$$k_{14} = k_0 \exp\left(-\frac{E^{\neq}_{14}}{kT}\right) = k_0 \exp\left(-\frac{E_0 - \frac{1}{2}h\nu_{14}}{kT}\right),$$

$$k_{15} = k_0 \exp\left(-\frac{E^{\neq}_{15}}{kT}\right) = k_0 \exp\left(-\frac{E_0 - \frac{1}{2}h\nu_{15}}{kT}\right), \quad (3)$$

where $E^{\neq}_{14}$ and $E^{\neq}_{15}$ are the activation energies of the $^{14}NO_{ads}$ and $^{15}NO_{ads}$ dissociation, respectively, E_0 is the potential energy barrier, k is the Boltzmann constant, h is the Planck constant, and T is the absolute temperature. By solving the system of equations (3) the activation energy of the $^{15}NO_{ads}$ dissociation results to be higher than the one of the $^{14}NO_{ads}$ dissociation by a factor of $\sim \frac{1}{2}h(\nu_{14} - \nu_{15})N_A \approx 180$ J/mol, where N_A is the Avogadro constant.

When the surface explosion is initiated in the mixture of $^{14}NO_{ads}$ and CO_{ads}, the rate of the CO_2 and N_2 evolution reaches the maximum at $T_0 \approx 380$ K [3]. Using the condition $k_{14} = k_{15}$ to solve system (3) we may estimate the value T_X of the temperature, corresponding to the maximum of the reaction rate in the $^{15}NO_{ads} + CO_{ads}$ co-adsorption layer, provided that the initial coverage and the heating rate are the same:

$$T_X = T_0 \frac{E_0 - \frac{1}{2}h\nu_{15}}{E_0 - \frac{1}{2}h\nu_{14}}. \quad (4)$$

Substitution of the corresponding values of T_0, ν_{14} and ν_{15} determined above and the value of 120 kJ/mol for E_0 [3] gives $T_X = 380.65$ K, i.e. the explosive TPR peaks of the N_2 reaction products would be expected to shift upwards in temperature by a $\Delta T \approx 0.65$ K substituting $^{14}NO_{ads}$ by $^{15}NO_{ads}$ in the co-adsorption layer.

In this work the surface explosion in co-adsorption layers prepared by subsequent adsorption of CO and isotopic mixtures of $^{14}NO + {}^{15}NO$ on the Pt(100)-(hex) surface was studied by TPR with a high temperature resolution in order to measure the KIE. The experiments were performed in a wide coverage range (θ_{NO} and θ_{CO}) and for both possible sequences of admission of the reactant gases. The KIE was evaluated from the shift of the desorption peak maxima for $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ obtained in the same heating run.

2. Experimental

Experiments were performed in the vacuum chamber of a VG ADES 400 electron spectrometer (base pressure $\leqslant 5 10^{-11}$ mbar). A Pt single crystal oriented along the (100) face within $< 0.5°$ was used. The cleaning procedure was performed according to a conventional technique involving Ar^+ ion etching and annealing in oxygen and in vacuum. The exposure was measured in langmuir (L) (1 L $\equiv 10^{-6}$ Torr s). The temperature was measured by a chromel/alumel thermocouple spot-welded to an edge side of the single crystal. TPR spectra were recorded by means of a VG QXK 400 quadrupole mass-spectrometer supplied with a double cathode assembly and a channeltron detector, using a constant heating rate of 10 K/s. In the range 300–900 K the heating rate deviations were not greater than ± 0.05 K/s.

A self-designed processor controlled device was interfaced to the spectrometer for the acquisition of up to ten different masses and for controlling temperature and heating rate of the sample during the TPR experiments. In order to study the KIE, TPR spectra of $^{14}N_2 + CO$ ($m/e = 28$), $^{14}N^{15}N$ ($m/e = 29$), and $^{15}N_2$ ($m/e = 30$) with a high temperature resolution were recorded using temperature steps between the measured points smaller than 0.2 K. The temperature of the peak maximum was determined by the least-squares method. The value of T_{max} was obtained by averaging ten independent evaluations. Thus an accuracy of ± 0.2 K or better in the determination of the position of the peak could be achieved.

3. Results and discussion

A typical set of TPR spectra, obtained by exposing a clean Pt(100)-(hex) first to CO (0.5 L) and then to ^{15}NO (1.5 L) at 300 K, is shown in figure 1. The evolution of CO ($m/e = 28$), $^{15}N_2$ ($m/e = 30$), ^{15}NO ($m/e = 31$), O_2 ($m/e = 32$), CO_2 ($m/e = 44$) and $^{15}N_2O$ ($m/e = 46$) is observed. The reaction is initiated by the desorption of NO and CO in the range of 355–375 K that, according to the model developed in ref. [3], produces vacant sites within the (1 × 1) islands. As a result of the reaction rate acceleration, the evolution of the products – N_2, CO_2 and N_2O – is observed in the form of very narrow peaks with FWHM ≈ 5–7 K in the range 375–385 K (the so-called "surface explosion" phenomenon). After the surface explosion, the unreacted initial substances and the products of the NO_{ads} dissociation – N_2 and O_2 – are desorbed.

It is easy to see (figure 1), that the NO_{ads} dissociation proceeds to end before complete CO desorption [13–15]. Taking into consideration the very high reactivity of

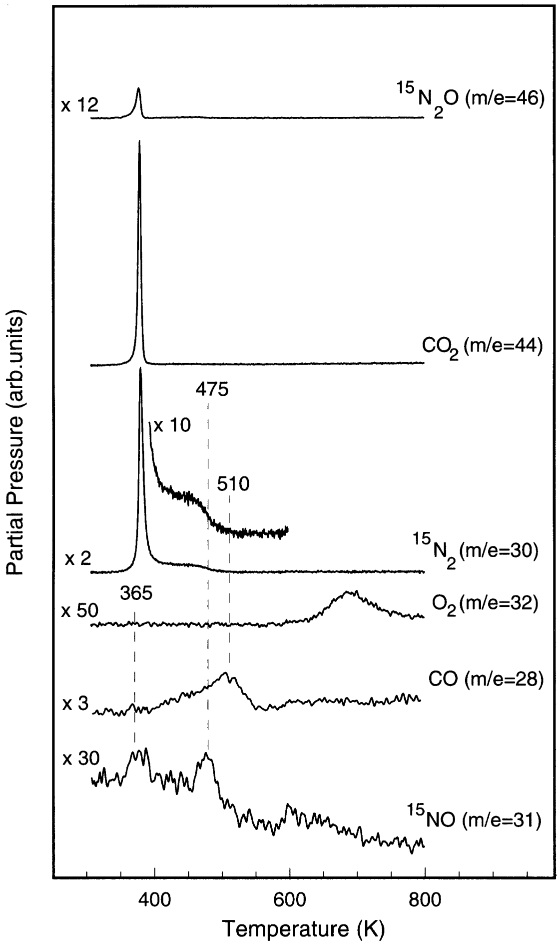

Figure 1. TPR spectra of ^{15}NO ($m/e = 31$), CO ($m/e = 28$), O_2 ($m/e = 32$), $^{15}N_2$ ($m/e = 30$), CO_2 ($m/e = 44$) and N_2O ($m/e = 46$) obtained for the co-adsorption layer prepared via subsequent exposures of 0.5 L of CO and 1.5 L of ^{15}NO on the Pt(100)-(hex) surface at 300 K. The heating rate is 10 K/s.

CO_{ads} towards O_{ads} [16] it is surprising that both carbon monoxide and oxygen are desorbed from the co-adsorption layer as displayed in figure 1. This means that CO_{ads} and O_{ads} coexist on the surface. This fact proves the statistical character of the growth of the adsorption islands of NO or CO, resulting in an excess of NO_{ads} into some of the (1×1) islands or an excess of CO_{ads} into the other (1×1) ones. However, the reaction between CO_{ads} and NO_{ads} takes place independently within each (1×1) island; the islands are separated from each other by the adsorbate-free (hex) phase or by the defects originated at the island boundaries during the (hex) → (1×1) reconstruction.

In order to measure the KIE the reaction between CO and the mixture of ^{15}NO and ^{14}NO (2.5 : 1) was performed in a co-adsorption layer under TPR conditions. The KIE should manifest itself by the shift of the maxima of the $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ desorption peaks. When a clean Pt(100)-(hex) is subsequently exposed to the $^{15}NO/^{14}NO$ mixture (2 L) and CO (1 L) at 300 K, a set of TPR spectra with a high temperature resolution for molecular nitrogen products with different isotopic composition are observed as shown in figure 2 (only the region of the surface explosion is presented). The desorption peak maxima appear at 381.0, 382.7 and 382.5 K for $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$, respectively. The KIE was observed in all experiments performed, regardless of the CO/NO ratio in the adsorption layer, the quantitative isotopic composition of NO and the inlet sequence of NO and CO.

Table 1 presents two experimental data sets where the KIE is clearly pronounced. It is evident that in all measurements T_{max} for $^{14}N^{15}N$ and $^{15}N_2$ coincide within an accuracy of 0.2 K whereas the maxima of the $^{14}N_2$ peaks appear at a 0.6–1.2 K lower temperature. The difference of T_{max} for the $^{14}N_2$ and $^{15}N_2$ peaks agrees with the value roughly estimated by the absolute reaction rate theory described above.

The elementary steps of the NO–CO reaction mechanism for the Rh surface have been discussed attentively in ref. [17]. They are:

$$NO_{ads} + * \rightarrow N_{ads} + O_{ads} \tag{5a}$$

$$CO_{ads} + O_{ads} \rightarrow CO_{2\,g} + 2* \tag{5b}$$

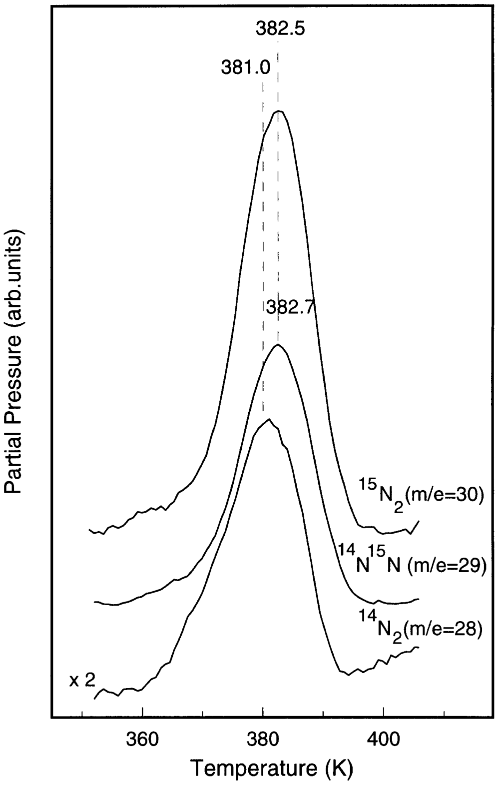

Figure 2. A set of TPR spectra of $^{14}N_2$ ($m/e = 28$), $^{14}N^{15}N$ ($m/e = 29$) and $^{15}N_2$ ($m/e = 30$) with a high temperature resolution for the demonstration of the KIE in the molecular nitrogen production. The initial co-adsorption layer is prepared by subsequent exposures of the $^{15}NO + ^{14}NO$ (2.5 : 1) mixture (2 L) and of CO (1 L) on the Pt(100)-(hex) surface at 300 K. The heating rate is 10 K/s.

Table 1
Temperatures of the desorption peak maxima for $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ measured for $CO_{ads} + NO_{ads}$ co-adsorption layers prepared using different sequences of NO and CO adsorption. Nitric oxide consists of a mixture of ^{14}NO and ^{15}NO (1 : 10)

The first reactant and its exposure	The second reactant and its exposure	$T_{max}(^{14}N_2)$ (K)	$T_{max}(^{14}N^{15}N)$ (K)	$T_{max}(^{15}N_2)$ (K)	$T_{max}(^{15}N_2) - T_{max}(^{14}N_2)$ (K)
CO, 0.5 L	NO, 0.5 L	381.5	382.1	382.1	0.6
CO, 0.5 L	NO, 1 L	380.4	381.3	381.2	0.8
CO, 0.5 L	NO, 1.5 L	378.5	379.6	379.5	1.0
CO, 0.5 L	NO, 2 L	379.5	380.7	380.5	1.0
CO, 0.5 L	NO, 3 L	382.6	383.8	383.7	1.1
CO, 0.5 L	NO, 4 L	384.5	385.6	385.5	1.0
NO, 2 L	CO, 0.5 L	381.6	382.8	382.8	1.2
NO, 2 L	CO, 1 L	382.4	383.3	383.5	1.1
NO, 2 L	CO, 1.5 L	382.9	383.7	383.7	0.8
NO, 2 L	CO, 2 L	384.6	385.7	385.7	1.1
NO, 2 L	CO, 3 L	385.5	386.2	386.2	0.7
NO, 2 L	CO, 4 L	385.6	386.4	386.3	0.7

$$NO_{ads} + N_{ads} \rightarrow N_2O_{ads} + * \qquad (5c)$$

$$NO_{ads} + N_{ads} \rightarrow N_{2\,g} + O_{ads} + * \qquad (5d)$$

$$N_2O_{ads} \rightarrow N_2O_g + * \qquad (5e)$$

$$N_2O_{ads} \rightarrow N_{2\,g} + O_{ads} \qquad (5f)$$

$$N_{ads} + N_{ads} \rightarrow N_{2\,g} + 2* . \qquad (5g)$$

The proposed reaction steps may be used to describe our TPR data presented in figure 1. The main question deals with the determination of the rate-determining step and the ability of N_2 production through the reaction $NO + N \rightarrow N_2$. Four steps can play the role of the rate-determining step: the dissociation of NO_{ads}, step (5a), the formation of N_2O_{ads}, step (5c), the production of N_2 through the reaction between NO_{ads} and N_{ads}, step (5d), the dissociation of N_2O_{ads}, step (5f). Let us assume that step (5c) is the rate-determining step. In this case $^{14}N{-}^{14}NO_{ads}$ and $^{14}N{-}^{15}NO_{ads}$ would be the favourite products, resulting in the evolution of $^{14}N_2$ and $^{14}N^{15}N$ at lower temperature than $^{15}N_2$. However, this N_2 desorption sequence was not observed experimentally. Moreover, this rate-determining step should cause the accumulation of N_{ads} on the surface and thus promote the recombination of nitrogen atoms. Really, the close inspection of TD spectra of the reaction products (figure 1) shows that nitrous oxide ($T_{max} = 376.5$ K) evolves before CO_2 and N_2 ($T_{max} = 377.7$ K and $T_{max} = 379.2$ K, respectively) indicating that N_2O_{ads} is formed rather easily and then, according to ref. [18], desorbs immediately into the gas phase.

The assumption that the N_2O_{ads} dissociation, step (5f), is the rate-determining step, implies the production of a lot of N_2O, in contrast to the insignificant N_2O formation observed in figure 1. The kinetic isotope effect in this case manifests itself in the difference between the amount of energy required in order to break the bond of ^{15}N–O and ^{14}N–O. If the N–O vibration turns into the translation along the reaction coordinate, $^{14}N^{14}NO_{ads}$ and $^{15}N^{14}NO_{ads}$ molecules should dissociate at lower temperature than $^{14}N^{15}NO_{ads}$ and $^{15}N^{15}NO_{ads}$, resulting into the following sequence of appearance of the nitrogen TD-peaks: $T_{max}(^{14}N_2) < T_{max}(^{14}N^{15}N) < T_{max}(^{15}N_2)$. Moreover, $^{14}N^{15}N$ should have a bigger FWHM than $^{14}N_2$ and $^{15}N_2$. Both these facts have been never observed during all experiments.

Finally, if the reaction between NO_{ads} and N_{ads}, step (5d), is the main step of the N_2 production and the rate-determining step, it should result in the evolution of $^{14}N_2$ and $^{14}N^{15}N$ at lower temperature than $^{15}N_2$ for the same reason as described above for step (5c). Thus, the assumption that the dissociation of NO_{ads}, step (5a), is the rate-determining step, agrees with all our experimental data. The same conclusion was made by Belton et al. in ref. [17] who examined the reaction of co-adsorbed nitric oxide and nitrogen atoms on the Rh(111) surface.

4. Concluding remarks

In the light of the assumption that the NO_{ads} dissociation is the rate-determining step a KIE was observed. Thus, in the case of the reaction of CO_{ads} with an isotopic mixture of NO_{ads} in the co-adsorption layer, the desorption of $^{14}N_2$ occurs first, because of the lower activation energy of the dissociation of $^{14}NO_{ads}$ in comparison to $^{15}NO_{ads}$. As the temperature rises, the $^{15}NO_{ads}$ dissociation rate increases causing the appearance of $^{14}N^{15}N$ and $^{15}N_2$ in addition to $^{14}N_2$. Since the $^{14}NO_{ads}$ consumes faster than $^{15}NO_{ads}$, it comes to a point where the $^{14}N^{15}N$ and $^{15}N_2$ evolution rates dominate over that of $^{14}N_2$.

Acknowledgement

The work described in this publication was possible in part due to the support of The Russian Foundation for Fundamental Studies (Project 96-03-33211) and INTAS (Project 93-0964). The authors would like to thank A.M. Badalyan, V.V. Kaichev and D.I. Nikitin for the realisation of the system for the TPR technique processing and V.A. Boronin for the software preparation. One of us (DYZ) would like to thank A. Hornung for help during the preparation of the manuscript.

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