The translational energy of desorbing products in NO and N$_2$O decomposition on Pd (110)

Yuichi Ohno
Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

Kazushi Kimura
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0811, Japan

Ming Bi$^{(b)}$ and Tatsuo Matsushima
Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

(Received 8 December 1998; accepted 22 February 1999)

The angular and velocity distributions of desorbing N$_2$, N$_2$O, and NO molecules were studied in the decomposition of NO and also N$_2$O on a palladium (110) surface by means of angle-resolved thermal desorption combined with cross-correlation time-of-flight techniques. The results were quite similar in both cases although the desorption of N$_2$, N$_2$O, and NO concurrently peaked at 490 K in the NO decomposition and, in the N$_2$O decomposition, the desorption of N$_2$ and N$_2$O peaked at 140 K. The desorption of N$_2$O and NO showed a cosine angular distribution and a Maxwellian velocity distribution at the surface temperature. On the other hand, the N$_2$ desorption collimated sharply at $\pm 41^\circ$--$43^\circ$ off the surface normal in a plane along the [001] direction. Then the velocity distributions of N$_2$ involved two hyperthermal components with the mean translational energy of 0.47 and 0.22 eV, respectively. A mechanism for the inclined N$_2$ desorption was proposed to be due to a highly exothermic reaction of N$_2$O(ad)$\rightarrow$N$_2$(g) + O(ad) and the strong repulsive force operative on the product N$_2$ from the surface. © 1999 American Institute of Physics.

I. INTRODUCTION

The decomposition of NO on noble–metal surfaces is one of the key processes on the actual three-way catalysts for controlling automotive exhausting gases.$^1$ The complete conversion into N$_2$ and O$_2$ is desirable, but it can hardly be achieved because of the outgrowth of other oxides, N$_2$O, etc. Knowledge of the relation of both N$_2$ and N$_2$O formation is requisite for improving such environmental catalysts. A Pd(110) surface is active towards thermal dissociation of NO although the reaction accompanies the emission of both N$_2$ and N$_2$O.$^2$–$^4$ Ikai and Tanaka reported interesting angular distributions of desorbing N$_2$ in the NO decomposition on Pd(110) and proposed the mechanism “desorption-mediated emission.”$^3$ The N$_2$ desorption was concentrated in a plane along the [001] direction and collimated very sharply $37^\circ$ off the surface normal. This inclined desorption was not found in the catalytic reaction of NO and H$_2$ in which the N$_2$ desorption was collimated along the surface normal.

The spatial and velocity distributions of desorbing surface species can yield both the structural and dynamic information of reaction sites and reaction itself when the molecules undergoes strong repulsive force from the surface.$^5$ The molecules being produced are released immediately (within the period of molecular vibration) from the surface before becoming accommodated with the surface. The direction of the repulsive force exerted towards the reaction site normal is preserved in the desorption dynamics. Furthermore, hot atoms or molecules produced in thermal- or photodissociation can participate in the reaction$^6$–$^7$ and, in some cases, induces desorption inclined far from the site normal.$^8$–$^{10}$ The latter desorption may occur whenever the dissociation of admolecules is able to emit translationally hot atoms or molecules.

In this communication, we first report the high velocity of desorbing N$_2$ which peaks at $\pm 41^\circ$–$43^\circ$ off the surface normal in a plane along the [001] direction, in both NO and N$_2$O decompositions on Pd(110). This confirms that N$_2$O(ad) is intermediate species for the conversion of NO into N$_2$. Furthermore, a mechanism for the inclined desorption of N$_2$ is proposed; i.e., the repulsive force is operative towards N$_2$ both from the surface and the remaining oxygen after the N$_2$–O bond rupture because of the high exothermicity in the reaction of N$_2$O(ad)$\rightarrow$N$_2$(g) + O(ad).

II. EXPERIMENT

The experiments were performed in the apparatus described in details elsewhere.$^{11}$ In brief, the UHV system consisted of three chambers; (i) a reaction chamber equipped with LEED-AES optics, an Ar$^+$ gun, and a quadrupole mass spectrometer (M$_1$), (ii) a chopper chamber with a pseudo-random chopper between the slit on each end, and (iii) an analyzer chamber with another mass spectrometer (M$_2$). A Pd(110) sample crystal in a disk-shaped slice (10 mm in diameter $\times$1.0 mm thick) was set on top of an L-shaped manipulator. It could be rotated at the top in order to change the desorption angle (the polar angle denoted as $\theta$). Inaccuracy in the angular determination was $\Delta \theta = \pm 1^\circ$.

For angle-resolved TDS experiments, a clean Pd(110)
surface was exposed to 0.20–0.50 L of $^{15}\text{N}^{16}\text{O}$ (1 Langmuir = $1.0 \times 10^{-6}$ Torr s) around the surface temperature $T_s = 350$ K and then heated at constant rates 5–9 K/s, while the product signals of $^{15}\text{N}_2$, $^{15}\text{N}_2^{16}\text{O}$, $^{15}\text{N}^{16}\text{O}$ were monitored in angle-integrated form by $M_1$, and also in angle-resolved form by $M_2$. For velocity measurements, the flow of product molecules passing the first slit was modulated by the chopper and the arrival time at the ionizer in $M_2$ was registered on a multichannel scaler running synchronously with the chopper blade. Appropriate time resolutions were 15 $\mu$s for $\text{N}_2$ and 30 $\mu$s for both NO and $\text{N}_2\text{O}$, attained with 130.72 and 65.36 Hz of chopper rotation rates, respectively. At low temperature experiments, a clean Pd(110) surface was exposed to 0.20 L of $^{15}\text{N}_2^{16}\text{O}$ below 130 K and then heated at a constant rate 7 K/s. A significant fragmentation of $\text{N}_2\text{O}$ was observed at the filament of $M_1$, with the cracking fraction was $\text{N}_2^{16}\text{O}:\text{NO} = 0.49:1.00:0.37$, meaning that 26% of $\text{N}_2\text{O}$ was converted into $\text{N}_2$, and 20% of $\text{N}_2\text{O}$ into NO. The cracking fraction at $M_2$ in the analyzer chamber was less than that at $M_1$.

III. RESULTS

The desorption of NO peaked at 490 K and was accompanied with the emission of $\text{N}_2$ and $\text{N}_2\text{O}$ when the surface covered by NO was heated. Figure 1(a) shows typical thermal desorption spectra of $\text{N}_2$ in angle-resolved form together with $\text{N}_2\text{O}$ and NO in angle-integrated form when the surface was exposed to 0.50 L of NO around 350 K. The major NO desorption peak was observed at 490 K and two shoulders were found at 380 and 520 K. Only the NO peak at 490 K was accompanied with $\text{N}_2$ and $\text{N}_2\text{O}$ emission. Otherwise, a small oxygen peak was observed around 800 K. These observations indicate that the desorption and the dissociation of NO(ad) proceed simultaneously above 440 K. The desorption of $\text{N}_2$ and $\text{N}_2\text{O}$ reached almost the maximum level at exposures above 0.50 L of NO.

The $\text{N}_2$ desorption was monitored in angle-resolved form at various desorption angles in a plane along the [001] direction. The $\text{N}_2$ signal was suppressed considerably at $\theta = 0^\circ$, whereas it was highly enhanced around $\theta = \pm 41^\circ$ as shown in Fig. 1(a). In fact, the angular distribution of $\text{N}_2$ peaked sharply along the off-normal direction. Figure 2(a) shows the distribution of $\text{N}_2$ emission in polar coordinates which was described as $\cos^n(\theta \pm 41^\circ)$ where $n = 28$. Iki and Tanaka found this inclined desorption as $\cos^n(\theta \pm 37^\circ)$ form with $n=46$. The discrepancy may be due to the difference in angular resolution between the two apparatus. After subtraction of this component, a normally-directed desorption remained in a small amount. The off-normal and sharp beams of $\text{N}_2$ suggest that the strong repulsive force is operative towards both parallel and perpendicular directions to the surface.

The above statement was confirmed by the velocity measurements of desorbing $\text{N}_2$. The velocity distribution observed at the collimation angle is shown in Fig. 2(b). Most of the actual desorbing $\text{N}_2$ molecules were hyperthermal. The experimental distribution curve as well presented by the deconvolution into two fast components, namely, ‘‘$F_1$’’ and ‘‘$F_2$’’. Each component of the distribution curve was described by the modified Maxwellian form as $y(v)dv \propto v^4 \exp\left(-\frac{(v-v_0)^2}{\alpha^2}\right)dv$. The $F_1$ component yielded the width parameter of $\alpha = 333$ m/s, the stream velocity of $v_0 = 1610$ m/s, and the mean translational energy of 0.47 eV or 2700 K in the temperature unit. The $F_2$ component delivered $\alpha = 408$ m/s, $v_0 = 942$ m/s, and the translational energy of 0.22 eV or 1300 K.

On the other hand, the angular distributions of NO and $\text{N}_2\text{O}$ were mostly described as a cosine function. These molecules are considered to be fully accommodated with the surface prior to desorption. This was confirmed further by the velocity measurements. The velocity distribution of desorbing $\text{N}_2\text{O}$ was well described by a Maxwellian distribution at the surface temperature as shown in Fig. 2(b). A similar velocity distribution was also observed for desorbing NO. Both the reactant NO and the product $\text{N}_2\text{O}$ desorb after a surface residence time long enough to be accommodated with the surface. These findings suggest a possibility that the decomposition of $\text{N}_2\text{O}$ is the elementary step to produce $\text{N}_2$ from the NO decomposition.

Furthermore, angular and velocity distributions of $\text{N}_2$ desorbing in the course of $\text{N}_2\text{O}$ decomposition were also studied. When the surface exposed to 0.20 L of $\text{N}_2\text{O}$ below 130 K was heated, the major desorption of $\text{N}_2\text{O}$ was accompa-
enhanced around the inclined direction of $\theta = 43^\circ$ rather than the normal direction. The angular distribution of N$_2$ is shown in Fig. 3(a). It again collimated sharply along the off-normal direction in a plane along the [001] direction. The distribution curve was described as $\cos^n(\theta - 43^\circ)$, where $n = 60 \pm 20$. Otherwise, the component of normally-directed desorption occurred as found in the NO decomposition. Its distribution curve was approximated as $\cos^n \theta$, where $n = 3 \pm 2$.

The velocity distribution of N$_2$ desorbing at $\theta = 43^\circ$ is shown in Fig. 3(b). The distribution was quite similar to that in the NO decomposition. Thus, the velocity distribution again consisted of two fast components, $F_1$ and $F_2$. The parameters yielded were $a = 258$ m/s and $v_0 = 1661$ m/s for the $F_1$ component, and $a = 408$ m/s and $v_0 = 942$ m/s for the $F_2$. The resultant translational temperature for each component was almost identical to that found in the NO decomposition. The contribution of the $F_2$ component was, however, enhanced slightly. The present results support the mechanism that N$_2$ molecules are emitted with an excess translational energy through the decomposition of N$_2$O on the surface.

FIG. 2. (a) Angular distributions of N$_2$ desorbing from a NO adsorbed Pd(110) surface. The relative peak height of N$_2$ is plotted in polar coordinates for the exposure to NO at 0.50 L (closed circles) and at 0.20 L (open triangles). The fitting curve (full line) is obtained by the deconvolution with the functions $\cos^{5\theta}(\theta = 41^\circ)$ and $\cos^3 \theta$, the latter being drawn by a broken line. (b) Velocity distributions of desorbing N$_2$ at $\theta = 41^\circ$ (closed circles) and N$_2$O at $\theta = 0^\circ$ (open circles). The fitting curve for N$_2$ (full line) was obtained by the deconvolution with two modified Maxwellian forms (broken lines). A Maxwellian distribution at the surface temperature is drawn for N$_2$O (dotted line).

FIG. 3. (a) Angular distribution of N$_2$ desorbing from a N$_2$O adsorbed Pd(110) surface. The relative peak height for N$_2$ at 0.20 L exposure to N$_2$O is plotted in polar coordinates (closed circles). The fitting curve (full line) was obtained by the deconvolution with the functions $\cos^{5\theta}(\theta = 41^\circ)$ and $\cos^3 \theta$ (broken lines). (b) Velocity distribution of desorbing N$_2$ at $\theta = 43^\circ$ (closed circles). The fitting curve (full line) was obtained by the deconvolution with two modified Maxwellian forms (broken lines). A Maxwellian distribution at the surface temperature is also drawn (dotted line).

IV. DISCUSSION

At low coverage of NO and at room temperature, a Pd(110)(2×1)–NO structure was confirmed by LEED, IRAS, and NEXAFS studies, indicative of NO adsorbed on the short bridge site on a Pd(110) surface that has undergone no substantial reconstruction. No dissociation of NO occurs below 440 K. With increasing surface temperature, a part of NO is desorbed and the remaining NO is dissociated to N(ad) and O(ad). NO admolecules migrate with a high mobility above room temperature and are likely to react rapidly with N(ad) and produce N$_2$O(ad). A part of the product N$_2$O(ad) desorbs thermally after full accommodation with the surface. Remaining N$_2$O(ad) is decomposed into N$_2$(g) and O(ad). N$_2$O admolecules are actually formed from NO(ad) and N(ad) at temperatures as low as 100 K on platinum.

The product N$_2$ is expected to carry away a high translational energy because the heat of decomposition of N$_2$O(ad)$\rightarrow$N$_2$(g) + O(ad) is highly exothermic by about $-46$ kcal/mol. This was estimated from the fact that the reaction in the gas phase, N$_2$O(g)$\rightarrow$N$_2$(g) + O(g), is endothermic by about $+39$ kcal/mol (Ref. 17) and the heat of formation of Pd–O bond is exothermic by about $-85$ kcal/mol. Furthermore, the activation energy for the N$_2$–O bond rupture on the surface was estimated to be of about 9 kcal/mol from the TDS peak temperature in the present work. This amounts to the heat of adsorption of N$_2$O. It is highly possible that a part of the heat of decomposition of N$_2$O(ad) is released and
partitioned into the translational mode of desorbing N₂ as well as the internal mode of the molecule.

The gaseous N₂O is a linear molecule. A possible geometry of N₂O at the instant of decomposition is drawn in Fig. 1(c), where the bond length of gaseous N₂O and a nondistorted Pd(110) surface are assumed. The size of N₂ molecule in a physical adsorption state is also shown by assuming the radius of 2.0 Å.²¹,²² N₂O molecules are adsorbed in a highly-inclined and linear form through the nitrogen end on Pt(111).¹⁹ The molecule is forced to lie on the surface prior to decomposition and then the oxygen is left on the adsorption site when the N₂–O bond rupture takes place. At the instant when this bond rupture is finished, the nascent N₂ molecules receive the strong Pauli repulsion in the direction normal to the surface in addition to the force of bond rupture parallel to the surface. This is because the position of the N–N portion of the molecule is in close contact with the surface compared with the equilibrium position of the physical adsorption or the weakly chemisorbed state of N₂.²¹,²² Eventually the molecule will leave the surface in the direction inclined from the surface normal.

The energy transfer to desorbing N₂ is reminiscent of the multidirectional desorption of O₂(ad) in a photoinduced reaction.¹⁰ In the latter, a hot atom emitted along the bond orientation of oxygen admolecules collides with neighboring O₂(ad). The direction of resultant desorption is controlled by the momentum transfer from the hot atom and also from the repulsive force operative along the surface normal. The latter force is induced by the change of surface electronic structure due to the formation of the Pt–O bond.²³ The collimation is shifted far from the surface normal when the former momentum transfer is significant. The decomposition of N₂O is analogous to the reaction mentioned above, since an excess amount of energy is released whenever N₂–O bond rupture takes place.

The dissociation step of NO(ad) is considered to be rate-determining in the NO conversion into N₂ and O₂ on Pd(110). This is confirmed from the fact that the reaction of NO(ad)+N(ad)→N₂O(ad) proceeds rapidly even around 100 K.¹⁹ and the decomposition of N₂O(ad)→N₂(g)+O(ad) occurs at temperatures as low as 140 K on Pd(110). The N₂O molecules formed in this way stay on the surface for a while enough to be thermalized. Then, some of the admolecules desorbs in to the gas phase, yielding a cosine angular distribution and a Maxwellian velocity distribution at the surface temperature. The other admolecules are likely to be oriented parallel the the [001] direction and watch for a chance to surmount the activation barrier for the decomposition into N₂(g) and O(ad). Thus, the reaction pathway for the NO decomposition on Pd(110) can be summarized as follows:

\[ \text{NO(ad)} \rightarrow \text{N(ad)} + \text{O(ad)}, \]  
\[ \text{NO(ad)} + \text{N(ad)} \rightarrow \text{N₂O(ad)}, \]  
\[ \text{N₂O(ad)} \rightarrow \text{N₂(g)} + \text{O(ad)}, \]  
\[ \text{N₂O(ad)} \rightarrow \text{N₂O(g)}, \]  
\[ 2\text{O(ad)} \rightarrow \text{O₂(g)}. \]