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The translational energy of desorbing products in NO and N₂O decomposition on Pd (110)

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The angular and velocity distributions of desorbing N₂, N₂O, and NO molecules were studied in the decomposition of NO and also N₂O 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 N₂, N₂O, and NO concurrently peaked at 490 K in the NO decomposition and, in the N₂O decomposition, the desorption of N₂ and N₂O peaked at 140 K. The desorption of N₂O and NO showed a cosine angular distribution and a Maxwellian velocity distribution at the surface temperature. On the other hand, the N₂ desorption collimated sharply at $\pm 41^\circ$ – 43° off the surface normal in a plane along the [001] direction. Then the velocity distributions of N₂ involved two hyperthermal components with the mean translational energy of 0.47 and 0.22 eV, respectively. A mechanism for the inclined N₂ desorption was proposed to be due to a highly exothermic reaction of N₂O(ad)→N₂(g)+O(ad) and the strong repulsive force operative on the product N₂ from the surface. © 1999 American Institute of Physics.
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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 N₂ and O₂ is desirable, but it can hardly be achieved because of the outgrowth of other oxides, N₂O, etc. Knowledge of the relation of both N₂ and N₂O 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 N₂ and N₂O.^{2–4} Ikai and Tanaka reported interesting angular distributions of desorbing N₂ in the NO decomposition on Pd(110) and proposed the mechanism “desorption-mediated emission.”³ The N₂ desorption was concentrated in a plane along the [001] direction and collimated very sharply 37° off the surface normal. This inclined desorption was not found in the catalytic reaction of NO and H₂ in which the N₂ 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 N₂ which peaks at $\pm 41^\circ$ – 43° off the surface normal in a plane along the [001] direction, in both NO and N₂O decompositions on Pd(110). This confirms that N₂O(ad) is intermediate species for the conversion of NO into N₂. Furthermore, a mechanism for the inclined desorption of N₂ is proposed; i.e., the repulsive force is operative towards N₂ both from the surface and the remaining oxygen after the N₂–O bond rupture because of the high exothermicity in the reaction of N₂O(ad)→N₂(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 (M₁), (ii) a chopper chamber with a pseudo-random chopper between the slit on each end, and (iii) an analyzer chamber with another mass spectrometer (M₂). A Pd(110) sample crystal in a disk-shaped slice (10 mm in diameter ×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 θ). 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 = 1.0×10^{-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 μs for N_2 and 30 μs for both NO and N_2O , attained with 130.72 and 65.36 Hz of chopper rotation rates, respectively.¹²

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 N_2O was observed at the filament of M_1 .¹³ The cracking fraction was $\text{N}_2:\text{N}_2\text{O}:\text{NO}=0.49:1.00:0.37$, meaning that 26% of N_2O was converted into N_2 , and 20% of N_2O 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 N_2 and N_2O when the surface covered by NO was heated. Figure 1(a) shows typical thermal desorption spectra of N_2 in angle-resolved form together with N_2O 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 N_2 and N_2O emission. Otherwise, a small oxygen peak was observed around 800 K. These observations indicate that the desorption and the dissociation of $\text{NO}(\text{ad})$ proceed simultaneously above 440 K. The desorption of N_2 and N_2O reached almost the maximum level at exposures above 0.50 L of NO .

The N_2 desorption was monitored in angle-resolved form at various desorption angles in a plane along the $[001]$ direction. The 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 N_2 peaked sharply along the off-normal direction. Figure 2(a) shows the distribution of N_2 emission in polar coordinates which was described as $\cos^n(\theta \pm 41)$ where $n=28$. Ikai and Tanaka found this inclined desorption as $\cos^n(\theta \pm 37)$ form with $n=46$.^{2,3} 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 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 N_2 . The velocity distribution observed at the collimation angle is shown in Fig. 2(b). Most of the actual desorbing N_2 molecules were hyperthermal. The experimental distribution curve as well presented by the deconvolution into two fast components, namely, “ F_1 ” and

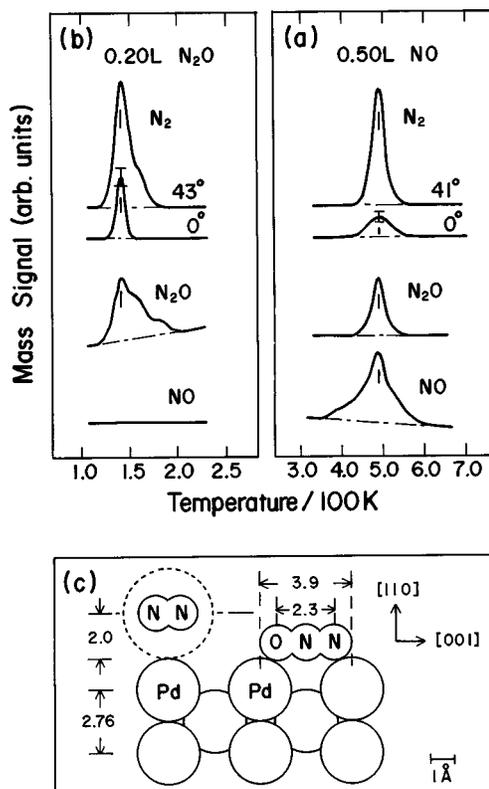


FIG. 1. (a) Thermal desorption spectra of N_2 in angle-resolved forms and N_2O and NO in angle-integrated forms, observed when a Pd(110) surface was exposed to 0.50 L of NO around 350 K. (b) Desorption spectra of the three species after 0.20 L exposure to N_2O below 130 K. The desorption angle is in a plane along the $[001]$ direction. (c) Geometry of N_2O at the instant of decomposition on Pd(110). The size of N_2O is referred to a gaseous molecule. The broken circle indicates the N_2 molecule estimated from van der Waals radius.

“ F_2 ”. Each component of the distribution curve was described by the modified Maxwellian form as $y(v)dv \propto v^4 \exp[-(v-v_0)^2/\alpha^2]dv$.⁵ 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 N_2O 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 N_2O 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 N_2O desorb after a surface residence time long enough to be accommodated with the surface. These findings suggest a possibility that the decomposition of N_2O is the elementary step to produce N_2 from the NO decomposition.

Furthermore, angular and velocity distributions of N_2 desorbing in the course of N_2O decomposition were also studied. When the surface exposed to 0.20 L of N_2O below 130 K was heated, the major desorption of N_2O was accompa-

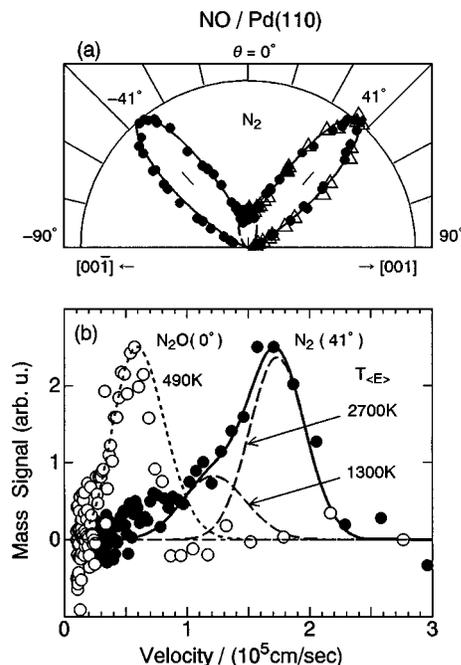


FIG. 2. (a) Angular distributions of N_2 desorbing from a NO adsorbed Pd(110) surface. The relative peak height of N_2 is plotted in polar coordinates for the exposure to NO at 0.50 L (closed circles) and at 0.20 L (open triangles). The fitting curve (full line) is obtained by the deconvolution with the functions $\cos^{28}(\theta \pm 41)$ and $\cos^5 \theta$, the latter being drawn by a broken line. (b) Velocity distributions of desorbing N_2 at $\theta=41^\circ$ (closed circles) and N_2O 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_2O (dotted line).

nied with a prompt N_2 desorption at 140 K and completed below 200 K as shown in Fig. 1(b). Here, no signal of NO desorption was found except for a trace amount of signal attributed to the N_2O fragmentation. The N_2 signal in angle-resolved form in a plane along the [001] direction was still 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 $\cos^n(\theta-43)$, 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 $\alpha=258$ m/s and $v_0=1661$ m/s for the F_1 component, and $\alpha=408$ 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_2O on the surface.

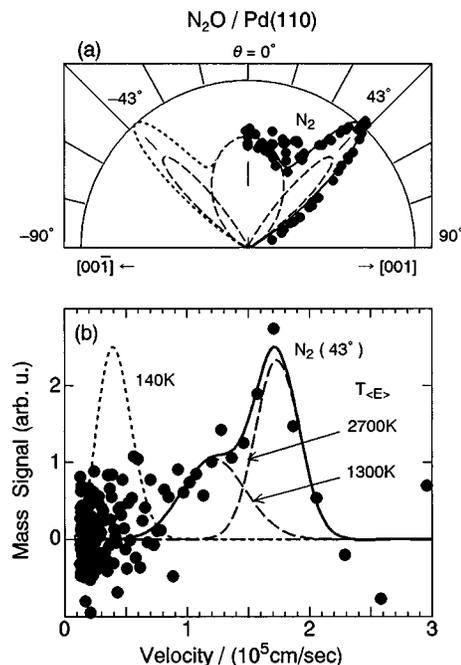


FIG. 3. (a) Angular distribution of N_2 desorbing from a N_2O adsorbed Pd(110) surface. The relative peak height for N_2 at 0.20 L exposure to N_2O is plotted in polar coordinates (closed circles). The fitting curve (full line) was obtained by the deconvolution with the functions $\cos^{60}(\theta \pm 43)$ 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.^{14,15} No dissociation of NO occurs below 440 K.¹³ With increasing surface temperature, a part of NO is desorbed and the remaining NO is dissociated to N(ad) and O(ad). NO ad molecules migrate with a high mobility above room temperature and are likely to react rapidly with N(ad) and produce $N_2O(ad)$. A part of the product $N_2O(ad)$ desorbs thermally after full accommodation with the surface. Remaining $N_2O(ad)$ is decomposed into $N_2(g)$ and O(ad). N_2O ad molecules are actually formed from NO(ad) and N(ad) at temperatures as low as 100 K on platinum.¹⁶

The product N_2 is expected to carry away a high translational energy because the heat of decomposition of $N_2O(ad) \rightarrow N_2(g) + O(ad)$ is highly exothermic by about -46 kcal/mol. This was estimated from the fact that the reaction in the gas phase, $N_2O(g) \rightarrow N_2(g) + O(g)$, 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.¹⁸ 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_2O .^{19,20} It is highly possible that a part of the heat of decomposition of $N_2O(ad)$ is released and

partitioned into the translational mode of desorbing N_2 as well as the internal mode of the molecule.

The gaseous N_2O is a linear molecule. A possible geometry of N_2O at the instant of decomposition is drawn in Fig. 1(c), where the bond length of gaseous N_2O and a nondistorted Pd(110) surface are assumed. The size of N_2 molecule in a physical adsorption state is also shown by assuming the radius of 2.0 \AA .^{21,22} N_2O 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 N_2 -O bond rupture takes place. At the instant when this bond rupture is finished, the nascent N_2 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 N_2 .^{21,22} Eventually the molecule will leave the surface in the direction inclined from the surface normal.

The energy transfer to desorbing N_2 is reminiscent of the multidirectional desorption of $O_2(ad)$ in a photoinduced reaction.¹⁰ In the latter, a hot atom emitted along the bond orientation of oxygen ad molecules collides with neighboring $O_2(ad)$. 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 N_2O is analogous to the reaction mentioned above, since an excess amount of energy is released whenever N_2 -O bond rupture takes place.

The dissociation step of $NO(ad)$ is considered to be rate-determining in the NO conversion into N_2 and O_2 on Pd(110). This is confirmed from the fact that the reaction $NO(ad)+N(ad)\rightarrow N_2O(ad)$ proceeds rapidly even around 100 K on platinum,¹⁶ and the decomposition of $N_2O(ad)\rightarrow N_2(g)+O(ad)$ occurs at temperatures as low as 140 K on Pd(110). The N_2O molecules formed in this way stay on the surface for a while enough to be thermalized. Then, some of the ad molecules desorb into the gas phase, yielding a cosine angular distribution and a Maxwellian velocity distribution at the surface temperature. The other ad molecules are likely to be oriented parallel to the [001] direction and watch for a chance to surmount the activation barrier for the decomposition into $N_2(g)$ and $O(ad)$. Thus, the reaction pathway for the NO decomposition on Pd(110) can be summarized as follows:



Finally, the combinative desorption of $N(ad)+N(ad)\rightarrow N_2(g)$ becomes a major reaction pathway in the N_2 emission at temperatures as high as 600 K.³ A study of such combinative desorption dynamics indicated that the highly energetic N_2 was emitted along the surface normal.²⁴ However, the component of normally-collimated desorption found in the present study may not be attributed to this combinative process. This is because the dissociated $N(ad)$ rapidly reacts with $NO(ad)$ to produce $N_2O(ad)$ around 500 K. In order to investigate this issue, we need further experiments of angular and velocity distributions of desorbing N_2 in a plane along the [110] direction.

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