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Spatial distributions of desorbing products in steady-state NO and N₂O reductions on Pd(110)

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The angular and velocity distributions of desorbing product N₂ were examined over the crystal azimuth in steady-state NO+CO and N₂O+CO reactions on Pd(110) by cross-correlation time-of-flight techniques. At surface temperatures below 600 K, N₂ desorption in both reactions splits into two directional lobes collimated along 41°–45° from the surface normal toward the [001] and [001] directions. Above 600 K, the normally directed N₂ desorption is enhanced in the NO reduction. Each product desorption component, as well as CO₂, shows a fairly asymmetric distribution about its collimation axis. Two factors, i.e., the anisotropic site structures and the reactant orientation and movements, are operative to induce such asymmetry, depending on the product emission mechanism. © 2006 American Institute of Physics. [DOI: 10.1063/1.2189855]

I. INTRODUCTION

The NO and N₂O reduction by CO and H₂ on palladium and rhodium surfaces has received much attention because of its importance in controlling automobile exhaust gas composition and the peculiar N₂ emission. N₂O is not only an undesirable by-product in the catalytic NO reduction but also the key intermediate in controlling the selectivity to N₂. Its decomposition largely shares the N₂ emission; however, knowledge of this emission process is still limited. The ordinary kinetic approach is not informative for this process because of the presence of several rapid surface-nitrogen removal pathways after the slow NO dissociation. This paper delivers the first extensive analysis of the angular distributions of desorbing N₂ as well as CO₂ in steady-state NO +CO and N₂O+CO reactions on Pd(110) over the whole crystal azimuth. Similarities and remarkable differences in the angular distributions have been observed for these two reactions, characterizing the surface-nitrogen removal processes. The N₂ and CO₂ desorption shows a fairly asymmetric distribution about their collimation axes.

The desorption dynamics (the spatial, velocity, and internal energy distributions) of reaction products with hyperthermal energy must be sensitive to the structure of reaction sites on which the molecules are formed. The relationship of the desorption dynamics to the site structure should provide the most direct site-identification method applicable in the course of a catalyzed reaction. The crystal azimuth dependence of the product distributions has been extensively studied only for the reactive CO₂ desorption on Pd(110) and Pt(110) surfaces. These data have provided the fundamental basis for understanding the relationship between the collimated product desorption and reaction-site structures. Such a relationship can be extended to the orientation of intermediate molecules emitting products directly, i.e., in N₂O decomposition. The detailed distribution analysis of desorbing fragment N₂ will provide information on the movement of parent N₂O as well as its orientation as observed in electron (or photon)-stimulated desorption ion angular distribution (ESDIAD).

The inclined N₂ desorption in N₂O decomposition on Pd(110) is useful to analyze the removal pathways of surface nitrogen because the concomitant associative desorption of N(a) emits N₂ sharply along the surface normal and other desorbing products N₂O and NH₃ show a cosine distribution. Measurements of the angular and velocity distributions will provide information on the reaction pathways whenever any step becomes rate determining because these distributions do not involve the reaction rate and are always controlled by their own desorption steps. The distributions of desorbing products in the NO reduction have been analyzed with several relaxation methods, such as modulated molecular beams, angle-resolved (AR) temperature-programmed desorption (TPD), or AR-pressure jumps. Steady-state conditions, however, could not be established for the reaction, and then both detailed kinetic and dynamic analyses of product desorption processes were seriously limited. In their AR-TPD work of NO on Pd(110) in the presence of CO, Ikai and Tanaka found that the N₂ peak at 490 K involves desorption collimated at 38° off normal toward the [001] direction and desorbing N₂, in the other peak at around 600 K, is collimated at the surface normal.
desorption was not involved in a catalytic cycle and assigned it as a stoichiometric reaction mediated by NO desorption.\textsuperscript{14} Later, we showed that this inclined N\textsubscript{2} desorption is well reproduced in N\textsubscript{2}O decomposition on Pd(110), Rh(110), and Ir(110) as well as in steady-state NO+CO (or H\textsubscript{2}) and N\textsubscript{2}O+CO (or H\textsubscript{2}) reactions on Pd(110).\textsuperscript{13,15–22} Thus, the intermediate N\textsubscript{2}O(a) formed from the NO(a)+N(a) fast reaction\textsuperscript{23–25} has been proposed to be oriented along the [001] direction before dissociation in the course of the catalyzed NO reduction. In the present work, AR-product desorption measurements have been successfully performed at different crystal azimuths for the steady-state NO (or N\textsubscript{2}O) +CO reaction and the resultant spatial distributions of all products have been constructed in a three-dimensional way.

Many studies on the collimated fragment desorption from surface molecules have been reported in ESDIAD.\textsuperscript{7,8} Fast-desorbing fragments are collimated along the ruptured bond axis, yielding structural information on the adsorbed parent molecules. In the thermal decomposition of adsorbed molecules, however, the released fragment has been believed to be quickly thermalized to the surface temperature before emission because these species interact with attractive forces due to their chemical or physical adsorption potential and the energy relaxation is very fast on metal surfaces.\textsuperscript{26} In fact, collimated product desorption in thermal surface reactions has been limited to some associative processes such as CH\textsubscript{4}(a)+H(a) → CH\textsubscript{3}(g) and CO(a)+O(a) → CO\textsubscript{2}(g).\textsuperscript{4} In these cases, significant repulsive forces are exerted from the surface toward the nascent products. Thus, the inclined N\textsubscript{2} emission in N\textsubscript{2}O decomposition on Pd(110), Rh(110), and Ir(110) is the first example to show collimated fragment desorption in thermal decompositions on solid surfaces.\textsuperscript{15–18} Its desorption dynamics will be informative regarding the energy partitioning in the dissociation event. The product N\textsubscript{2} effectively receives repulsive forces along the N\textsubscript{2}O molecular axis since recent density-functional theory (DFT) calculations with generalized gradient approximations\textsuperscript{27,28} (GGA) and scanning tunneling microscope (STM) and near-edge x-ray-absorption fine structure (NEXAFS) work have confirmed the presence of [001]-oriented N\textsubscript{2}O on Pd(110).\textsuperscript{29,30} Sharp fragment desorption was once reported in a thermal hydrazine decomposition on Ir(111).\textsuperscript{31} The product N\textsubscript{2} desorption around 290 K was sharply collimated along the surface normal in AR-TPD procedures after N\textsubscript{2}H\textsubscript{4} exposures at 260 K. However, the reliability of the AR signal is not clear because angle-resolved signals become very poor in thermal desorption work unless the apparatus has at least two slits and a very large pumping speed in either a collimator or a reaction chamber.\textsuperscript{32}

II. EXPERIMENT

The apparatus used has three separately pumped chambers.\textsuperscript{21} The reaction chamber is equipped with x-ray photoelectron spectroscopy (XPS) optics, reverse-view low-energy electron diffraction (LEED), an ion gun, and a quadrupole mass spectrometer (QMS) for angle-integrated (AI) measurements. The chopper house has a large pumping rate of about 7 m\textsuperscript{3}s\textsuperscript{-1}. This high pumping rate can satisfactorily yield angle-resolved measurements.\textsuperscript{32} The chopper house has a narrow slit facing the reaction chamber and a cross-correlation random chopper blade. Another QMS was set in the analyzer connected through a narrow tube-type slit for AR-product desorption and time-of-flight (TOF) analyses. The distance from the ionizer to the chopper blade was 377 mm and the time resolution was selected at 20 μs.\textsuperscript{33}

A palladium crystal with a (110) plane (Surface Preparation Laboratory, Netherlands) in a disk-shaped slice (with 1 mm thickness and a 10 mm diameter) was mounted on top of a rotatable manipulator. The crystal was rotated to change the desorption angle (polar angle, θ) in the normally directed plane at various crystal azimuths between the [001] and [1\textbar{}10] directions. The crystal azimuth (φ) is defined in the (110) plane as the angle rotated from the [001] direction, i.e., φ=0° at the [001] direction [Fig. 1(a)]. The LEED pattern showed a sharp (1 × 1) form after the surface was cleaned by Ar\textsuperscript{+} ion bombardments in the surface temperature (T\textsubscript{s}) range between 800 and 900 K, heating in 5 × 10\textsuperscript{-8} Torr oxygen at 850 K, and annealing at 1100 K.

\textsuperscript{15}N\textsubscript{2}O was introduced through a doser with a small orifice (diameter: 0.1 mm) about 2 cm from the sample crystal, while \textsuperscript{13}CO and \textsuperscript{15}NO were backfilled. The partial pressures of \textsuperscript{13}C\textsubscript{16}O(P\textsubscript{CO}) and \textsuperscript{15}NO(P\textsubscript{NO}) were kept constant by continuously dosing the gas. Hereafter, the isotopes \textsuperscript{15}N and \textsuperscript{13}C are, respectively, denoted by N and C in the text. The product N\textsubscript{2}, CO\textsubscript{2}, and N\textsubscript{2}O signals were monitored in both AI and AR forms. The N\textsubscript{2} signals in both QMS’s were corrected for
the contribution of the fragmentation of N$_2$O. The pressures of reactant gases were also corrected by their mass spectrometer sensitivities.

III. RESULTS
A. General features

The AR signal was obtained with the analyzer QMS as the difference between the signal at the desired angle and the signal when the crystal was away from the line-of-sight position. The above gas doser with a small orifice was effective to reduce the N$_2$ formation in the N$_2$O exposure on the reaction chamber wall. Under this construction, the flux of incident N$_2$O toward the surface decreased proportionally to the cos(θ) when the angle shifted from the normal direction. This decrement was evaluated and the signal intensity was corrected.

For the steady-state NO+CO reaction at different $P_{NO}/P_{CO}$ ratios, Figs. 2(a) and 2(b) shows the AR signals at around the collimation angles (the maximum flux position) against $T_S$, at $\theta=0^\circ$ for desorbing N$_2$, CO$_2$, and N$_2$O, and at $\theta=41^\circ$ for the N$_2$ in the plane along the [001] direction. All the signals were negligible below 490 K. The N$_2$ signal at $\theta=41^\circ$ increased rapidly above 500 K, reached a maximum at around 550 K, and then decreased at higher temperatures. This signal is due to the inclined N$_2$ desorption in the intermediate N$_2$O decomposition. The N$_2$ signal at $\theta=0^\circ$, on the other hand, increased slowly and peaked at about 600 K. This comes from the associative desorption of N(a). The AR CO$_2$ signal at the normal direction increased at around 500 K and decreased above 570 K with increasing $T_S$, more slowly than the N$_2$ signal at $\theta=41^\circ$. The temperature dependence of the N$_2$O signal was very similar to that of N$_2$ at $\theta=41^\circ$. It should be noted that the ratio of the N$_2$ signal at $41^\circ$ to that at $0^\circ$ decreases with increasing $T_S$, indicating that the reaction pathway shifts at high temperatures. Nevertheless, the reaction stoichiometry was already confirmed as $x$NO+CO→$y$N$_2$+$z$N$_2$O+CO$_2$ where $2x+y+z$. At the pressure ratio of $P_{NO}/P_{CO}=1$, the N$_2$ signal at $\theta=0^\circ$ was much less than that at $41^\circ$ below 550 K, i.e., the product N$_2$ mostly comes from the intermediate N$_2$O dissociation. Above 650 K, the normally directed N$_2$ signal overcomes the other. At high temperatures, the amount of NO(a) is reduced, and the N$_2$O formation is suppressed, whereas the association of N(a) is enhanced because of the higher activation energy. This situation became clear when the CO pressure was increased at the location in which the amount of N(a) was increased by the fast removal of O(a) and the resultant enhanced NO dissociation [Fig. 2(b)]. At higher CO pressures, the N$_2$ signal at $\theta=0^\circ$ was highly enhanced and the N$_2$ formation shifted from the N$_2$O decomposition pathway to the association of N(a). Thus, N$_2$ desorption in the two pathways was examined at both $P_{NO}/P_{CO}=1$ ($T_S=550$ K) and 1/4 ($T_S=640$ K) in this work.

The AR N$_2$ signal in the N$_2$O+CO reaction was measurable because of the sharply collimated desorption although the Al N$_2$ signal involved large experimental uncertainty. The maximum N$_2$ flux was located at $\theta=43^\circ$–$46^\circ$ in the N$_2$O+CO reaction. The signals at their collimation angles at $3.3 \times 10^{-6}$ Torr of N$_2$O and $0.5 \times 10^{-6}$ Torr of CO are plotted versus the surface temperature [Fig. 2(c)]. The AR N$_2$ signal became noticeable above around 450 K. The signal was peaked at 510 K and decreased quickly at higher temperatures. No AR N$_2$ signal was found in the normal direction. The desorption of the other product CO$_2$ collimated along the surface normal. The difference in the signal between N$_2$ and CO$_2$ was mostly due to different angular distributions.

In the range of $T_S=400$–800 K, only the (1×1) pattern was observed in LEED measurements during the steady-state CO+NO reaction at a total pressure of $1 \times 10^{-7}$ Torr of the equimolar mixture of NO and CO. This indicates a reducing surface conditions at $P_{NO}/P_{CO}=1$. On the other hand, under a constant N$_2$O flow at $T_S$ below 350 K, a streaky c(2×4) structure was observed. Increasing $T_S$ to 470 K resulted in the appearance of (2×3)-1D superstructure spots. They are due to oxygen adsorption. LEED structures were also examined around the kinetic transition under steady-state conditions at different CO pressures. With increasing CO pressure, the intensity of the fractional spot became weaker. When the N$_2$O/CO pressure ratio was about 13 at the kinetic...
transition or above it, the pattern was converted from a (1 × 1) structure to (2 × 3)-O lattice. Both N₂O and NO reductions are seriously retarded by adsorbed oxygen, and thus the rate-limiting steps of the reactions are likely to proceed on clean parts free from oxygen.

B. Angular distribution and crystal azimuth

In the N₂O+CO reaction desorbing N₂ always split in a two-directional way in the plane along the [001] direction and collimated at θ=43° ± 46° off the surface normal in the temperature range studied, 460–800 K. No normally directed desorption was found even at 800 K. The distribution became somewhat broader from a cos²(45° − θ) form at 460 K to a cos²(45° − θ) at 750 K, but the collimation angle remained invariant. The angular distributions at different crystal azimuths at 520 K, P₅₂₀=3.3 × 10⁻⁶ Torr and Pₐ₁₀=0.5 × 10⁻⁶ Torr, are shown in Fig. 3. The surface was under the reducing condition because the CO pressure was above the kinetic critical point (P₅₂₀=Pₐ₁₀=13 at 520 K), i.e., CO(a) ≫ O(a). The observed maximum flux position remains fairly invariant when the crystal azimuth is shifted from the [001] direction. The signal at φ=0° (along the [001] direction) is approximated by a form of \( \cos^2(θ+45°) + \cos^2(θ-45°) \). The distribution becomes broader with an increasing azimuth. The signal intensity itself decreases quickly and is mostly suppressed at around φ = 40°. The remaining signal above φ=60° is mostly due to the normally directed and cosine components.

At temperatures above 550 K and smaller P₅₂₀/Pₐ₁₀ ratios, the distributions change significantly. The typical results are shown for Tₛ=640 K and a ratio of P₅₂₀/Pₐ₁₀=1/4 in Fig. 5. The angular distribution at 640 K involved three decomposition components. The normally directed and cosine components are drastically enhanced. The distribution at φ=0° is approximated by a form of \( 0.91 \cos^3(θ+41°)+0.03 \cos^5(θ)+0.06 \cos(θ) \). The latter two components were estimated from the velocity distribution analysis to be described in the following section. The intensity of these components in the normal direction is independent of the φ position. The distribution again becomes broader with increasing azimuth. The signal intensity itself decreases quickly and is mostly suppressed at around φ = 40°. The remaining signal above φ=60° is mostly due to the normally directed and cosine components.

The CO₂ desorption collimates sharply along the surface normal in both N₂O and NO reduction. No differences have been found in the CO₂ distribution between them. The results for N₂ formation from an equimolar (NO+CO) mixture.

FIG. 3. Angular distributions of desorbing N₂ at different crystal azimuths (φ=0°, 18°, 25°, and 40°) in the steady-state N₂O reduction at P₅₂₀=3.3 × 10⁻⁶ Torr, Pₐ₁₀=0.5 × 10⁻⁶ Torr, and Tₛ=520 K. The signal is normalized to the maximum value at the collimation angle. The solid curves are simulated by the inserted equations.

FIG. 4. Angular distributions of desorbing N₂ at different crystal azimuths (φ=0°, 18°, 40°, 62°, and 90°) in the steady-state NO reduction at P₅₂₀=Pₐ₁₀=5 × 10⁻⁶ Torr and Tₛ=550 K. The signal is normalized to the maximum value at the collimation position. Typical deconvolutions are shown by broken and dotted curves. The solid curve indicates the sum of the components.
Spatial distribution of NO and N2O desorbing from Pd

C. Velocity distribution

The extent of the thermalized component has been estimated from the fraction of the Maxwellian distribution with a translational temperature equal to the surface temperature in the velocity distribution curve. This estimation becomes important for the NO+CO reaction above 600 K where both the normally directed and thermalized components are enhanced. These components have been separated at the normal direction where the contribution from the inclined component is negligible. The translational energy can be used to judge the collimation angle of desorption components because it is peaked at this angle in the repulsive desorption.\textsuperscript{1,38}

Each velocity distribution of desorbing N\textsubscript{2} clearly shows the thermalized component in the NO+CO reaction above 550 K. Typical velocity distributions at $T_{S}=550$ K and $P_{NO}=P_{CO}=5 \times 10^{-6}$ Torr are shown in Fig. 7. The resultant mean kinetic energy is shown in the temperature units as $T_{(E)}=(E)/2k$, where $\langle E \rangle$ is the mean kinetic energy and $k$ is the Boltzmann constant. In the previous paper reporting the desorption angle dependence in the plane along the [001] direction,\textsuperscript{21} this value peaked at around $\phi=0^\circ$ and $\phi=40^\circ$, reaching about 3400 K. This time, the crystal-azimuth was varied at a fixed desorption angle of $40^\circ$. The translational temperature decreases quickly with increasing azimuth, showing that the desorption is fairly concentrated in the plane along the [001] direction [Fig. 7(e)]. Each velocity distribution curve was too wide to be fitted to one modified Maxwellian form. Especially, the distribution at around $\theta=40^\circ$ and $\phi<18^\circ$ is wide, extending to 4 km s\textsuperscript{-1} [Figs. 7(b) and 7(e)].

It should be noted that the distribution curve in the normal direction ($\theta=0^\circ$) involves the component expected by the Maxwellian distribution at the surface temperature, supporting the presence of the cosine component. This component can also be seen at the crystal azimuth above $\phi=40^\circ$, where the inclined desorption component is mostly suppressed. The contribution from this cosine component becomes relatively small at around the collimation angle of the inclined component. The translational temperature of desorbing N\textsubscript{2} after subtraction of the thermalized component has been estimated as shown in the figure as the fast component.

This value is peaked at 3420 K at the collimation angle and decreases slowly with increasing shift from the collimated position. It is still 2280 K in the surface normal direc-
mostly supplied from the intermediate N2O decomposition at this temperature. The average kinetic energy is shown in temperature units and the kinetic energy after subtraction of the thermalized component. The N2 is isotropic, i.e., a broader distribution in the plane along the [110] direction. Second, a small fraction of the intermediate N2O may be decomposed when it is oriented along the [110] direction. The former is likely to take place because of no such component in the N2O+CO reaction. In fact, the DFT calculations predict that the [110] oriented N2O is about 19 kJ mol⁻¹ less stable than the [001] oriented species.  

The velocity distribution is still wide even after the subtraction of the thermalized component, yielding 1.05–1.10 for the speed ratio defined as \((\bar{v}^2/(\bar{v})^2 - 1)^{1/2}/(32/9\pi - 1)^{1/2}\), where \(\bar{v}\) is the velocity of the molecule, \(\langle v \rangle\) is the mean velocity, and \(\langle \bar{v}^2 \rangle\) is the mean square velocity. The speed ratio is usually below unity for a hyperthermal component at around the collimation position.  

A translational temperature of 3420 K corresponds to an energy of 0.59 eV, which is higher than the excitation energy of the molecular vibration of N2 at the ground state, 0.28 eV.  

Desorbing fast N2 may involve vibrationally and/or rotationally excited molecules. In other words, no suitable distribution functions can be invoked for the involved components. Experiments with higher-energy resolutions are highly desired. In order to show the presence of very fast components, the distribution curve has been deconvoluted into two components of the modified Maxwellian distribution, \(f(u) = u^2 \exp(-u - u_0)^2 / \alpha^2\), where \(u_0\) is the stream velocity and \(\alpha\) is the width parameter. Here, we have simply assumed a common width parameter to both components for the deconvolution procedures.  

The resultant deconvolutions are shown by broken curves. The faster component (in the fast one) is 5600–6100 K wide and the slower one, 2000–2400 K (Fig. 7).  

The contributions of both the thermalized and normally directed desorption components are enhanced at higher temperatures and smaller \(P_{NO}/P_{CO}\) ratios. The results at 640 K are shown in Fig. 8. The velocity distribution in the normal direction involves a large fraction of the thermalized component [Fig. 8(a)]. This component is significant even at around the inclined collimation angle [Figs. 8(b) and 8(c)]. The translational temperature estimated from the average kinetic energy is lower than that at 550 K although it is peaked at the collimation position, indicating the enhanced contribution from the thermalized component. In fact, the translational temperatures for the fast component obtained after subtraction of the thermalized component are comparable to those obtained at 550 K [Fig. 8(e)]. The velocity curve in the normal direction exhibits the fast component except for the inclined desorption. It should be again noted that the fast component is still significant at \(\phi=90^\circ\) and \(\theta=40^\circ\) [Fig. 8(d)]. The decay of the fast component flux is less than that at 550 K [Fig. 7(e)] when the azimuth angle shifts from \(\phi =0^\circ\) to \(\phi=90^\circ\) at \(\theta=40^\circ\). We examine the N2 desorption in the plane along the [110] direction where no inclined N2 desorption is contributed from the N2O decomposition (Fig. 9). The average kinetic energy is not high and insensitive to the desorption angle, consistent with the large fraction of the thermalized component. The kinetic energy of the fast component decreases slowly with increasing desorption angle \(\theta\). The flux of the fast component follows roughly a \(\cos^2(\theta)\) form.
The translational temperature of CO$_2$ is 1490 K at the normal direction at 640 K (Fig. 6, top-right panel). The velocity distribution contains the thermal component represented by the Maxwellian distribution at the surface temperature. This thermalized CO$_2$ component was estimated to be about 20% of the total signal at the normal direction. The fast component after subtraction of the thermalized one gives a translational temperature of 1740 K. This component is sharply collimated along the surface normal and becomes very weak at around 45°. The velocity distribution curve at the translational temperature of 1490 K, $T_\text{E}$, is the long-axis of the velocity distribution. The fast component broadens from a cos$^{13}\theta$ form at $\phi=90^\circ$ to a cos$^5\theta$ form at $\phi=0^\circ$. A very similar distribution has been also observed for the CO$_2$ product in the N$_2$O +CO reaction and is found to be insensitive to the surface temperature. This anisotropy is also similar to that in the CO oxidation.

IV. DISCUSSION

A. Three-dimensional distribution

The CO$_2$ desorption that is collimated along the surface normal shows remarkable anisotropy. The angular distribution was approximated in a (0.8 cos$^4\theta + 0.2 \cos \theta$) form at $\phi=90^\circ$ and a (0.8 cos$^{13}\theta + 0.2 \cos \theta$) form at $\phi=0^\circ$ in the NO + CO reaction at 640 K (Fig. 6). The angular distribution of the fast component broadens from a cos$^{13}\theta$ form at $\phi=0^\circ$ to a cos$^5\theta$ form at $\phi=90^\circ$. A very similar distribution has been also observed for the CO$_2$ product in the N$_2$O +CO reaction and is found to be insensitive to the surface temperature. This anisotropy is also similar to that in the CO oxidation.

It is interesting to examine the extent of anisotropy of the normally directed N$_2$ desorption. The deconvolution into the three components could be well performed for the data at 640 K as shown in Fig. 5. The signal intensity at around the normal direction is mostly contributed from the normally directed and cosine components. Their relative intensity was well determined from the velocity distribution analysis at the surface normal direction. On the other hand, the signal at around the collimation angle of 41° is merely contributed from the inclined and cosine components. The resultant normally directed component shows an anisotropy, represented by a cos$^{7\theta}$ form at $\phi=0^\circ$ and shifts to a cos$^5\theta$ form at $\phi=90^\circ$. The distribution is sharper along the [001] direction in a similar way to that of CO$_2$.

For the anisotropy analysis of the inclined N$_2$ desorption, the following transformation from the polar coordinates to another polar angle system was necessary. The desorption direction can be defined with two new angles (n, m) and (θ, φ) is given by cos $\theta$ = cos n cos β and tan $\phi$ = −tan β/ sin $\alpha$. $\alpha$ is the longitude measured from the normal direction [110] about the [110] axis when the polar axis is taken to be parallel to the
crystal azimuth [110], whereas β becomes the longitude shifted from the plane along the [001] direction when the polar axis is parallel to the [001] axis. When β=0°, the value of α becomes equal to the desorption angle (θ) in the plane along the [001] direction. The experimental AR signals at definite (θ, φ) values were converted into the signal intensity at new coordinates (α, β) after smoothing the data points against varying θ values at fixed φ values. The resultant correction due to the smoothing procedures, however, was less than 10% of each signal because of the measurement at every 5° of the θ value. The signals estimated at α=45° for the N₂O+CO reaction are shown as a function of β in Fig. 10(a). The β value is always less than φ at a fixed α value, and then the distribution at a fixed α value against β becomes sharper than that against φ. The resultant distribution at α=45° has been approximated by a cos² β form with n =17±3. Very similar β dependences have been obtained at α=41° from the inclined N₂ desorption in the NO+CO reaction at 550 and 640 K.

The spatial distributions of desorbing N₂ and CO₂ are shown in three-dimensional polar coordinates in Figs. 10(b) and 11, which were derived from the angular distribution data in Figs. 4–6. These were drawn by assuming a distribution with twofold symmetry around the collimation axis at θ=45° and φ=90° for the inclined N₂, and at θ=0° for CO₂ and the normally directed N₂ desorption component. The distribution below 550 K for desorbing N₂ mostly consists of a single desorption component that is merely controlled by the N₂O decomposition. In this new three-dimensional way, the N₂ distribution for the N₂O+CO reaction is approximated by cos²⁸(α±45)cos¹⁷(β). The N₂ distribution for the NO+CO reaction has the form of cos²²(α±41)cos¹⁷(β) at 550 K. This distribution form describes almost all the signal intensity of the fast component.

Similarly, the fast CO₂ component is approximated as a cos¹³ α cos⁴ β form, commonly for the N₂O+CO and NO +CO reactions. This anisotropy is very close to that in the CO+O₂ reaction on Pt(110). The normally directed N₂ desorption is approximated by a cos⁷ α cos² β form. The distribution is commonly sharper in the plane along the [001] direction.

B. Intermediate structure

A Pd(110) plane shows a stable (1×1) form, whereas it is reconstructed into missing-row forms when it is covered by oxygen. The resultant surface consists of three- or four-atom-wide microfacets with a (111) structure declining alternatively about +30° or −30° in the [001] direction. The repulsive force exerting from its formation site to the product CO₂ in CO oxidation on noble metals is strong enough to hold the site orientation in the angular distributions. In fact, the reactive CO₂ desorption in AR-TPD as well as steady-state (SS) CO oxidation experiments collimates fairly along the local normal of declining microfacets on reconstructed Pt(110), Ir(110), and Rh(110), indicating the CO₂ formation on inclined (111) facets. On the other hand, no inclined CO₂ desorption has been found on Pd(110) under either TPD or SS conditions, although the c(2×4)-O lattice due to the missing-row structure was observed. The lack of inclined CO₂ desorption on this surface is due to either the instability of the (1×2) reconstruction without oxygen above 355 K, or high oxygen coverage. The CO₂ desorption shifts to the surface normal direction when the (1×2) surface is highly covered by oxygen. The observation of inclined CO₂ desorption requires low-oxygen coverage conditions. However, the reconstructed Pd(110)(1×2) stabilized by oxygen is
converted into the \((1 \times 1)\) form when the surface oxygen is removed above 355 K.\(^{43}\) The \((1 \times 2)\) reconstruction by CO appears only at high CO coverage.\(^{49-52}\)

LEED observations were consistent with the absence of bidirectional CO\(_2\) desorption in N\(_2\)O or NO reduction. The LEED pattern due to \(c(2 \times 4):O\) or \((2 \times 3):1D-O\) was suppressed with increasing CO pressures, yielding more products. The rate-determining NO or N\(_2\)O dissociation proceeds on \((1 \times 1)\) parts without oxygen. The CO\(_2\) formation takes place on the oxygen-covered area where the oxygen density is high enough to emit CO\(_2\) along the surface normal.

On the other hand, the inclined N\(_2\) desorption takes place on \((1 \times 1)\) parts because of the severe retardation by oxygen toward N\(_2\)O dissociation.\(^{17,53}\) The intermediate N\(_2\)O is easily formed from the reaction N(a) + NO(a) in NO reduction on palladium, platinum, and rhodium surfaces.\(^{12,23-25}\) The reaction pathway through N\(_2\)O decomposition is operative at low temperatures where NO(a) is significant, more than N(a).\(^{54}\) N\(_2\)O is easily decomposed on Pd(110) below 150 K, emitting N\(_2\) in the inclined way.\(^{15-18}\) This peculiar desorption has been proposed to be due to the decomposition of N\(_2\)O oriented along the [001] direction although the vibrational spectroscopy work indicates the terminal nitrogen atom interacting with the surface at around 100 K,\(^{55}\) or no N\(_2\)O(a) signal has been observed in the catalyzed NO reduction above 500 K.\(^{56-58}\) On clean Pd(110), DFT-GGA,\(^{27,28}\) STM,\(^{29}\) and NEXAFS\(^{30}\) studies commonly support the presence of two adsorption forms below 60 K, i.e., one lying form oriented along the [001] direction and another tilted form with the terminal nitrogen atom interacting with the metal. This is consistent with the results from vibrational spectroscopy which is insensitive to the lying form according to the surface-selection rule.\(^{39}\) The activation energy barrier between the tilted and lying forms has been estimated to be only 4 kJ mol\(^{-1}\) by DFT-GGA and 8 kJ mol\(^{-1}\) in the reverse way, i.e., the conversion between them seemed to be facile.\(^{28}\) The lying N\(_2\)O oriented along the [001] direction bridges the palladium-atom trough running along the [110] direction and is located on the on-top site.

### C. Different collimation angles

The above collimation angle of desorbing N\(_2\) shows noticeable differences between NO and N\(_2\)O reduction, i.e., 41 ± 2° and 45 ± 2°, respectively. It is not likely that the intermediate N\(_2\)O in the NO reduction is in different adsorption states from those of N\(_2\)O(a) supplied from gaseous N\(_2\)O as proposed by Ikai and Tanaka,\(^{10}\) because some fraction of the intermediate desorbs without dissociation after thermalization as observed in its cosine distribution. Rather, the intermediate N\(_2\)O may be affected by coadsorbed species, such as NO(a) and/or N(a) which are absent in the N\(_2\)O + CO reaction.

In fact, the collimation angle of desorbing N\(_2\) from N\(_2\)O decomposition has been reported to be affected by coadsorbed species and the kind of metal. In AR-TPD work on adsorbed N\(_2\)O on Pd(110), the collimation angle of desorbing N\(_2\) shifts at low N\(_2\)O density.\(^{17}\) There are four N\(_2\) desorption peaks in the range of 100–160 K, i.e., \(\beta_1\)-N\(_2\) peaked at 110 K at very low N\(_2\)O(a) density, collimated at 50°, and shifted to 44° with increasing N\(_2\)O coverage. The \(\beta_3\)-N\(_2\) peak at 123 K and \(\beta_1\)-N\(_2\) at around 150 K appearing at higher N\(_2\)O density are collimated at 44 ± 2°. The N\(_2\)O density above 470 K is very low because of the small heat of adsorption, about 37 kJ mol\(^{-1}\). Thus, the intermediate N\(_2\)O is decomposed in a situation similar to \(\beta_1\)-N\(_2\), which suggests that the collimation angle of N\(_2\) emission is affected by the coadsorbed species in the steady-state NO reduction rather than N\(_2\)O reaction.

The Pd(110) surface is covered by CO(a) or O(a) in the course of N\(_2\)O reduction. The collimation angle of N\(_2\) desorption remains invariant even when the reaction shifts from the active region into the inhibited region, i.e., the main surface species changes from O(a) to CO(a) although the amount of O(a) is very small. Thus, the effect to the collimation from CO(a) is minor or nonexistent, since the CO coverage increases by as much as 0.2 monolayer at the kinetic transition.\(^{60}\) This is close to the coverage of the p(2 \(\times\) 2)-CO lattice.\(^{49,50}\) The coverage of O(a) and N(a) may increase to much higher levels in the active region of the NO reduction than that in the N\(_2\)O reaction because the sticking probability of NO is much larger than that of N\(_2\)O.\(^{54}\) In fact, adsorbed oxygen atoms play a role of not only an inhibitor toward N\(_2\)O dissociation but also a stabilizer of it. In the presence of adsorbed oxygen, the heat of N\(_2\)O adsorption increases from around 30 to 43 kJ mol\(^{-1}\) on Ru(0001).\(^{61}\) However, no collimation angle shift has been observed on Rh(110) as a result of the addition of O(a) although the TPD decomposition peak shifted from 70 to 140 K.\(^{13,19}\) Rather, the intermediate N\(_2\)O may be affected by coadsorbed species, such as N(a) and NO(a). The coverage of N(a) may also be significant in the NO reduction.\(^{54}\) The N(a)-covered palladium was reported to be active toward N\(_2\) adsorption even at room temperature,\(^{62}\) probably toward N\(_2\)O as well.

The collimation angle of the product N\(_2\) depends on metal, i.e., 70° ± 5° on Rh(110), 65° ± 5° on Ir(110), and 43°–50° on Pd(110). This sequence is consistent with the hot atom-assisted desorption model. In this model, a nascent oxygen atom (hot atom) provides a surface-parallel momentum to desorbing N\(_2\) when N\(_2\)O(a) molecules oriented along the [001] direction are decomposed. This hot atom-assisted model predicts larger collimation angles and higher kinetic energy on rhodium and iridium than on palladium because larger amounts of energy are released in the metal-O bond formation.\(^{63}\) During stabilization of the nascent product O(a) in N\(_2\)O dissociation, a large amount of the energy due to the O-metal bonding must be dissipated; the available energy that can be delivered to the product comes primarily from the metal-O bond formation.\(^{63}\) The released energy may be reduced when the N\(_2\)O dissociation site is affected by either N(a) or O(a). The decreased amount of released energy may provide less momentum transfers toward desorbing N\(_2\) and then yield smaller collimation angles.

### D. Anisotropy in desorption

The anisotropy of the spatial distribution of desorbing products has been due to either the anisotropic structures of
the product formation site or the anisotropic movements of the parent molecules. The former was proposed for anisotropic CO$_2$ distributions in the CO oxidation on Pd(110), Pt(110)(1×2), Ir(110)(1×2), and other stepped platinum surfaces. The movement at the transition state (TS) is restricted by the potential-energy field of the atoms involved and particularly, strongly depends on the structural anisotropy of the reaction site. The distribution is sharp when the movement is restricted, while facile movements will yield a broader angular distribution. This model originated from the theoretical treatment of the associative desorption dynamics of adsorbed hydrogen atoms. In the other case, anisotropy in dissociative desorption is explained to be due to the motion of the parent molecule. This model has been frequently used in ESDIAD. For example, this is the case of excited CO desorption in ESDIAD on a stepped Pt(112) surface, in which the angular distribution becomes broader in the plane where the molecule is easily vibrated (i.e., the restricted vibration immediately before bond breaking). These two models are applicable for the present N$_2$ desorption in the different pathways.

The sharpness of the angular distribution of desorbing molecules is related to the extent of repulsive forces operative toward the molecules. The stronger the repulsive force the higher is the velocity and the sharper is the distribution of desorbing molecules. The sharpness is reduced by the TS motions perpendicular to the rupturing bond axis, typically, the thermal motions of TS or the parent molecules. This latter factor induces anisotropy in the product distribution. In the normally directed N$_2$ desorption, the product is formed in an associative process of adsorbed nitrogen atoms and the resultant bulky N$_2$ molecule is repulsed from the formation site, being emitted along the local normal of the site. Anisotropic motions of the nascent bulky N$_2$ molecule may be expected. On Pd(110), the motion along the [110] direction is facile since the palladium atoms are closely packed allowing the molecule to move easily. On the other hand, the movement along the [001] direction may be restricted because of the high atomic corrugation. In fact, nitrogen adatoms are proposed to be located on the long-bridge site in the trough from high-resolution electron energy-loss spectroscopy (HREELS) work. The transition state of N$_2$ being desorbed may be moved along the [110] direction more easily than that along the [001] direction.

The inclined N$_2$ emission requires another anisotropy mechanism available to dissociative desorption since N$_2$ is directly emitted in the N$_2$O dissociation event. The angular distribution of desorbing N$_2$ in the inclined way is sharper in the plane along the [001] direction than that perpendicular to it. The sharpness parameter of the distribution is $n=28$ at $T_S=400$ K, where the distribution is represented in a $\cos^4(\delta)$ form. $\delta$ is the angle shift from the collimation position. The parameter increases to $n=50$ at $T_S=110$ K in the AR-TPD work and decreases to $n=18$ at 750 K. On the other hand, the parameter in the inclined plane passing $\alpha=45^\circ$, was estimated to be $n=17\pm3$ at 550 K. The movement of the N$_2$O molecule is more restricted in the plane along the [001] direction. This is consistent with the results from DFT-GGA, which predict that the dissociation is much easier from the bridge site although the [001] oriented N$_2$O is more stable over the on-top sites. The potential-energy surface around the bridge site shows an extremely shallow local minimum, hence the movement around the bridge site would be very facile toward the [110] direction.

In ESDIAD, the orientation of the parent molecule immediately before dissociation is clear since the reactant is in a stable adsorption state and the (electronic) transition from it to the dissociative form is faster than the nuclear motions. At present, a reliable model to predict the inclined $N_2$ collimation angle is not available. Indeed, even the dissociation sequence of N$_2$O is not clear, i.e., the DFT work predicts that the N–O bond is first broken in N$_2$O(a) because the adsorption through the terminal oxygen is not predicted on clean Pd(110). On the other hand, the first scission may take place in the N-metal bond when that adsorption is possible. This adsorption form has been proposed on several oxides. The restricted vibration of N$_2$O obliquely standing through the terminal oxygen is suitable for anisotropic desorption as expected in the ESDIAD model. There must be a limited angle range suitable for the NN–O bond scission on oxygen-modified Pd(110).

V. CONCLUSIONS

The product desorption in the steady-state NO+CO and N$_2$O+CO reactions on Pd(110) has been studied by using angle-resolved flux and velocity distribution measurements and LEED observations. The following results have been obtained:

1. N$_2$ desorption in both reactions splits into two directional lobes collimated along 41°–45° from the surface normal toward the [001] and [011] directions. This N$_2$ is emitted in the decomposition of the intermediate N$_2$O oriented along the [001] direction.
2. Above 550 K, the normally directed N$_2$ desorption is enhanced in the NO reduction. This comes from the associative desorption of N(a).
3. Reactive CO$_2$ desorption is collimated sharply along the surface normal in both reactions.
4. Each product desorption component shows a remarkable asymmetric distribution around their collimation axis. Commonly, the distribution is sharper in the plane along the [001] direction than in that perpendicular to it.

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