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N₂ emission-channel change in NO reduction over stepped Pd(211) by angle-resolved desorption

Tatsuo Matsushima,⁎, Anton Kokalj, Hideo Orita, Toshitaka Kubo, Masataka Sakurai, Takahiro Kondo, and Junji Nakamura

a Catalysis Research Center, Hokkaido University, Sapporo, 001-0021, Japan
b Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
c Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
d Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
e Faculty of Pure and Applied Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8573, Japan

⁎ Corresponding author; Tatsuo Matsushima
Tel/Fax: +81-29-874-1508
E-mail: tatmatsu@mbr.nifty.com
Postal address; Catalysis Research Center, Hokkaido University, Sapporo, 001-0021, Japan

Abstract
A sharp change in the N₂ emission channel from N₂O(a)→N₂(g)+O(a) to N(a)+N(a)→N₂(g) has been found at around 500 K in a steady-state NO+D₂ reaction over stepped Pd(211)=[(S)3(111)×(100)] by means of angle-resolved desorption. The desorbing N₂ is highly collimated at around 30° off normal toward the step-down direction below about 500 K due to the intermediate N₂O decomposition, whereas, above 500 K, the near normally directed desorption due to the recombination of N(a) is relatively enhanced. The N₂O decomposition channel is promoted when the reaction is carried out with hydrogen (deuterium) and the channel change is accelerated by quick changes of the amounts of surface hydrogen and oxygen (or NO(a)) into the opposite directions, and enhanced nitrogen removal as ammonia on the resultant hydrogen-rich surface. In the steady-state NO+CO reaction, the N₂ emission channel gradually changes above 500 K toward recombination. A model for the off-normal N₂ emission is briefly described.

Key words; Nitrogen oxide, Nitrous oxide, Reduction, Nitrogen, Palladium, Stepped surface
1. Introduction

The N\textsubscript{2} emission in the steady-state NO reduction on palladium and rhodium, the best deNO\textsubscript{x} catalysts, takes place through either (i) an N\textsubscript{2}O(a) intermediate, which then decomposes to N\textsubscript{2}(g)+O(a), or (ii) N(a)+N(a)→N\textsubscript{2}(g) [1]. This paper reports a sharp change in the N\textsubscript{2} emission channel at around 500 K from N\textsubscript{2}O(a)→N\textsubscript{2}(g)+O(a) toward the N(a)+N(a)→N\textsubscript{2}(g) reaction in the steady-state NO+D\textsubscript{2} reaction on stepped Pd(211)=[(S)3(111)×(100)] and the limited extent of the channel change in the NO+CO reaction over the range of 450 K to 700 K. The N\textsubscript{2}O decomposition channel is promoted when the reaction is carried out with hydrogen (deuterium) and then the channel change is accelerated by quick changes of surface oxygen (or NO(a)) and hydrogen into the opposite directions, and enhanced N(a) removal as ammonia on the resultant hydrogen-rich surface. The two different N\textsubscript{2} emission channels mentioned above can be separately examined by angle-resolved (AR) desorption because, in the N\textsubscript{2}O decomposition channel, the product N\textsubscript{2} is sharply emitted off normal, whereas, in the nitrogen recombination, it is desorbed nearly along the surface normal in a broader form.

The above off-normal N\textsubscript{2} emission was first found in temperature-programmed desorption (TPD) of NO-covered Pd(110) by Ikai and Tanaka [2-4]. Using an isotope tracer, they confirmed that, on Pd(110) and stepped Pd(211), this N\textsubscript{2} comes from the reaction of NO(a) with N(a); i.e., the heating of a surface with \textsuperscript{15}N(a) and \textsuperscript{14}NO(a) results in the emission of \textsuperscript{14}N\textsuperscript{15}N off normal and \textsuperscript{15}N\textsuperscript{2} along the surface normal [5,6]. For the peculiar N\textsubscript{2} emission, they proposed a desorption-mediated reaction model in which desorbing NO was suggested to affect this off-normal emission. Although a significant amount of product N\textsubscript{2}O was found in the temperature range of the off-normal N\textsubscript{2} emission in their TPD work as well, they omitted the decomposition (before desorption) of intermediate N\textsubscript{2}O(a) toward N\textsubscript{2}[5,6]. Furthermore, from the absence of such inclined N\textsubscript{2} emission in the subsequent cooling in the presence of H\textsubscript{2} and NO, they argued that this off-normal desorption channel is not involved in the catalyzed NO reduction [7,8]. On the other hand, Matsushima et al. reproduced this inclined N\textsubscript{2} emission in the absence of NO(a) in TPD procedures of N\textsubscript{2}O-covered Pd(110), Rh(110), Ir(110), and Rh(100) or N\textsubscript{2}O exposures on clean Rh(110) above 60 K, as well as the steady-state NO or N\textsubscript{2}O reduction on Pd(110), Rh(110), and Rh(100) [1,9]. The lack of difference in the desorption dynamics (spatial and/or velocity distributions) of hyper-thermal product N\textsubscript{2} between steady-state NO+CO (or H\textsubscript{2}) below about 550 K and thermal decomposition or reduction of N\textsubscript{2}O indicates the off-normal product emission from a common transition state [1] and moreover that the state of desorbing NO has no effects on the off-normal emission.

These findings have, at long last, confirmed the participation of intermediate N\textsubscript{2}O in the main pathway of catalyzed NO reduction to N\textsubscript{2} on Pd and Rh. In fact, this intermediate or N\textsubscript{2}O-like transition state emitting N\textsubscript{2} has been frequently proposed in kinetic simulations [10-14]. The origin of the inclined N\textsubscript{2} emission is due to the decomposition of N\textsubscript{2}O oriented along the [001] direction.
The oriented \( \text{N}_2\text{O} \) was later confirmed on Pd(110) by scanning tunneling microscopy [15] and near-edge X-ray absorption fine structure [16] as well as density functional theory (DFT) with generalized gradient approximation (GGA) on Pd(110) and Rh(110) [17,18]. According to the last AR measurements providing three-dimensional (3D) distributions, the inclined \( \text{N}_2 \) emission is highly concentrated around the normally directed plane along the [001] direction on Pd(110) and Rh(110) [19-21]; i.e., the orientation of the parent \( \text{N}_2\text{O} \) is preserved in the spatial distribution of desorbing \( \text{N}_2 \) even at high temperatures around 800 K.

The pathway to \( \text{N}_2 \) via the intermediate \( \text{N}_2\text{O} \) has the potential to remove nitrogen on catalyst surfaces even at around room temperature because of its fast formation and decomposition [1,22,23]. It may play a major role in surface nitrogen removal, for example, in automobile gas convertors (involving active Pt-Rh sites [7,24]) working at the start of a cold engine or in the catalyzed reduction of aqueous nitrate and nitrite ions [25-27]. However, its kinetic and dynamic behavior is still unclear. Only AR-desorption analysis can selectively examine this process because of the absence of spectroscopic observations of \( \text{N}_2\text{O}(a) \) in the course of catalyzed deNOx processes [28,29]. Stepped Pd(211) provides a stage suitable to examine this pathway because it is rather stable toward reconstructions [30] and significantly produces \( \text{N}_2\text{O} \) in the NO reduction as observed on other stepped Pd surfaces [31,32].

2. Experimental
The apparatus consists of three ultrahigh-vacuum chambers as described previously [33]. Briefly, a reaction chamber has low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy optics, and a mass spectrometer for angle-integrated (AI) signals in an analog mode. An analyzer, which is separately evacuated, has a mass spectrometer for angle-resolved (AR) measurements with a pulse counting mode. The chopper house between the reaction chamber and the analyzer is rapidly and separately evacuated. The \( \text{N}_2 \) flux is measured with the AR mass spectrometer without sensitivity corrections due to different velocities as a function of the desorption angle (\( \theta \); polar angle) because no serious shift is caused when constructing the angular distribution [20]. The angle is scanned in the normally directed plane along the \( \{111\} \) (step up-and-down) direction (see Fig. 1) because of the maximized product \( \text{N}_2 \) desorption in the decomposition of adsorbed \( \text{N}_2\text{O} \) on Pd(211) [34]. The polar angle sign is defined as negative on the side of inclined \( \text{N}_2 \) emission, referring to Ikai-Tanaka’s work (Fig. 1) [5].

A palladium crystal (from Surface Preparation Laboratory, Netherlands) in a disk-shape slice was mounted on the top of a manipulator. The LEED pattern showed a sharp (1×1) form after cleaning by \( \text{Ar}^+ \) ion bombardments, heating in oxygen, and subsequently reducing in \( \text{D}_2 \). Without further purification, commercial \( ^{15}\text{NO} \) (isotope purity: 99%), \( \text{D}_2 \) (purity: 99%) and \( ^{13}\text{CO} \) (purity: 99%) were separately backfilled. Hereafter, isotopes \( ^{15}\text{N} \) and \( ^{13}\text{C} \) are simply designated as N and C in the text.
The AI- or AR signal is determined as the signal difference between a desired surface temperature and room temperature.

3. Results

3.1 Temperature dependence

The steady-state NO+D\textsubscript{2} reaction is noticeable above \(T_s\) (surface temperature)=410 K and shows a steep N\textsubscript{2} peak at around 475 K and a broad one above 550 K (Fig. 2(a)). The AR-N\textsubscript{2} signal is monitored at \(\theta=-31^\circ\) off normal, which is the collimation (maximum flux) angle. It is well reproduced in the subsequent cooling. The former peak is large in the AR form but small in the AI form. The ratio of the AR signal to the AI one is largely decreased above 500 K, indicating changes in the angular distribution. At high D\textsubscript{2} pressures (Fig. 2(b)), the N\textsubscript{2} formation peaks are well separated; i.e., the peak at 475 K is reduced, and the N\textsubscript{2} formation above 550 K is enhanced. In this case, the ammonia formation is significant, peaking at around 550 K. In general, at low D\textsubscript{2} pressures, the surface nitrogen deposited from NO dissociation is merely removed as N\textsubscript{2} since the amounts of formed N\textsubscript{2}O and ND\textsubscript{3} are much lower (Fig. 2(a)). On the other hand, at high D\textsubscript{2} pressures, surface nitrogen is removed as N\textsubscript{2} and ND\textsubscript{3} depending on the surface temperature.

For comparison with the TPD work in Ikai-Tanaka’s report [5], the AR-N\textsubscript{2} signal at \(\theta=-31^\circ\) was recorded while the surface was heated at a constant rate of 3.3 K/s in the presence of NO and D\textsubscript{2} as well as in the subsequent cooling (Fig. 3(a)). The sharp peak is observed at around 490 K only during heating, and the broad maximum around 600 K is reproduced in both procedures, as reported. The peak at 490 K becomes sharper at higher D\textsubscript{2} pressures and is suppressed at low pressures.

3.2 Angular distribution

The AR-N\textsubscript{2} signal at 490 K during TPD is shown against the desorption angle \(\theta\) after being normalized to the unit surface area (Fig. 3(b)). It shows a distribution form of \(\cos^2(\theta+30)\). On the other hand, the signal at 600 K shows a \(\cos^2(\theta+5)\) form (Fig. 3(c)). By using the power series of the cosine of the desorption angle shift from the collimation angle, the observed distribution is de-convoluted into two components, a sharp component collimated around -30° as \(\cos^2(\theta+30)\) and a broad one directed close to the surface normal. The factor \(R\) in the figure indicates the ratio of the maximum signal between the broad and sharp component. These distributions agree well with the results in the report by Ikai and Tanaka except for the very weak \(\cos^2(\theta+5)\) component in the desorption at 490 K [5]. This may be due to the slower heating rate in the present work.

The AR-N\textsubscript{2} signal in the steady-state NO reduction is plotted versus the desorption angle in Fig. 4. The distribution is sensitive to the surface temperature, especially around 500 K. The N\textsubscript{2} desorption is sharply collimated around -30° off normal below about 490 K. Above 500 K, the signal in the normal direction is relatively increased, and the component collimated off normal is reduced.
At 590 K, the desorption flux is approximated as \( \cos^{1.5}(\theta+5) \). The observed distribution is again de-convoluted into two power components of the cosine of the desorption angle shift, a sharp off-normal component and a broad one directed close to the surface normal. The factor \( R \) sharply increases around 500 K. Below 480 K, \( \text{N}_2 \) is mostly emitted into the inclined way, whereas, above 500 K, it mostly consists of the broad component. These results agree well with those in the TPD procedures. The resultant two desorption components are the main players to emit the product \( \text{N}_2 \) even in the steady-state NO reduction on stepped Pd as well [1]. The former inclined desorption is due to the decomposition of intermediate \( \text{N}_2\text{O} \), and the latter comes from the recombination of adsorbed nitrogen atoms, as described in the Introduction [1]. The \( \text{N}_2 \) emission channel sharply changes from the decomposition of intermediate \( \text{N}_2\text{O(a)} \) to nitrogen atom recombination at around 500 K.

### 3.3 \( \text{D}_2 \) pressure effect

The \( \text{N}_2 \) emission channel change also depends on the hydrogen (deuterium) pressure. There is a critical deuterium pressure for \( \text{N}_2 \) emission. Below this point, the \( \text{N}_2 \) formation increases with increasing \( \text{D}_2 \) pressure but decreases or remains fairly constant above this point (Fig. 5). It should be noted that the \( \text{ND}_3 \) signal steeply increases above the critical point. The pathway of surface nitrogen removal changes toward ammonia formation, since the total NO consumption still increases with \( \text{D}_2 \) pressure, as seen from a continued increase of \( \text{D}_2\text{O} \) formation over the critical point and small amounts of \( \text{N}_2\text{O} \) formation. The ratio of the AR-N\(_2\) signal at -31° to the AI-N\(_2\) at 470 K somewhat decreases over the critical point, indicating a small contribution from the N(a) recombination; i.e., the decrease of \( \text{N}_2 \) signal is mostly due to the ammonia formation. At temperatures above 465 K, the ammonia formation is enhanced above the critical \( \text{D}_2 \) pressure. The kinetic transition point shifts to lower \( \text{D}_2 \) pressures at higher temperatures. The AI signals of \( \text{D}_2\text{O} \) and \( \text{ND}_3 \) are largely shifted to higher values in the procedure of decreasing \( \text{D}_2 \) pressure due to the memory of their adsorption on the chamber wall (Fig. 5).

The flash-desorption technique has been applied to determine the amounts of adsorbed species during the catalyzed NO reduction [35]. The crystal is heated from a steady-state condition at a fixed temperature to 930 K, where there are no adsorbed species except for oxygen, while AI signals due to \( \text{D}_2, \text{D}_2\text{O}, \text{ND}_3, \text{N}_2, \text{NO}, \) and \( \text{N}_2\text{O} \) are simultaneously monitored. The amount of surface nitrogen-containing species initially adsorbed (mostly NO(a) and N(a) [30,36]) is calculated as the sum of peak areas due to \( \text{ND}_3, \text{N}_2, \text{NO}, \) and \( \text{N}_2\text{O} \) although their amounts are not separately determined. Indeed, the peak areas of \( \text{ND}_3 \) and \( \text{N}_2\text{O} \) signals are negligible. With increasing \( P_{\text{D}_2} \) at fixed \( P_{\text{NO}}=1.5\times10^{-5} \) Pa and 460-480 K, the adsorbed N-containing species increases to the critical point and then decreases above it [35]. The amount of deuterium-containing species is negligible below the critical point, and above it, the amount is not determined because of the large memory effect of
3.4 NO+CO reaction

The temperature dependence of the steady-state NO+CO reaction is different from that for the NO+D₂ reaction; i.e., no sharp N₂ formation peak is found at around 480 K when CO is used (Fig. 6(a)). The reaction is noticeable above 410 K, increases sharply around 460 K, shows a broad maximum around 510 K, and then decreases at higher temperatures. In the subsequent cooling, both AI-N₂ and AI-CO₂ signals are well reproduced. The products from this reaction are N₂, CO₂ and a small amount of N₂O. The ratio of AI-signal CO₂ to that of N₂ is fortunately about 2 although these species may have differences in the mass spectrometer sensitivity and the pumping rate. The AR-N₂ signal at θ=-30° off normal (the collimation angle) also follows a similar temperature dependence except for the peak temperature around 490 K and faster decrease at higher temperatures. The AR/AI N₂ signal ratio is slowly decreased above 490 K, suggesting a slow change of the N₂ emission channel.

The AR-CO₂ signal normalized to the unit surface area at 531 K is plotted versus the desorption angle in Fig. 6(b). The desorption is collimated at around -10° off normal. By using a power series of the cosine of the desorption angle shift, the observed distribution is de-convoluted into two components, a sharp component collimated at -10° and a cosine one. The cosine component is always observed in desorbing CO₂ in the CO oxidation on palladium, showing a Maxwellian velocity distribution at the surface temperature [33]. The sharp component is approximated to a form of \(\cos^{10}(\theta+13)\) at 450 K and \(\cos^{14}(\theta+11.5)\) at 555 K. These distributions were well reproduced in the CO+O₂ reaction at a pressure ratio of \(P_{\text{CO}}/P_{\text{O₂}}=2\). It has been confirmed that the amount of surface CO in the steady-state NO+CO reaction is noticeable but below one fourth of the value equilibrium to the CO pressure (without NO), whereas the amount of surface N-containing species increases with increasing NO pressure.

The counter product N₂ desorption is sharply collimated at around -30° off normal over a wide temperature range (Figs. 6(c-d)). The distribution is again de-convoluted into two components, sharp off-normal and broader components, as shown by the broken curves. The inclined component is in a form of \(\cos^{30}(\theta+30)\) at 475 K, \(\cos^{20}(\theta+31)\) at 531 K, and \(\cos^{12}(\theta+28)\) at 610 K (not shown for brevity). This component is major even at 531 K and relatively decreases with increasing surface temperature. The ratio \(R\) of the two components increases to 0.83 at 610 K.

4. Discussion

4.1 N₂ emission via intermediate N₂O

The N₂ emission channel from the decomposition of N₂O intermediate via the reaction of NO(a)+N(a) was not accepted on Pd and Rh surfaces until a long time after the earlier proposals as
described in the Introduction [10-12,14]. The emission of N$_2$O itself was treated as a bypath yielding a harmful byproduct [37]. For example, Belton et al. confirmed the fast N$_2$O formation from N(a)+NO(a) on Rh(111), but did not succeed in confirming the subsequent decomposition emitting N$_2$ [23,38]. The same N$_2$O(a) formation pathway was repeatedly proposed on open Pd surfaces such as Pd(110), stepped Pd(211) and Pd(331) or Pd(111) with defects since N$_2$O and N$_2$ as well are significantly found in TPD procedures of NO-covered surfaces at relatively low temperatures [30-32]. However, spectroscopic observations of N$_2$O(a) are not successful in the course of the catalyzed NO reduction on Pd and Rh surfaces with or without supporting materials [28,29,39]. This is in high contrast to the N$_2$O intermediate yielding N$_2$ on Cu-oxide or metal-exchanged zeolite catalysts, which has been supported with infrared spectroscopy [14]. The above consideration of N$_2$O species on Pd and Rh surfaces as unreactive was merely due to the lack of direct evidence of N$_2$ emission from adsorbed N$_2$O before AR desorption analysis for steady-state NO reduction [1].

We consider the reason why adsorbed intermediate N$_2$O is not found with surface spectroscopy. The adsorption heat of N$_2$O on Pd(110), about 35 kJ mol$^{-1}$, is larger than the activation energy of N$_2$O(a) dissociation to N$_2$ and O(a) [1,40,41]. This tendency is common on open surfaces such as Pd(211) [34], Rh(110), Rh(100), Ir(110), and Ni(775) [42]; i.e., the intermediate N$_2$O(a) quickly decomposes and desorbs as well, yielding a very short life time at high temperatures for NO reduction although its branching to decomposition/desorption largely depends on the amount of co-adsorbed species and the surface temperature [1,41,43]. An estimated surface residence time of N$_2$O is on the order of nanoseconds, which is not long enough to allow detection of the species with surface vibration spectroscopy [29,30,39]. On the other hand, such a short surface residence is still long enough for nascent N$_2$O(a) on Pd and Rh surfaces to be oriented into a direction suitable for dissociative adsorption because of no differences in the desorption dynamics of desorbing N$_2$ between steady-state NO+CO (or H$_2$) below about 550 K and thermal decomposition or reduction of N$_2$O. It is also consistent with the fact that un-reacted N$_2$O is found in the products at low temperatures where the N$_2$O decomposition channel prevails. AR product desorption analysis for the NO or N$_2$O reduction on Pd(110), Rh(110) and Rh(100) shows the inclined N$_2$ emission characterizing the decomposition of oriented N$_2$O even at 700-800 K [1]. In fact, the collimation angle for this off-normal emission is insensitive to the surface temperature from 60 K to 800 K.

In general, the transition state (TS) of the process N(a)+NO(a)→N$_2$O(a) is different from that for the subsequent dissociation N$_2$O(a)→N$_2$(g)+O(a). The first TS is horse-like, where (N-N-O)* is attached to the surface via both nitrogen atoms [44], whereas the latter is hat-like attached to the surface via terminal nitrogen and oxygen atoms [45]. According to our recent DFT calculations [46], the former horse-like N$_2$O(a) can not dissociate directly to N$_2$(g)+O(a), but it rather transforms via highly tilted linear N-bonded TS into hat-like N$_2$O(a), which then dissociates into N$_2$ and O(a). Such a transformation of horse-like to hat-like N$_2$O via tilted N-bonded form is also compatible with the
DFT study of Ricart et al [47]. Thus, we may even expect in some specific cases different desorption
dynamics of N\textsubscript{2} in the NO reduction from that in the N\textsubscript{2}O reduction/decomposition, in particular,
when nascent N\textsubscript{2}O(a) in the former reaction displays different adsorption structures from that of the
latter, because several stable forms with very similar adsorption energy have been recently predicted
for adsorbed N\textsubscript{2}O [46,48].

Cho (kinetically) and Belton (with IR spectroscopy) drew negligible re-adsorption of N\textsubscript{2}O on
NO- or CO-covered surfaces [13,39]. It is noteworthy that this intermediate N\textsubscript{2}O is formed in the
adsorption state. The branching as a result of the subsequent decomposition/desorption is largely due
to the difference in the activation energy between both processes and co-adsorbed species; i.e., it
does not involve an adsorption process of gaseous N\textsubscript{2}O. Thus, the participation of this intermediate
in the NO reduction cannot be examined from the reactivity of gaseous N\textsubscript{2}O.

4.2 N\textsubscript{2} emission channel change

For the formation of intermediate N\textsubscript{2}O(a), NO(a) must partly dissociate to yield N(a). The N\textsubscript{2}
formation via N\textsubscript{2}O(a) is noticeable at around 410 K, much below the temperature of 490 K estimated
with high-resolution electron energy loss spectroscopy [30]. The overall reaction at low temperatures
is controlled by either NO dissociation or N\textsubscript{2}O(a) formation, since nitrogen-containing species (N(a)
and NO(a) [30,36]) are present in a significant amount and both the decomposition and desorption of
resultant N\textsubscript{2}O(a) are so fast that it cannot be detected with surface spectroscopy [1,28,29]. On this
surface, the dissociation of NO(a) and the reaction of NO(a)+N(a) proceed with comparable rates
since a mixture of \textsuperscript{15}N(a) and \textsuperscript{14}NO(a) can be simply prepared just below the temperature of NO
dissociation and desorption [6]. On the other hand, the recombination of N(a) is relatively enhanced
at higher temperatures because of the high activation energy [1,5,49,50] and depleted NO(a) by
increased desorption and dissociation [36]. Surface nitrogen atoms are also removed as ammonia,
especially above the critical D\textsubscript{2} pressure.

The reaction of 2D(a)+O(a)→D\textsubscript{2}O(a) is very fast on Pd surfaces above 400 K [51]; i.e., either
\( \Theta_D \gg \Theta_O \) or \( \Theta_O \ll \Theta_D \) is possible in steady-state NO reduction under a high vacuum, where \( \Theta_D \) and
\( \Theta_O \) stand for the coverage of O(a) and D(a), respectively. At lower temperatures or low D\textsubscript{2}
pressures, the reaction of D(a) with O(a) is still very fast, providing unoccupied sites suitable for the adsorption
and dissociation of NO as well as for the decomposition of N\textsubscript{2}O(a). This enhances the NO
dissociation with increasing D\textsubscript{2} pressure thus increasing the content of nitrogen atoms on the surface
without accumulation of D(a) leading to the enhanced N\textsubscript{2}O pathway. The amount of oxygen atoms
deposited from NO(a) is significant below the critical point and is sharply suppressed above it
because of the fast 2D(a)+O(a) reaction and depleted NO(a); i.e., at the transition point, the amounts
of surface hydrogen and oxygen sharply change into the opposite directions. Thus, D(a) is
accumulated above the kinetic transition point, and then the ammonia formation is enhanced and the
N₂O formation itself and its decomposition are reduced. The reaction with N(a) is not as fast as that with O(a), and the ammonia formation then competes with both N₂O formation and N-atom recombination, since its activation energy is in between the latter two processes.

In the N₂O pathway when CO is used, either N₂O formation or decomposition (NO dissociation as well) is retarded by CO(a) [1]. In fact, CO(a) remains significantly below about 500 K and occupies adsorption or dissociation sites. It removes O(a) as CO₂ but with a slower rate than hydrogen does [51,52], yielding slower switching of the amounts of CO(a) and O(a). Actually, no sharp critical point is found in the CO dependence for the NO+CO reaction.

A similar change of the N₂ emission channel is also observed on Pd(110) and Rh(100) in a slower manner [1,53]. The sharp change on Pd(211) is largely due to the enhanced N₂O pathway because both the reduced NO(a) and enhanced nitrogen removal as ammonia are also observed on Pd(110) where the N₂O pathway is not sharply enhanced [53]. The following factors may contribute to acceleration of this pathway: (i) Intermediate N₂O(a) dissociates rather than desorbs; i.e., it has higher selectivity to N₂ than that on Pd(110) [53]; and (ii) There is high accumulation of N(a) due to the rapid dissociation of NO(a) on stepped Pd(211) without hydrogen accumulation [30].

4.3 Off-normal N₂ emission

The mechanism of the inclined N₂ emission has not been fully understood, even in the dissociation of adsorbed N₂O on the widely studied Pd(110). The nascent product N₂ on Pd(211) may move in a way similar to that in the N₂O+CO (or H₂) reaction on Pd(110) and Rh(110) because of the similar spatial distribution [1,20,21,34].

The following findings are reported for the N₂O dissociation on Pd(110) [1,45]. (i) No N₂O is adsorbed through the terminal oxygen, and a tilting form through the terminal nitrogen is not reactive. (ii) Reactive N₂O is oriented along the [001] direction; this species is bent and bonded to the surface via terminal N and O atoms. (iii) The inclined N₂ desorption is initiated by the dissociation of N₂O, where the N-O bond is broken first.

Immediately after this bond rupture, the resultant nascent N₂ is attracted to the metal surface (the N₂-surface bond is similar in strength and length to the N₂O-surface bond) [45]. Nevertheless, the N-metal bond in the nascent product is likely to be broken before being thermalized/stabilized to the ground state because of considerable repulsive forces received from the counter product O(a). Indeed, off-normal N₂ emission is observed considerably below the desorption temperature of adsorbed N₂; i.e., at 85-100 K on Pd(110) [41,54], 100 K on Ir(110) [43], and about 60 K on Rh(110) [55]. Adsorbed N₂ is desorbed at around 120 K on Pd(110), 200 K on Ir(110) [43] and 160 K on Rh(110) [1]. Furthermore, consecutive N₂ emission after the N-O bond rupture is suggested from the spatial distribution highly concentrated around the normally directed plane along the orientation of the parent molecule. In the steady-state N₂O reduction on Pd(110) and Rh(110) as well as NO
reduction on Pd(110) below about 550 K, the N\textsubscript{2} distribution is sharp versus the azimuth angle shift, yielding a width of about 30° at half maximum [19-21]. This suggests the repulsive desorption from the site bonding to the nascent N\textsubscript{2} without transfers to other sites. After the N-O bond rupture, the nascent N\textsubscript{2} fragment is proposed to be swung over the bonding metal atom because of the repulsive force operative from the counter product oxygen. The sequential (delayed) break of the N-metal bond lets the N\textsubscript{2} fragment finally leave the surface. According to recent DFT-GGA calculations, the adsorption energy of N\textsubscript{2} to the metal surface is reduced with increasing the tilting of the molecular axis from the stable normal direction. The N\textsubscript{2}-surface bond is the weakest at around 35° off normal on Pd(110) and Rh(110) [46], suggesting inclined desorption after the N\textsubscript{2} is swung over the bonding metal atom. The resultant collimation angle will be shifted more off normal over the weakest bonding angle when the repulsive forces from the counter oxygen are strong enough because of the presence of high kinetic energy (desorption before stabilization). Significant repulsive forces to the nascent N\textsubscript{2} have already been predicted on Pd(110) from DFT-GGA [45]. This will lead to larger collimation angles on surfaces with smaller work functions or smaller lattice constants because of the resultant more polarized or closer oxygen. Thus, by considering the extent of repulsive forces, we may explain the reported order of the collimation angles on different surfaces; i.e., 60-75° on Rh(110), 66-71° on Rh(100) [1] > 50-65° on Ir(110) [43,56] > 40-45° on Pd(110). The large angle shift is expected on Rh(110) and Rh(100) with a lower work function [57] and a smaller lattice constant, yielding the more polarized oxygen at closer distances than those on Pd(110). The shift on Ir(110) will be between the others because of the intermediate work function and lattice constant [57]. Generally, the collimation angle is affected from (i) the repulsive forces from the counter product O(a), (ii) the shape of the potential energy surface of the N\textsubscript{2}(a) above the metal surface, and (iii) the amount of released energy and its partitioning [9]. The cumulative effect from these factors must be theoretically examined.

According to this model of the transition state for N\textsubscript{2}O decomposition, we can examine active forms of N\textsubscript{2}O(a) on the present surface because the off-normal (around -25°) N\textsubscript{2} emission has been reported in the N\textsubscript{2}O decomposition on Pd(211) at around 110 K under AR-TPD conditions as well [34]. Its emission is highly concentrated in the plane along the step up-and-down direction. This collimation is close to that in the present work. A suitable candidate of adsorbed N\textsubscript{2}O should be oriented along the [111] direction; i.e., at the transition-state, the terminal oxygen atom will interact with step atoms so that the nascent N\textsubscript{2} is emitted over the (111) facet toward the (100) step normal side. According to preliminary DFT calculations, a suitable form of N\textsubscript{2}O(a) is adsorbed through a terminal nitrogen atom and tilted in the [111] direction toward the step edge. In the course of dissociation, the N\textsubscript{2}O tilts further and bends with the terminal O toward the bridge site at the step edge, and the N-O bond concomitantly elongates [46]. The resulting transition state is similar to that
reported by Burch on Pt(211) [58]. The nascent N$_2$ emitted from the N$_2$O is swung in the [111] direction toward the (111) facet and finally leaves the surface. The resultant collimation angle shifts toward the surface normal more than that on Pd(110) (40°-45° off normal) because of the inclination (19.5°) of the (111) facet and a similar distance between the product oxygen and the nascent N$_2$. Indeed the difference in the collimation angle between Pd(110) and Pd(211) is similar to the angle of inclination of the (111) facet of Pd(211).

5. Conclusions

The product N$_2$ distribution has been studied in the steady-state NO+D$_2$ reaction on stepped Pd(211) by angle-resolved desorption measurements. The following conclusions were reached.

(1) The desorbing N$_2$ is highly collimated at about 30° off normal toward the step down direction in the intermediate N$_2$O decomposition. On the other hand, it is broadly collimated near along the surface normal in the recombinant of N(a).

(2) A sharp change of the N$_2$ emission channel from N$_2$O(a)→N$_2$(g)+O(a) to N(a)+N(a)→N$_2$(g) takes place at around 500 K. In the steady-state NO+CO reaction, the pathway gradually changes above 500 K. This channel change is promoted by hydrogen (deuterium) to limited extents.

(3) A model for the off-normal N$_2$ emission on late transition metals and an active intermediate N$_2$O form on Pd(211) have been proposed.

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References

Our recent AR-work shows that in a steady state N$_2$O+CO reaction on Ir(110), the desorption of the product N$_2$ is split into two components in the plane along the [001] direction as a form of $\cos^{10}(\cos(\theta-\theta_0)+\cos(\theta+\theta_0))$ at 500 K-700 K with $\theta_0=50^\circ$-$60^\circ$. 


Figure Captions

Fig. 1 Top and side views of stepped Pd(211), definition of crystal axes, and the definition of the desorption angle, $\theta$.

Fig. 2 Surface temperature dependence of Al product signals and AR $^{15}$N$_2$ signals at -31° off normal in a steady-state $^{15}$NO+D$_2$ reaction with $P_{NO}$= 1.5×10$^{-5}$ Pa and $P_{D2}$= (a) 1.2×10$^{-5}$ Pa and (b) 3.2×10$^{-4}$ Pa. The temperature was increased stepwise to 800 K and then decreased. AR-N$_2$ signals observed in the direction of increasing surface temperature are designated by filled squares and those in the downward direction by open squares. Only Al signals in the direction of increasing temperature are shown for clarity. No D$_2$O signals are shown in (b) because of the large uncertainty in the presence of a high D$_2$O background. AI-N$_2$: ▲, D$_2$O:○, N$_2$O:◇, ND$_3$:▽, and AR-$^{15}$N$_2$:■, □.

Fig. 3 (a) Traces of the AR-N$_2$ signal at -31° off normal in the heating and subsequent cooling in the presence of a $^{15}$NO+D$_2$ mixture ($P_{NO}$= 1.5×10$^{-5}$ Pa, and (i) $P_{D2}$= 4.4×10$^{-5}$ Pa or (ii) 1.1×10$^{-5}$ Pa). Angular distributions of desorbing $^{15}$N$_2$ in the plane along the step up-and-down direction; (b) peak at 490 K and (c) desorption at 600 K. Typical deconvolutions are shown by broken curves. The solid lines indicate the summation. The value of $R$ represents the ratio between the maximum signals of the resultant broad and sharp components.

Fig. 4 Angular distributions of desorbing $^{15}$N$_2$ in the plane along the step up-and-down direction in the $^{15}$NO+D$_2$ reaction at $T_s$=450-590 K. The steady-state $^{15}$NO + D$_2$ reaction was established at $P_{NO}$= 1.5×10$^{-5}$ Pa and $P_{D2}$= 2.9×10$^{-5}$ Pa. The surface temperature is (a) 450 K, (b) 478 K, (c) 500 K and (d) 590 K. The signals observed in the direction of the increasing desorption angle (from the negative region toward the positive) are designated by closed symbols, and those in the decreasing desorption angle, by open symbols. Typical deconvolutions are shown by broken curves. The solid lines indicate the summation. The value of $R$ represents the ratio between the maximum signals of the resultant broad and sharp components.

Fig. 5 Variation of the product AI mass signals and the AR-$^{15}$N$_2$ signals at -31° off normal in the steady-state NO reduction with D$_2$ pressures. The vertical lines indicate the kinetic transition point. The signals observed in the direction of the increasing D$_2$ pressure are designated by closed symbols, and those in the decreasing pressure, by open symbols. AI-N$_2$:▲,△, D$_2$O:●, N$_2$O:◆,◇, ND$_3$:▽,◇, and AR-$^{15}$N$_2$:■, □.
Fig. 6 (a) $T_S$ dependence of AI product signals and AR $^{15}\text{N}_2$ signal at -30° off normal in a steady-state $^{15}\text{NO} + ^{13}\text{CO}$ reaction with $P_{\text{NO}}=1.5\times10^{-5}$ Pa and $P_{\text{CO}}=2.9\times10^{-5}$ Pa. Signals observed in the direction of the increasing surface temperature are designated by filled symbols, and those in the downward direction, by open symbols. Angular distributions of desorbing products in the plane along the step up-and-down direction; (b) $^{13}\text{CO}_2$ at 530 K, (c) $^{15}\text{N}_2$ at 531 K, and (d) $^{15}\text{N}_2$ at 475 K. The signals observed in the direction of the increasing desorption angle are designated by closed symbols, and those in the decreasing desorption angle, by open symbols. Typical deconvolutions are shown by broken curves. The solid lines indicate the summation. The value of $R$ represents the ratio of the maximum signals of the resultant components.
Fig. 1 Mat
(a) $P_{D_2}/P_{NO}=0.8$

AR-N$_2$ at -31$^\circ$

(b) $P_{D_2}/P_{NO}=22$

AR-N$_2$/100 c/s

Fig. 2 Mat
(b) 490 K in TPD
$R = 0.1$

(30$^\circ$, 0$^\circ$, $\cos^2(\theta + 5)$, $\cos^2(\theta + 30)$)

(c) 600 K in TPD
$R > 100$

Fig. 3 Mat
\[ \cos^2(\theta + 5) \]

(a) 450 K
\[ R = 0.09 \]

(b) 478 K
\[ R = 0.11 \]

(c) 500 K
\[ R = 0.80 \]

(d) 590 K
\[ R = 33 \]

Fig. 4 Mat
Fig. 5 Mat
Fig. 6 Mat