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Title	An Experimental Approach to Transition States of Surface Reactions; Energy Partitioning in Repulsive Desorption
Author(s)	Matsushima, Tatsuo; Orita, Hideo; Kokalj, Anton
Citation	e-Journal of Surface Science and Nanotechnology, 11, 65-71 https://doi.org/10.1380/ejsnt.2013.65
Issue Date	2013
Doc URL	https://hdl.handle.net/2115/56515
Type	journal article
File Information	e-JSSNT2013 Matsushima Transition State approach.pdf



An Experimental Approach to Transition States of Surface Reactions; Energy Partitioning in Repulsive Desorption*

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(Received 24 February 2013; Accepted 18 March 2013; Published 27 April 2013)

In a chemical reaction, both material conversions and energy partitioning take place simultaneously. Then its mechanism must be characterized from the viewpoints on both sides. Energy partitioning in surface reactions can be examined on product desorption processes when these are repulsive. This principle is exemplified in $\text{CO(a)} + \text{O(a)} \rightarrow \text{CO}_2\text{(g)}$ on $\text{Pd(110)(1}\times\text{1)}$, and its application is proposed for $\text{N}_2\text{O(a)} \rightarrow \text{N}_2\text{(g)} + \text{O(a)}$ on the same surface. Structural information of desorption sites and active intermediates, as well as transition states, can be delivered from desorption- and azimuth-angle dependences of physical quantities of desorbing hyper-thermal products; i.e., anisotropic distributions of their flux, and translational and internal energies. [DOI: 10.1380/ejsnt.2013.65]

Keywords: Angle-resolved thermal desorption; Surface chemical reaction; Palladium; Carbon dioxide; Nitrous oxide; Nitrogen; Single-crystal surfaces

I. INTRODUCTION

In a chemical reaction, both material conversions and energy partitioning take place simultaneously. It is clear that, referring to dynamic analysis of gaseous reactions by means of molecular beams [1], a reaction mechanism must be examined from the viewpoints on both sides. On the other hand, chemical reactions on metal surfaces have long been analyzed in chemical kinetics dealing only with material conversions; i.e., its conversion frequency (reaction rate) is followed as a function of both the amounts of adsorbed reactants and the surface temperature, proposing a consistent mechanism. This treatment omits the energy information of nascent products, counts only the number of product molecules, and neglects energy partitioning during the reaction event. Of course, very fast energy flow from nascent products into a metal surface prevents the energy partitioning from being analyzed [2]. There is still a chance to examine this energy partitioning in a product desorption event, even on metal surfaces, when the desorption is repulsive. The analysis of this partitioning will provide an approach to transition states (TS). This review delivers desorption dynamics sensitive to structures of desorption sites and active intermediates, as well as TS species. It is derived from anisotropic distributions of desorbed product flux and their translational and internal energies. The principle of this dynamics is based on energy partitioning in repulsive desorption into translational and rotational modes of nascent products.

II. SPATIAL DISTRIBUTION AND SURFACE STRUCTURE

In desorption dynamics, the flux and both the translational and internal energies of hyper-thermal products are analyzed before energy dissipation as a function of desorption angle (polar angle: θ . It is measured with respect to surface normal) along different crystal azimuths [3]. The resultant desorption dynamics can deliver surface-structure information only when significant anisotropy is found in these physical quantities. On the other hand, no structural information is derived when the nascent product is trapped on a surface due to chemisorption or dispersion forces before desorption. The resultant distribution is in an isotropic cosine form because of the fast energy relaxation in the order of picosecond on metal surfaces [2]. The structural information is also not derivable when desorbed products are hyper-thermal but show no anisotropy, although the potential energy surface (PES) can be examined along the surface normal direction.

In order to leave a surface before being thermalized, nascent products must be formed on a repulsive part of PES; i.e., they are more closely formed to the surface than the equilibrium position. The resultant desorption yields hyper-thermal products and is sharply collimated along the direction of repulsive force, yielding the maximum flux position (collimation angle). The translational energy is also maximized at this angle. The angle between the molecular axis of TS and the repulsive force direction is an important key in the repulsive desorption event; i.e., the nascent molecule torques when it is inclined against the surface just before desorption, as described in detail in the next chapter. This principle (well-known in gaseous reaction dynamics [4]) is applicable to repulsive desorption in surface reactions.

Surface atom arrangements and structures of adsorbed molecules have been clear after remarkable developments of surface-vibration spectroscopy since the 1960s and of

*This paper was presented at the 32nd Annual Meeting of the Surface Science Society of Japan, Tohoku University, Sendai, Japan, November 20-22, 2012.

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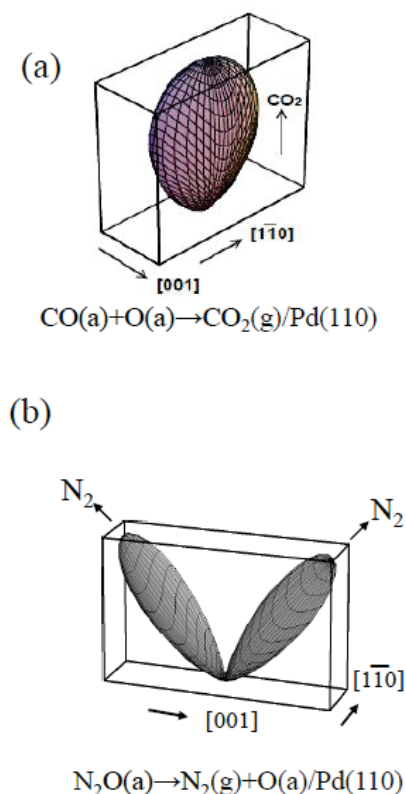


FIG. 1: Three-dimensional spatial distributions on Pd(110) of (a) desorbing product CO_2 in CO oxidation under TPD conditions [8] and of (b) N_2 in a steady-state $\text{N}_2\text{O} + \text{CO}$ reaction at 520 K [9].

scanning probe microscopy since the 1980s [5, 6]. However, the identification of reaction sites (active centers [7]) or active intermediates is still indirect because the above structure information is static and far from the reactions. Here, we need a method to derive structural information concerned with reaction sites or active species through the reaction itself. Such information can be provided from desorption dynamics. The structure sensitivity of desorption dynamics has been clearly exemplified in both an associative desorption as $\text{CO(a)} + \text{O(a)} \rightarrow \text{CO}_2\text{(g)}$ on Pd(110)(1 $\times$ 1) and a dissociative one as $\text{N}_2\text{O(a)} \rightarrow \text{N}_2\text{(g)} + \text{O(a)}$ on the same surface. In these processes, the product desorption flux and its translational energy show remarkable anisotropy (Fig. 1) [8, 9]. In the CO oxidation step, the product CO_2 is emitted immediately after the strong bond of Pd–O(a) in TS is broken, and the resultant spatial distribution of desorbed CO_2 is affected by the slope of the O(a) adsorption site and the symmetry around it [10]. In the N_2 desorption, the orientation of parent N_2O molecules is preserved in the spatial distribution, i.e., desorbing N_2 is highly concentrated in an inclined way in the plane along the [001] direction, and adsorbed N_2O is also oriented along the same direction [11]. The above structure information is mostly derived from the anisotropic spatial distribution. Our understanding of desorption dynamics shifted into a new stage in 2008. Remarkable desorption- and crystal azimuth-angle dependences have been found in the rotational and vibrational energies of desorbing CO_2 in CO oxidation on palladium

surfaces [12].

III. ENERGY PARTITIONING IN REPULSIVE DESORPTION

The translational energy (or temperature) of hyperthermal products is maximized in the surface normal direction when their desorption is sharply collimated along the surface normal and commonly decreases with increasing desorption angle, for example, in $2\text{H(a)} \rightarrow \text{H}_2\text{(g)}$ on Ni(111) [13], $\text{CO(a)} + \text{O(a)} \rightarrow \text{CO}_2\text{(g)}$ on Pt(111) [14], and $2\text{N(a)} \rightarrow \text{N}_2\text{(g)}$ on Rh(111) [15]. Comsa and his co-workers have carefully analyzed the velocity distribution of desorbed H_2 on Ni(111) and confirmed translational temperatures below the surface value (about 70%) at desorption angles above 60° following a steep decrease from the maximum value at the surface normal (about twice the surface temperature) with increasing desorption angle [16]. Here, desorption models involving quantum effects are requested, and on experimental sides, the desorption-angle dependence must be examined for the internal energy.

Yamanaka has reported the desorption- and azimuth-angle dependences of the rotational and vibrational energies of desorbed CO_2 in the CO oxidation on Pd in 2008 [12]. Two representative infrared (IR) emission spectra from the nascent product CO_2 in CO oxidation at 700 K on Pd(111) are reproduced in Fig. 2(a). The IR emission spectrum observed from CO_2 emitted along the surface normal direction is narrower than that at 30° off normal. The spectra were monitored with a wave number resolution of 4 cm^{-1} . The resultant spectrum becomes broader at higher rotational temperatures. Thick, solid lines show the optimum simulations. For comparison, the best simulations in the surface normal direction are drawn by the broken line in the spectrum at 30° . The resultant rotational temperature is plotted against the desorption angle in Fig. 2(b). The rotational temperature is about half the surface temperature at the surface normal and steeply increases about 1.5 times at 30° with increasing desorption angle. On Pd(110)(1 $\times$ 1), the decrease of the rotational temperature depends on the crystal azimuth; i.e., it remains fairly constant along the surface trough (along the $[1\bar{1}0]$ direction) and decreases quickly in the plane perpendicular to it (along the [001] direction). On this surface, the anisotropy is remarkable in the spatial distribution and in both translational and internal energies. Both the energy and the product are highly released into the plane along the $[1\bar{1}0]$ direction.

The vibrational temperature of CO_2 on Pd(111) and Pd(110)(1 $\times$ 1) is higher than the surface value. It decreases at higher desorption angles on Pd(111) or changes differently on Pd(110)(1 $\times$ 1) depending on the azimuth. A mechanism has been proposed for these changes [17]; however, conclusive discussions are difficult until the angle dependence is determined at each rotation-vibration mode. The vibrational modes are unlikely to be directly related to the desorption event because the energy level is largely separated, as compared with that in the rotational level, and its relaxation is much slower. In fact, the product molecules with hot vibration but cooled rotation and translation have been reported for $2\text{N(a)} \rightarrow \text{N}_2\text{(g)}$

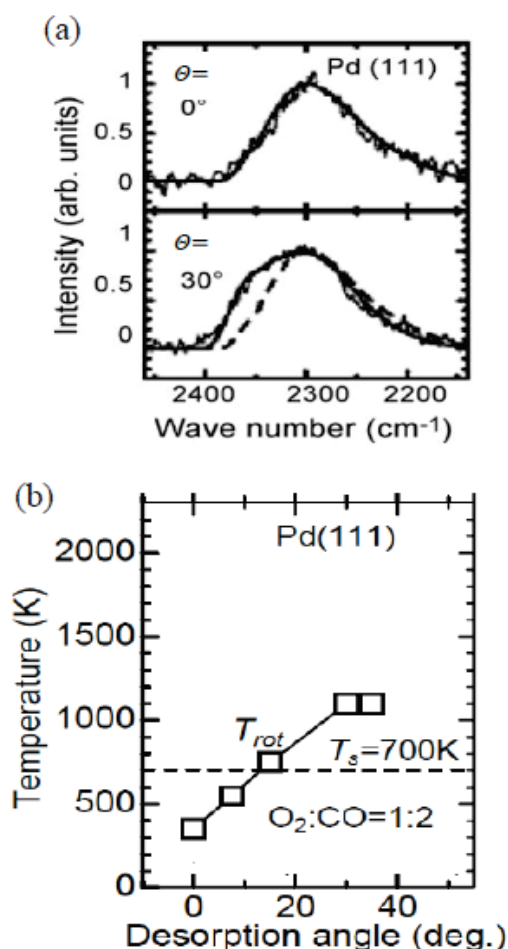


FIG. 2: (a) Infrared emission spectra from the product CO_2 emitted along the surface normal and 30° off normal directions in a steady-state CO oxidation at 700 K on Pd(111) [12a]. The total pressure in front of the surface is 0.49 Pa with a CO/O_2 flux ratio of 2:1. Thick, solid lines show the optimum simulations. For comparison, the best simulations at the surface normal are drawn by the broken line in the spectrum at 30° . (b) Desorption-angle dependence of the rotational temperature.

on Pd(110) [18]. In this review, as first order approximation, the vibration is handled independently from the rotational and translational modes.

A model with new concepts is required for this repulsive desorption, because the translational temperature decreases with increasing desorption angle, whereas the rotational temperature increases or remains constant, showing remarkable anisotropy. The model must be experimentally confirmed in quantitative way to deliver the surface structural information. The former decrease of the translational energy has been explained by introducing a width parameter for the activation energy barrier for *activated adsorption* and by assuming the *detailed balance principle* (DBP) for adsorption and desorption processes without effects on the anisotropic rotational and translational modes [18, 19]. The newly proposed model explains the desorption-angle dependence of both quantities, being based on energy partitioning into rotational and translational modes in the repulsive desorption event [12]. The

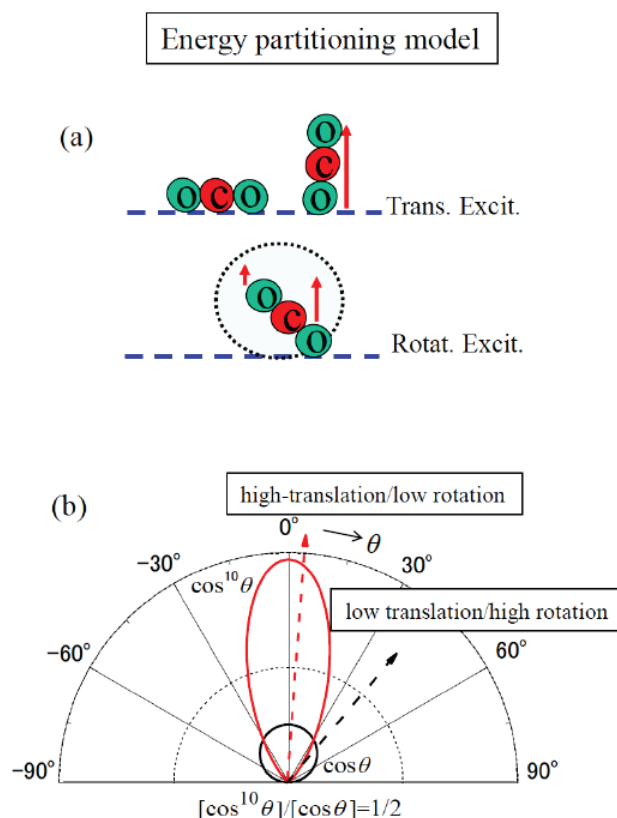


FIG. 3: (a) An energy-partitioning model in a repulsive-desorption event. Arrows show repulsive forces exerted from reaction sites. Standing or lying TS is translationally excited, whereas an inclined TS molecule torques at the desorption. (b) Flux simulations of two desorption components with $\cos^{10}\theta$ (hot translation) and cosine (hot rotation) forms. The total flux ratio of $[\cos^{10}\theta]$ to $[\cos\theta]$ is assumed to be 1/2.

transient O–C–O molecule torques when it is inclined against the surface just before desorption because the repulsive force (due to Pauli repulsion) decreases steeply with increasing distance from the surface (Fig. 3(a)). The resultant angular distribution becomes broad, since the released energy is transferred into the rotational mode. On the other hand, the translational mode is excited when the transient O–C–O stands or lies down, yielding sharply collimated desorption. Typical flux distributions for this simplified model are shown in Fig. 3(b), where the cosine distribution is assumed for the former rotational excitation and a $\cos^{10}\theta$ form is used for the latter translational excitation. Here, the total flux ratio of the former to the latter is assumed to be 2. It is clear that the molecules desorbing along the surface normal have high translational and low rotational energies because of the predominant fast component, whereas the product emitting at large desorption angles has lower translational and higher rotational energies because of the relatively enhanced cosine component. Translational temperatures below the surface value will appear when the repulsive forces are mostly converted into the rotational mode. Actually, the TS orientation is distributed around the most stable form, and the energy partitioning depends on this distribution. In order to confirm this energy partitioning model, both

the rotational and translational energies must be determined simultaneously as a function of desorption angle; i.e., the correlation between the rotational and translational energies must be examined at different desorption and azimuth angles. For this purpose, the population at each internal energy level and the velocity distribution of the molecules there must be determined simultaneously.

The roto-translational correlation versus desorption angle will be used to examine the orientation of TS. The first trial to examine the TS orientation has been proposed on Pd(110) [12, 17]. The molecular axis of transient O–C–O has been proposed to be inclined in the plane along the $[1\bar{1}0]$ direction immediately before desorption, since both the rotational and translational energies, as well as the product CO₂ molecules, are highly released into the plane along the $[1\bar{1}0]$ direction.

IV. STRUCTURE-INSENSITIVE DESORPTION DYNAMICS

The structural information of reaction (desorption) sites can be derived from desorbing products only when the physical quantities of desorbing products are anisotropic over the surface plane. As the product is repulsively desorbed from the site, the memory of this repulsive force is preserved in the physical quantities of each desorbing product in an anisotropic way; i.e., each product molecule holds only a piece of structural information after desorption. Eventually, the site structure is constructed by gathering these pieces over all of the desorption and azimuth angles. Although we can examine the potential energy curve along the surface normal, we cannot derive structural information parallel to the surface plane when no anisotropy is found in these physical quantities (for example, in the case that a sharp, angular distribution is common along any azimuth angle). This is why the angle-resolved analysis is indispensable to deriving structural information from desorbing products.

Resonance-enhanced multiphoton ionization (REMPI) is widely used to ionize desorbing products in a state-selective way and to provide the resultant ions to time-of-flight (TOF) measurements. This ion source is useful to simultaneously determine the rotational and vibrational energies as well as the translational energy. However, no structural information has ever been discussed in the work of desorption analysis using REMPI because of the lack of angle-resolved procedures (Fig. 4) [19–22]. Commonly, the desorption-angle dependence has been neglected with regard to the internal and translational energies of desorbing products. Along this line, the desorption results from REMPI-TOF in non-AR fashion are frequently combined with the adsorption probabilities measured as functions of the energy of incident molecules in an incident-angle-resolved way, by assuming DBP for adsorption and desorption processes [19, 20]. It is clear that this makes the explanations consistent. In such a way, neither structure sensitive desorption dynamics nor suitable models for the steep desorption-angle dependence of both the translational and internal energies are desirable. Nevertheless, no clear inconsistency has ever been noted in the usage of DBP, probably because it was fortunately used for the early REMPI-TOF work focused to $2\text{H(a)} \rightarrow \text{H}_2\text{(g)}$ on

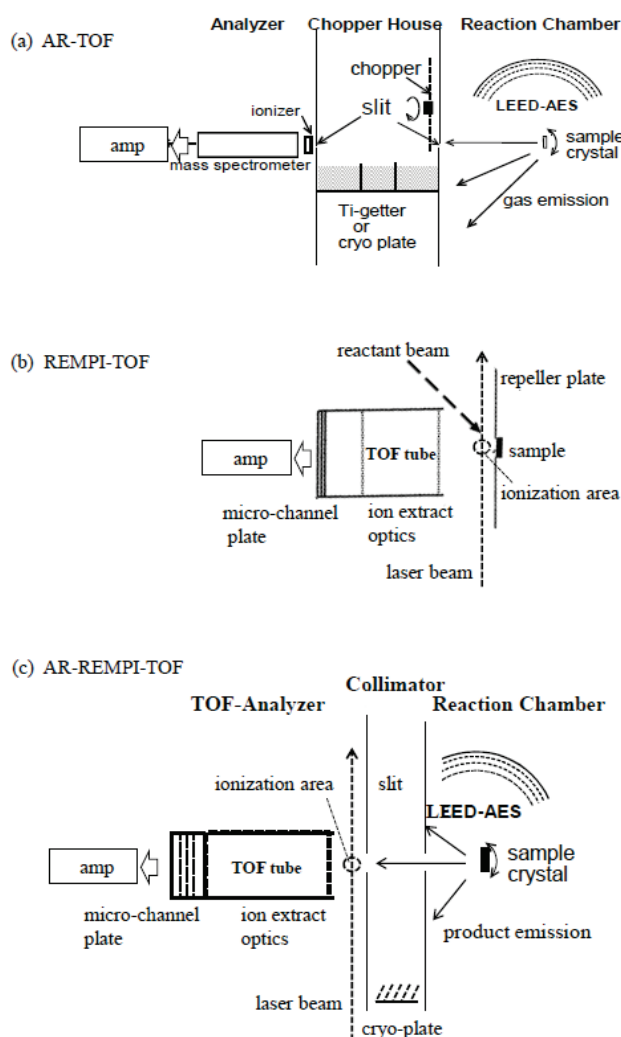


FIG. 4: Principles of three different systems for energy measurement of desorbing products. The reaction chamber is an ordinary ultra-high vacuum apparatus with standard facilities for surface analysis and a mass spectrometer. (a) Angle-resolved thermal- and steady-state-desorption measurements incorporating cross-correlation time-of-flight techniques. (b) State-resolved translational energy measurements with REMPI. A sample crystal is in the path of reactant beams. The beams are interrupted by an electronic shutter prior to the laser firing. The laser light is focused near the front of the surface, and the resulting ions are timed into a microchannel plate detector. (c) Angle- and state-resolved translational energy measurements with REMPI.

Cu(111) or Cu(100), in which no anisotropy exists in the very sharp spatial distribution of desorbing H₂ [19, 23, 24], i.e., negligible contributions from H₂ desorption at largely off-normal directions. The energy partitioning into translational and rotational modes in repulsive desorption has been examined from the viewpoints of theoretical simulations for desorbing H₂, but no discussions have focused on the resultant spatial distribution or energy distributions, probably because of the lack of experimentally observed desorption-angle dependences of internal energy [25].

On the other hand, the situation is different for the desorption of product CO₂ or N₂, since their mass is heavy (20-50% of that of metal atoms) and the bond en-

ergy of chemisorbed reactants CO(a), O(a), or N(a) is close to that of metal-metal bonds. The scattering of TS molecules into products is more inelastic (surface metal atoms are likely to move during desorption). Here, the energy partitioning into each mode of leaving products, as well as the surface, becomes important for the angle dependence of the physical quantities of leaving products more than the couplings between each mode of TS molecules. The latter couplings play important roles in the hydrogen desorption [19, 20, 22]. In fact, for example, the desorbing N₂ product in 2N(a) → N₂(g) on Pd(110) yields high vibrational energy, lowered rotational and translational energies, and a broad spatial distribution; i.e., only the vibrational excitation survives because of the slow relaxation [18].

Principles of three typical apparatuses for desorption analysis are shown in Fig. 4.

- (Angle resolved but non-state selective) Angle-resolved mass spectrometry is combined with cross-correlation chopper techniques for TOF measurements [13]. Two slits and high pumping of the space between the slits are necessary [26]. It is useful to measure spatial distributions of any product, as well as angle-resolved translational energy distributions in either temperature-programmed desorption (TPD) or steady-state reactive desorption [10, 13].
- (State selective but non-angle resolved) REMPI is used to ionize products in a state-selective way, and the resultant ions are pulled into a TOF tube. Reactants are supplied from modulated molecular beams (MB) to the front surface or diffused from a crystal back side (via permeation [27]) or inside (via absorption [22]) when hydrogen desorption is studied. Laser light beams are focused near the front of the sample surface and synchronized with MB pulses to reduce the background signal [19, 21, 22].
- (Angle resolved and state selective) A new system is designed for simultaneous analysis of both internal and translational energies in an AR way. Laser beams for REMPI are focused just outside the exit of the slits to ionize desorbing products after angle-resolved procedures. The product density in the ionization area is about 2 orders of magnitude smaller than that in non-AR REMPI. This type of apparatus can examine the concept of energy partitioning into the rotational and translational modes in the repulsive-desorption event.

V. REMARKABLY ANISOTROPIC DESORPTION

New desorption analysis with AR-REMPI-TOF (Fig. 4(c)) should be applied for reactions with the following characteristics: (1) Desorbing product molecules provide remarkable anisotropy in their physical quantities. (2) The molecules can be state-selectively ionized by means of REMPI. (3) The energy partitioning takes place in the translational and rotational modes in desorption.

The combinative desorption of H(a) into H₂(g) does not satisfy condition (1) [23]. CO₂ from the CO oxidation

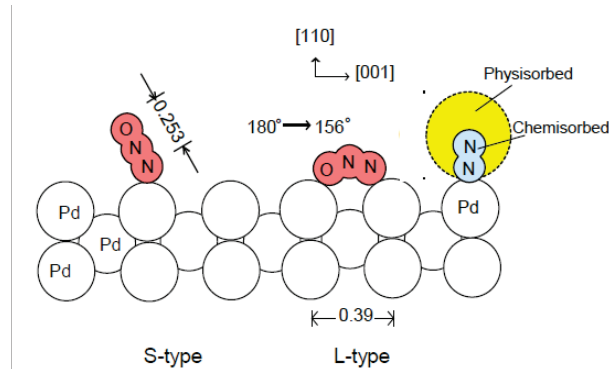


FIG. 5: Adsorption forms of N₂O and N₂ on Pd(110) [32]. The dotted circle indicates the size of an N₂ molecule estimated from van der Waals' radii. The numbers indicate the distance in nm units.

does not clear condition (2) [28, 29]. Desorbing product N₂ in N₂O(a) → N₂(g)+O(a) on Pd(110), Rh(110) or Rh(100) fulfils all three conditions [11]. The dissociative desorption of the intermediate N₂O(a) is the final N₂ emission process in the NO reduction on the best de-NO_x metal catalysts (Pd and Rh) at lower temperatures. Spatial distributions very similar to the results in Fig. 1(b) are found for desorbing N₂ in a steady state NO+CO or NO+D₂ reaction on Pd(110) below about 550 K [9]. At higher temperatures, the combinative desorption of N(a) into N₂(g) becomes predominant, yielding less anisotropy.

The desorption of N₂ is sharply collimated in an inclined way in the plane along the [001] direction on fcc metal surfaces, such as Pd(110) and Rh(110). The collimation angle of desorbing N₂ is 40-51° off normal on Pd(110) and 64-71° off normal on Rh(110) and Rh(100) [11]. Four-directional and inclined desorption is found on Rh(100) [30]. Adsorbed N₂O is oriented along the [001] direction (and also the [010] direction on Rh(100) [31]) before dissociation [11]. Kokalj has predicted two adsorption forms on Pd(110) by using density functional theory with generalized gradient approximations (DFT-GGA) as shown in Fig. 5. A tilting (on-top) form is bonding through the terminal nitrogen to the surface atom (S-type) and a lying form is oriented along the [001] direction (L-type) [32]. The L-type was later confirmed by scanning tunneling microscopy at 14 K [33]. The co-adsorption of the two forms was also confirmed with near-edge X-ray absorption fine structure at 60 K [34]. In fact, the adsorption energy of N₂O on Pd(110) is around 35 kJ/mol, close to the physical adsorption energy, and the activation energy to dissociation is also close to it.

The active species that dissociates is the L-type, since the terminal oxygen must be deposited on the surface (Fig. 6(a)). According to DFT-GGA calculations by Kokalj, this species is bonded to the surface via terminal N and O atoms and considerably bent because of the charge backdonation from the metal [32]. The N₂ desorption is initiated by breaking the N-O bond in N₂O(a) [35]. Immediately after this bond rupture, highly repulsive forces are induced between the resultant nascent N₂ and the counter product oxygen ad-atom (Fig. 6(b)) [35]. At this

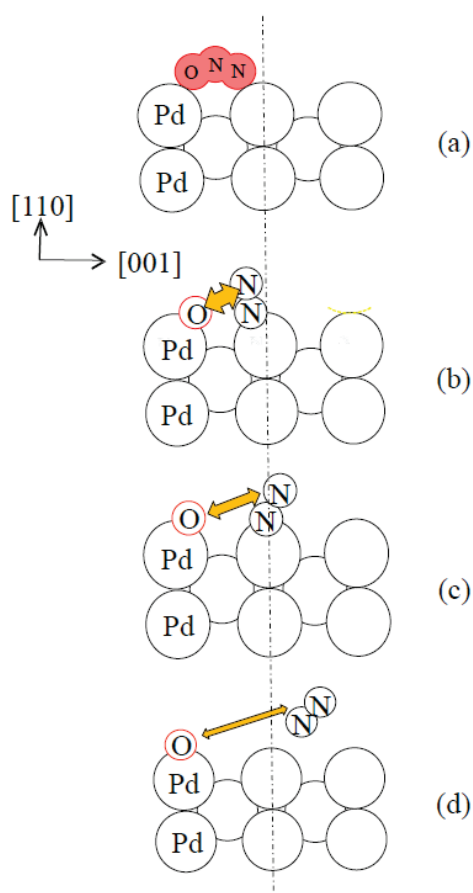


FIG. 6: Proposed N_2 desorption from $\text{N}_2\text{O}(\text{a})$. (a) The bent N_2O is oriented along the $[001]$ direction. (b) At $\text{N}-\text{O}$ dissociation, large repulsive forces are induced between the nascent N_2 and the counter product $\text{O}(\text{a})$ [35]. (c) The nascent N_2 is swung over the bonding metal atom. (d) The N_2 fragment is left around the weakest N -metal bonding position. The arrows show repulsive forces.

moment, the position of the nascent N_2 above the surface is slightly farther than the equilibrium position of chemisorbed $\text{N}_2(\text{a})$, hence the bonding of the terminal nitrogen to the metal atom is not yet broken. It is proposed that the nascent N_2 is then swung over the bonding metal atom (passing the most stable standing form) to an inclined position on the opposite side (Fig. 6(c)). The sequential break of the terminal N -metal bond lets the N_2 fragment finally leave the surface (Fig. 6(d)). According to recent DFT-GGA calculations [36], the adsorption energy of N_2 to the metal surface is reduced by increasing the tilting of the molecular axis from the surface normal. The N_2 -surface bond is the weakest at around 35° off normal on $\text{Pd}(110)$ and $\text{Rh}(110)$, suggesting inclined desorption after the N_2 fragment is swung to this angle. The resultant collimation angle will shift 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. This model predicts larger collimation angles with stronger repulsive forces operative toward the nascent N_2 from the counter-oxygen atom. Thus, the collimation angle on $\text{Pd}(110)$ may be smaller than that on $\text{Rh}(110)$ or $\text{Rh}(100)$ because the repulsion

is expected to be larger on rhodium than on palladium, considering smaller work functions [37] and smaller lattice constants on rhodium; i.e., more polarized or closer oxygen is formed on Rh surfaces [38].

This swing-desorption model clearly explains the new measurements concerned with N_2 emission on stepped $\text{Pd}(211)=[(\text{S})3(111)\times(100)]$. N_2 desorption is sharply collimated at $25\text{--}31^\circ$ off normal toward the step-down direction in either the thermal decomposition of $\text{N}_2\text{O}(\text{a})$ at around 110 K [39] or a steady-state $\text{NO}+\text{D}_2$ (or $\text{NO}+\text{CO}$) reaction below about 550 K [38]. In the latter, of course, the intermediate $\text{N}_2\text{O}(\text{a})$ emits the product N_2 . According to the above swing model, a suitable pre-dissociation state of adsorbed N_2O should be oriented along the step up-and-down direction, and the terminal oxygen atom will be deposited on step Pd atoms. On this stepped surface, N_2O adsorbs through the terminal nitrogen atom bonding to step Pd atoms in a bridge form [40]. This adsorption form is too far to release the terminal oxygen onto the step Pd atoms. Hence, the DFT-GGA calculations have predicted that, in the course of dissociation, the N_2O tilts toward the nearest step in the step-up direction and bends with the terminal O toward the bridge site at the step edge. The $\text{N}-\text{O}$ bond concomitantly elongates [38] and the terminal nitrogen atom of the dissociating molecule moves from the stable bridge site onto Pd atoms on the (111) terrace [38, 40]. A very similar dissociation was first proposed on stepped $\text{Pt}(211)$ by Burch [41]. Eventually, the nascent N_2 is swung on the terrace (not on the step edge), being affected by repulsive forces from oxygen deposited on the step atoms toward the step-down direction. Thus, the N_2 desorption will be collimated at $40\text{--}51^\circ$ off normal from the terrace normal direction in a way similar to that on $\text{Pd}(110)$, yielding $21\text{--}32^\circ$ off normal from the (211) surface normal because of the inclination (19.5°) of the (111) facet.

The above swing-desorption model predicts the emission of N_2 with hot rotation and translation. It is different from the cooled rotation of desorbing N_2 from combinative desorption in $2\text{N}(\text{a}) \rightarrow \text{N}_2(\text{g})$ on $\text{Ag}(111)$, $\text{Ru}(0001)$, and $\text{Pd}(110)$ [21]. The correlation of the rotational energy to the translational energy should be examined as a function of the desorption angle around the collimation angle. The energy-partitioning model predicts an increasing rotational temperature (or decreasing translational energy) with increasing shift from the collimation position. This can be examined only by means of the above proposed AR-REMPI-TOF method. This confirmation will make AR desorption analysis useful to separately analyze the $\text{N}(\text{a})+\text{NO}(\text{a}) \rightarrow \text{N}_2\text{O}(\text{a}) \rightarrow \text{N}_2(\text{g})+\text{O}(\text{a})$ pathway in catalyzed NO reduction [11]. The pathway will yield effective NO reduction catalysts working at low temperatures.

VI. SURFACE SPECTROSCOPY AND DESORPTION DYNAMICS

Surface-vibration spectroscopy is a powerful tool to identify surface species in the course of catalyzed reactions, but its application is limited above about 0.01 monolayer. The identification becomes more difficult when active species with low adsorption heat are co-adsorbed with reactants having higher adsorption ener-

gies. The intermediate $\text{N}_2\text{O}(\text{a})$ has been proposed frequently since 1978 for NO reduction on rhodium surfaces [42, 43]. However, the N_2O pathway has long been treated as a side reaction not yielding the final product N_2 [44] because of the lack of spectroscopic observations of $\text{N}_2\text{O}(\text{a})$ in the course of NO-catalyzed reduction [45, 46]. This lack is not surprising, since the surface residence time of adsorbed N_2O is in the order of nanosecond or less above 450 K for usual NO-reduction conditions, as estimated from a simple first order kinetics with a small adsorption heat of about 35 kJ/mol and a similar activation energy to dissociation. Furthermore, the surface is mostly covered by NO(a), N(a), and O(a) etc. It is clear that the time domain is available only by desorption dynamics and is inaccessible to surface-vibration spectroscopy since the dynamics can identify active intermediates through the reaction. The desorption dynamics also can identify active species among different adsorption forms of the same chemical species. For example, the vi-

bration spectroscopy can observe S-type $\text{N}_2\text{O}(\text{a})$ but not L-type $\text{N}_2\text{O}(\text{a})$ on Pd(110) [47], although the latter is active. Such superiority of desorption dynamics appears because of its surface-structure sensitivity. This method and surface spectroscopy are complementary to each other because the former surveys species at the exit of the reaction, whereas the latter monitors species at the reaction entrance.

Acknowledgments

This work was partly supported by a 1996 Center of Excellence (COE) Special Equipment Program of the Ministry of Education, Sports, and Culture of Japan and by Grant-in-Aid No. 21550004 for General Scientific Research from the Japan Society for the Promotion of Science.

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