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Running title; *N<sub>2</sub> distribution in N<sub>2</sub>O decomposition / T. Matsushima*

## **Angular distributions of desorbing N<sub>2</sub> in thermal N<sub>2</sub>O decomposition on Rh(100)**

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### Abstract

The angular distribution of desorbing N<sub>2</sub> was studied in the decomposition of N<sub>2</sub>O(a) on Rh(100) at 60-140 K by means of angle-resolved temperature-programmed desorption. N<sub>2</sub> desorption shows two peaks at around 80 K and 110 K. At low N<sub>2</sub>O coverage, the former collimates far from the surface normal toward the [001] direction, whereas at high coverage, the desorption sharply collimates along the surface normal. The adsorption form of N<sub>2</sub>O and its dissociation were also examined by DFT-GGA

calculations. Dissociating  $\text{N}_2\text{O}$  is proposed to be lying along the [001] direction at low coverage and to change to an upright form bonding through the terminal oxygen at high coverage.

**Key words;** Thermal desorption, Nitrous oxide, Rhodium, Surface chemical reaction, Angle-resolved DIET, Catalysis, Density functional theory calculations.

## I. Introduction

The reduction of nitrous oxide on rhodium surfaces has received much attention because of its importance in controlling the catalytic deNO<sub>x</sub> process.  $\text{N}_2\text{O}$  is not only an undesirable byproduct in the NO reduction on this best catalyst but also the key intermediate in controlling the selectivity toward  $\text{N}_2$  [1]. Knowledge of this intermediate is still limited because of the presence of several surface-nitrogen removal pathways in the deNO<sub>x</sub> process. This paper is the first to deliver the angular distribution of desorbing  $\text{N}_2$  in the thermal decomposition of adsorbed  $\text{N}_2\text{O}$  on Rh(100).  $\text{N}_2$  desorption shows two peaks at around 80 K ( $\beta_2\text{-N}_2$ ) and 110 K ( $\beta_1\text{-N}_2$ ). The former sharply collimates at 66° off normal in the plane along the [001] direction at low  $\text{N}_2\text{O}$  coverage, indicating four-directional desorption, whereas, at high coverage, its desorption shifts along the surface normal. The adsorption form of  $\text{N}_2\text{O}$  and its dissociation were also examined by density-functional theory calculations (DFT) with the generalized gradient approximation (GGA).

The characteristic spatial distribution of desorbing  $N_2$  in the deNO<sub>x</sub> process is useful to identify the intermediates emitting products. The desorption of  $N_2$  with hyper-thermal energy in the  $N_2O$  decomposition is sharply collimated in an inclined way in the plane along the N-N-O bond on Pd(110) and Rh(110), i.e., the parent molecule orientation is preserved in the distribution. On Rh(100), similar inclined  $N_2$  desorption along the [001] direction is observed only at limited  $N_2O$  coverage. At high coverage, another  $N_2O$  adsorption form is suggested.

## II. Technical details

### 2.1 Experimental

Two UHV apparatuses were used. One has low-energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) facilities for the survey of surface-cleaning procedures, and the other has three chambers for angle-resolved temperature-programmed desorption (AR-TPD) [2]. The reaction chamber has a mass spectrometer for angle-integrated (AI) desorption analysis as well as a cryo-plate cooled to about 25 K yielding a pumping rate of about  $9 \text{ m}^3/\text{s}$ , which is large enough to prevent the  $N_2$  scattered in the reaction chamber from penetrating the analyzer [3].

A rhodium crystal with (100) planes (1 mm thick with a 9 mm diameter) was rotated to change the desorption angle (polar angle;  $\theta$ ) in the normally directed plane at the crystal azimuth along either the [001] or [011] direction. The LEED pattern showed a sharp  $(1 \times 1)$  form after the surface was cleaned by  $Ar^+$  ion bombardments, heating in

$5 \times 10^{-8}$  Torr oxygen at a surface temperature ( $T_S$ ) of 850 K and then in  $6 \times 10^{-8}$  Torr hydrogen. The crystal was heated in  $H_2$  before every  $N_2O$  exposure to remove the surface oxygen [4]. The  $^{15}N_2O$  coverage,  $\theta_{N_2O}$ , was determined from the  $^{15}N_2O$  exposure relative to the value to a monolayer. The completion of a monolayer was defined by the appearance of a sharp  $^{15}N_2O$  desorption peak from multilayers at 84 K. The density of the monolayer was estimated to be one fourth of the surface rhodium atom density from a comparison with the  $^{13}C^{18}O$  desorption [5]. Hereafter, the isotope  $^{15}N$  is described as N in the text. No super-structures were found in LEED observations after  $N_2O$  adsorption at 78 K.

## 2.2 Computational

The calculations were performed in the framework of DFT-GGA [6] using the plane-wave basis set and ultrasoft pseudopotentials [7,8] as implemented in the PWscf code contained in the Quantum ESPRESSO package [9], while molecular graphics were generated using the XCRYSDEN program [10]. The perfect Rh(100) surface was modeled by periodically repeated slabs consisting of five (100) layers and  $N_2O$  adsorption was modeled at 1/4 and 1/9 ML coverages using (2×2) and (3×3) supercells respectively. Further computational details are described elsewhere [11]. Transition states and activation energies for  $N_2O$  dissociation have been calculated by climbing-image nudged-elastic-band method [12] using the (2×2) supercells.

## III. Results

### 3.1 AR-TPD results

$\text{N}_2\text{O}$  was introduced at  $T_s = 50\text{-}55$  K.  $\text{N}_2\text{O(a)}$  is either desorbed in the subsequent heating or decomposed, emitting  $\text{N}_2$  at  $60\text{-}130$  K (Fig. 1a). The  $\text{N}_2\text{O}$  desorption is noticeable above  $\Theta_{\text{N}_2\text{O}} = 0.5$  in the range of  $100\text{-}130$  K. The  $\text{N}_2$  desorption peaks at  $100\text{-}120$  K ( $\beta_1\text{-N}_2$ ) and  $70\text{-}95$  K ( $\beta_2\text{-N}_2$ ). The  $\beta_1\text{-N}_2$  signal above  $\Theta_{\text{N}_2\text{O}} = 0.7$  is largely corrected by the  $\text{N}_2\text{O}$  fragmentation in the analyzer. The  $\beta_2\text{-N}_2$  signal shows remarkable enhancement in the surface normal direction. It increases rapidly above  $\Theta_{\text{N}_2\text{O}} = 0.3$ , whereas the  $\beta_1\text{-N}_2$  signal increases slowly. Below  $\Theta_{\text{N}_2\text{O}} = 0.20$ , the  $\beta_2\text{-N}_2$  signal is intensified at around  $66^\circ$  off normal toward the  $[001]$  direction. The  $\beta_2\text{-N}_2$  signal at this position decreases with increasing  $\text{N}_2\text{O}$  coverage (Fig. 1b). On the other hand, the  $\beta_1\text{-N}_2$  signal increases and its peak shifts to lower temperatures. These comparisons indicate that the angular distribution of  $\beta_2\text{-N}_2$  changes from an inclined form to a normally directed way with increasing  $\text{N}_2\text{O}$  coverage.

The AR-TPD spectra of  $\beta_2\text{-N}_2$  below  $\Theta_{\text{N}_2\text{O}} = 0.15$  are intensified at around  $\theta = 68^\circ$  in the plane along the  $[001]$  direction (Fig. 2(a)). In the analysis of the noisy AR signals, the average level was estimated by curve fitting, in which a Gaussian form was assumed [13]. The resultant angular distribution along the  $[001]$  direction is sensitive to the coverage (Fig. 2b). The distribution changes from a three-directional form to the normally directed one with increasing  $\text{N}_2\text{O}$  coverage. The inclined desorption component is sharp as approximated in a  $\cos^{25}(\theta \pm 66)$  form at  $\Theta_{\text{N}_2\text{O}} = 0.16$ . The collimation angle slightly shifts to smaller values at higher coverage. The normally directed component was approximated into a  $\cos^{7-8}(\theta)$  form at  $\Theta_{\text{N}_2\text{O}} = 0.68$ . On the

other hand, in the plane along the [011] direction, the N<sub>2</sub> desorption is sharply directed along the surface normal even at low coverage. The other peak ( $\beta_1$ -N<sub>2</sub>) shows a cosine distribution.

### 3.2 DFT results

Two kinds of adsorption forms of N<sub>2</sub>O were characterized by DFT-GGA, i.e., (i) an upright (or slightly tilted—precise estimation of the tilt angle is difficult due to the flatness of the potential energy surface) form with the terminal nitrogen bonding to the surface, and (ii) a lying form attached to the surface with both terminal N and O atoms (Fig. 3). The upright form prefers to adsorb on the top site with an adsorption energy ( $E_{\text{ads}}$ ) of 0.46 eV at 1/9 ML coverage, whereas on the bridge site it is about 0.1 eV smaller. In the lying form, both terminal atoms are bonded to neighboring top sites. The [011]-oriented form ( $E_{\text{ads}}= 0.50$  eV at 1/9 ML) is more stable than the [001]-oriented one ( $E_{\text{ads}}= 0.40$  eV at 1/9 ML). The adsorption energies at larger 1/4 ML coverage are slightly smaller than at 1/9 ML, the largest difference being 0.05 eV for the lying [011]-oriented form, which is due to close distance between the terminal O and N atoms of neighboring molecules. The upright and lying adsorption forms are very similar to those on Rh(110), but the current adsorption energies are smaller [11]. This is reasonable because the surface metal atoms on (110) surface are less coordinated and thus more reactive. The dissociation to N<sub>2</sub>(a)+O(a) proceeds during the geometry optimization of the lying form with both terminal atoms bonded to the adjacent bridge sites. Special attention has been given to the search for either an upright or a tilted form attached through the O atom to the surface because such an

adsorbed structure could be a precursor in the desorption of  $N_2$  along the surface normal. The calculations suggest, however, that  $N_2O$  cannot adsorb with its O-atom in an upright (or titled) configuration.

## 4. Discussion

### 4.1 Desorption components

$N_2O$  decomposition yields two  $N_2$  desorption peaks at 60-130 K. Because of its cosine distribution,  $\beta_1-N_2$  is desorbed from adsorbed  $N_2$ . Such  $N_2(a)$  may be formed either at the adsorption temperature or in the subsequent heating. The desorption from  $N_2(a)$  on Rh(100) was reported to take place at around 110 K [14].

At low  $N_2O$  coverage,  $\beta_2-N_2$  appears at lower temperatures. This is due to direct desorption from the  $N_2O$  decomposition because of the sharp angular distribution. For highly inclined  $N_2$  desorption, the decomposition of  $N_2O$  oriented in the [001] direction was first proposed on Pd(110) (1×1), where desorbing  $N_2$  collimated at 43° off normal [1]. On Rh(110), the  $N_2$  desorption collimates 65-68 ° off normal along the [001] direction [2]. The [001]-oriented  $N_2O$  as well as the tilted form bonded through the terminal nitrogen was predicted on Rh(110) and Pd(110) by DFT-GGA calculations [13,15]. Both forms were later confirmed on Pd(110) by scanning tunneling microscope and the near-edge X-ray absorption fine structure [16].

According to the DFT-GGA calculations, the [001]-oriented  $N_2O(a)$  is bent on Pd(110) and Rh(110) with the terminal nitrogen and oxygen atoms pointing toward the surface. On Rh(100), the bending is enhanced along the [011] direction because of the

shorter nearest-neighbor rhodium atom distance. These lying forms are plausible precursors for the dissociation to release the oxygen. The adsorption heat was estimated to be about 0.28 eV from the desorption peak temperature (ca 110 K). The calculated values (0.4 ~ 0.5 eV) are therefore overestimated. We also estimated activation energies for the dissociation of [001]- and [011]-oriented N<sub>2</sub>O, and located the respective transition states (TS). The activation energies are fairly small, about 0.1 eV for both lying [001]- and [011]-oriented forms. Both TS are reactant-like and the reaction coordinate is mainly along the N-O distance, which is elongated by about 0.19 and 0.24 Å at the TS of the [001]- and [011]-oriented forms, respectively. The calculated activation energies, however, are too small to account for the dissociation at around 70 K. The dissociation in the subsequent heating might be retarded by oxygen deposited at the adsorption temperature as observed on Rh(110) [2]. At present, on the basis of DFT-GGA calculations, we are not able to explain why the [001]-oriented N<sub>2</sub>O dissociates easily. Possibly the dispersion interactions, which are not treated properly in DFT-GGA, may be important in this context and account for this discrepancy.

#### **4.2 Inclined and normally directed desorption**

The sharp inclined N<sub>2</sub> desorption comes from the dissociation of the [001]-oriented N<sub>2</sub>O in a similar way to that on Rh(110) and Pd(110). From the surface symmetry of Rh(100), it shows four-directional desorption. This inclined desorption shows a similar collimation angle to that on Rh(110), where the distribution is a form of  $\cos^{10}\{\theta - (65 \pm 4)\}$ . There are remarkable differences in their angular distributions, i.e., the co-existence of normally directed desorption and sharper inclined desorption.

No upright (or tilted) N<sub>2</sub>O adsorption bonding through the terminal oxygen has been found on clean Pd(110) and Rh(110) surfaces in the DFT-GGA calculations [11,15] and experimentally no normally directed N<sub>2</sub> desorption has been found on these surfaces [2]. However, it is unlikely that the product N<sub>2</sub> is sharply emitted along the surface normal without such an adsorption form because of the lack of an associative process of N(a) in the N<sub>2</sub>O dissociation. For the normally directed desorption, the lying form is unlikely to be the precursor.

It should be noted that the inclined component is enhanced at small N<sub>2</sub>O coverage and the normally directed desorption is increased above about  $\theta_{\text{N}_2\text{O}} = 0.20$ . In other words, the inclined desorption is remarkable on oxygen-free surfaces and the normally directed component takes place in the presence of deposited oxygen. The adsorption form of N<sub>2</sub>O may be changed in the presence of oxygen. In fact, the heat of adsorption was reported to increase on Ru(001) by the addition of a small amount of oxygen [17]. In fact, the present experiments show that  $\beta_2$ -N<sub>2</sub> formation is extended to higher temperatures when more oxygen is deposited. Surface rhodium atoms modified by oxygen may be positively charged, yielding adsorption sites for standing N<sub>2</sub>O with the terminal oxygen bonding to the surface. Such a form has been proposed on rhodium oxides [18].

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## References

- [1] T. Matsushima, Surf. Sci. Rep. 52 (2003) 1 and there in.
- [2] K. Imamura and T. Matsushima, Catal. Lett. 97 (2004) 197.
- [3] M. Kobayashi and Y. Tuzi, J. Vac. Sci. Technol. **16** (1979) 685.
- [4] G. B. Fisher and S. J. Schmieg, J. Vac. Sci. Technol. A 1 (1983) 1064.
- [5] A.P. Van Bavel, M.J.P. Hopstaken, D. Curulla, J.W. Niemantsverdriet, J.J. Lukklen and P. A. Hilbers, J. Chem. Phys. 119 (2003) 524.
- [6] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [7] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
- [8] Ultrasoft pseudopotentials (US PP) for the nitrogen and rhodium atoms were obtained from the PWscf's pseudopotential download page, <http://www.pwscf.org/pseudo.htm>. Files: N.pbe-rrkjus.UPF, and Rh.pbe-rrkjus.UPF. The pseudopotential for oxygen atom is the one used in the reference: A. Dal Corso, Phys. Rev. B 64 (2001) 235118.
- [9] S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, R. Car, N. Marzari and A. Kokalj: Quantum ESPRESSO: Open-Source Package for Research in Electronic Structure, Simulation, and Optimization, <http://www.pwscf.org/> (2005).

- [10] A. Kokalj: *Comput. Mater. Sci.* 28 (2003) 155 [Code, <http://www.xcrysden.org/> (2005)]
- [11] A. Kokalj, T. Matsushima, *J. Chem. Phys.* 122 (2005) 034708.
- [12] G. Henkelman, B. P. Uberuaga, and H. Jonsson, *J. Chem. Phys.* 113 (2000) 9901.
- [13] H. Horino, S. Liu, A. Hiratsuka, Y. Ohno and T. Matsushima, *Chem. Phys. Lett.* 341 (2001) 419.
- [14] H. A. C. M. Hendrickx, A. Hoek and B. E. Nieuwenhuys, *Surf. Sci.* 135 (1983) 81.
- [15] A. Kokalj, I. Kopal and T. Matsushima, *J. Phys. Chem. B* 107 (2003) 2741.
- [16] K. Watanabe, A. Kokalj, H. Horino, I.I. Rzeznicka, T. Takahashi, N. Nishi and T. Matsushima, *Jpn. J. Appl. Phys.* 45 (3B) (2006) 2290.
- [17] H.H. Huang, C.S. Seet, Z. Zou and G.Q. Xu, *Surf. Sci.* 356 (1996) 181.
- [18] A. L. Yakovlev, G. M. Zhidomirov and R. A. Van Santen, *Catal. Lett.* 75 (2001) 45.

## Figure captions

Fig. 1 AR-TPD spectra of desorbing  $^{15}\text{N}_2$  from Rh(100) exposed to various amounts of  $^{15}\text{N}_2\text{O}$  at 60 K. The desorption angles  $\theta$  are (a)  $0^\circ$  and (b)  $68^\circ$  toward the [001] direction. Closed symbols; observed signal of mass/e = 30. Open symbols; signals after fragment correction. The heating rate was 1.5 K/s.

Fig. 2 (a) AR-TPD spectra of  $^{15}\text{N}_2$  observed at different desorption angles in the plane along the [001] direction.  $\Theta_{\text{N}_2\text{O}} = 0.15$ . The curves were deconvoluted into two Gaussian peaks for smoothing. (b) Angular distributions of desorbing  $\beta_2$ - $^{15}\text{N}_2$  in the plane along the [001] direction at  $\Theta_{\text{N}_2\text{O}} = 0.16, 0.32$  and  $0.68$ . The ordinate was normalized to the  $\beta_2$ - $\text{N}_2$  signal at the surface normal direction at  $\Theta_{\text{N}_2\text{O}} = 0.68$ . The distributions were deconvoluted into two inclined components and a normally directed component, as shown by broken curves. The solid lines indicate their summations. A top view of the surface and its azimuth are shown on the top.

Fig. 3 Top and side views of DFT-GGA optimized  $\text{N}_2\text{O}(\text{a})$  structures on Rh(100) at 1/9 ML. The larger gray balls are Rh atoms, while the smaller red (blue) balls are oxygen (nitrogen) atoms. The corresponding chemisorption energies are also shown.

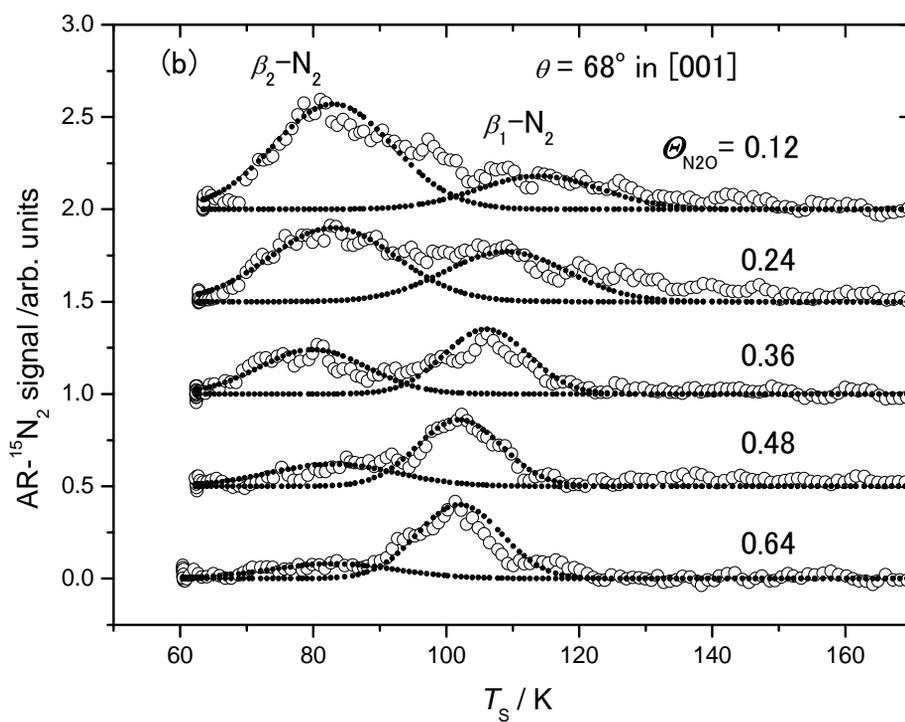
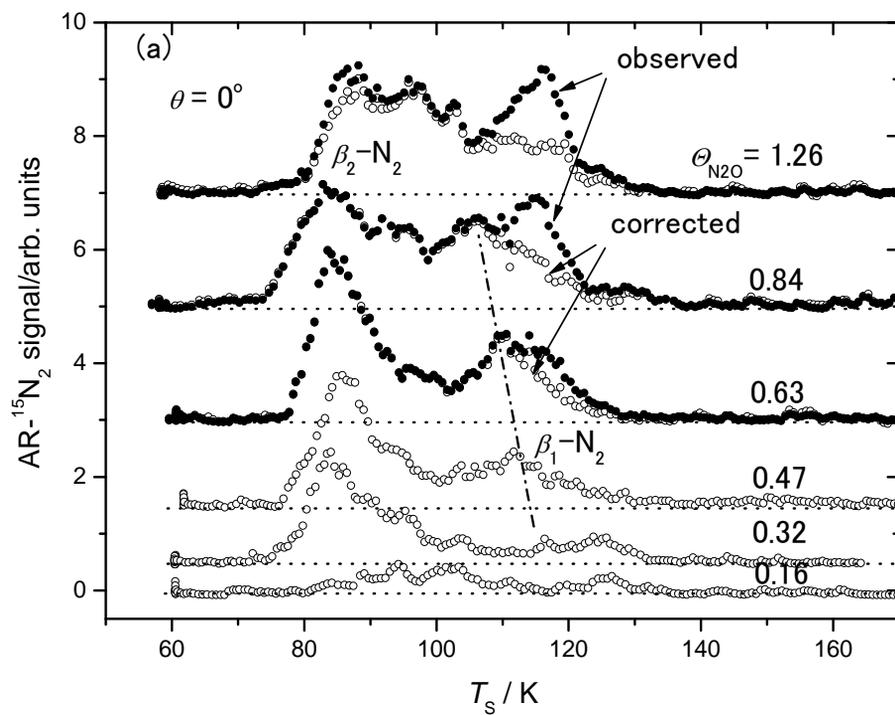
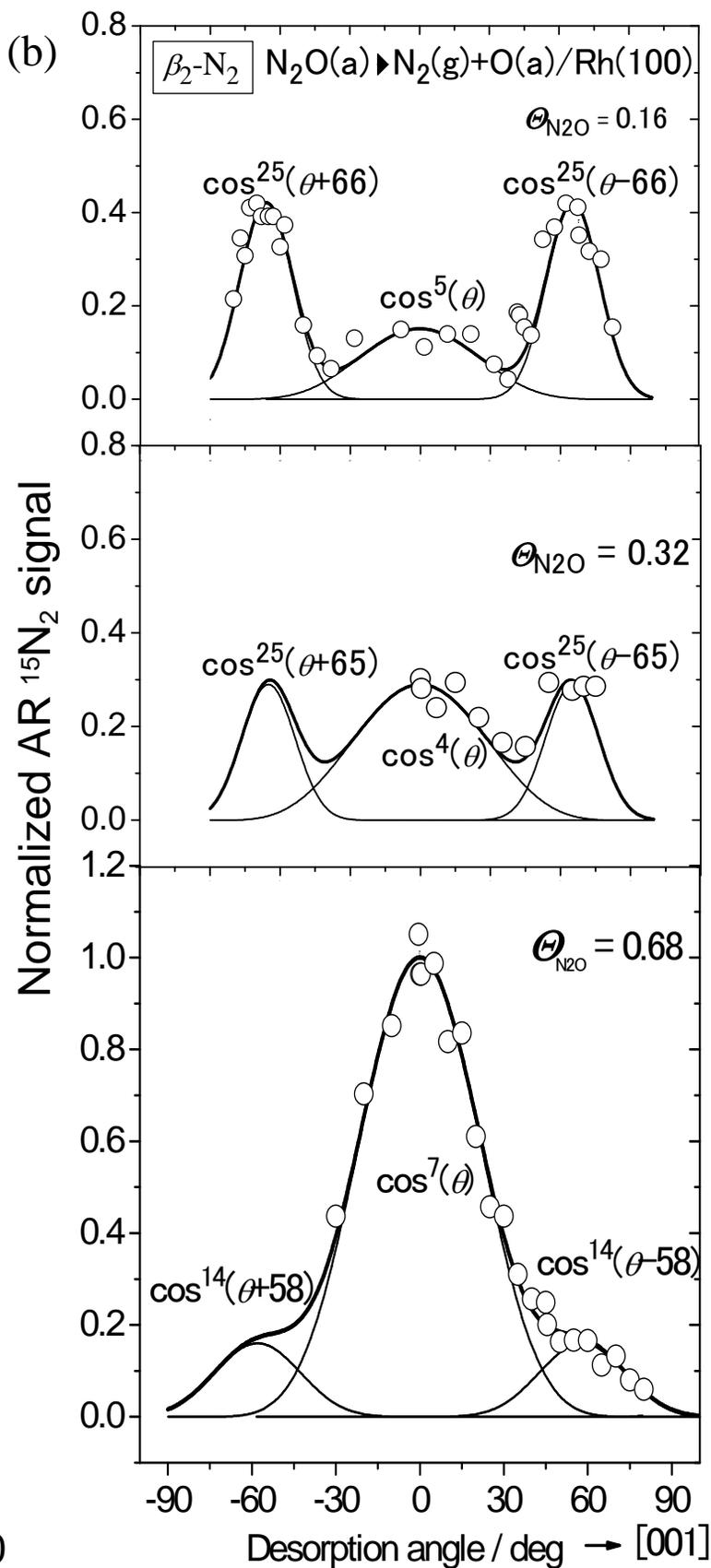
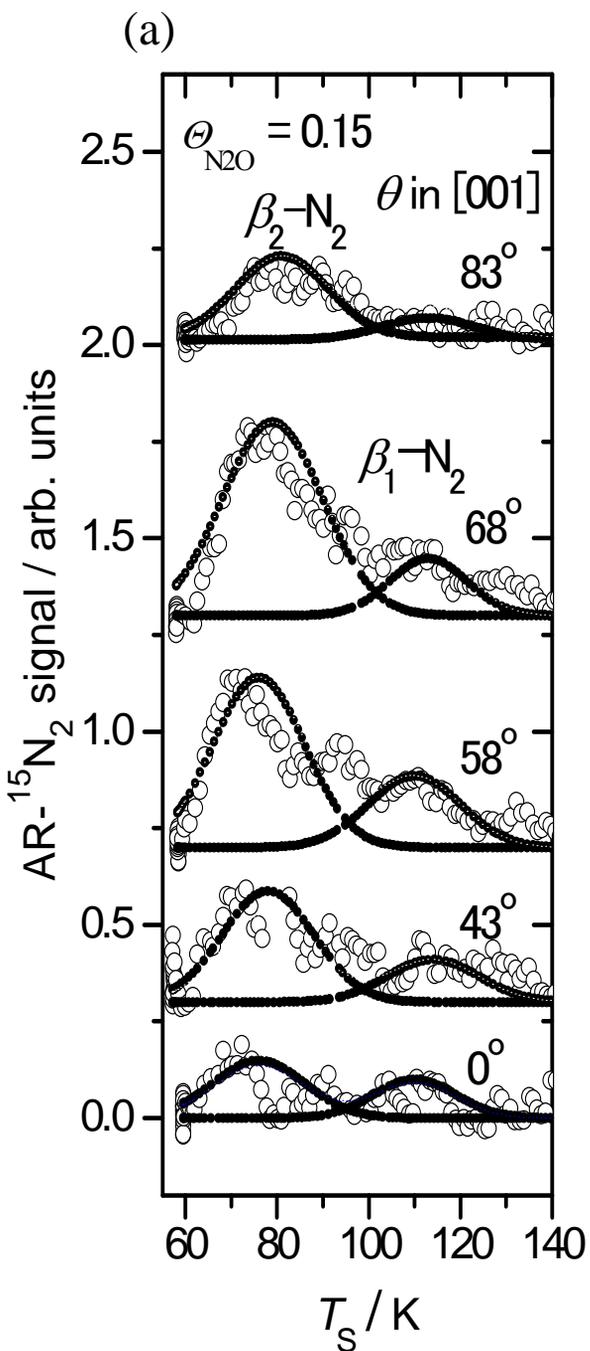
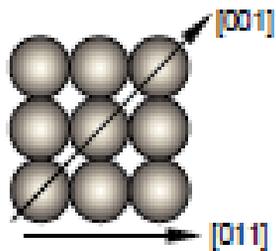


Fig.1 Mat

Fig.2Mat



(3 × 3)-N<sub>2</sub>O/Rh(100)

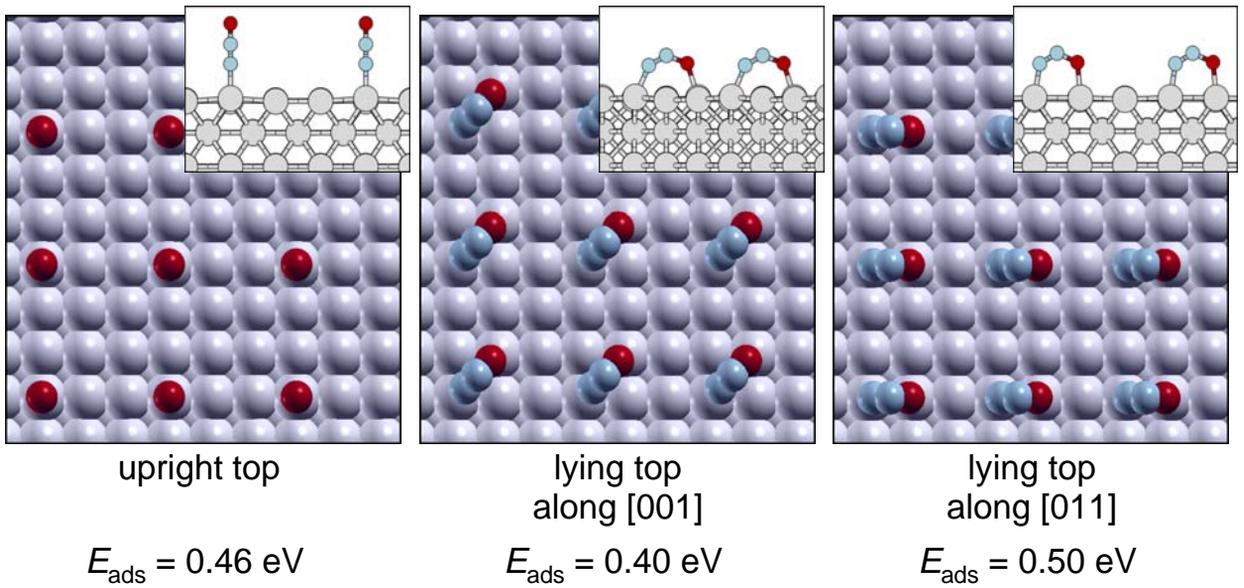


Fig. 3 Mat