Angular distributions of desorbing N_2 in thermal N_2O decomposition on Rh(100)

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Abstract

The angular distribution of desorbing N_2 was studied in the decomposition of N_2O(a) on Rh(100) at 60–140 K by means of angle-resolved temperature-programmed desorption. N_2 desorption shows two peaks at around 80 K and 110 K. At low N_2O 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_2O and its dissociation were also examined by DFT-GGA calculations. Dissociating N_2O 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.
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1. Introduction

The reduction of nitrous oxide on rhodium surfaces has received much attention because of its importance in controlling the catalytic $deNO_x$ process. N_2O is not only an undesirable byproduct in the NO reduction on this best catalyst but also the key intermediate in controlling the selectivity toward N_2 [1]. Knowledge of this intermediate is still limited because of the presence of several surface-nitrogen removal pathways in the $deNO_x$ process. This paper is the first to deliver the angular distribution of desorbing N_2 in the thermal decomposition of adsorbed N_2O on Rh(100). N_2 desorption shows two peaks at around 80 K (β_2-N_2) and 110 K (β_1-N_2). The former sharply collimates at 66° off normal in the plane along the [001] direction at low N_2O coverage, indicating four-directional desorption, whereas, at high coverage, its desorption shifts along the surface normal. The adsorption form of N_2O 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 $deNO_x$ 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.

2. Technical details

2.1. Experimental

Two UHV apparatuses were used. One has low-energy electron diffraction (LEED) and X-ray photon-electron spectroscopy (XPS) facilities for the survey of

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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 m^3/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; θ) in the normally directed plane at the crystal azimuth along either the [001] or [011] direction. The LEED pattern showed a sharp (1 × 1) form after the surface was cleaned by Ar$^+$ ion bombardments, heating in 5×10^{-8} Torr oxygen at a surface temperature (T_S) of 850 K and then in 6×10^{-8} Torr hydrogen. The crystal was heated in H$_2$ before every N$_2$O exposure to remove the surface oxygen [4]. The ^{15}N$_2$O coverage, Θ_{N_2O}, was determined from the ^{15}N$_2$O exposure relative to the value to a monolayer. The completion of a monolayer was defined by the appearance of a sharp ^{15}N$_2$O 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$_2$O 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$_2$O 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$_2$O dissociation have been calculated by climbing-image nudged-elastic-band method [12] using the (2 × 2) supercells.

3. Results

3.1. AR-TPD results

N$_2$O was introduced at T_S = 55–60 K. N$_2$O(a) is either desorbed in the subsequent heating or decomposed, emitting N$_2$ at 60–130 K (Fig. 1a). The N$_2$O desorption is noticeable above $\Theta_{N_2O} = 0.5$ in the range of 100–130 K. The N$_2$ desorption peaks at 100–120 K (β_1-N$_2$) and 70–95 K (β_2-N$_2$). The β_1-N$_2$ signal above $\Theta_{N_2O} = 0.7$ is largely corrected by the N$_2$O fragmentation in the analyzer. The β_2-N$_2$ signal shows remarkable enhancement in the surface normal direction. It increases rapidly above $\Theta_{N_2O} = 0.3$,
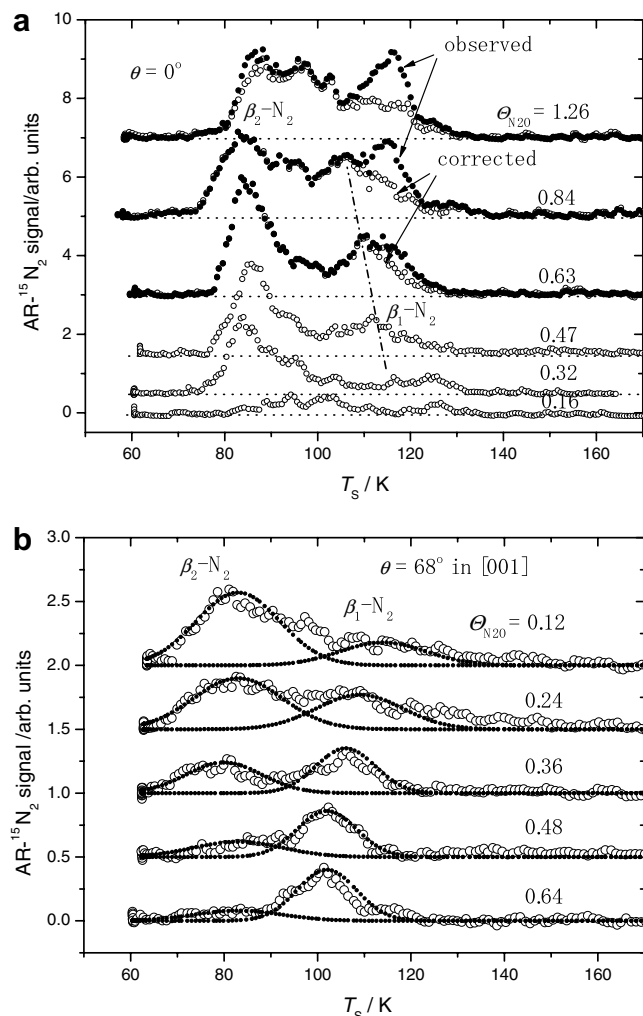

Fig. 1. AR-TPD spectra of desorbing ^{15}N$_2$ from Rh(100) exposed to various amounts of ^{15}N$_2$O at 60 K. The desorption angles θ are (a) 0° and (b) 68° toward the [001] direction. Closed symbols; observed signal of mass/e = 30. Open symbols; signals after fragment correction. The heating rate was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

whereas the β_1-N$_2$ signal increases slowly. Below $\Theta_{N_2O} = 0.20$, the β_2-N$_2$ signal is intensified at around 66° off normal toward the [001] direction. The β_2-N$_2$ signal at this position decreases with increasing N$_2$O coverage (Fig. 1b). On the other hand, the β_1-N$_2$ signal increases and its peak shifts to lower temperatures. These comparisons indicate that the angular distribution of β_2-N$_2$ changes from an inclined form to a normally directed way with increasing N$_2$O coverage.

The AR-TPD spectra of β_2-N$_2$ below $\Theta_{N_2O} = 0.15$ are intensified at around $\theta = 68°$ in the plane along the [001] direction (Fig. 2a). 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 N$_2$O coverage. The inclined desorption component is sharp as approximated in a cos$^{25}(\theta \pm 66)$ form at