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Editor's Choice

Adsorption Configuration Changes and Reactions of N_2O on V(110) between 80 and 200 K

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Adsorption and reactions of N_2O on V(110) have been investigated. The N_2O molecule is adsorbed on V(110) through the terminal nitrogen atom at 80 K. The molecular axis of N_2O is tilted from the surface, and the tilt angle is greater than 55°. The adsorption configuration of N_2O changes in the temperature range of 80 to 120 K, and decomposition of N_2O takes place to produce N_2.

The reaction of nitrogen oxides (NO_x) on metal and metal oxide surfaces has been the subject of numerous surface science studies. Nitrogen oxides are major components of air pollution, and the catalytic reaction of NO_x on solid surfaces is important in environmental chemistry. In surface science studies of NO_x, nitric oxide (NO) has been most extensively studied.[1] In the process of the NO reaction on solid surfaces, formation and desorption of nitrous oxide (N_2O) has been frequently observed.[2] To better understand the surface reaction of NO, it is crucial to investigate the adsorption and reactions of N_2O on solid surfaces.

In the present study the adsorption and reactions of N_2O on V(110) have been investigated using X-ray photoelectron spectroscopy (XPS) and a near-edge X-ray absorption fine structure (NEXAFS) techniques. We will discuss the adsorption geometry change of N_2O on V(110) in the process of the N_2O reaction in the temperature range of 80 to 200 K.

The XPS and temperature-programmed desorption (TPD) experiments were carried out in an ultrahigh vacuum (UHV) system whose base pressure was lower than 2×10^{-10} Torr. The XPS spectra were recorded using a 300 W Al Kα X-ray source and a hemispherical analyzer (model VG Cram 2). The NEXAFS experiment was performed at the 2B1 beam line of the Pohang Accelerator Laboratory, Korea. NEXAFS spectra were obtained by measuring partial electron yield using a hemispherical electron energy analyzer. The V(110) crystal was purchased from Metal Crystals and Oxides and cleaned by using a standard procedure. N_2O was introduced to the analysis chamber using a leak valve.

TPD was utilized to investigate the desorption products from the surface reaction of N_2O on V(110). Figure 1 shows TPD profiles from N_2O adsorbed on V(110) at 80 K. Exposure of N_2O was (a) 0.1 and (b) 1.0 L and the heating rate was 3 K s^{-1}. When N_2O exposure is 0.1 L, the only desorption product is N_2 (28 amu) and the maximum desorption temperature is 100 K. As the exposure of N_2O increases, 44 and 30 amu desorption features are observed in addition to the 28 amu feature. The intensity ratio of the 44 to 30 amu feature is very close to the fragmentation pattern of N_2O in the mass spectrometer, and both 44 and 30 amu features represent N_2O desorption. Maximum desorption temperatures of N_2 and N_2O are very close, but N_2O desorption takes place over a wider temperature range. This result implies that N_2 is desorbed from decomposition of N_2O in the temperature range of 80 to 200 K while N_2O desorption is from the molecularly adsorbed form. No desorption was observed at temperatures higher than 200 K.

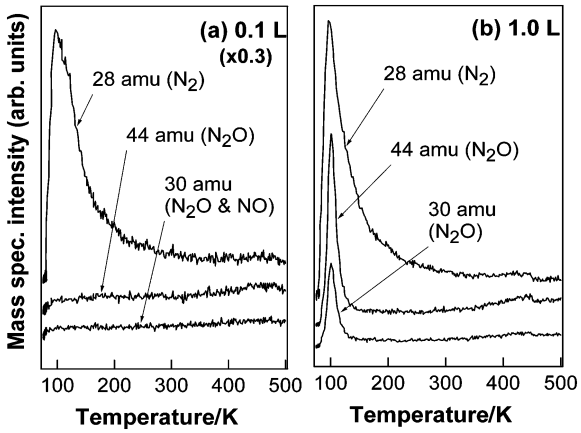

Figure 1. TPD profiles from N_2O adsorbed on V(110) at 80 K. Exposure of N_2O was (a) 0.1 and (b) 1.0 L. Heating rate was 3 K s^{-1}.

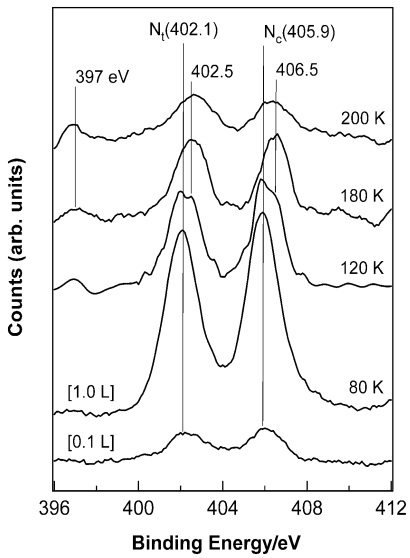

Figure 2. Change of N 1s XPS spectra of N_2O adsorbed on V(110) as a function of the surface temperature.

The adsorption state of N_2O on V(110) was investigated by using XPS. Figure 2 shows the N 1s XPS spectra of N_2O adsorbed on V(110). Initial adsorption of N_2O at 80 K on V(110) produces two XPS features at 402.1 and 405.9 eV. Two nitrogen atoms of N_2O, N_t (terminal) and N_c (central), are in different chemical environments. Two XPS features at 402.1 and 405.9 eV correspond to the terminal (N_t) and central (N_c) nitrogen of

N_2O, respectively. The binding energies of N_2O do not change as the surface coverage of N_2O increases.

The V(110) surface dosed by 1.0 L of N_2O at 80 K was heated, and the change of the N 1s XPS features was investigated. As the surface temperature increases, nitrogen 1s binding energies of N_2O shift to higher energies. At 200 K, N 1s binding energies of N_2O shift to 402.5 and 406.5 eV, and the intensity of the peaks substantially attenuated. The new feature at 397 eV corresponds to atomic nitrogen. This result indicates that both desorption and decomposition of N_2O take place in the temperature range of 80 to 200 K. Surface defects could be responsible for the decomposition of N_2O to produce atomic nitrogen on the surface. This observation agrees very well with the TPD results.

The shift of the binding at 120 K is not caused by the adsorption of N_2O at different adsorption sites or surface defects. The shift of XPS features was not observed when N_2O exposure was increased from 0.1 to 5.0 L. The shift of binding energy to higher values indicates stronger interaction between adsorbed N_2O and the surface; the charge transfer from N_2O to the surface upon adsorption on V(110). The molecular orbitals of N_2O are well-known[3] and the HOMO is the 2π orbital. For the effective interaction of the N_2O 2π orbital with metal d orbitals, N_2O should be oriented parallel to the surface. The shift of the binding energy in the temperature range of 80 to 120 K indicates that the adsorption geometry of N_2O on V(110) changes in this temperature range. Note that the binding energy shift of center nitrogen is greater than that of terminal nitrogen. This observation implies that the adsorption geometry of central nitrogen is more affected than that of terminal nitrogen upon heating.

The adsorption geometry of N_2O on V(110) was further investigated by utilizing nitrogen K-edge NEXAFS. Figure 3 shows nitrogen K-edge NEXAFS features of N_2O adsorbed on V(110). The surface was prepared by dosing 1.0 L of N_2O at 80 K. Curves (a) and (b) were obtained at 80 K, and Curve (c) was obtained after heating the surface to 200 K. The incident photon beam was 20° glancing to the surface for the spectrum (a), and the beam was normal to the surface for the spectra (b) and (c). The spectra were normalized to have the same edge jump. The N K-edge spectra of N_2O show two intense resonance features. They can be assigned to the transitions of 1s electrons of terminal and central nitrogen to the 3π orbital (LUMO) of N_2O. Two features at 400.0 and 403.8 eV correspond to terminal and center nitrogen, respectively.

Nitrogen K-edge NEXAFS spectra of N_2O adsorbed on V(110) show angular dependency. The NEXAFS spectrum obtained with the incident photon beam normal to the surface shows stronger resonance for the transition of N 1s electrons to the 3π orbital of N_2O. Notice that the 3π orbital is oriented perpendicular to the molecular axis of N_2O. This observation clearly indicates that the N_2O molecule adsorbed on V(110) at 80 K is tilted from the surface. We are not going to calculate the exact adsorption angle simply based on the NEXAFS results, but we can estimate that the angle between the molecular axis of N_2O and the surface should be greater than 55°.

The N_2O molecule can be attached to the metal surface through terminal (N_t) or central (N_c) nitrogen. There have been efforts to determine which nitrogen atom of N_2O is bonded to the surface based on the relative intensities of terminal (N_t) and central (N_c) nitrogen π^* resonance features of NEXAFS.[4] However, controversial results have been reported. In the case of

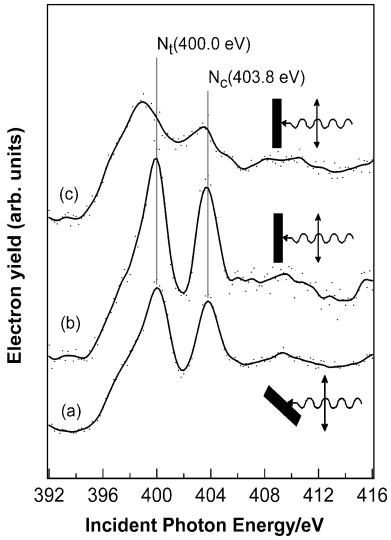

Figure 3. NEXAFS features of N_2O adsorbed on V(110). The surface was prepared by exposing V(110) to 1.0 L of N_2O at 80 K. The spectrum (a) was recorded with the photon beam glancing to the surface by 20° while the spectrum (b) was measured at normal incident of the photon beam. The spectrum (c) was obtained after heating the surface to 200 K.

N_2O on V(110), the N_2O molecule is tilted on V(110). The N_2O molecule should be bent for the adsorption through the central nitrogen atom in the tilted geometry. Adsorption-induced bending of N_2O is well known,[5] but the molecule should be bent significantly to maintain the tilting angle, 55°, between the N–N bond and the surface. We conclude that the N_2O molecule is adsorbed on V(110) through the terminal (N_t) nitrogen atom. At 200 K, the N 1s NEXAFS feature is significantly attenuated but does not show strong angular dependency. This observation shows that the adsorption geometry and the molecular structure of N_2O are changed.

In summary, N_2O is adsorbed on V(110) through the terminal nitrogen atom at 80 K. In the temperature range of 100 to 200 K, the adsorption geometry of N_2O changes, which results in stronger interaction between the central nitrogen atom and the surface. Desorption of N_2 takes place in this temperature range.

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