Reaction of NO on Vanadium Oxide Surfaces: Observation of the NO Dimer Formation

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The adsorption and surface reactions of NO on a VO/V(110) surface have been investigated using X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure, and temperature programmed desorption (TPD) technique. NO is molecularly adsorbed on VO/V(110) at 80 K. As the surface coverage of NO increases, the NO dimer is formed on the surface at 80 K. Both NO and $(NO)_2$ are adsorbed on the surface with the N-O bond perpendicular to the surface. $(NO)_2$ decomposes at ~100 K and the reaction product is desorbed as N_2O. Decomposition of NO takes place when the surface temperature is higher than 273 K.

Key Words : VO, NO, NO dimer, XPS, NEXAFS

Introduction

The adsorption and reactions of NO on metal and metal oxide surfaces have been the topic of numerous surface science studies. Nitrogen oxides are major components of air pollution, and the catalytic reduction of nitrogen oxides is the important reaction in the automobile three-way catalyst. To better understand real catalyst systems, it is very important to investigate adsorption and reactions of reactant molecules on well-characterized metal and metal oxide surface on a molecular level.

Because NO has an unpaired electron in the $2\pi^*$ orbital, adsorption of NO on solid surfaces is rather complicated compared with that of CO. The dissociation energy of NO (6.53 eV) is much lower than that of CO (11.15 eV),[1] and NO is dissociatively adsorbed on most metal surfaces except Cu, Pt, Ag, Pt, and Au at room temperature.[2] Because of high reactivity, adsorption of NO on metal surfaces results in a variety of surface species such as N_2O, $(NO)_2$, NO_2, $(NO_2)_2$, and NO_3 in addition to NO, N, and O.

The reaction of NO on solid surfaces is sometimes very confusing. The interaction of NO on Ag(111) is so weak that no reaction is observed between NO and the surface at room temperature.[3] However, formation of N_2O on Ag(111) was observed when NO was adsorbed on the surface as low as 80 K.[4] In the case of the NO reaction on MgO, Rodriguez and co-workers suggested that the defective MgO surface was responsible for the production of N_2O from NO,[5] while Kim and co-workers reported that more N_2O was formed on a "low-defect" MgO surface below 75 K.[6] The anomaly in NO reactivity to form N_2O at low temperatures on less-reactive surfaces can be explained by formation of $(NO)_2$.[7-9] If the interaction of NO and the surface is week, NO molecules form dimeric NO on the surface. Thermal reaction of $(NO)_2$ produces N_2O.

$$NO(a) + NO(a) \rightarrow (NO)_2(a) \rightarrow N_2O(a) + O(a)$$

In the present study of NO adsorption on the surface, we used a partially oxidized vanadium (110) surface to reduce the surface reactivity toward adsorbing NO. We have concentrated on the formation and thermal reaction of the NO dimer on the surface. We will also report possible orientations of NO and $(NO)_2$ adsorbed on the VO/V(110) surface.

Experimental Methods

The X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) experiments reported here were carried out in an ultra-high vacuum (UHV) chamber whose base pressure was lower than 2×10^{-10} Torr. The photoelectron spectra were recorded using a non-monochromatic 300 W Al $K\alpha$ X-ray source and a 100 mm radius hemispherical analyzer (model VG Cram2).[10]

The near-edge X-ray absorption fine structure (NEXAFS) experiment was performed at the 2B1 beam line of the Pohang Accelerator Laboratory, Korea. The 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. The VO/V(110) surface was prepared by exposing a vanadium (110) surface to 10 L of oxygen at 80 K followed by annealing at 400 K. (1 L corresponds to 10^{-6} torr·sec gas exposure) The oxygen dosing-annealing cycle was repeated 15 times to produce a VO surface. By repeating the oxygen dosing-annealing cycle, a uniform VO layer can be produced on a V(110) surface.[11] Gases were introduced to the analysis chamber using a leak valve.

Results and Discussion

XPS Results. Figure 1 shows the N 1s XPS spectra of NO_x species adsorbed on a VO/V(110) surface at different NO exposures. Adsorption temperature was 80 K. Initial adsorption of NO at 80 K produces two features at 403.7 eV and 399.2 eV. As NO exposure increases, the intensity of the 399.2 eV feature increases and a new feature appears at

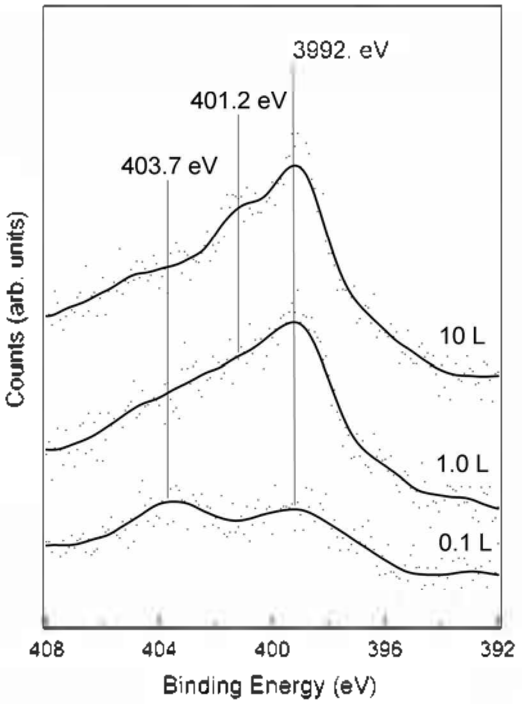


Figure 1. N 1s XPS spectra of NO_X species adsorbed on a VO/V(110) surface at 80 K.

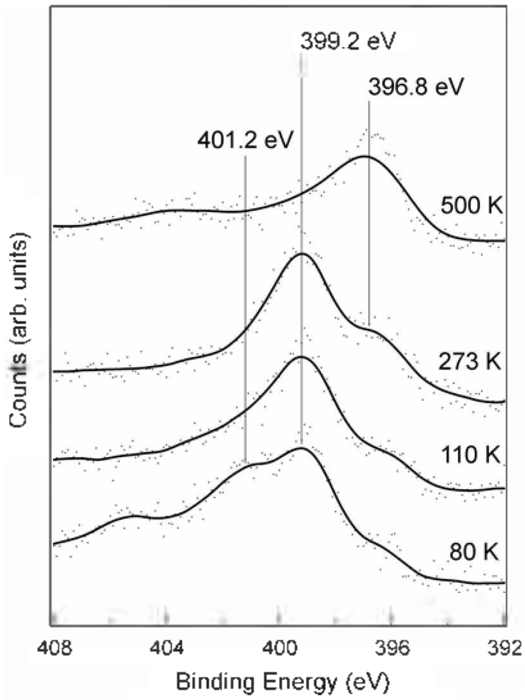


Figure 2. Change of N 1s XPS spectra of NO_X species adsorbed on a VO/V(110) surface as a function of the surface temperature. The surface was prepared by exposing VO/V(110) to 10 L of NO at 80 K followed by brief heating at indicated temperatures. All of spectra were taken at 80 K.

401.2 eV. The XPS result clearly shows that NO is molecularly adsorbed on a partially-oxidized vanadium surface (VO/V(110)) at 80 K. If dissociated N atoms exist on the surface, a peak should be observed at ~397 eV. (Typical binding energy values of NO_X species adsorbed on solid surfaces are listed in Table 1.) The XPS feature at 399.2 eV can be easily assigned as molecularly adsorbed NO. The peak around 403.7 eV can be originated from NO_2 or NO_3 species but the exact stoichiometry cannot be determined based on only XPS results. When NO exposure exceeds 1.0 L, the NO XPS feature splits into 399.2 eV and 401.2 eV, and there are several possibilities for this splitting. The N 1s binding energy is sensitive to the molecular angle relative to the surface and binding energies of perpendicular and lying-down NO are different.[13] Generally, the binding energy of lying-down NO is lower than that of perpendicular NO and lying-down NO decomposes at lower temperatures. As it is shown in Figure 2, the 401.2 eV feature disappears first when the surface is heated to 110 K, which implies that 401.2 eV feature cannot be lying down NO. In addition to that, the NEXAFS investigation shows that the orientation of two NO species are the same. (NEXAFS results will be explained later.) Other possibility is the adsorption of NO at different adsorption sites. On metal surfaces, NO molecules are frequently adsorbed on different adsorption sites such as atop, bridge, and hollow sites. In the case of NO adsorption on a vanadium oxide surface, however, bridge and hollow sites composed of vanadium atoms are not available and it's not likely that NO is adsorbed on bridge or hollow sites. We assign the 401.2 eV feature as the NO dimer, $(NO)_2$. When NO molecules form a dimer, the N 1s XPS feature splits into two peaks .[18] The appearance of a doublet in the N 1s energy level can be explained in terms of different screening of the core electrons. The screening effect from the same NO molecule (intramolecular screening) should be different from the screening effect of the other NO molecule forming the dimer (intermolecular screening). The energy splitting due to these two different screening effects is 2-3 eV[13,19] and corresponds to the two N 1s XPS features at 399.2 eV and 401.2 eV in Figure 1. The evidence of the NO dimer formation will be discussed in more detail later.

Table 1. Typical N 1s binding energy values of NO_X species adsorbed on solid surfaces

chemical state	surface	binding energy, eV	references
N(ads)	W(111), 600 K	397.1	12
NO(lying down)	Ni(100), <150 K	398.1	13
NO(perpendicular)	Ni(100), <150 K	399.9	13
NO(ads)	VO, 80 K	399.2	this work
$(NO)_2$(ads)	VO, 80 K	401.2	this work
NO(ads)	MoS_2, 80 K	401.6	14
$(NO)_2$(ads)	MoS_2, 80 K	403.3	14
$(NO_2)_2$(condensed)	Ni(poly), 77 K	404.2	15
NO_2(ads)	Ag(111), 90 K	404.8-406	16
NO_3(ads)	Ag(111), 140 K	405.8	16
N_2O(ads)	Rh/CeO_2	403.8, 407.7	17

Thermal reaction of NO adsorbed on a VO/V(110) surface has been investigated with XPS. Figure 2 shows the change

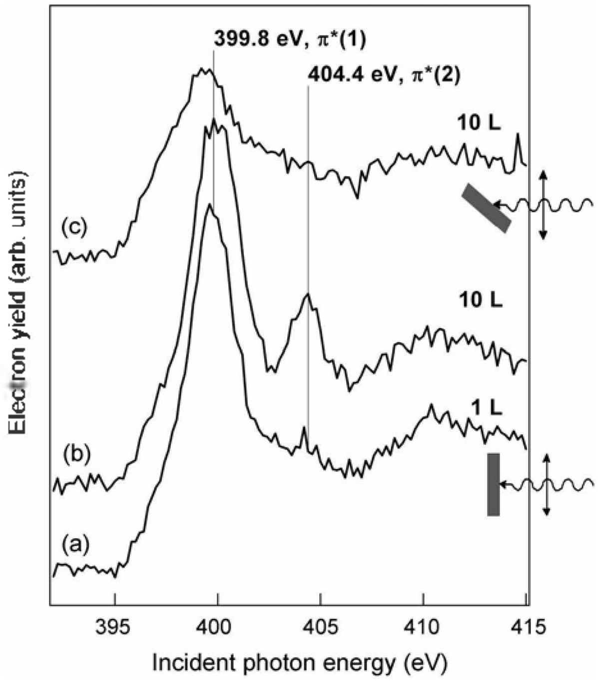
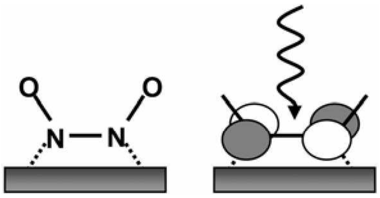


Figure 3. Nitrogen K-edge NEXAFS features of NO_X species adsorbed on a VO/V(110) surface. Spectra (a) and (b) were recorded with the incident photon beam normal to the surface. Spectrum (c) was recorded with the incident photon beam glancing to the surface by 20°.

of N 1s XPS features of NO as a function of the surface temperature. The surface was prepared by exposing the VO/V(110) surface to 10 L of NO at 80 K. When the surface is heated to 110 K, the XPS feature at 401.2 eV disappears completely. As the 401.2 eV feature disappears, the intensity of the 399.2 eV feature does not change and any other new feature shows up. This observation indicates that desorption of $(NO)_2$ takes place in the temperature range of 80 to 110 K. At higher temperatures, a new feature appears at 396.8 eV. At 500 K, the 399.2 eV feature disappears and only the 396.8 feature remains, which shows that NO decomposes into atomic nitrogen at higher than 273 K on a VO/V(110) surface.

NEXAFS Results. Figure 3 shows the nitrogen K-edge NEXAFS features of NO species adsorbed on a VO/V(110) surface at 80 K. Curves (a) and (b) were obtained as the incident photon beam was normal to the surface and Curve (c) was recorded when the photon beam was 20° glancing to the surface. Adsorbed NO shows a strong resonance feature at 399.8 eV when NO exposure is 1.0 L. This NEXAFS feature corresponds to π^* resonance of NO[20] and we label this feature as $\pi^*(1)$ resonance. When the NO exposure is increased to 10 L, a new resonance feature appears at 404.4 eV (Curve (b)). We label the 404.4 eV feature as $\pi^*(2)$ resonance. When the incident photon beam is glancing to the surface, the $\pi^*(2)$ resonance feature disappears and the $\pi^*(1)$ feature is substantially suppressed (Curve (c)). This observation clearly indicates that both π^* orbitals related to $\pi^*(1)$ and $\pi^*(2)$ transitions are orientated toward the same direction and they should be parallel to the surface. From NEXAFS results, we can exclude the possibility that N 1s XPS peaks at 399.2 eV and 401.2 eV in Figure 1 correspond to differently-oriented NO molecules. The splitting of π^* resonance features indicates the formation of the NO dimer.[21] When two NO molecules form a dimer, two singly occupied NO π^* orbitals couple to form a doubly occupied bonding combination and an unoccupied antibonding combination. Only the latter one is available for the excitation of nitrogen 1s electrons. The NEXAFS result shows that both NO and $(NO)_2$ species are present on the surface and agrees very well with the XPS result.

The orientation of adsorbed molecules can be determined based on the angular dependency of NEXAFS features. Because π^* orbitals are oriented parallel to the surface, both NO and $(NO)_2$ should be oriented with the NO bond perpendicular to the surface as shown below, even though the precise angle cannot be determined.



In NEXAFS experiment, the orientation of the adsorbed molecule can be determined precisely by comparing the change of relative intensity of π^* and σ^* resonance features as a function of the angle of the incident photon beam. Unfortunately, the experimental evidence in the present case is not conclusive, because the resonance features are not well-resolved for conclusive evidence in the σ^* resonance region. There are several different NO_X species on the surface including NO, NO_2, and $(NO)_2$, and the σ^* resonance energies of these species seem to be superimposed. In addition to that, NO bonds can be tilted from the surface normal as $(NO)_2$ and NO_2 are formed.

TPD Results. Temperature programmed desorption (TPD) technique was utilized to investigate the desorption products from the surface reaction of NO on VO/V(110). Figure 4 presents a series of TPD profiles corresponding to increasing exposures of NO from 0.1 L to 10 L. NO was dosed at 80 K and heating rate was 3 K/sec. Figure 4 shows the desorption profiles of $m/e = 44$ and $m/e = 30$. The 44 *amu* curve represents desorption of N_2O and the 30 amu curve represents both desorption of NO and fragmentation of N_2O.

If we compare TPD profiles in Figure 4 with XPS features in Figure 2, we can conclude that disappearance of 401.2 eV XPS feature in the temperature range of 80 to 110 K is closely related to N_2O desorption. Formation of N_2O from NO adsorbed on solid surfaces has been frequently reported.[1] There are two possible mechanisms for the formation of N_2O from NO adsorbed on the surface.

$$\mathrm{NO(a)} \rightarrow \mathrm{N(a)} + \mathrm{O(a)}$$

$$\mathrm{NO(a)} + \mathrm{N(a)} \rightarrow \mathrm{N_2O(g)} \tag{1}$$

$$\mathrm{NO(a)} + \mathrm{NO(a)} \rightarrow \mathrm{(NO)_2(a)} \rightarrow \mathrm{N_2O(g)} + \mathrm{O(a)} \tag{2}$$

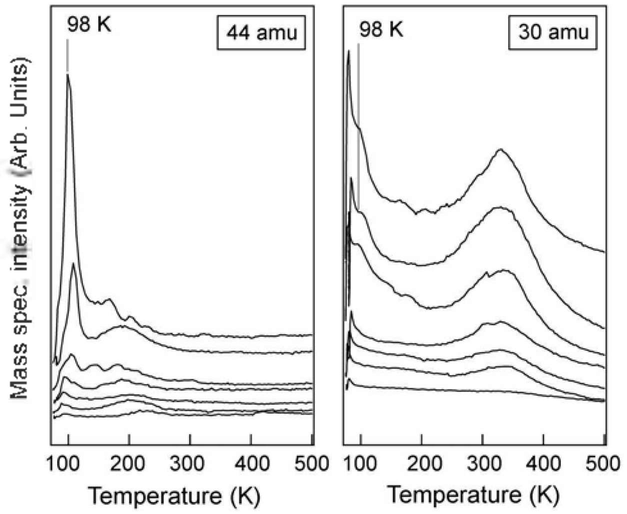


Figure 4. TPD profiles corresponding to increasing exposure of VO/V(110) to NO at 80 K. The dosing amounts were 0.1, 0.3, 0.5, 1.0, 2.0, 5.0, 10 L. Heating rate was 3 K/sec.

In our study of NO adsorption on the vanadium oxide surface using XPS and TPD, atomic nitrogen is not observed on the surface below 273 K while N_2O desorption takes place at ~100 K. This observation clearly indicates that N_2O is formed from adsorbed NO via mechanism (2) and implies that $(NO)_2$ is present on the surface at 80 K. TPD results support the formation of $(NO)_2$ from adsorbed NO on VO/V(110) and are consistent with XPS and NEXAFS results.

Conclusion

The adsorption and reactions of NO on a partially-oxidized vanadium (110) surface have been investigated with XPS, NEXAFS, and TPD technique. The results obtained with three different techniques agree very well and the main conclusions are the following:

(1) NO is molecularly adsorbed on VO/V(110) at 80 K.

(2) As the surface coverage of NO increases, $(NO)_2$ is formed on the surface at 80 K. Both NO and $(NO)_2$ are adsorbed on the surface with the N-O bond perpendicular to the surface.

(3) $(NO)_2$ decomposes at ~100 K and the reaction product is desorbed as N_2O.

(4) Decomposition of NO takes place when the surface temperature is higher than 273 K.

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