Interaction of SO_2 with Oxygen on Ni(100) Studied by XPS and NEXAFS

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The adsorption and surface reactions of SO_2 on Ni(100), c(2x2)_O/Ni (100) and NiO(111)/Ni(100) surfaces have been investigated using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) technique. On Ni(100), chemisorbed SO_2 is formed at 160 K. When SO_2 is adsorbed on c(2x2)_O/Ni(100) at 160 K, SO_2 reacts with oxygen to form SO_3 and trace amount of SO_4 species. SO_3 is adsorbed on this surface with its C_3 axis perpendicular to the surface. On a NiO(111)/Ni(100) surface, both SO_3 and SO_4 species are formed at 160 K from adsorbed SO_2.

Key Words : Ni, NiO, SO_2, NEXAFS, Surface

Introduction

The adsorption and reactions of SO_2 on metal and metal oxide surfaces have received a great deal of attention in surface science studies of catalysis.[1] Sulfur dioxide is used for the production of sulfuric acid. On the other hand, SO_2 is the major component of air pollutants. In addition to the industrial and environmental importance, SO_2 could be a good probe molecule for the fundamental studies of chemisorption on metal and metal oxide surfaces. Compared to CO, SO_2 is a stronger π acceptor and it is more reactive with co-adsorbed species on the surface and its adsorption geometry is more complicated.

The structure of SO_2 adsorbed on Ni single crystal surfaces has been characterized using X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), and surface extended X-ray absorption fine structure (SEXAFS). Based on NEXAFS and SEXAFS studies, Yokoyama and co-workers reported that SO_2 was chemisorbed on both Ni(100) and Ni(111) at ~170 K with its molecular plane parallel to the surface.[2] They also reported that the S atom directly interacted with substrate Ni, located at the bridge sites. The normal incident X-ray standing wave (NIXSW) technique study also showed that SO_2 was adsorbed molecularly on Ni(111) at 140 K with its molecular plane parallel to the surface but the S and O atoms were in off-atop sites.[3] On Ni(110), SO_2 partly decomposes at 160 K to produce SO_2 and SO_3 species.[4]

We investigated the reaction of SO_2 with oxygen on a Ni (100) surface using XPS and NEXAFS technique. We used c(2x2)_O/Ni(100) and NiO(111)/Ni(100) surfaces for the model study of the interactions of SO_2 with oxygen on Ni surfaces. It was found that SO_2 interacted strongly with co-adsorbed oxygen on Ni(100) and surface oxygen on NiO to produce SO_3 and SO_4 species, which were clearly identified using NEXAFS.

Experimental Procedures

The XPS experiment reported here was carried out in an ultra-high vacuum chamber (UHV) whose base pressure was lower than 2×10^{-10} Torr. The photoelectron spectra were recorded using a non-monochromatic 300 W Al Kα X-ray source and a 100 mm radius hemispherical analyzer (model VG Cram2).[5]

The NEXAFS experiment was performed at the BL-11B beam line of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF). The NEXAFS spectra were obtained by measuring fluorescence yield. The setup of the beam line and the analysis chamber has been described in detail elsewhere.[3]

The Ni(100) crystal was purchased from Metal Crystals and Oxides and cleaned by using a standard procedure. The c(2x2)_O/Ni(100) surface was prepared by exposing the Ni (100) surface to 40 L of oxygen at 300 K.[6] (1 L corresponds to 10^{-6} torr·sec exposure) The NiO(111) surface was produced by exposing the Ni (100) surface to 300 L of oxygen at 300 K.[7] Gases were introduced to the analysis chamber using a leak valve.

Results and Discussion

XPS analysis. Figure 1 shows the S_2p XPS features of SO_2 adsorbed on Ni(100), c(2x2)_O/Ni(100), and NiO(111)/Ni(100) surfaces. Curve (A) was obtained by exposing the Ni (100) surface to 3 L of SO_2 at 80 K. At this temperature, SO_2 multilayer is formed and the peak at 167.6 eV can be easily assigned as molecularly adsorbed SO_2.[8] When the Ni (100) surface covered with SO_2 multilayer is heated to 160 K, a new S_2p XPS peak is observed at 165.3 eV (Curve (B)). The peak at 165.3 eV can be assigned as chemisorbed SO_2.[4] When the surface is heated up to 350 K, SO_2 is completely decomposed and an atomic sulfur peak is observed at 161.8 eV (the spectrum is not shown). Curve (C) and Curve (D) of Figure 1 correspond to XPS features of SO_2 adsorbed on c(2x2)_O/Ni(100) and NiO(111)/Ni(100) surfaces at 160 K, respectively. Both surfaces were prepared by dosing 3 L of SO_2 at 80 K followed by annealing briefly at 160 K to desorb multilayer SO_2. When SO_2 is chemisorbed on a c(2x2)_O/Ni(100) surface, the S_2p XPS peak shows up at

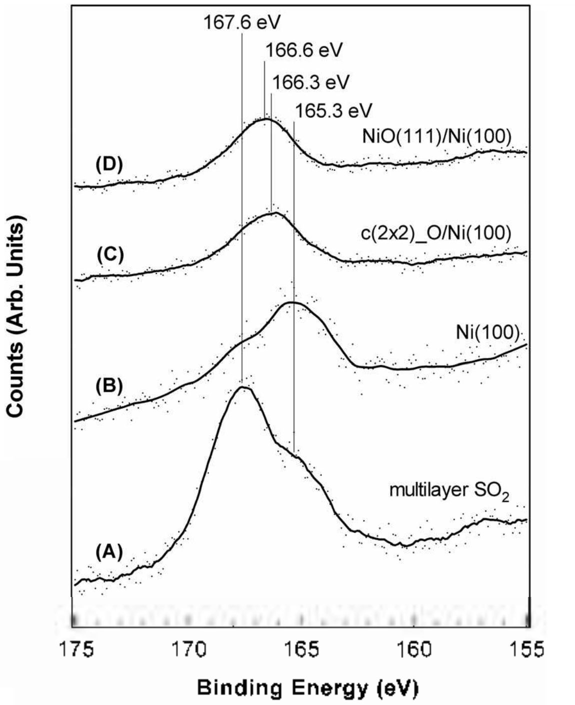

Figure 1. XPS spectra of SO_x species formed on clean and oxygen-modified Ni(100) surfaces. Each surface was prepared as follows. (A) The Ni(100) surface was exposed to 3 L of SO_2 at 80 K (multiplayer SO_2). (B) The Ni(100) surface was exposed to 3 L of SO_2 at 80 K followed by annealing at 160 K for 30 seconds (chemisorbed SO_2). (C) The c(2x2)_O/Ni(100) surface was exposed to 3 L of SO_2 at 80 K followed by annealing at 160 K for 30 seconds. (D) The NiO(111)/Ni(100) surface was exposed to 3 L of SO_2 at 80 K followed by annealing at 160 K for 30 seconds. All spectra were obtained at 80 K.

166.3 eV. The S_2p XPS peak shifts to 166.6 eV when SO_2 is adsorbed on a NiO(111)/Ni(100) surface. It is clear that sulfur is more highly oxidized if SO_2 is co-adsorbed with oxygen on Ni(100). However, it's difficult to tell the difference of SO_x species formed on c(2x2)_O/Ni(100) and NiO(111) surfaces in XPS spectra. In addition to that, the exact stoichiometry of SO_x species adsorbed on oxygen-modified Ni surfaces cannot be determined based on XPS results. The chemical states of the SO_x species adsorbed on c(2x2)_O/Ni(100) and NiO(111)/Ni(100) surfaces were further investigated using sulfur K-edge NEXAFS technique.

NEXAFS investigation. A near-edge X-ray absorption fine structure (NEXAFS) technique has been utilized to investigate SO_x species produced from the surface reaction of SO_2 and oxygen on Ni surfaces. Figure 2 shows the sulfur K-edge NEXAFS features of multiplayer SO_2 (Curve (A)) and chemisorbed (Curve (B) and (C)) SO_2 on Ni(100). Multilayer of SO_2 was prepared by doing 20 L of SO_2 on Ni(100) at 80 K. Chemisorbed SO_2 was produced by dosing 3 L of SO_2 at 80 K followed by annealing at 160 K. The NEXAFS features at 2473.2 eV and 2478.6 eV correspond to the transition of the sulfur 1s-electron to $3b_1$ (π^* resonance) and $9a_1$ (σ^* resonance) molecular orbitals of SO_2, respectively.[2] The sulfur K-edge NEXAFS feature of chemisorbed SO_2 shows strong angular dependency. The π^*

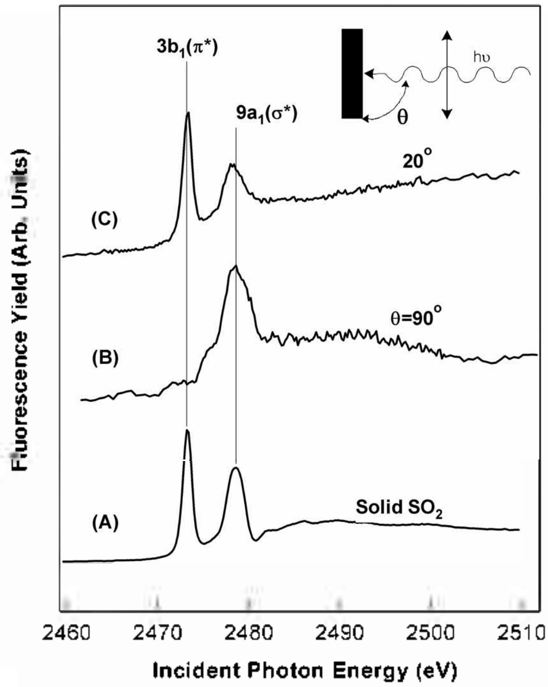

Figure 2. NEXAFS features of SO_2 adsorbed on Ni(100). (A) Solid SO_2 was produced by dosing 20 L of SO_2 on Ni(100) at 80 K. (B) Chemisorbed SO_2 was formed by dosing 3 L of SO_2 on Ni(100) at 80 K followed by annealing at 160 K. The incident photon beam was normal to the surface. (C) Chemisorbed SO_2. The photon beam was 20° glancing to the surface.

resonance feature shows maximum intensity when the incident photon beam is glancing to the surface (Curve (C)). This feature disappears completely if the photon beam becomes normal to the surface (Curve (B)). This observation clearly indicates that SO_2 is adsorbed on Ni(100) with its molecular plane parallel to the surface. This result agrees very well with the previous report.[2]

The adsorption and surface reactions of SO_2 on c(2x2)_O/Ni(100) were also investigated by utilizing NEXAFS. Figure 3 shows the sulfur K-edge NEXAFS features of SO_x species adsorbed on c(2x2)_O/Ni(100) at 160 K. The surface was prepared by exposing the c(2x2)_O/Ni(100) surface to 3 L of SO_2 at 80 K followed by annealing briefly at 160 K. It clearly shows three features at 2478.0 eV, 2480.0 eV, and 2482.4 eV. The intensities of two features at 2478.0 eV and 2480.0 eV show strong angular dependency on the angle of the incident photon beam. The 2480.0 eV feature disappears completely when the photon beam is perpendicular to the surface. This observation indicates that the upper state molecular orbital related to this transition is orientated perpendicular to the surface. That the feature at 2482.4 eV does not show clear angular dependency implies that the upper state molecular orbital related to this transition is totally symmetric. Based on these interpretations, we assign three K-edge features of SO_x species in Figure 3 as follows. The 2478.0 eV and 2480.0 eV features correspond to the transitions of sulfur 1s electrons to e*(3pπ) and a_1*(3s+3pσ) orbitals of SO_3 species, respectively.[9] The 2482.2 eV feature cannot be assigned as the transition to a_1*($3d_{z^2}$) or two

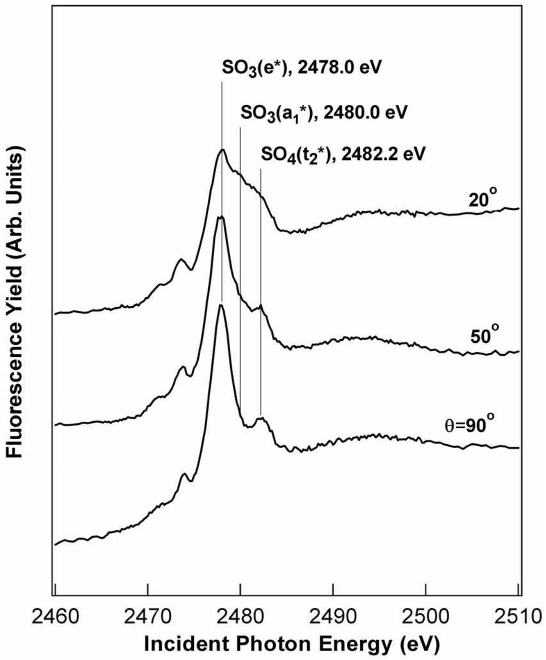

Figure 3. NEXAF features of SO_x species formed on c(2x2)_O/Ni(100). The surface was prepared by exposing the c(2x2)_O/Ni(100) surface to 3 L of SO_2 at 80 K followed by annealing at 160 K. The angle θ indicates the angle of the incident photon beam.

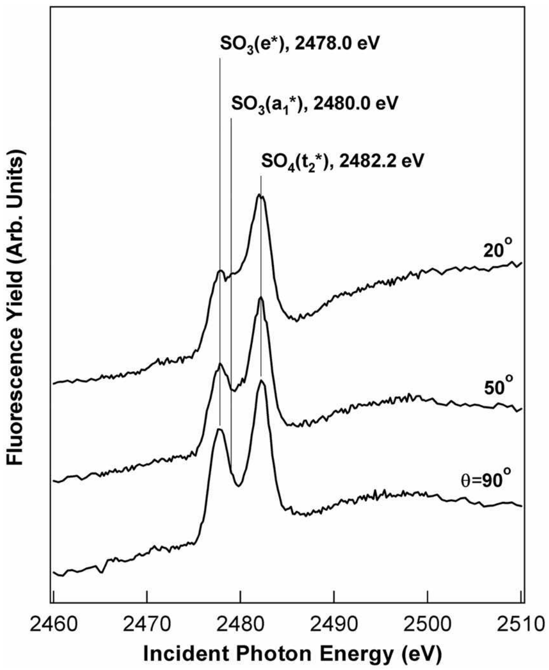

Figure 4. NEXAF features of SO_x species formed on NiO(111)/Ni(100). The surface was prepared by exposing the NiO(111)/Ni(100) surface to 3 L of SO_2 at 80 K followed by annealing at 160 K. The angle θ indicates the angle of the incident photon beam.

e*($3d_{x^2-y^2}+3d_{xy}$, $3d_{xz}+3d_{yz}$) orbitals of SO_3 species. The transition to a_1* orbital should be suppressed if the photon beam is normal to the surface and the transition energies to e* orbitals are much higher than 2482.2 eV. We conclude that the 2482.2 eV feature is related to the transition of sulfur 1s electrons to the t_2* orbital of SO_4 species. This observation clearly indicates that SO_2 mainly forms SO_3 on a c(2x2)_O/Ni(100) surface at 160 K. Angular dependency of NEXAFS features also suggests that SO_3 is adsorbed on the surface with its C_3 axis perpendicular to the surface.

The reaction of SO_2 on a NiO surface was investigated using NEXAFS. The NEXAFS features of SO_x species formed at 160 K on a NiO(111)/Ni(100) surface is shown in Figure 4. The surface was prepared by depositing 3 L of SO_2 on the NiO surface at 80 K followed by heating up to 160 K. The sulfur K-edge NEXAFS spectrum of SO_x species formed on NiO(111) shows three absorption features at 2478.0 eV, 2480.0 eV, and 2482.2 eV. The energies of these features are the same as those of SO_x species formed on c(2x2)_O/Ni(100). In addition to that, the angular dependency of these features is very similar to that of NEXAFS features of SO_3 and SO_4 species formed on c(2x2)_O/Ni(100). These observations clearly indicate that both SO_3 and SO_4 species are formed on NiO(111)/Ni(100). The relative amount of SO_3 and SO_4 cannot be determined exactly based on NEXAFS. However, the amount of SO_4 formed on NiO(111) at 160 K should be much greater than that of SO_4 formed on c(2x2)_O/Ni(100) at the same temperature.

Conclusion

The interaction of SO_2 with oxygen on Ni(100) has been investigated with XPS and NEXAFS. The main conclusions are the following:

(1) SO_2, SO_3, and SO_4 species formed on the surface have been clearly identified.

(2) When SO_2 is adsorbed on c(2x2)_O/Ni(100) at 160 K, it forms mainly SO_3. SO_3 is adsorbed on this surface with its C_3 axis perpendicular to the surface.

(3) On NiO(111)/Ni(100), both SO_3 and SO_4 are formed from SO_2 at 160 K.

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