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 $\pi$ 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. 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$_3$ and SO$_4$ 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 $\times$ 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).$^2$

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$_2$. 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$_2$.$^2$ 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$_2$. 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
The S\textsubscript{2p} XPS peak shifts to 166.6 eV when SO\textsubscript{2} is adsorbed on a NiO(111)/Ni(100) surface. It is clear that sulfur is more highly oxidized if SO\textsubscript{2} is co-adsorbed with oxygen on Ni(100). However, it's difficult to tell the difference of SO\textsubscript{x} species formed on c(2x2)\textsubscript{O}/Ni(100) and NiO(111) surfaces in XPS spectra. In addition to that, the exact stoichiometry of SO\textsubscript{x} species adsorbed on oxygen-modified Ni surfaces cannot be determined based on XPS results. The chemical states of the SO\textsubscript{x} species adsorbed on c(2x2)\textsubscript{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\textsubscript{x} species produced from the surface reaction of SO\textsubscript{2} and oxygen on Ni surfaces. Figure 2 shows the sulfur K-edge NEXAFS features of multilayer SO\textsubscript{2} (Curve (A)) and chemisorbed (Curve (B) and (C)) SO\textsubscript{2} on Ni(100). Multilayer of SO\textsubscript{2} was prepared by doing 20 L of SO\textsubscript{2} on Ni(100) at 80 K. Chemisorbed SO\textsubscript{2} was produced by dosing 3 L of SO\textsubscript{2} at 80 K followed by annealing at 160 K for 30 seconds. The NiO(111)/Ni(100) surface was exposed to 3 L of SO\textsubscript{2} at 80 K followed by annealing at 160 K for 30 seconds. All spectra were obtained at 80 K.

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The adsorption and surface reactions of SO\textsubscript{2} on c(2x2)\textsubscript{O}/Ni(100) were also investigated by utilizing NEXAFS. Figure 3 shows the sulfur K-edge NEXAFS features of SO\textsubscript{x} species adsorbed on c(2x2)\textsubscript{O}/Ni(100) at 160 K. The surface was prepared by exposing the c(2x2)\textsubscript{O}/Ni(100) surface to 3 L of SO\textsubscript{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\textsubscript{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 ε\textsuperscript{5}(3pπ) and a\textsubscript{1g}\textsuperscript{5}(3s+3pσ) orbitals of SO\textsubscript{2} species, respectively.\textsuperscript{9} The 2482.2 eV feature cannot be assigned as the transition to a\textsubscript{1g}\textsuperscript{5}(3d\textsubscript{2}) or two
NEXAFS Characterization of SOx Formed on NiO  


The interaction of SO2 with oxygen on Ni(100) has been investigated with XPS and NEXAFS. The main conclusions are the following:

1. SO2, SO3, and SO4 species formed on the surface have been clearly identified.
2. When SO2 is adsorbed on c(2x2)_O/Ni(100) at 160 K, it forms mainly SO3. SO3 is adsorbed on this surface with its C3 axis perpendicular to the surface.
3. On NiO(111)/Ni(100), both SO3 and SO4 are formed from SO2 at 160 K.

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References