Adsorption of SO₂ on Pd(100) Studied by S K-Edge XAFS

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Abstract. Surface structure and an electronic property of SO₂ adsorbed on Pd(100) were studied by S K-edge NEXAFS, SEXAFS and S1s XPS. The molecule was found by the polar-angle dependent NEXAFS to adsorb with the molecular plane normal to the Pd(100) surface. This is a clear contrast to the SO₂/Ni(100) case where the molecule lies flat on the surface. From the peak position of XPS and the π^* peak height of the NEXAFS spectra, we can deduce that the amount of the charge transfer from Pd to SO₂ is smaller than that from Ni. The SEXAFS analysis indicates that the S atom of the molecule is located at the bridge site and that one O atom also directly interacts with the metal surface. The difference of the adsorbate structure between SO₂/Pd and SO₂/Ni can be explained in terms of chemical bonding between the substrate and SO₂.

1. INTRODUCTION

Although many studies of the adsorbed SO₂ on metal surfaces have been reported from the environmental and industrial interests, there have been few studies for the quantitative structure determination of the systems. Very recently we have carried out the XAFS studies of SO₂ adsorbed on Ni(100), (111) [1,2] and (110) [3] and concluded that the molecule adsorbs on the surfaces with the molecular plane parallel to the surface. On the other hand, Burke et al. [4] concluded by means of HREELS that on Pd(100) the molecule adsorbs with the molecular plane normal to the surface. It is interesting to examine the different adsorption behavior of the molecule depending on the metal surfaces. In order to reveal the nature of this difference, we have investigated XAFS of SO₂/Pd(100). Comparing with that on Ni surfaces, we have clarified the differences of the amount of charge transfer and of the surface structure between these two systems.

2. EXPERIMENTAL

A Pd(100) single crystal was mechanically polished using 0.05 μm alumina and subsequently electrolyzed in ethanol solution of 10 vol% hydrochloric acid at ~ 273 K. The clean and (1 $\times$ 1)-ordered Pd(100) was prepared by means of repeated cycles of the Ar⁺ bombardment and annealing up to ~ 1100 K in an UHV chamber. The crystal was dosed with 5 L SO₂ (1L = 1×10^{-6} Torr $\cdot$ s; 1 Torr = 133 Pa) at ~ 170 K. At that temperature only submonolayer molecule can adsorb on the surfaces since multilayer SO₂ desorbs around ~ 120 K. During all the spectroscopic measurements the sample temperature was kept at 100 K. All the experiments were carried out at BL-11B of Photon Factory. S-K edge XAFS spectra were taken by the fluorescence yield mode. The polar-angle dependent spectra were recorded for NEXAFS [$\theta = 90^\circ$ (normal X-ray incidence), $\theta = 55^\circ$, $\theta = 15^\circ$] and SEXAFS ($\theta = 90^\circ$, $\theta = 55^\circ$). S 1s photoemission spectra were also measured using a synchrotron radiation X ray of 2550 eV.

3. RESULTS AND DISCUSSION

3.1 S K-edge NEXAFS

Figure 1 shows the polar-angle dependent S K-edge NEXAFS spectra of submonolayer SO₂ adsorbed on Pd(100) together with that on Ni(100) for comparison. The S coverage was estimated to be 0.35 ML for Pd(100) and 0.41 ML for Ni(100) from the edge jump of the NEXAFS spectra. We can

Figure 1. S K-edge NEXAFS spectra of SO₂/Pd(100) (a) and SO₂/Ni(100) (b).

find a clear difference of the polarization dependence from each other. The lower energy peaks (~ 2473 eV) are attributed to the S1s-to- π^* resonance and the higher-energy ones to the σ^* resonances. From the polarization dependence of the π^* peaks, we can deduce that on Pd(100) SO_2 adsorbs with the molecular plane normal to the surface, while on Ni(100) the molecule lies flat. The suppression of the π^* peaks ($\theta=55^\circ$; polarization-averaged spectrum) compared to the multilayer spectrum (not shown) indicates that the charge transfer from Pd to the SO_2 π^* orbital occurs. The amount of the charge transfer is estimated to be $0.8 e$, which is smaller than that of $\text{SO}_2/\text{Ni}(100)$ ($1.2 e$). The spectral analysis of the two σ^* peaks (a_1^* , b_2^*) revealed that the C_2 axis of the molecule is considerably tilted from the surface normal.

3.2 S 1s XPS

We have also measured the S 1s photoemission spectra for the $\text{SO}_2/\text{Pd}(100)$ (not shown). The principal peak locates at the 2474.2 eV which is lower than that of multilayer SO_2 (2476.6 eV) by 2.4 eV. This energy shift is smaller than that on Ni(100) (3.8 eV), implying that the amount of the charge transfer is smaller than that of $\text{SO}_2/\text{Ni}(100)$. This is consistent with the NEXAFS remarks.

3.3 S K-edge SEXAFS

Figure 2 shows the Fourier transforms of the S-K edge SEXAFS functions $k^2\chi(k)$ of $\text{SO}_2/\text{Pd}(100)$. We could not obtain the reliable grazing-incidence spectrum because of considerable scattering X rays. The feature at ~ 1.0 Å is attributed to the S-O coordination and the ~ 2.1 Å one is to the S-Pd scattering. From the analysis of the S-O shell, we concluded that the S-O distance is elongated to 1.48 Å (1.43 Å for gaseous SO_2) because of the charge transfer to the antibonding π^* orbital, although it is shorter than that on Ni(100) (1.51 Å). From the polarization dependence of the S-O effective coordination number, the C_2 axis of the molecule is found to be tilted by $\sim 34^\circ$ from the surface normal. This indicates that one O atom of the molecule interacts directly with the surface. Comparing the ratio of the S-Pd effective coordination number $N^*(\theta=90^\circ)/N^*(\theta=55^\circ) = 0.52 \pm 0.06$ with the calculated ones (0.57 for bridge, 1.12 for hollow, 0.00 for atop), S atom is found to locate on the bridge site.

Figure 3 shows a schematic surface structure of $\text{SO}_2/\text{Pd}(100)$. Difference of the surface structures between SO_2/Pd and SO_2/Ni is explained in terms of the nature of the chemical interaction between the molecule and the substrates. The NEXAFS and XPS results imply that on the Pd(100) the π interaction is weaker than that on Ni and not dominantly contribute to the adsorbed structure. On the Ni surfaces the nature of the π acceptor of SO_2 mainly determines the surface structure. In contrast, on Pd(100) we can deduce that the nature of the σ donor of the molecule plays an important role.

Figure 2. Fourier transforms of the S K-edge EXAFS functions $k^2\chi(k)$ of $\text{SO}_2/\text{Pd}(100)$.

Figure 3. Schematic view of the surface structure of $\text{SO}_2/\text{Pd}(100)$.

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