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Adsorption and Surface Reaction of SO₂ on Cu(100) Studied by S K-Edge XAFS and STM

T. Nakahashi, H. Hamamatsu, S. Terada, M. Sakano, F. Matsui, T. Yokoyama, Y. Kitajima* and T. Ohta

Dept. of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

** Photon Factory, National Laboratory for High Energy Physics, 1-1 oho, Tsukuba, Ibaraki 305, Japan*

Abstract. Adsorption and reaction of SO₂ on Cu(100) at room temperature has been studied by means of S K-edge XAFS, AES, LEED, XPS and STM. It has been revealed that there are atomic S and SO₃ with the stoichiometric ratio of 1:2 on the surface. This indicates that a disproportionation reaction of 3SO₂(a)→S(a)+2SO₃(a) occurs at room temperature. The atomic S locates in the fourfold hollow site. SO₃ adsorbs with its trigonal pyramid upright on the surface. The (2×2) and c(4×6) domains were observed by STM. The former contains only one SO₃ species in the unit cell without atomic S, while the latter involves one SO₃ and two atomic S. This implies the occurrence of drastic migration of resultant products.

1. INTRODUCTION

The industrial and environmental importance of SO₂ has motivated the studies of adsorption and surface reaction of sulfur dioxide SO₂ on metal and metal oxide surfaces[1-8]. Leung et al.[3] studied the surface reaction of SO₂/Cu(100) by means of EELS and observed the presence of SO₃(a), suggesting that a disproportionation reaction occurs on the surface. Recently, Policik et al.[6] studied the decomposition process of SO₂ on Cu(100) by high resolution XPS and showed that SO₂ decomposes into SO+O+S on heating to room temperature. The above results appear to be inconsistent to each other and further studies on the same system are needed. We have studied the surface structures of low coverage SO₂ on Ni(100), (110) and (111) at low temperature by the surface XAFS method and found that the SO₂ molecules lie down flat on the surface with a slight S-O bond elongation for all the cases[7,8]. These studies demonstrated the effectiveness of the surface XAFS method for surface adsorbate systems. In this report, we applied this method to the study of SO₂ adsorption and decomposition on Cu(100) at room temperature. AES, XPS and STM were also applied to clarify the surface structures in more detail. First, we focused on the coverages of the adsorbates by measuring AES, S 1s XPS and S K-edge NEXAFS. Second, we evaluated the orientation angle of the SO₃ species by NEXAFS, and determined the adsorption geometries of atomic S and SO₃ by SEXAFS. STM clarified the nature of weak long-range ordered islands, one of which was observed by LEED as a weak (2×2) overlayer and the other was newly detected. A structural model for the whole surface is consequently proposed.

2. EXPERIMENTAL

A clean, (1×1)-ordered Cu(100) surface was dosed with ~5 L SO₂ at room temperature. Polarization dependent S K-edge XAFS spectra and S 1s XPS were taken at 100K at the soft X-ray double crystal monochromator station BL-11B of the Photon Factory. In order to estimate the coverage of S from the normalized S-K fluorescence intensity (edge jump), a reference spectrum of (√17×√17)R14°S/Cu(100) whose S coverage is 0.47 ML [9] was also taken. S 1s XPS was recorded at a temperature of ~100 K using monochromatized synchrotron radiation at 2550 eV and the Rigaku XPS-7000 concentric hemispherical electron energy analyzer. After all the spectroscopic measurements, no changes in NEXAFS spectra were detected, implying that the present phase is quite stable for rather a long time at ~100 K. The AES, LEED and STM measurements were carried out at room temperature in our laboratory. AES and LEED were examined using an Omicron four-grid reverse view LEED/AES optics. As the coverage references for O and S, we employed (√2×√2)R45°O/Cu(100) (0.50 ML) [10] and (√17×√17)R14°S/Cu(100). Although the electron beam destroys the molecules on the surface and possibly induces desorption of adsorbed species, the AES/LEED measurements were carried out within a few minutes and the electron-irradiated sample was not used for further experiments. STM images were observed using an Omicron bolt-on module STM apparatus. The STM images were recorded using a W tip in the constant-current mode of I_t=2.87 nA for SO₂/Cu(100). The gap voltage, typically 100 mV, was applied to the sample with the tip at virtual ground, implying tunneling of electrons to unoccupied levels of the sample. The lateral calibration was conducted by observing STM images of clean Cu(100). For the vertical direction the relative calibration was performed using the height of S atoms in (√17×√17)R14°S/Cu(100) [9].

3. RESULTS AND DISCUSSION

At the saturation coverage reached by exposing to 5 L SO_2 , LEED exhibited a weak (2x2) pattern. From the AES intensity ratio, S-KLL(152 eV)/Cu-LMM(920 eV) or O-KLL(503 eV)/Cu-LMM(920 eV), the absolute saturation coverages were estimated to be 0.15 ± 0.01 ML for S and 0.30 ± 0.03 ML for O, respectively. The S and O coverages were invariable at least for a few days.

A Si1s photoemission spectrum of the surface exhibited two distinguished peaks at 2469.8 eV and 2475.3 eV. The former peak is attributed to the atomic S species since the S 1s peak of the $(\sqrt{17} \times \sqrt{17})\text{R}14^\circ\text{S}/\text{Cu}(100)$ phase has exactly the same binding energy. The latter peak is located between those of $\text{SO}_2/\text{Pd}(100)$ (2473.8 eV) and $\text{SO}_4/\text{Pd}(100)$ (2476.2 eV), and is exactly the same as that of $\text{SO}_3/\text{Ni}(100)$ (2475.3 eV). Thus, we determined that the peak comes from SO_3 . These findings are in good agreement with the previous HREELS study[3]. The coverage of each species was estimated from the integral intensity of the peak using the reference phase, $(\sqrt{17} \times \sqrt{17})\text{R}14^\circ\text{S}/\text{Cu}(100)$. The results are 0.05 ± 0.01 ML for atomic S and 0.10 ± 0.01 ML for SO_3 . The total amount of S is 0.15 ML, which agrees with the above-described AES result. It should be noted that the surfaces obtained in these measurements were the same with each other in spite of the independent experiments using different chambers. The above results indicate that upon adsorption of SO_2 at room temperature a disproportionation reaction of $3\text{SO}_2(\text{a}) \rightarrow \text{S}(\text{a}) + 2\text{SO}_3(\text{a})$ occurs quantitatively on the Cu(100) surface and no other species such as SO or SO_4 are observed.

Fig. 1 shows the polarization-dependent S K-edge NEXAFS spectra of 5 L $\text{SO}_2/\text{Cu}(100)$, together with some reference spectra. From the edge jump, the S coverage was estimated to be 0.15 ± 0.01 ML by comparing to that of the reference phase, $(\sqrt{17} \times \sqrt{17})\text{R}14^\circ\text{S}/\text{Cu}(100)$. The coverage obtained is again in good agreement with the values given by AES and XPS. In Fig. 1, three peaks are observed at 2469.8, 2477.4 and 2479.3 eV. The first peak is usually observed for atomic S systems. The second and third peaks exhibit opposite polarization dependence to each other. These peaks are assigned to the SO_3 species by comparing with the S K-edge spectrum of SO_3^{2-} salts[11]: the second peak is assigned to the transition to the e^* and the third one to the a_1^* final states. It should be noted that the SO_3 species maintains the molecular structure of a trigonal pyramid (C_{3v}) with the formal charge of -2. Any other peak ascribed, for instance, to SO or SO_4 could not be observed in the spectra. These findings are well consistent with the XPS results. Since the peaks ascribed to the SO_3 species show significant polarization dependence, the SO_3 species should adsorb with a specific orientation. By the curve fitting analysis of the e^* and a_1^* peaks, the orientation angle of the C_3 axis was determined to be nearly perpendicular to the surface.

The S K-edge EXAFS function $k^2\chi(k)$ was obtained according to well-established procedures. Fig.2 shows the Fourier transformed spectra at $\theta=15^\circ$ and 90° , together with calculated spectra for two structural models, depicted in the top. The peak at $\sim 1\text{\AA}$, which is ascribed to the intramolecular S-O shell, is significantly enhanced at normal X-ray incidence, while the peak at $\sim 2\text{\AA}$, attributable to the S-Cu shell, shows less polarization dependence. The curve-fitting analysis of the EXAFS spectra gave the surface atomic structure: $R(\text{S-O}) = 1.49 \pm 0.03\text{\AA}$, which is close to that of Na_2SO_3 ($1.50\text{\AA}$) and $R(\text{S-Cu}) = 2.30 \pm 0.02\text{\AA}$. The NEXAFS analysis could not determine whether the SO_3 trigonal pyramid sits upright with O-Cu direct

Figure 1: S K-edge NEXAFS spectra of 5L $\text{SO}_2/\text{Cu}(100)$, compared with those of some references.

Figure 2: Fourier transforms of the SEXAFS spectra at $\theta=15^\circ$ and 90° , compared with the FEFF6 simulated curves for model 1 and 2.

chemical bonds or sits upside down with a direct S-Cu interaction. In order to determine which of these two surface models is correct, EXAFS simulations using FEFF6 [12] were performed. Here we employed a Cu cluster with 25 (or 31) atoms (bulk lattice constant assumed) and one adsorbate species (either atomic S or SO_3). The polarization dependent EXAFS spectra were resultantly calculated by taking the average of the spectra for atomic S and SO_3 with the population ratio of $\text{S}:\text{SO}_3=1:2$ obtained by XPS. As shown in Fig. 2, model 1 assumes the upright SO_3 , while in model 2 SO_3 is directed downward. The calculated Fourier transforms for both models are depicted in Fig. 2. Model 1 gives good agreement with the observed spectra, and we can conclude that the trigonal SO_3 species is oriented with the sulfur away from the surface, this leading to direct O-Cu interaction. In model 1 we examined several possibilities of S and O geometries and found that the configuration as in Fig. 2 where $\text{S}(\text{SO}_3)$ locates closely above the bridge site is most probable. When $\text{S}(\text{SO}_3)$ was placed in the vicinity of the hollow or atop site, the Fourier transformed spectrum did not fit with the experimental one. This suggests that two O atoms should occupy the adjacent bridge sites, although we have to perform the O K-edge SEXAFS analysis for the direct determination of the O adsorption site.

Since the S-Cu shell at $\sim 2.0 \text{ \AA}$ was found to be attributed only to atomic S, the adsorption site can unambiguously be determined to be the hollow site, which is common for atomic S adsorption geometry.

Fig.3 shows an STM image of 5L $\text{SO}_2/\text{Cu}(100)$ over an area of $65 \times 100 \text{ \AA}^2$. No data processing was done except flat background subtraction. The quality of the image is not so high possibly due to the observation of mobile adsorbates, but the surface image is clearly seen with an atomic resolution. We can see two types of domains in addition to diffused random spots. One is the domain forming (2×2) square lattice, while the other domain has spots forming the rhombic $c(4 \times 6)$ structure, in which there are two faint small spots. The results of AES, XPS and NEXAFS tell us that there are only SO_3 and S species on the surface in the 2:1 stoichiometric ratio. Thus, all the bright spots can be assigned to SO_3 species and the dim spots appearing in $c(4 \times 6)$ to atomic S.

It should be noted that in the (2×2) domain only SO_3 is present and correspondingly in the $c(4 \times 6)$ domain the population ratio of S/SO_3 is not 0.5 but 2.0. These findings imply that noticeable migration of reacted species should take place around room temperature to form two different domains. The $c(4 \times 6)$ domain did not give a LEED pattern and only the (2×2) one provided weak half-integer spots, while the STM image clearly shows the two domains. This successfully demonstrates the usefulness of STM for the detection of long-range ordered structure of small islands.

Figure 3: STM image($65 \times 100 \text{ \AA}^2$) taken in the constant mode of $I_t=2.87 \text{ nA}$ and $V_{\text{gap}}=100 \text{ mV}$.

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