Structure of CH₃SH on Cu(100) Studied by S-K SEXAFS and NEXAFS

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Abstract. A surface structure of submonolayer methanethiol CH₃SH molecularly adsorbed on Cu(100) has been investigated by means of S K-edge SEXAFS and NEXAFS. From the analysis of these spectra, it was revealed that the CH₃SH molecule adsorbs as a methanethiolate (CH₃S⁻) with the S-C bond nearly perpendicular to the surface. SEXAFS has clarified that the S atom locates at the fourfold hollow site and the S-C and S-Cu bond distances are, respectively, 1.82±0.02 and 2.29±0.03 Å. Although it was reported that the adsorption of methanethiol induces surface reconstruction on the Cu(111) surface, we have observed neither reconstruction nor large strain on the Cu(100) surface.

1. INTRODUCTION

Adsorption of sulfur-containing organic compounds on metal surfaces has been an important subject for understanding the mechanisms of the hydrodesulfurization process. Prince *et al.* [1] investigated the surface structure of methanethiol on Cu(111) by means of S K-edge SEXAFS and NEXAFS, and found that the CH₃SH molecule is adsorbed with the S-C bond perpendicular to the surface and the S atom locates at the hollow site. Additionally, they reported that the adsorbed molecules penetrate the top Cu layer, causing a little expansion of the top Cu layer spacing. In the present work, the adsorption of methanethiol on Cu(100) has been studied using S K-edge SEXAFS and NEXAFS spectroscopies.

2. EXPERIMENTAL

A Cu(100) single crystal was mechanically and electrochemically polished. Cleaning of the surface was carried out by argon ion bombardment (500 V) and annealing (~1000 K) in an UHV chamber. The surface cleanliness and order were confirmed by NEXAFS and LEED, respectively. Submonolayer CH₃SH adsorption was performed by dosing the clean Cu(100) with ~5 L CH₃SH (1 L = 1.0×10⁻⁶ Torr·s; 1 Torr = 133 Pa) at ~280±10 K. The sample was kept at 100 K during the spectroscopic measurements.

3. RESULTS AND DISCUSSION

3.1 S-K NEXAFS

Figure 1 shows polar angle dependent S K-edge NEXAFS spectra of submonolayer CH₃SH on Cu(100), together with that of randomly oriented multilayer CH₃SH. The S coverage of submonolayer CH₃SH on the Cu(100) surface was estimated from the S-K edge jump (normalized S-K fluorescence intensity). Using the (√17×√17)R14° atomic S/Cu(100) system as a reference (0.47 ML), the coverage was found to be 0.27 ML.

Peak A in the spectrum of multilayer CH₃SH is assigned to the superposition of the σ*(S-H) and σ*(S-C) transitions from the SCF-MO calculation. Peak B in the submonolayer spectrum shows noticeable polarization dependence and locates at a higher energy side compared to peak A. In our previous study for benzenethiol (C₆H₅SH) on Ni(100), a similar higher energy shift was observed and was ascribed to the cleavage of the S-H bond (adsorbed species is benzenethiolate C₆H₅S⁻) [2,3]. This indicates that the adsorbed species in the present system is also thiolate

Figure 1: S K-edge NEXAFS spectra of the CH₃SH multilayer at X-ray incidence angle θ of 55° and the submonolayer at $\theta=90^\circ$ (short-dashed, normal incidence) and 15° (solid line, grazing incidence). All the spectra were taken at 100 K.

(CH_3S^*) and peak B can be assigned to the $\sigma^*(\text{S-C})$ transition. The spectral analysis of the polarization dependence revealed that the polar angle ω of the S-C bond is $10 \pm 10^\circ$; namely, the S-C bond is nearly perpendicular to the surface. This finding is consistent with the following SEXAFS analysis.

Figure 2: Fourier transforms of the S K-edge SEXAFS oscillation functions $k^2\chi(k)$ of the submonolayer at $\theta = 90^\circ$ (short-dashed), 55° (long-dashed) and 15° (solid line).

surface, although the possibility of tilting vibration around the polar axis cannot be ruled out. The first-NN S-Cu distance was found to be 2.29 ± 0.02 Å. The adsorption site of S can be determined from the ratio of the effective coordination number $N_r = N^*(90^\circ)/N^*(15^\circ)$. The ratio $N_r = N^*(90^\circ)/N^*(15^\circ)$ derived experimentally was 0.87 ± 0.10 , while the calculated values for typical adsorption sites were 0.830 (hollow), 0.242 (bridge) and 0.000 (atop). It is clear that the hollow-site adsorption is the most probable. The second-NN S-Cu distance was 3.23 ± 0.03 Å, which indicates that no relaxation between first and second layers occurs (the distance is 3.22 Å without relaxation). Figures 3 and 4 show the adsorption models for $\text{CH}_3\text{SH}/\text{Cu}(100)$ given by our present results.

It should be noted that the strain of the surface Cu atoms around S as observed for $\text{CH}_3\text{SH}/\text{Cu}(111)$ was not found in the present $\text{CH}_3\text{SH}/\text{Cu}(100)$ case. Such a difference may be caused by the different atomic densities; the present (100) surface gives a smaller atomic density and thus a smaller surface stress upon adsorption.

Figure 3: Side view of the adsorption structure of submonolayer $\text{CH}_3\text{SH}/\text{Cu}(100)$ derived from S-K SEXAFS. CH_3SH is assumed to adsorb as CH_3S^* .

Figure 4: Schematic view of the surface structure of submonolayer $\text{CH}_3\text{SH}/\text{Cu}(100)$. The S-C bond is nearly perpendicular to the surface and the S atom adsorbs at the fourfold hollow site.

References

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