

Adsorption Behavior of (CH₃)₂S on Rh(100) Studied by Sulfur K-Edge NEXAFS and XPS

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We have studied dimethyl sulphide (CH₃)₂S (DMS) on Rh(100) system using polarization dependent S K-edge near edge X-ray absorption fine structure (NEXAFS) and S 1s, S 2p and C 1s X-ray photoelectron spectroscopy (XPS) techniques. At 90 K, the XPS results show that some of DMS molecules dissociate to methanethiolate CH₃S- and atomic sulfur. A noticeable polarization dependence is observed in the S K-edge NEXAFS spectra for submonolayer phase. The NEXAFS results imply that DMS molecule is lying flat on Rh(100) surface. On the other hand, the tilt angle of S-C bond axis of methanethiolate is nearly surface normal.

INTRODUCTION

In the recent years, we pay attention to the researches related to environmental problems, which mostly caused by automobile exhaust gas. For this reason it is important to study the reaction of exhaust gas on platinum family (Pt, Pd, Rh) which are often used for catalyst. Particularly if sulfur containing molecules adsorb on the surface of pure catalyst, these molecules causes electron-backdonation from surface and then catalyst loses its activity, which is named "Sulfur Poisoning". Previously we have investigated the adsorption systems of sulfur containing molecules on transition metal surfaces, such as nickel and copper, using XAFS and XPS [1-5] and where we found a relation between the adsorption structure of the molecule and the adsorption site on the surface. DMS molecule has two S-C single bonds and a bond angle of 105°. For DMS/Ni(100) system, we found that DMS molecule adsorbs with the molecular plane nearly parallel to the surface with intramolecular S-C bonds without cleavage at 80 K, however the chemical shift of C 1s has not occurred [6]. In the case of DMS/Cu(100) system, it has not occurred similarly and the tilt angle of the S-C bonds with respect to the surface normal is

57±8° [7]. On the other hand, there are several researches about platinum family. However researches about Rh are very few and their viewpoints are macroscopic. Therefore microscopic study is required for revealing the reaction of sulfur poisoning about Rh. In this study, we have investigated the molecular adsorption system, DMS/Rh(100), by use of S K-edge NEXAFS and XPS measurements and compared this system with the other transition metal surface systems.

EXPERIMENTAL DETAILS

A commercially available Rh(100) single crystal (10 mm diameter, 3 mm thickness and 99.9 % purity) was mechanically polished using 0.05 μm Al₂O₃ to a mirror finish. The Rh(100) crystal was cleaned by repeating cycles of Ar⁺ ion sputtering (3 keV) and anneal up to ~ 900 K by electron bombardment in an ultrahigh vacuum chamber (base pressure less than 2 × 10⁻⁸ Pa). The cleanliness of Rh(100) surface was verified by XPS measurement (S 2p, C 1s and O 1s). The research grade DMS was purified by means of a few cycles of freezing with liquid N₂ under high vacuum and melting at ambient temperature. In order to obtain a submonolayer phase,

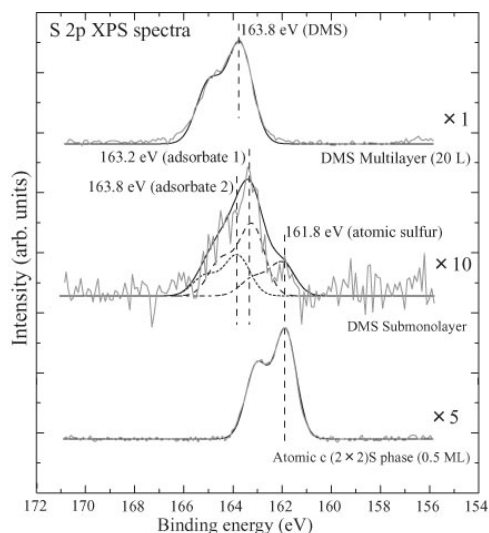


Fig. 1 S 2p XPS spectra for DMS multilayer (20 L), submonolayer at 90 K, and atomic c(2×2)S/Rh(100) phase (0.5 ML).

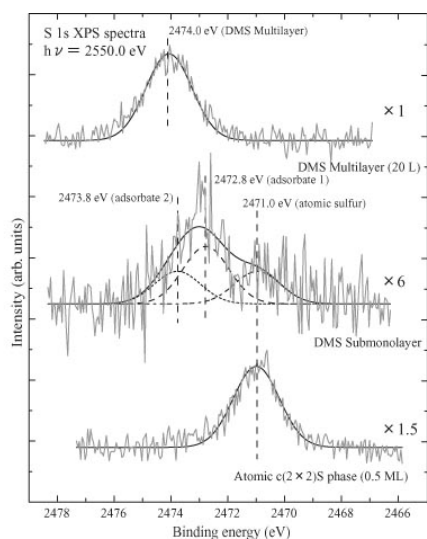


Fig. 2 S 1s XPS spectra for DMS multilayer (20 L), submonolayer at 90 K, and atomic c(2×2) S/Rh(100) phase (0.5 ML).

the DMS gas was introduced with an exposure of 0.5 L (8.3×10^{-8} [Torr] \times 6 [s]) to the Rh(100) crystal which was cooled down to 90 K using liquid N₂.

Polarization dependent S K-edge NEXAFS measurements were carried out at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center (HSRC) [8]. The photon energy was calibrated on the assumption

that the first peak of K₂SO₄ appear at 2481.70 eV. The S-K fluorescence yield detection was employed using an UHV-compatible gasflow type proportional counter with P-10 gas (10 % CH₄ in Ar). S 1s XPS spectra were recorded for submonolayer, multilayer and atomic S phases, using synchrotron radiation X-rays of 2550 eV and a concentric hemispherical electron energy analyzer (ULVAC-Φ OMNI-V). On the other hand, S 2p and C1s spectra were measured for submonolayer, multilayer and atomic S phases using MgKα (1253.6 eV) X-ray.

RESULTS AND DISCUSSION

XPS

S 2p XPS spectra for multilayer, submonolayer at 90 K and sulfur saturation phase are shown in Fig. 1. Sulfur saturation phase coverage is 0.5 ML which corresponds to c(2×2) structure on Rh(100) surface [9-11]. By comparing the integral intensity between submonolayer and atomic c(2×2)S/Rh(100) system, the sulfur amount of submonolayer phase is estimated to be 0.1 ML. There are obviously two peaks on S2p XPS spectrum for submonolayer phase. These peak positions are corresponding to DMS multilayer and atomic sulfur respectively. On the other hand, S K-edge NEXAFS spectra discussed in chapter 3.2 has another peak (adsorbate 2) between DMS and atomic sulfur peak positions. Therefore we assign this peak to methanethiolate (CH₃S⁻) and deconvolute the XPS spectrum for submonolayer phase by means of defining the peak position of CH₃S⁻ as a free parameter. The peak position of atomic sulfur is decided by atomic c(2×2)S/Rh(100) phase. S 2p^{3/2} binding energies for multilayer, adsorbate 1, adsorbate 2 and atomic sulfur are found to be 163.8, 163.2, 163.8 and 161.8 eV, respectively. The peak components for S 1s spectra are consistent with S 2p XPS results, which are shown in Fig. 2. We assign adsorbate 1 and adsorbate 2 to CH₃S⁻ (methanethiolate) and (CH₃)₂S (DMS) for these binding energy respectively [7, 12] and the relative peak position of CH₃S⁻ in comparison with atomic sulfur is almost the same as reported by Gang Liu et al [13]. These results imply three things. The first, DMS molecule adsorbs on Rh(100) surface with dissociation of S-C bonds at 90 K. The second, the

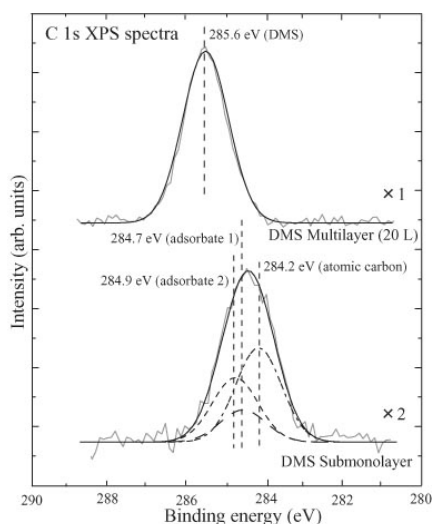


Fig. 3 C 1s XPS spectra for DMS multilayer (20 L), submonolayer phase on Rh(100) at 90 K.

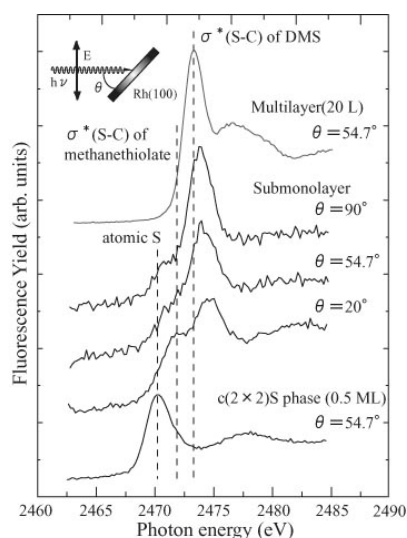


Fig. 4 S K-edge NEXAFS spectra for DMS multilayer (20 L), atomic c(2x2)S/Rh(100) phase (0.5 ML) and submonolayer phase on Rh(100) at 90 K with the X-ray beam incident angle (90°, 54.7° and 20°) to the surface.

two adsorbates (methanethiolate and DMS) adsorb through sulfur atoms, since the peak position of S 1s shift to lower binding energy side comparing with that of multilayer. The third, from the XPS intensity analysis, the ratio of existence for methanethiolate : DMS : atomic S at submonolayer phase is found in the ratio 3 : 2 : 2.

Fig. 3 shows C 1s XPS spectra of multilayer and submonolayer phase at 90 K. Since the peak position of methanethiolate is correspond to that on Mo(110) [14], the carbon atom has no interaction with Rh(100) surface. On the other hand, that of DMS has 0.7 eV shift to lower binding energy relative to that of multilayer. Therefore DMS molecule does not only bond with the sulfur atom but also the carbon atom. It is thought that one or two atomic carbon adsorb on the surface when DMS molecules decompose to methanethiolate or atomic sulfur. Thus, the ratio of C 1s XPS intensities is not contradictory to that of S 1s and S 2p XPS results.

S K-edge NEXAFS

Fig. 4 shows the S K-edge NEXAFS spectra of multilayer, submonolayer phases at 90 K and atomic c(2x2)S/Rh(100) phase, taken with the X-ray incident angle θ of 90° (normal), 54.7° (magic) and 20° (grazing). The glancing angle θ is also the polar angle of electric field vector of the incident X-rays with respect to the surface normal. We can find three features in the NEXAFS spectra in Fig. 4. The first feature is caused by atomic sulfur. Noticeable polarization dependence can be seen in the NEXAFS spectra; for grazing X-ray incidence ($\theta = 20^\circ$) the second feature at 2471.6 eV is enhanced, but it is suppressed for normal X-ray incidence ($\theta = 90^\circ$). On the other hand, for normal X-ray incidence ($\theta = 90^\circ$) the third feature at 2473.5 eV is enhanced, however that of grazing X-ray incidence ($\theta = 20^\circ$) is suppressed. For the XPS analysis, they can be ascribed to the σ^* (S-C) resonance of methanethiolate and DMS respectively. This result indicates that the S-C bond of methanethiolate molecule is nearly perpendicular on Rh(100) surface and that of DMS molecule is almost lying flat. In order to quantitatively estimate the molecular tilt angle, the angular dependence of the σ^* (S-C) resonant intensity is examined by a curve-fitting analysis of the NEXAFS spectra [15]. Fig. 5 and Fig. 6 show the curve-fitting results and the plots of the σ^* (S-C) resonance intensities as a function of $(3\cos^2\theta-1)$. The threshold energies of the step function peaks are determined from the S 1s XPS results (Fig. 2). The tilt angle of S-C bond axis of methanethiolate with

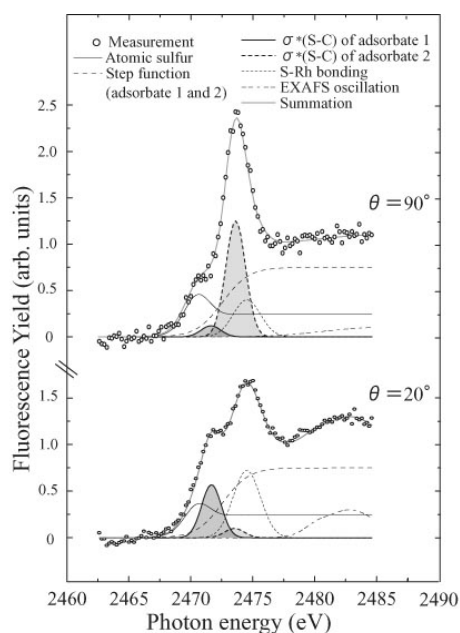


Fig. 5 The curve-fitting analysis of S K-edge NEXAFS spectra for submonolayer phase.

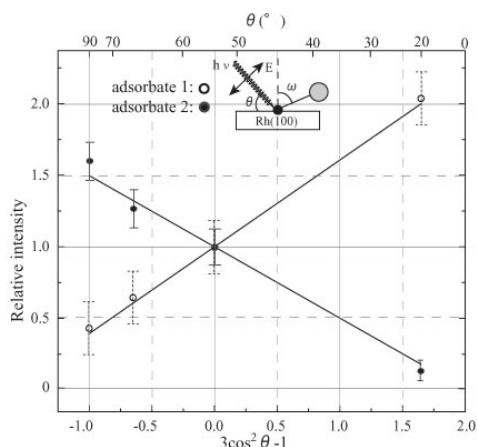


Fig. 6 The intensity of the σ^* (S-C) resonance of adsorbate 1 (methanethiolate) and adsorbate 2 (DMS) as a function of $(3\cos^2\theta-1)$.

respect to the surface normal is estimated to be $31\pm 7^\circ$. For DMS molecule, it was determined to be $87\pm 5^\circ$. These tendencies of the tilt angle are similar to the other transition metal surfaces, such as Ni(100) [6] and Cu(100) [7, 12, 16]. The adsorption model for DMS/Rh(100) system at 90 K is shown in Fig. 7. The analyzed results of XPS and NEXAFS have a good agreement with each other.

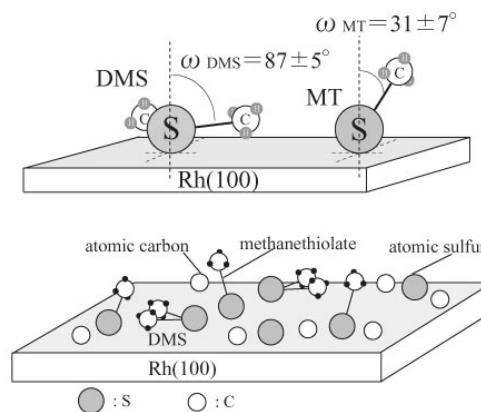


Fig. 7 The adsorption model of submonolayer DMS/Rh(100) at 90 K.

Charge transfer

The chemical shift of S 1s XPS binding energy implies that some charge transfer from Rh(100) substrate to the molecules has occurred. The peak position (2473.8 eV) of DMS submonolayer phase has 0.2 eV shift to lower binding energy relative to that of multilayer (2474.0eV). This values, however, are very smaller than that of Ni(100) system, of which chemical shift is 1.0 eV [6]. In the case of Cu(100) system, it is 0.7 eV [7]. For these results, Rh(100) has the lower activity of the reaction with sulfur atom than Ni(100) and Cu(100). On the other hand, the shift of the binding energy for C 1s XPS spectra, comparing multilayer and submonolayer phase, is larger than that of S 1s binding energy. In this result, carbon atom more drastically reacts with Rh(100) surface than sulfur atom and the dissociation of DMS molecule has caused by means of the back-donation from Rh(100) surface to the carbon atom. It is also thought that the higher activity between carbon atom and Rh(100) surface causes the slightly larger tilt angles of methanethiolate and DMS than these of Ni(100) [6] and Cu(100) [7, 12, 16].

Temperature dependence

Fig. 8 shows temperature dependence of submonolayer DMS/Rh(100). After the sample was prepared at 90 K, it was annealed up to 110 K by use of W-filament. The main peak is DMS doublet at 90 K. On the other hand, the main peak position indicates

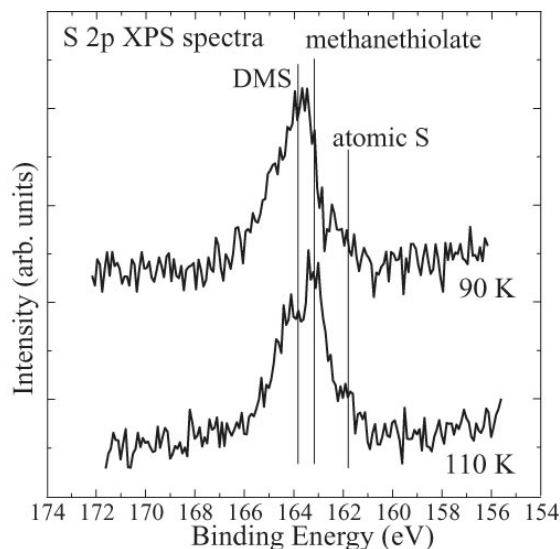


Fig. 8 Temperature dependence of submonolayer DMS/Rh(100)

methanethiolate at 110 K. The amount of atomic sulfur don't increase through this annealing process. Therefore it is found that DMS molecule on Rh(100) dissociates into methanethiolate by annealing up to 110 K, however atomic S doesn't form from DMS and methanethiolate under this process.

CONCLUSION

We have investigated DMS molecular adsorption on Rh(100) surface at 90 K by use of NEXAFS and XPS techniques. It is found that some DMS molecules decompose to methanethiolate and atomic sulfur on Rh(100) at 90 K. The tilt angle of DMS molecule is nearly surface parallel and its both sulfur and carbon atoms have bonding with substrate. On the other hand, that of methanethiolate molecule is nearly perpendicular and only its sulfur atom bonds with substrate. For XPS studies, sulfur atom does not react with Rh(100) surface strongly in comparison with carbon atom. By temperature dependence study, it is found that DMS molecule on Rh(100) dissociates into methanethiolate by annealing up to 110 K, but adsorbates don't compose atomic S under this condition. We would like to emphasize that a combination NEXAFS and XPS measurements is very powerful tool in determining the molecular adsorption structure and the interaction between the

molecule and the substrate.

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