Adsorption behavior of $(\text{CH}_3)_2\text{S}$ on sputtered and annealed Rh(100) surface by AFM, XPS and NEXAFS*

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The temperature dependent reaction of dimethyl sulfide $(\text{CH}_3)_2\text{S}$: DMS on Rh(100) over the temperature range of 90-300 K and the surface reaction of DMS depending on the morphology of Rh(100) surface have been studied with Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS) and Sulfur K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) techniques. DMS molecules adsorb molecularly on 850 K annealed Rh(100) surface at 90 K, and some of DMS are dissociated into methanethiolate CH_3S - : MT or atomic sulfur as the temperature of the substrate increases. The temperature dependent reduction of the total coverage of sulfur indicates that some of sulfur-containing molecules desorb from the surface. On the other hand, it is found that DMS decomposes into atomic S on 1000 K annealed Rh(100) surface at 90 K. These results indicate that the dissociative reaction of DMS/Rh(100) is more sensitive to the surface morphology than that of Cu(100).
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I. INTRODUCTION

The catalytic activity of most transition metals is drastically reduced by the adsorption of sulfur-containing compounds even at extremely low concentrations [1]. Particularly this effect, so called "Sulfur Poisoning", is well known as one of the deactivated factors for the automobile exhaust catalyst materials using the platinum family elements (Pt, Pd and Rh). It is found that the Rh catalyst has a high resistance for Sulfur Poisoning and a high purification ability of CO and NO_x [2]. Therefore the highly efficient catalyst is expected by use of Rh. Due to the use of Rh catalysts for the automobile emissions control the interaction of sulfur-containing molecules with Rh surface at wide temperature range is of great interest. Moreover in the field of molecular adsorption on metal surface, it is well known that step-edge structures are more effective for the catalytic reactions [3]. Therefore the morphology of the catalyst surface seem to influence the catalytic activities and reactions. Previously we have investigated the adsorption systems of sulfur-containing molecules on transition metal surfaces, such as nickel and copper, using XAFS and XPS [4, 5] and where we found a relation between the adsorption structure of the molecule and the adsorption site on the surface. On the other hand, there are several researches about platinum family. Jeffrey and Harvey have reported about significant loss of the activity for NO reduction when Al_2O_3 -Supported Rh, Pd and Pt catalysts are poisoned with SO_2 [6]. Their work shows

Rh to be most resistant to poisoning while Pt is severely inhibited. However researches about Rh are very few and their viewpoints are macroscopic investigation. Therefore microscopic study is required for revealing the reaction of sulfur poisoning about Rh. In this study, we pay attention to the adsorption system of the sulfur containing molecules on Rh surface and the reaction related with the surface morphology. The aim of this work is to investigate the temperature dependent surface reaction of DMS on Rh(100) and the surface reaction related with the morphology of Rh(100) surface by AFM, XPS and Sulfur K-edge NEXAFS techniques.

II. EXPERIMENTAL DETAILS

A commercially available Rh(100) single crystal (10 mm ϕ diameter, 3 mm thickness and 99.9% purity) was mechanically polished using 0.05 μm Al_2O_3 to a mirror finish. The Rh(100) crystal was cleaned by the combination of Ar^+ sputtering (3 keV) to remove sulfur, carbon and oxygen impurities and annealing up to ~ 900 K by electron bombardment in an ultrahigh vacuum chamber, operating with a base pressure below 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 N_2 under high vacuum and melting at ambient temperature. The morphology of Rh(100) and Cu(100) surface was controlled by adjusting the flash annealing temperature (up to any temperature or as-sputtered) after 3 keV Ar^+ sputtering (30 min). In order to obtain a submonolayer phase, the research grade DMS was admitted via the variable leak valve at a constant chamber pressure of 5.0×10^{-8} Torr, maintaining Rh(100) sample

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FIG. 1: Temperature dependent S 2p XPS core level spectra for DMS multilayer, submonolayer and atomic S on Rh(100).

at 90 K with liquid N₂. The exposure was kept up for 10 sec (0.5 L). The temperature of substrate (90 K ~room temperature) was adjusted by W-filament resistive heating.

The AFM images of each substrate were measured by NanoScope III-a (Veeco Instruments) with non-contact tapping mode at Innovation Plaza Hiroshima JST. S 2p and C 1s XPS were recorded by use of Al K_α X-ray (1486.6 eV) and a concentric hemispherical electron energy analyzer (ULVAC-Φ OMNI-V). 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) [7]. 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).

III. RESULTS AND DISCUSSION

A. Temperature dependent dissociation of DMS on Rh(100) surface

Figure 1 shows a set of S 2p XPS spectra for multilayer, submonolayer on Rh(100) at 90, 250 K and room temperature : RT (300 K) and atomic S/Rh(100) recorded after exposure to DMS and heating the adsorption sample up to any temperature. The corresponding Rh(100)

FIG. 2: Temperature dependent C 1s XPS core level spectra for DMS multilayer and submonolayer on Rh(100).

substrate was prepared with 850 K flash annealing after Ar⁺ sputtering. The vertical lines are superimposed at the binding energies corresponding to the S 2p_{3/2} peak energies of the various adsorbates discussed below. It is most readily found that the spectra recorded at the highest (RT) and/or lowest (90 K) temperatures have special features, which show a single spin-orbit split doublet. With regard to the highest temperature, this same state has been seen in atomic S/Rh(100) phase shown below the spectrum of RT phase. It is characterized by a binding energy significantly lower than that of any molecular states, which is investigated by many researches of the decomposition of sulfur-containing molecules on transition metal surfaces [8]. Therefore this component can be obviously identified as atomic S adsorption. On the other hand, the binding energy of the lowest temperature phase is exactly corresponding to that of multilayer DMS. This highest energy state is evidently DMS which has a interaction with Rh(100) by considering of our previous study about DMS/Rh(100) system [9]. At the temperature range between 90 K and RT, however, the spectra are more complex. It is clear that an additional component is generated in proportion to increase of the temperature, which takes the position of the binding energy between atomic S and DMS. This middle state can be assigned to MT, and has been seen in studies of the dissociation of DMS on Rh(100) [9] and Cu(111) [8].

Figure 2 shows the corresponding C 1s XPS spectra for multilayer, submonolayer at 90, 130, 200 K and RT. The suitable back-ground spectrum measured before exposure of DMS has been already subtracted from all of spectra.

FIG. 3: Temperature dependent sulfur coverage estimated from S 2p peak intensity of DMS submonolayer on Rh(100).

FIG. 4: Temperature dependent carbon coverage peak of DMS submonolayer on Rh(100); closed markers and open markers are estimated from C 1s XPS intensities and sulfur coverage, respectively.

It is similar to S 2p XPS results that the spectrum measured at 90 K shows a single phase associated with DMS. The spectrum recorded at RT also indicates a single peak shape. This state can be ascribed to hydrocarbon: CH_x ($x > 1$) species owing to the higher binding energy than that of C or CH on Rh(111) [10]. For the middle range of temperature, MT appear with DMS and CH_x .

XPS results show that DMS molecules molecularly adsorb on Rh(100) at 90 K, and some of molecules dissociate into MT, atomic S and CH_x species as the substrate temperature increases. Finally all of DMS on Rh(100) decompose to atomic S and CH_x at RT. The tendencies of temperature dependent dissociation of DMS on Rh(100) have a good agreement with between S 2p and C 1s analyses.

More quantitatively detailed analysis can be carried out with the investigation about the coverage changes of each adsorbate. The coverage of sulfur saturation phase is 0.5

FIG. 5: Incident angle dependence of S K-edge NEXAFS spectra for DMS submonolayer on Rh(100) at 90 K.

ML which corresponds to $c(2 \times 2)$ structure on Rh(100) surface [11–13]. By comparing the integral intensity between submonolayer and S/Rh(100) system (shown in Fig. 1), the sulfur amount of each species can be estimated. The standard coverage of carbon is established in C 1s spectrum at 90 K, whose intensity is equal to 0.32 ML of carbon coverage. Figure 3 shows the sulfur coverage of each adsorbate as a function of the substrate temperature. The temperature dependent reduction of the total coverage of sulfur (open circle) indicates that some of adsorbates desorb from Rh(100) surface above 150 K. MT (open diamond) keeps its regular coverage during the temperature range of 150–250 K, which implies that the amount of dissociated MT is roughly equal to that of generated from DMS (open star). Particularly the equivalence of the reduction of MT coverage and the increase of atomic S coverage is found in the heating range of 250–300 K. Moreover there is the same relationship between the reduction of total coverage and that of DMS coverage. At the temperature range of 250–300 K, therefore, it is supposed that all of MT decompose and form atomic S species. On the other hand, DMS molecules adsorbed on Rh(100) entirely lead to thermal desorption from the surface.

The temperature dependent carbon coverage has been estimated from C 1s XPS, which is shown as closed markers and solid lines in Figure 4. In order to reveal the detailed reactions, a certain set of reaction models is assumed as follows;

Here all of species formed from DMS are supposed to stay on Rh(100) surface after this reactions. Being based on this reaction models, the carbon coverage of each adsorbate has made an estimate from the results of sulfur coverage (shown as open markers and dotted lines in Fig. 4). The quantitative variations of each coverage calculated by the two ways agree with each other over the whole temperature range. Therefore the assumed set of

FIG. 6: The AFM images of Cu(100); the substrate is annealed up to 950 K (well-annealed) and as-sputtered.

FIG. 7: S 2p XPS spectra for DMS/Cu(100) at 90 K; the substrates are annealed up to 950 K, 850 K and as-sputtered.

reactions is confirmed. Because the total coverage of remained elements gives the ratio of Carbon : Sulfur = 2 : 1, that of the thermal desorption species should indicate the same ratio of elements. Dohmae have reported that atomic S on Rh can not desorb even if it is annealed up to 1000 K in ultrahigh vacuum condition [2], and S 2p XPS results of Figs. 1 and 3 implies that all of MT stay and/or dissociate on Rh(100) surface. Consequently the thermal desorption state can be identified only DMS molecule.

Figure 5 shows the S K-edge NEXAFS spectra of submonolayer at 90 K, taken with the X-ray incident angle θ of 90° (normal) and 20° (grazing). The main feature indicates the transition of $S1s \rightarrow \sigma^*(S-C)$ of DMS. Notice-

FIG. 8: S K-edge NEXAFS spectra for DMS/Cu(100) at 90 K with the X-ray incident at 90° and 20° ; the substrates are annealed up to 950 K, 850 K and as-sputtered.

able polarization dependence can be seen in the NEXAFS spectra; for normal X-ray incidence ($\theta = 90^\circ$) the peak of $\sigma^*(S-C)$ is enhanced, however that of grazing X-ray incidence ($\theta = 20^\circ$) is suppressed. This result indicates that the S-C bond of DMS molecule is almost lying on Rh(100) surface. This tendency of the tilt angle is similar to the other transition metal surfaces, such as Ni(100) [14] and Cu(100) [15–17].

FIG. 9: The AFM images of Rh(100); the substrates are annealed up to 1000 K and 1200 K.

B. DMS on sputtered and annealed Cu(100) surface

After 3 keV Ar^+ sputtering, we annealed the Cu(100) sample at different temperatures and obtained the surface morphologies shown in Fig. 6. At 950 K, the surface is smooth. On the other hand, small hills and holes ~ 5 nm height are randomly distributed on as-sputtered Cu(100) surface. It is obviously found that the more annealing temperature increases, the more the Cu(100) surface smoothes. This changes of the surface morphology are caused by the diffusion of adatoms and vacancies produced by sputtering [18]. Figure 7 shows S 2p XPS spectra for Cu(100) annealing temperature of 950 K (well-annealed), 850 K and as-sputtered. The all spectra (950 K, 850 K and as-sputtered) show a single spin-orbit split doublet, and their S 2p_{3/2} peak positions are corresponding each other. Therefore DMS molecules do not dissociate and molecularly adsorb on all Cu(100) surface at 90 K. The dissociation of molecules is not also confirmed from S K-edge NEXAFS shown in Fig. 8. The orientation of DMS molecule does not change with the annealing temperature, because there is almost no change in the polarization dependent spectral shapes and peak intensities.

C. DMS on sputtered and annealed Rh(100) surface

Rh(100) sample was annealed at different temperatures after sputtering, and we obtained the surface morphologies by means of AFM measurement. Figure 9 shows two kinds of well-annealed Rh(100) surface; the left and right images show 1000 K and 1200 K annealed sample respectively. At 1000 K, the surface has a lot of wrinkled structures which is not observed at any annealing temperatures of Cu(100). Similar to well-annealed Cu(100), Rh(100) heated up to 1200 K becomes a smooth surface. Figure 10 shows S 2p XPS spectra for Rh(100) annealing temperature of 1200 K, 1000 K, 850 K and as-sputtered. Since the peak of atomic S exists in the spectrum of 1000 K, DMS decomposes into atomic S on 1000 K heating Rh(100) surface at 90 K. On the other hand, the spectra of 1200 K, 850 K and as-sputtered do not include

FIG. 10: S 2p XPS spectra for DMS/Rh(100) at 90 K; the substrates are annealed up to 1200 K, 1000 K, 850 K and as-sputtered.

the component of atomic S. The peak position and the shape of XPS and NEXAFS, shown in Fig. 11, indicates that DMS molecules adsorb molecularly on the 1200 K and 850 K annealing surface, and dissociate into CH_3S -(MT) on as-sputtered surface at 90 K. Four peaks are obviously found to S K-edge NEXAFS spectra. According to previous study of DMS/Rh(100) system [9], these

FIG. 11: S K-edge NEXAFS spectra for DMS/Rh(100) at 90 K with the X-ray incident at 90° and 20°; the substrates are annealed up to 1200 K, 1000 K and as-sputtered.

components were assigned to atomic S (around 2470 eV), MT (2471.6 eV), DMS (2473.5 eV) and S-Rh bonding (around 2475 eV), respectively. Polarization dependence can be observed for all of these peak intensities. The polarization dependent spectral shapes and peak intensities of S K-edge NEXAFS are quite changeable in regard to Rh(100) annealing temperature. Therefore the orientation angles of DMS and MT on Rh(100) at 90 K are quite sensitive to the surface morphology.

D. Surface reactivity

We can discuss about the reactivity of the adsorption systems investigated in above. It is found with the changes of XPS and NEXAFS spectra that the dissocia-

tive reaction for DMS/Rh(100) at 90 K is more sensitive to the surface morphology than on Cu(100). The higher reactivity and sensitivity of DMS/Rh(100) are caused by the higher electron density at near Fermi level of Rh(100) surface [19] than that of Cu(100) [20], because the reactivity of surface is in proportion to the electron density at near Fermi level. According to investigated systems in this paper, 1000 K annealed surface has the highest reactivity. We supposed that the wrinkled structures shown in Fig. 9, whose surface may consist of lots of step-edge structures, supply the activated adsorption sites.

IV. CONCLUSION

We have investigated the temperature dependent reaction of dimethyl sulfide DMS on Rh(100) over the temperature range of 90-300 K and the surface reaction of DMS related with the morphology of Rh(100) surface structure with AFM, XPS and S K-edge NEXAFS techniques. DMS molecules adsorb on Rh(100) molecularly at 90 K, and some of DMS molecules form the dissociated compounds; MT or atomic S upon heating. The temperature dependent reduction of total coverage indicates that thermal desorption has gradually occurred above 150 K. Moreover comparing S 2*p* and C 1*s* XPS, it is supposed that the thermal desorption species are only DMS molecules and the other adsorbates are decomposed and remain on the surface. S K-edge NEXAFS study implies that the S-C bond axes of DMS molecule are almost lying flat on Rh(100) surface. In sputtered and annealed Rh(100) surfaces, 1000 K annealed surface has the highest reactivity, because DMS molecules decompose into atomic S only on the surface. It is supposed that the high reactivity is caused by the wrinkled structures seen in the AFM image at 1000 K heating, which correspond to lots of step-edge structures, and there are activated adsorption sites on these step-edges.

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