

# Coadsorption behavior of $(\text{CH}_3)_2\text{S}$ with $\text{H}_2\text{O}$ or $\text{D}_2\text{O}$ on Rh(100) studied by XPS and NEXAFS

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The coadsorption reaction of  $(\text{CH}_3)_2\text{S}$  with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  on Rh(100) surface has been studied by XPS and S K-edge NEXAFS techniques. The  $(\text{CH}_3)_2\text{S}$  gradually dissociate into methanethiolate:  $\text{CH}_3\text{S}$ -, as the temperature of the sample is elevated. S K-edge NEXAFS results indicate that the H/D exchange between  $(\text{CH}_3)_2\text{S}$  and  $\text{D}_2\text{O}$  yields the angular change in the S-C bond to more flat-lying, when  $\text{D}_2\text{O}$  is introduced into this coadsorption system.

**Keywords:** Coadsorption Reaction;  $(\text{CH}_3)_2\text{S}$ ;  $\text{H}_2\text{O}$ ;  $\text{D}_2\text{O}$ ; XPS; S K-edge NEXAFS.

## 1. Introduction

Platinum group metal catalysts are widely applied to some purification reaction of exhaust gases, particularly in the field of automobile exhaust cleaning. "Sulfur Poisoning" is an important factor in the deactivation of these catalysts. Many studies have paid attention to such problems [1-4, 5, 6]. These studies mainly investigate the interaction between the sulfur-containing molecules and the metal surfaces. We also have studied the adsorption system of  $(\text{CH}_3)_2\text{S}$  [dimethyl sulfide: DMS] on clean Rh surface, where the temperature dependent dissociation and desorption reactions have been revealed [7, 8]. These results conclude that sulfur poisoning is essentially due to the adsorption of the atomic sulfur, which blocks the contact of the exhaust gas and the catalyst surface. Therefore, the dissociative reaction of a sulfur-containing molecule is of great interest.

Actually the catalyst in practical use is set under the environment of  $\text{H}_2\text{O}$ -rich. Thus, the coadsorption reaction between sulfur-containing molecules and  $\text{H}_2\text{O}$  will give us the more actual knowledge of sulfur-poisoning. T. We have studied the coadsorption system of  $(\text{CH}_3)_2\text{S}$  and  $\text{H}_2\text{O}$  on Rh(100) [9]. The S-C cleavage occurs more easily in the coadsorption with  $\text{H}_2\text{O}$  than on clean or oxygen

pre-covered surface during heating process. The paper shows that the coadsorbed species, such as  $\text{H}_2\text{O}$  and O, seriously affect the dissociation of S-C bonds.

Hydrogen isotopes (H and D) have some different properties in the chemical reactions of molecules each other. The exchange between H and D yields the change in the bond energy and the bond length. The rate of the reaction related with that bond undergoes a change (first-order isotope effect) [10]. For example, the bond energy of O-D becomes higher than that of O-H in the water isotopomers. This induces the difference in the rate of O-H scission; the dissociation constant of  $\text{H}_2\text{O}$  is six times as large as that of  $\text{D}_2\text{O}$ . These isotopic differences are reported to influence the adsorption/desorption behavior on/from transition metal surfaces [11]. Therefore, some isotope effects are expected in such a coadsorption system with water isotopomers.

The aim of this work is to reveal the coadsorption reaction and the isotope effect of  $(\text{CH}_3)_2\text{S}$  : DMS with water isotopomers, such as  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ , on Rh(100) surface by means of X-ray photoelectron spectroscopy (XPS) and sulfur K-edge near edge X-ray absorption fine structure (NEXAFS) techniques.

## 2. EXPERIMENTAL

A commercially available  $\text{Rh}(100)$  single crystal (10 mm $\phi$  diameter, 3 mm thickness and 99.9 % purity) was mechanically polished using 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  to a mirror finish. The  $\text{Rh}(100)$  crystal was cleaned by the alternating cycles of  $\text{Ar}^+$  ion sputtering (3 keV, 2 $\mu\text{A}$ , 300 K, 30 min) to remove sulfur, carbon and oxygen impurities and annealing up to 1200 K by an electron bombardment in an ultrahigh vacuum (UHV) chamber, operating with a base pressure below  $2 \times 10^{-8}$  Pa. The cleanliness of  $\text{Rh}(100)$  surface was verified by XPS measurements (S 2p, C 1s and O 1s). The research grade DMS was purified by means of a few cycles of freezing with liquid  $\text{N}_2$  under high vacuum condition and melting at ambient temperature. The ordered  $\text{Rh}(100)$  surface was promoted by the flash annealing up to 1200 K after 3 keV  $\text{Ar}^+$  sputtering for 30 min.  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$  and DMS were admitted via the variable leak valve into the UHV chamber in this procedure, as the  $\text{Rh}(100)$  substrate was cooled down to 90 K with liquid  $\text{N}_2$ . The dosages were 0.2 L for  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  and 0.3 L for DMS, respectively. The temperature of substrate (90 ~ 200 K) was controlled by resistive heating with the W-filament, which was set behind the crystal.

S 2p, C 1s and O 1s XPS were recorded by use of  $\text{AlK}\alpha$  X-ray (1486.6 eV) and a concentric hemispherical electron energy analyzer (ULVAC-PHI OMNI-V). The binding energy was calibrated on the assumption that the peak position of  $\text{Rh } 3d_{5/2}$  appear at 307.2 eV. The coverage of sulfur adsorbed on  $\text{Rh}(100)$  was estimated by comparison with the integral intensity of sulfur saturated phase, which corresponds to 0.5 monolayer (ML) of sulfur on  $\text{Rh}(100)$  [12-14]. 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) [15, 16]. The photon energy was calibrated on the assumption that the first peak of  $\text{K}_2\text{SO}_4$  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 which means the mixed gas of 10 %  $\text{CH}_4$  and 90 % Ar.

## 3. RESULTS AND DISCUSSIONS

### 3.1. XPS results

Fig. 1 shows the temperature dependent S 2p XPS

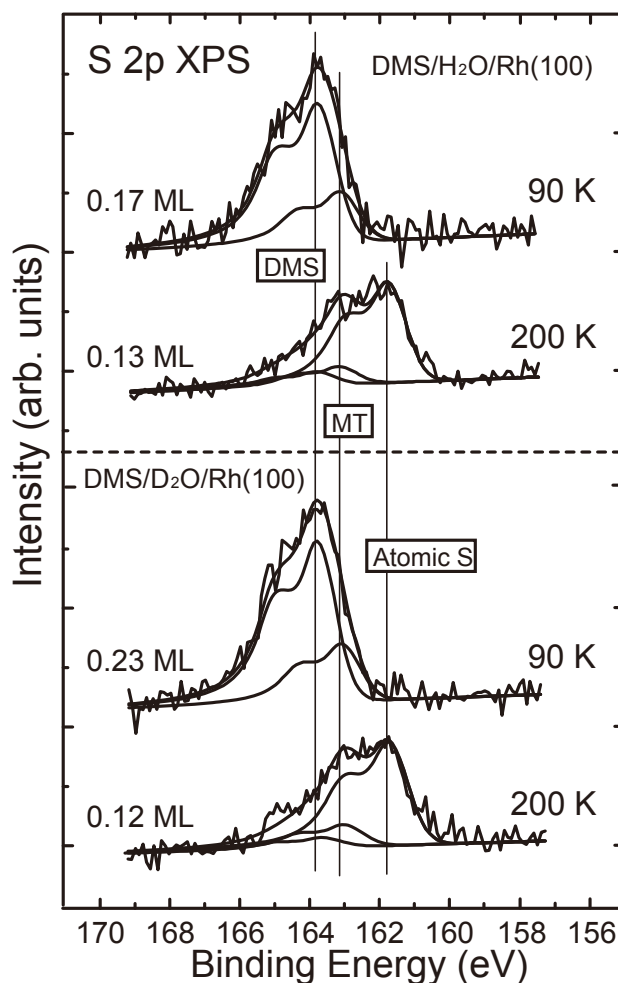


Fig. 1. Thermal dependent S 2p XPS spectra for the coadsorption system of DMS with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  on  $\text{Rh}(100)$ .

spectra for the coadsorption of DMS with water isotopomers ( $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ ) on  $\text{Rh}(100)$  surface. The estimated sulfur coverages for each sample are shown in Fig. 1. These amounts are small enough for ruling out the second layer. At 90 K, the spectra for DMS with each water isotopomers can be deconvoluted into two chemical states, where the solid lines are superimposed on the S  $2p_{3/2}$  position. These peaks are assigned to DMS and methanethiolate ( $\text{CH}_3\text{S}^-$ : MT) [5]. MT is formed by the cleavage of the S-C bonds in DMS molecule. Thus, DMS molecules partially dissociate at 90 K. The sulfur included in MT is seemed to directly bond to the substrate at 90 K, because the peak position of MT (163.2 eV) is corresponding to that on clean  $\text{Rh}(100)$  surface [5]. When the samples are heated up to 200 K, the peak intensities of DMS and MT drastically decrease on both surfaces. Another peak appears additionally at around 162 eV, which

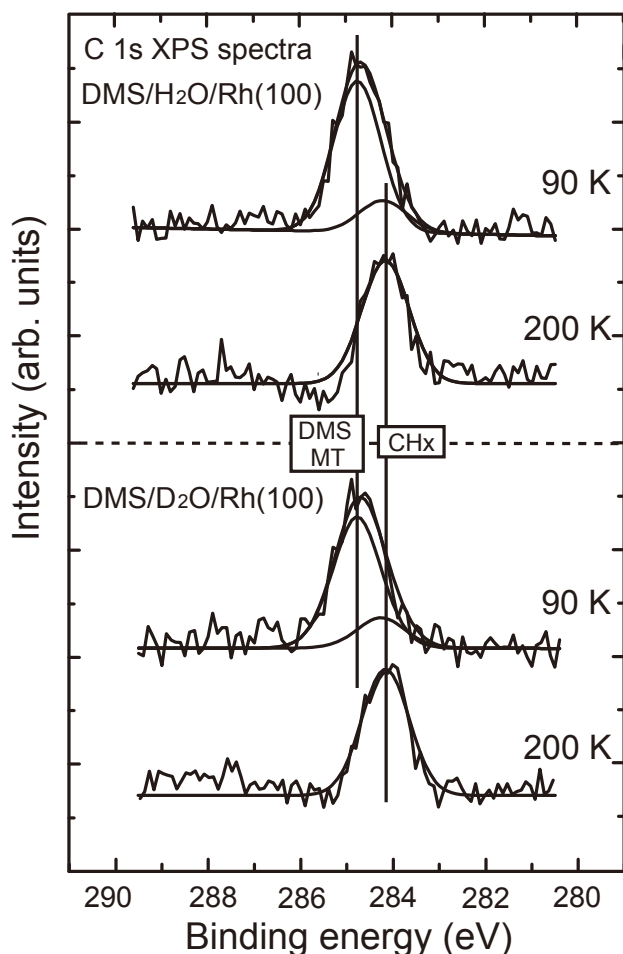


Fig. 2. Thermal dependent C 1s XPS spectra for the coadsorption system of DMS with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  on  $\text{Rh}(100)$ .

represents the formation of atomic sulfur chemisorbed on  $\text{Rh}(100)$  [7]. Most of the S-C bonds in DMS and MT are broken at 200 K, because quite a small amount of DMS and MT remains on  $\text{Rh}(100)$  surface. There is also the desorption of adsorbates from the surface. According to the previous study [8], the main desorbed species seem to be the chemisorbed DMS molecules, and most of MT decomposed into atomic sulfur.

The C 1s XPS spectra of the same samples are also shown in Fig. 2, where these spectra have already been subtracted the suitable background spectrum measured before DMS adsorption. Two peaks are found in these spectra. The first peak at 284.2 eV is assigned to  $\text{CH}_x$  ( $x = 2$  or 3) species chemisorbed on  $\text{Rh}(100)$ , which is formed by the scission of S-C bonds [17]. The second peak presents the methyl bonding to sulfur atom, such as DMS and MT. There has already been the peak for  $\text{CH}_x$  at 90 K, which indicates the decomposition of DMS molecules. That peak intensity is enhanced as the temperature rises, and simultaneously the decrease of the

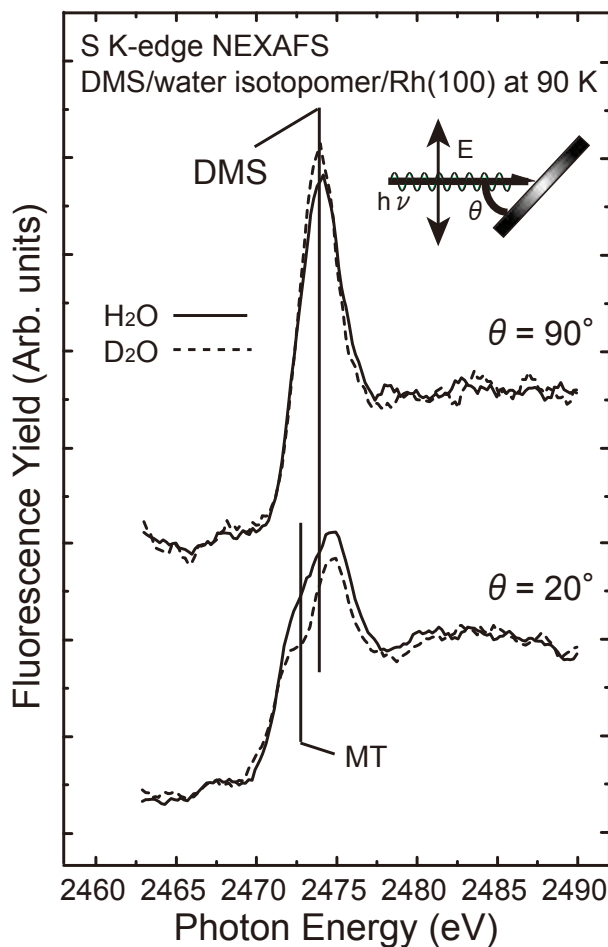


Fig. 3. Sulfur K-edge NEXAFS spectra for the coadsorption system of DMS with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  on  $\text{Rh}(100)$  at 90 K.

peak intensity for MT and DMS occurs. Therefore, we can observe the thermal dissociation of DMS and MT in the C 1s XPS spectra. When the sample is heated up to 200 K, the C 1s XPS spectrum becomes having a single peak of  $\text{CH}_x$  species. Thus, most of the S-C bonds have already been cleaved. The results of S 2p and C 1s XPS are corresponding to each other. One cannot obtain any isotopic differences in the thermal reaction between DMS and water isotopomers.

### 3.2. S K-edge NEXAFS results

Fig. 3 shows the S K-edge NEXAFS spectra for the coadsorption of DMS with water isotopomers on  $\text{Rh}(100)$  surface at 90 K. The glancing angle  $\theta$  is also the polar angle of electric field vector of the incident X-rays with respect to the surface normal. One can obtain the tilt angle of the chemical bond by means of the dipole selection rule between electric field vector and the transition moment. These spectra are normalized by the edge-jump with each other. We can find a peak at  $90^\circ$  and a shoulder

structure at  $20^\circ$  in the spectra. The main peak at 2474.0 eV is assigned to the transition on  $\text{S } 1s \rightarrow \sigma^*(\text{S-C})$  of DMS. The shoulder structure at 2472.5 eV is ascribed to that on  $\text{S } 1s \rightarrow \sigma^*(\text{S-C})$  of MT [7]. The polarization dependence for the intensity of the  $\sigma^*(\text{S-C})$  indicates that the tilt angle of S-C bond in DMS is almost lying flat on  $\text{Rh}(100)$  surface, because the maximum of the peak intensity occurs at  $\theta = 90^\circ$ . On the other hand, the S-C bond of MT is located to be perpendicular to the surface qualitatively. These tendencies for the S-C orientations are similar between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  as the coadsorbates. However, a little difference depending upon the water isotopomers can be seen in the peak intensities. For normal X-ray incidence ( $\theta = 90^\circ$ ), the peak of DMS is enhanced more on the coadsorption with  $\text{D}_2\text{O}$  than  $\text{H}_2\text{O}$ . On the other hand, the peak height for DMS and MT is intensified with  $\text{H}_2\text{O}$  at grazing X-ray incidence ( $\theta = 20^\circ$ ). These tendencies represent that the coordination angle of the S-C bonds becomes more flat-lying in regard to  $\text{Rh}(100)$  surface, when  $\text{D}_2\text{O}$  is introduced to this coadsorption system. This structural change in the tilt angle of the S-C bond is attributed to the H/D exchange reaction in the methyl group. The H/D exchange between  $\text{D}_2\text{O}$  and other molecules, as in  $\text{H}_2\text{O}$  and an amide group, have reported [18, 19]. The displacement into deuterium leads to shorten the bond length between a certain atom and hydrogen because of the vibrational change [20]. In this study, some of the C-H bonds are speculated to be replaced into the C-D bonds. These methyl groups can come to approach more to the  $\text{Rh}(100)$  surface, because the S-C bond axes of DMS molecule is almost lying flat on the surface [7]. Simultaneously, the coordination angle of the S-C bond makes closer to parallel to the surface qualitatively.

#### 4. CONCLUSION

We have investigated the coadsorption behavior of DMS with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  on  $\text{Rh}(100)$  surface by XPS and S K-edge NEXAFS techniques. A part of DMS molecules coadsorbed with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  dissociates into MT on  $\text{Rh}(100)$  surface at 90 K. DMS and MT gradually decompose into atomic sulfur, when the samples are annealed. Most of the S-C bonds undergo a scission at 200 K. There is little difference between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  in the coadsorption reaction. On the other hand, S K-edge NEXAFS study shows that the tilt angle of the S-C bond

change into more flat-lying, when  $\text{D}_2\text{O}$  is admitted into this coadsorption system. The change in the adsorption structure is supposed to be caused by the H/D exchange between DMS and  $\text{D}_2\text{O}$ .

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