

# SURFACE REACTION OF $(\text{CH}_3)_2\text{S}$ ON Rh NANOHOLE SURFACE

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**Abstract.** The noble metal membrane with nanosize hole structure is synthesized by rhodium nanoparticle, which are protected by poly-vinylpyrrolidone (PVP) as surfactant. There are many nanoholes on the Rh(PVP) membrane surface. We have measured the nanohole sizes by means of AFM (Atomic Force Microscope) with tapping measurement mode. The distributions of the nanoholes are from 30 nm to 400 nm in diameter. We have investigated the temperature dependent adsorption behavior of dimethylsulfide  $[(\text{CH}_3)_2\text{S}]$  on the Rh(PVP) membrane surface by sulfur K-edge NEXAFS (Near-Edge X-ray Absorption Fine Structure) and XPS (X-ray Photoelectron Spectroscopy) measurements. It is found that this surface has a high reactivity at 80K for the desulfurization of the sulfur-including molecule. At all substrate temperature region from 80 to 600K, a very large peak is observed at around 2482 eV in sulfur K-edge NEXAFS spectra. This result means DMS molecules stably adsorb with the membrane surface oxygen and form  $\text{SO}_4^{2-}$  structure.

## 1. INTRODUCTION

There are many origins of an environmental pollution in an automobile and/or industrial exhaust gases. Especially an activity of the purification catalyst is suppressed in a sulfuric atmosphere. That is named 'Sulfur Poisoning'. It is found that the sulfur poisoning is caused by the adsorption reaction of the sulfur including molecule on the catalyst surface. For example, the sulfur poisoning is originated by the dissociation of the S-C bond and continuously the sulfur atom adsorption on active site on the catalyst surface. The adsorbed sulfur atom picks some electrons from the catalyst surface at the active site. Therefore, the surface results in electronically inert.

In previous study, K. Dohmae reports that rhodium surface has a high resistance to the sulfur poisoning with existing oxygen atoms [1]. The adsorbed sulfur atom is desorbed at around 600K. That is named 'Healing effect'. At 90K, T. Nomoto *et al.* report that the adsorption behavior of dimethyl sulphide  $((\text{CH}_3)_2\text{S}$ ; DMS) on Rh(100) single crystal surface, with using sulfur K-edge NEXAFS and XPS techniques [2]. It is found from the XPS results that some DMS molecules dissociate to methanethiolate  $\text{CH}_3\text{S}$ - and atomic sulfur at 90K. Polarization dependent sulfur K-edge NEXAFS spectra for submonolayer phase imply that the DMS molecule is lying flat on Rh(100) surface. On the other hand, the tilt angle of the S-C bond axis of the

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methanethiolate is nearly surface normal. At annealing temperature up to 1000K, many of sulfur atom desorbs from Rh(100) surface and the surface becomes partly clean situation again [3]. Due to the healing effect, the catalyst with using rhodium has the high resistance to the sulfur poisoning.

The catalytic effect is proportional to the surface area of the substrate. If the substrate can be made a porous surface, the catalytic effect can be increased easily. We have achieved to synthesize the newly structured rhodium membrane with nanosized holes from Rh(PVP; poly-vinylpyrrolidone) nanoparticle in these years. In this work, we have studied the morphology by using AFM and the adsorption behavior of DMS molecules on the rhodium membrane surface by means of sulfur K-edge NEXAFS and XPS measurements at from 80 to 600K.

## 2. EXPERIMENTAL

The Rh(PVP) was purchased from TANAKA PRECIOUS METALS and used as initial membrane materials without purification. The Rh(PVP) nanoparticles, stabilized with poly-vinyl pyrrolidone, have a nanoscale size of 1-3 nm in diameter. The Rh(PVP) colloidal solution was diluted with the Milli-Q water by 10%(V). The synthesized rhodium membrane was made by use of the spin-coating method. A nickel sheet, which surface was mechanically polished by using  $0.05 \mu\text{m}^{\varnothing} \text{Al}_2\text{O}_3$  compounds, was used as a substrate. The conventional spin-coating method was employed to spread the membrane on wide areas of the nickel substrate. The spin-coating was done by means of rotational speed at 8000 rpm and keeping rotation for 30 seconds for drying at 300K. The Rh(PVP) colloidal solution was dark-brown color before casting. The Rh(PVP) membrane color was changed to dark-blue after spin-coating. Following the spin-coating process the membrane was annealed up to 600K in the air and cooled down to 300K gradually. The surface morphology was observed by AFM (Digital Instrument, Veeco, Nanoscope III-a) with tapping mode. The scan rate and the pixel size were 0.5 Hz and 512x512 pixels, respectively.

An initial contaminant level of the membrane surface was verified by XPS measurement (S 2p, C 1s, N 1s and O 1s). After Ar<sup>+</sup> sputtering (ion energy: 500 eV, ion current: 200 nA, for 20 min) there were rhodium, carbon, nitrogen and oxygen atoms, but not sulfur atoms on the membrane surface.

In order to obtain a submonolayer phase, research grade DMS (>99.0%, Katayama Chemical),

which was purified by a few freeze-pump-thaw cycles at ambient temperature, was introduced with an exposure of 0.5 L for submonolayer ( $5 \cdot 10^{-8}$  Torr  $\times 10$  s) to the membrane surface at 80K with using liquid N<sub>2</sub>. The base pressure of the UHV chamber was less than  $2 \cdot 10^{-8}$  Pa. The substrate temperature could control with using tungsten filament (20 W, 100 V), which set at the behind side of the substrate, and monitor by the K-type thermocouple, which directly spot-welded on the substrate.

Temperature dependent sulfur K-edge NEXAFS measurements were carried out at the soft X-ray double crystal monochromator beamline BL-3 on Hiroshima Synchrotron Radiation Center (HSRC) [4]. The photon energy was calibrated on the assumption that the first peak of K<sub>2</sub>SO<sub>4</sub> located at 2481.70 eV. The sulfur-K fluorescence yield detection was employed using an UHV-compatible gas-flow type proportional counter with P-10 gas (10% CH<sub>4</sub> in Ar) and applied voltage of about 2 kV to the gold-coating tungsten wire (10  $\mu\text{m}$  in diameter). Since we wanted to investigate the adsorption behavior inside of the nanoholes, all NEXAFS spectra was obtained with normal incidence of synchrotron light. Rh 3d, S 2p, C 1s, N 1s and O 1s spectra were measured for the submonolayer adsorption phase using a concentric hemispherical electron energy analyzer (ULVAC- $\Phi$  OMNI-V) and AlK <sub>$\alpha$</sub>  X-ray source at 300 W and 15 kV.

## 3. RESULTS AND DISCUSSION

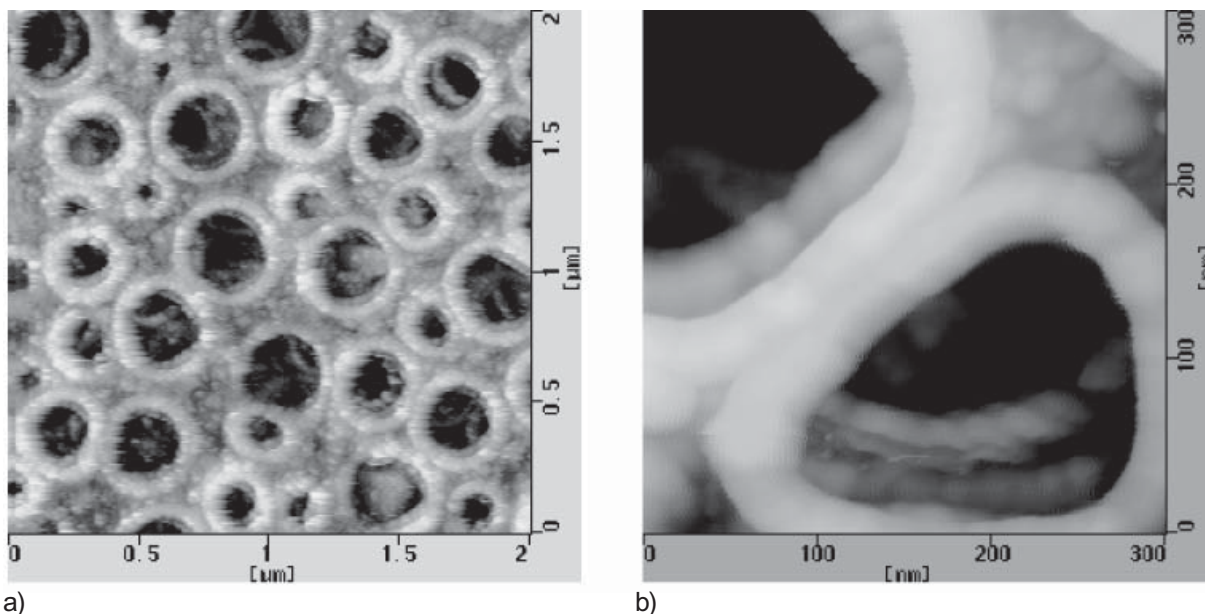
### 3.1. Surface morphology of the membrane by AFM

Figs. 1a and 1b show a surface morphology of the Rh(PVP) membrane. There are many rings on the membrane surface and also inside of each hole. It looks many rhodium ring tires are built up. These ring sizes are from 30 to 400 nm in diameter. It is found that all of the edges of the ring rise up to a few 10 nm high and there are many grains at the ring edges. The grains have a size from several nm to 10 nm and a round shape. Although we can not obtain an element information by AFM measurement, the grains seems to be made from Rh(PVP) nanoparticles.

### 3.2. XPS results of DMS submonolayer phase on the Rh(PVP) membrane

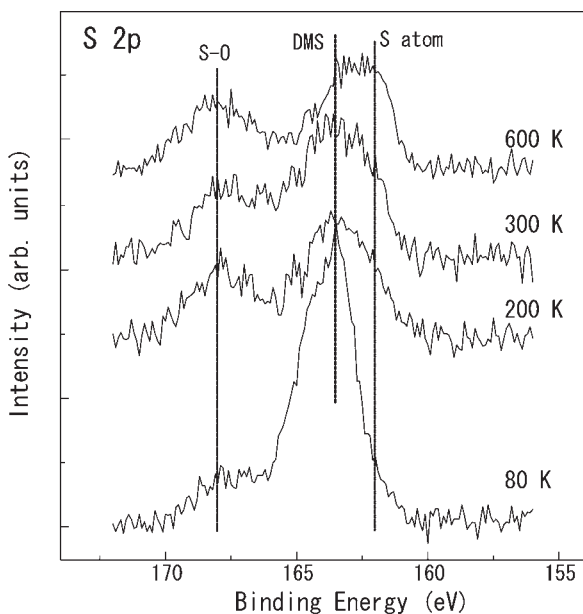
#### 3.2.1. S 2p XPS

Fig. 2 shows the temperature dependent S 2p XPS spectra for submonolayer phase. All spectra have



**Fig. 1.** (a) AFM topographical image ( $2 \times 2 \mu\text{m}$ ) showing nanosize hole rings at Rh(PVP) membrane by tapping measurement mode. (b) narrow section AFM topographic image ( $300 \times 300 \text{ nm}$ ).

been already subtracted the background spectrum, which is obtained before DMS molecular dosing. For adsorption phase at 80K, three peaks are observed at around 168, 163.6, and 162 eV. The peak at 162 eV shows that some of DMS molecules dissociate and form an atomic sulfur adsorption. Since



**Fig. 2.** Temperature dependent S 2p XPS core level spectra using  $\text{AlK}\alpha$  X-ray. All spectra are subtracted background data from original spectrum, which background is obtained before DMS molecular dosing.

the sulfur 2p peak for the physisorbed DMS molecule, such as multilayer phase, is located at 163.8 eV [2,3], the peak at 163.6 eV indicates that DMS molecule, which remains without dissociation, adsorbs chemically. The peak at 168 eV finds at higher binding energy side than the physisorbed DMS molecule. Because the peak at around 168 eV is assigned to S-Ox ( $x = 3$  or 4) bonding of sulphate group by M-D. Appay et al and P. Velázquez *et al.* [5, 6], the chemisorbed DMS molecules have two chemical situations. One is a chemisorbed with the rhodium atom of the membrane and the other is a bond with an oxygen atom of the membrane.

After annealing up to 200K, the peak at 163.6 eV is suppressed, the peaks at 168 and 162 eV are increasing. These results suggest that the chemisorbed DMS molecules with the rhodium atom dissociate to atomic sulfur and re-bond with the oxygen atom. Judging from the decreasing of the peak intensity at 163.6 eV, it seems that some of the chemisorbed DMS molecules desorbs from the membrane surface. More high temperature annealing up to 300K, the spectrum does not change in comparison with the spectrum at 200K.

After annealing up to 600K, the peak at 163.6 eV is more suppressed, the peaks at 168 and 162 eV are more increasing. It can be described that these surface reactions are the chemisorbed DMS molecular dissociation and the chemical bonding between DMS molecule and oxygen atom of the

membrane. Although it is natural that the sulfur atoms bind with the metal at high temperature, it is surprised that the SO<sub>x</sub> species are existing at 600K.

### 3.2.2. C 1s XPS

The temperature dependent C 1s XPS spectra are not shown here. There is an only peak at 284.7 eV at 80K, which is assigned to molecularly chemisorbed, without dissociation, methyl group (CH<sub>3</sub>-) of DMS molecule and no peak at 285.6 eV, which is assigned to physisorbed DMS molecule [2,3]. It seems that the methyl group of DMS molecule has an interaction with the membrane surface at 80K, same as the adsorption system of DMS on Rh(100) [2,3]. For annealing at 200K phase, the spectrum is slightly changed and the peak top moves 0.3 eV to lower binding energy side in comparison with the spectrum at 80K phase. There is no change among annealing at 200, 300, and 600K phases. This result suggests that the methyl group of DMS molecule has more strong interaction with the membrane surface.

### 3.2.3. O 1s XPS

The temperature dependent O 1s XPS spectra are not shown here. There are two peaks in oxygen 1s core level energy region at 531.4 and 529.8 eV. Before DMS dosing, a giant single peak and a small shoulder structure are observed at 532.4 and 530 eV, respectively. The peak at 532.4 eV is assigned to the oxygen atom in PVP surfactant. The peak at 529.8 eV is assigned to the chemisorbed atomic oxygen on the membrane. That peak has no dependence with the substrate temperature. On the other hand, the peak at 531.4 eV is increasing at 200K. This peak is assigned to the bonding the sulfur of DMS and the oxygen in PVP. This peak is originated from S-O bonding and gradually increasing at above 200K. This result is correspond to the result of sulfur 2p XPS at above 200K.

### 3.2.4. Rh 3d XPS

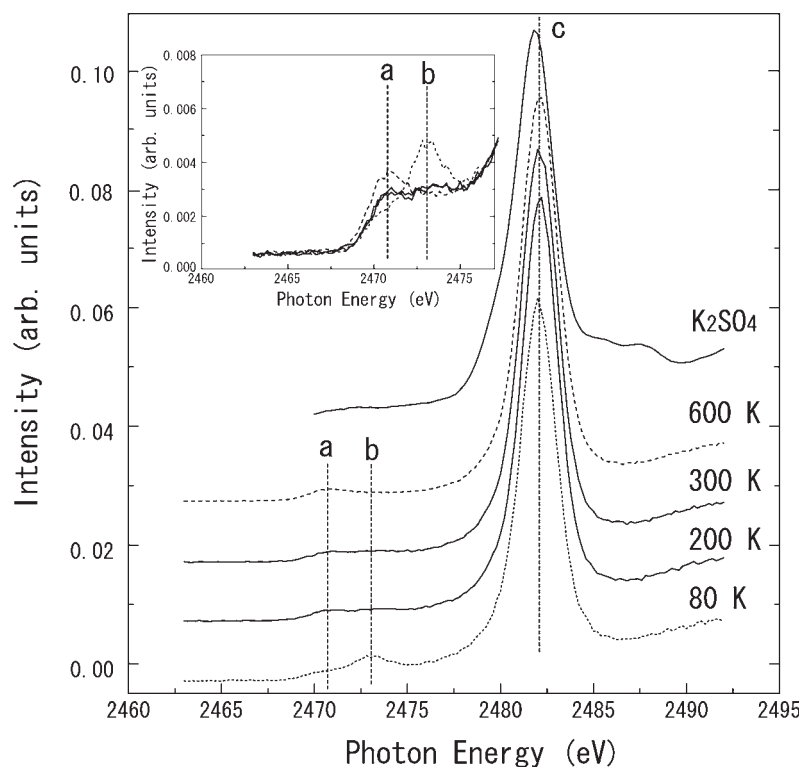
The Rh(PVP) membrane before DMS molecular dosing and the temperature dependent Rh 3d XPS spectra are not shown here. There are two peaks at Rh 3d<sub>5/2</sub> region in the before DMS molecular dosing phase. These peaks seem to be assigned to the Rh atom inside of the nanoparticle and the surface Rh atom, which interacts with PVP polymer. The XPS spectrum at 80K drastically changes in comparison with the spectrum in the before DMS molecular dosing phase. This result indicates that all

chemisorbed DMS molecule and atomic sulfur have an interaction with the rhodium atoms at the membrane surface. The intensity and peak position of 3d spectra hardly change at from 200 to 600K.

## 3.3. Sulfur K-edge NEXAFS results of DMS submonolayer phase on the Rh(PVP) membrane

Fig. 3 shows the temperature dependent sulfur K-edge NEXAFS spectra of DMS submonolayer phase on the Rh(PVP) membrane and K<sub>2</sub>SO<sub>4</sub> powder species as a standard. An inset, which is inserted as the partial expansion figure in the energy region between 2463 and 2477 eV, is also shown in Fig. 3. All NEXAFS spectra are normalized by the edge-jump intensity, which intensity is a difference between pre-edge and post-edge, at the photon energy of 2490 eV. There are three peaks at 80K, which are observed at 2470.7 eV (peak **a**), 2473.1 eV (peak **b**) and 2482 eV (peak **c**), respectively. The first peak **a** is assigned to atomic sulfur bonding with rhodium atom [2,3]. The second peak **b** is assigned to chemisorbed DMS molecule with rhodium atom [2,3], which is the transition from sulfur 1s to antibonding σ\*(S-C) molecular orbital. The third peak **c** is almost same as the peak position of K<sub>2</sub>SO<sub>4</sub> powder. Therefore the third peak **c** is assigned to SO<sub>4</sub><sup>2-</sup> phase. This adsorption reaction has a same reaction of the chemisorbed ethylmethylsulfide (C<sub>2</sub>H<sub>5</sub>SCH<sub>3</sub>) molecule on Ag nanoparticle membrane surface [7], which still remains oxygen atoms. These results indicate that DMS molecules dissociate and form an atomic sulfur, molecularly chemisorbed DMS bind with surface rhodium and with oxygen atom in the Rh(PVP) membrane at initial adsorption phase. In comparison with the adsorption behavior on Rh(100) single crystal at 90K [2,3], the peak intensity of atomic sulfur at 2470.4 eV is almost same as this result. It is found that this adsorption reaction is strong same as on Rh(100) surface. Moreover this adsorption reaction is stronger than that of on Cu(100) [8], Ag(111) [9] and Ni(100) [10]. Because DMS adsorption does not dissociate and form atomic sulfur on Cu(100), Ag(100) and Ni(100) surfaces.

On the next adsorption phase at 200K, the second peak **b** is suppressed because of the intramolecular S-C bonds dissociation. The substitution of that reaction, the first peak **a** increases. However, the intensity of the third peak **c** hardly changes. On the third adsorption phase at 300K, DMS adsorption behavior is almost same as the reaction at 200K.



**Fig. 3.** Temperature dependent S K-edge NEXAFS spectra of DMS adsorption phase on Rh(PVP) membrane.

The final adsorption phase at 600K, the second peak **b** is more decreasing and the first peak **a** is more increasing. However, the intensity of the third peak **c** hardly changes. These results are correspond to the results of sulfur 2p XPS. There are three adsorption species of atomic adsorption sulfur, chemisorbed DMS with rhodium atom and with oxygen atom, forms  $\text{SO}_4^-$ , on the Rh(PVP) membrane. It seems that  $\text{SO}_4^-$  adsorption species are very stable.

#### 4. CONCLUSION

We have investigated the morphology of the surface nanohole structure of the Rh(PVP) membrane by AFM measurement and also the adsorption behavior of DMS molecule on the membrane surface from 80 to 600K by sulfur K-edge NEXAFS and XPS techniques. The nanohole sizes have a size distribution from 30 nm to 400 nm in diameter. DMS molecules dissociate and form the atomic sulfur, molecularly chemisorbed DMS bind with surface rhodium and with oxygen atom in the Rh(PVP) membrane, which form  $\text{SO}_4^{2-}$  species, at initial ad-

sorption phase at 80K. During anneal up to 600K, it is found that some of DMS molecules dissociate and  $\text{SO}_4^{2-}$  species still remain. It seems that the Rh(PVP) membrane has a large effect at 80K, which is related with desulfurization, in comparison with the single crystal surfaces of Rh(100), Cu(100), Ag(111) and Ni(100).

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