Adsorption and Removal Reactions of (CH$_3$)$_2$S on Rh/Al$_2$O$_3$/NiAl(100): Structural and Spectroscopic Study*

T. Nomoto,$^1$ S. Yagi, and K. Soda

Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

H. Namatame and M. Taniguchi

Synchrotron Radiation Center, Hiroshima University, 2-313 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan

(Received 2 June 2008; Accepted 1 December 2008; Published 4 April 2009)

We have studied the adsorption reaction of (CH$_3$)$_2$S on Rh/Al$_2$O$_3$/NiAl(100) and sulfur removal reaction depending upon heat-treatment using X-ray Photoelectron Spectroscopy and Atomic Force Microscopy techniques. The results show a difference in the adsorption reaction between the as-deposited Rh/Al$_2$O$_3$/NiAl(100) and that heat-treated at 1000 K. (CH$_3$)$_2$S dissociates on the Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface at 300 K, and the sulfur removal reaction occurs at 523 K induced by O$_2$ dosing. In contrast, the heat-treated surface is quite inert against the dissociative reaction of (CH$_3$)$_2$S, because the Rh atoms dissolve into the NiAl(100) substrate through the Al$_2$O$_3$ layer by the high temperature treatment (1000 K). The AFM results also show the morphological changes in these systems, such as many stripe structures for the Al$_2$O$_3$/NiAl(100), nanoclustered surface for the Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface, and nano-hole structures for the Rh/Al$_2$O$_3$/NiAl(100) heated at 1000 K. [DOI: 10.1380/ejssnt.2009.239]

Keywords: Rhodium/alumina; Dimethyl sulfide; Sulfur-poisoning; Nano materials; Surface chemical reaction; Catalysis; Atomic force microscopy; X-ray photoelectron spectroscopy

I. INTRODUCTION

Platinum group metals supported on oxides, such as Al$_2$O$_3$, CeO$_2$ and ZrO$_2$, are widely used as the typical catalysts in the purification process of the automobile exhaust gas. For example, Rh/Al$_2$O$_3$ catalyst is noticeable in the reduction of NO, and Pd/Al$_2$O$_3$ is available in the oxidation of CO. Those performances are frequently degraded by some deactivation factors because of the use in the severe environment. Especially, the poisoning of catalyst surface and the aggregation of catalyst metals under high temperature are regarded as the main problems [1].

The sulfuric atmosphere as low as few ppm causes the sulfur adsorption on the catalyst surface, which disturbs the other purification reactions; the so-called “Sulfur-Poisoning” is one of the most important deactivation reaction for metal catalysts [2, 3]. Therefore not only the resistance against poisoning but also the removal of adsorbed sulfur is required for those catalysts to apply into the purification of the automobile and industrial exhaust gases. In this regard, many works have investigated the interactions between the sulfur-containing molecules and the transition metal surfaces [4–7]. These studies show that the sulfur poisoning is mainly caused by the adsorption of the atomic sulfur generated by the dissociation of the chemical bonds around sulfur atom. On the other hand, some studies take notice of the removal reaction of sulfur atoms from platinum group metal surfaces [8]. For example, Kohmoe reveals that the adsorbed sulfur atoms on Rh polycrystalline surface desorb as SO$_2$ at around 500 K under O$_2$ environment [2]. This work also compares with Pt and Pd surfaces, and shows the excellent performance of Rh for the sulfur removal reaction. In recent years, the collection of those poisoned metals is difficult because of the low cost performance. Thus, the easy recycle of the catalyst metals can be expected by means of the sulfur removal reaction.

A high temperature environment (≈1000 K) also gives damages to the catalyst metals supported on Al$_2$O$_3$. One of the problems is the migration of metal atoms under high temperature, and it leads to the aggregation of catalyst metals. The metal dissolution into Al$_2$O$_3$ is the second problem. It was reported that a part of Rh atoms was dissolved into Al$_2$O$_3$ support material by oxidation at 873 K [9]. Both of these two problems are related to the decrease in the reaction area.

In our previous studies, the adsorption system of (CH$_3$)$_2$S (dimethyl sulfide: DMS) on Rh(100) single crystal surface have been revealed, where we have investigated the temperature dependent dissociative reaction and the sulfur removal reaction [8, 10–12]. However, these systems are too fundamental to apply into practical use. Therefore, we are required to obtain the more actual findings of the sulfur poisoning by clarifying the adsorption behavior of DMS on Rh/Al$_2$O$_3$ system. The aim of this work is firstly to study the growth of Rh on Al$_2$O$_3$/NiAl(100) depending upon heat treatment, and secondary to reveal the adsorption reaction of DMS on Rh/Al$_2$O$_3$/NiAl(100) surface and the sulfur removal reaction by means of X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) techniques.

II. EXPERIMENTAL

A commercially available NiAl(100) single crystal (10 mm φ diameter, 2 mm thickness, Surface Preparation Laboratory Inc.) was mechanically polished with 0.05 µm abrasive paper, and the surface was further cleaned in a vacuum chamber using a standard UHV procedure with standard cleaning cycles of Ar$_2$ sputtering and heating to 1000 K, and then the surface was exposed to a 0.05 Torr of Ar$_2$ for 10 minutes before use. Rh metal was deposited by electron-beam evaporation with a deposition rate of 0.05 Å/s and the Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface was heat-treated at 1000 K in vacuum (≤10$^{-8}$ Torr). In this work, the heat-treated surface and the aggregation of catalyst metals under high temperature are regarded as the main problems [1].
The surface morphology was obtained by ex-situ AFM measurement with NanoScope III-a (Veeco Instruments) with tapping mode at Innovation Plaza Hiroshima JST. XPS measurements were performed by use of the concentric hemispherical electron energy analyzer (PHOIBOS 100-5ch, SPECS) with MgKα X-ray (1253.6 eV). All binding energies were referenced to Ni 3p3/2 peak position of NiAl at 853.0 eV [14]. The initial thickness of Al2O3 layer was 4.5 Å estimated from the signal ratio of I\textsubscript{Al2p}/I\textsubscript{NiAl}, where I\textsubscript{Al2p} and I\textsubscript{NiAl} were the Al 2p peak intensities of Al2O3 and NiAl as shown in Fig. 3 [15]. The coverages (ML) of Rh and sulfur were obtained with their XPS peak intensities in Rh 3p and S 2p regions (1ML corresponds to the area density of fcc Rh(100) surface atoms, 1.37×10\textsuperscript{13} atoms/mm\textsuperscript{2}).

III. RESULTS AND DISCUSSIONS

A. S 2p XPS

Figure 1 shows the temperature dependent S 2p XPS spectra for DMS on Rh(1.0 ML)/Al2O3/NiAl(100) as-deposited, Rh(1.0 ML)/Al2O3/NiAl(100) heated at 1000 K, and Al2O3/NiAl(100). The samples were treated with O2 gas above 423 K.
TABLE I: The intensity (%), peak position (eV) and FWHM (eV) of the Rh 3d_{5/2} peak for Rh(111) bulk, Rh/Al_{2}O_{3}/NiAl(100) as-deposited, and Rh/Al_{2}O_{3}/NiAl(100) heated at 1000 K surfaces.

| Rh 3d_{5/2} | peak intensity (%) | position (eV) | FWHM (eV) |
|-------------|--------------------|---------------|-----------|
| Rh(111)     | —                  | 307.45        | 1.51      |
| as-deposited | 100                | 307.50        | 1.26      |
| heated at 1000 K | 78             | 307.20        | 1.24      |

FIG. 2: Thermal dependence of Rh 3d_{5/2} XPS spectra for DMS on Rh/Al_{2}O_{3}/NiAl(100) as-deposited, and Rh/Al_{2}O_{3}/NiAl(100) heated at 1000 K surfaces.

peak position shifts to the lower binding energy side from that of the Al_{2}O_{3}/NiAl(100) surface. This shift gives the interaction between DMS and Rh layer. More than half the molecules (0.18 ML) remain on the surface at 200 K without desorption. Some of those molecules undergo the scission in the S–C bonds. The dissociation is promoted as the temperature rises, and most of the S–C bonds are cleaved at 300 K. Thus the Rh over-layer possesses a catalytic performance for the dissociative reaction of DMS. In the case of the Rh/Al_{2}O_{3}/NiAl(100) heated at 1000 K, the dissociative reaction and the desorption behavior are quite equivalent to that on the Al_{2}O_{3}/NiAl(100) surface meaning inert against the dissociation process of DMS.

The sulfur-poisoned Rh/Al_{2}O_{3}/NiAl(100) as-deposited surface was heated under O_{2} environment to remove the sulfur atoms. The main peak is located at 162.0 eV showing the adsorption of the atomic sulfur. One can find the broad peak at 166 eV to 169 eV, when the sample is annealed at 423 K and 473 K. This chemical state is assigned to SO_{2} species [2]. The broad peak disappears at 523 K, and simultaneously the total coverage of sulfur decreases. Those changes indicate the oxidation of sulfur and the desorption of SO_{2} from the Rh/Al_{2}O_{3}/NiAl(100) as-deposited surface. The desorption onset temperature is higher than that reported with polycrystalline Rh and Rh(100) surfaces, on which the sulfur atoms desorb at 423 K [2, 8]. Therefore, the performance of Rh in the sulfur removal reaction is weakened on the Al_{2}O_{3} layer.

B. Rh 3d XPS

Figure 2 shows the Rh 3d_{5/2} peaks for the Rh/Al_{2}O_{3}/NiAl(100) systems before DMS adsorption. The peak shape and the FWHM were estimated using a Shirley background and a mixed Gaussian-Lorentzian function with an asymmetric parameter. Table I shows these intensities, peak positions and FWHM of the Rh 3d_{5/2} peak. Metallic Rh state has a single peak at 307.2 eV, shown as the spectrum of Rh(111) bulk [16]. The Rh 3d_{5/2} peak of Rh/Al_{2}O_{3}/NiAl(100) as-deposited becomes broader than that of Rh(111) bulk. The peak position also shifts from that of Rh(111) bulk to 0.25 eV higher binding energy side. Therefore, the spectrum for Rh/Al_{2}O_{3}/NiAl(100) as-deposited seems to contain other components at the higher binding energy side in addition to the peak for metallic Rh state. The Rh atoms in second layer or more shows their peak at the corresponding position with metallic Rh state at 307.2 eV, because the spectrum becomes similar shape to the Rh(111) bulk spectrum as Rh coverage increases. On the other hand, the additional components shift from the metallic Rh state to the higher energy side, indicating the oxidation or the interaction with the Al_{2}O_{3} layer. The oxidized Rh state is reported to represent the Rh 3d_{5/2} peak at 308.0 eV or more; for Rh_{2}O_{3} at 308.35 eV and for RhOOH at 308.55 eV [16]. Thus, these components are confirmed the first layer Rh atoms on the surface which interact with Al_{2}O_{3} layer. These Rh atoms are squeezed some electrons by the Al_{2}O_{3} layer, which causes the Rh 3d_{5/2} peak shift to the higher binding energy side. We can also find the reverse shift of the Al_{2}O_{3} peak in Al 2p and O 1s spectra shown in Figs. 3 and 4. These results indicate multilayer or nanocluster structure composed with Rh more than two layers.

In contrast, the peak shape of the Rh/Al_{2}O_{3}/NiAl(100) heated at 1000 K can be described with a single state at 307.50 eV. The state extremely stabilizes against various treatments, such as the DMS adsorption, the heating and the O_{2} exposure. The integral intensity decays in comparison with that of the Rh as-deposited sample by 22%. Hence, two possible processes can engender the stability and the decrease in the Rh 3d_{5/2} peak intensity; the morphology of the Rh over-layer changes from a flat structure to a cluster structure; and the Rh atom dissolves into the substrate. We confirm the dissolution of Rh into the substrate under high temperature treatments because of the
low reactivity to DMS dissociation. Al 2p and O 1s XPS results also agree with that standpoint in next chapter. Rh 3d5/2 XPS result reveals the significantly different environment between Rh atoms on the as-deposited surface and that on the heat-treated surface (1000 K).

C. Al 2p and O 1s XPS

Figure 3 shows the temperature dependent Al 2p XPS spectra for Rh/Al2O3/NiAl(100) as-deposited, Rh/Al2O3/NiAl(100) heated at 1000 K, and Al2O3/NiAl(100) surfaces before/after the adsorption of DMS and the O2 treatments. Three peaks centered at 74.8-75.3 eV, 72.6 eV and 66.8 eV are assigned to Al 2p in the Al2O3 layer, Al 2p and Ni 3p of metallic Al and Ni in the NiAl(100) substrate, respectively [17]. The Al 2p binding energy of the Al2O3 layer decreases from 75.3 eV to 74.8 eV when it is covered with 1.0 ML of the Rh layer (as-deposited surface). The shift indicates the strong interaction between the Al2O3 layer and the deposited Rh atoms. The lower shifted peak position does not move any longer in the adsorption system of DMS on Rh/Al2O3/NiAl(100) as-deposited surface, indicating that those adsorption reaction is exclusive on the Rh surface. A dramatic change is observed in the signal ratio of I\textsubscript{Al2O3}/I\textsubscript{Al2O3} after O2 treatment at 423K, 473 K and 523 K. Thereby, the oxide thickness increases significantly after heating under O2 environment. The Al2O3 thicknesses are calculated to be 8 Å, 11 Å and 13 Å at 423 K, 473 K and 523 K, respectively (the pristine Al2O3 thickness is about 5 Å). As mentioned by Song et al., the pristine Al2O3 layer thickness is stable even at 1070 K without over-layer [17]. This result indicates that Rh layer behaves as a catalyst for oxidation of aluminum by supplying reactive oxygen atoms formed by dissociation of oxygen on Rh surface. A similar catalytic mechanism was reported in Pd/Al2O3/NiAl(110) system [17, 18]. A part of the reactive oxygen atoms also have an important role in the sulfur removal reaction as revealed in our previous study [8].

When the Rh as-deposited sample is heat-treated at

**FIG. 3:** Thermal dependence of Al 2p XPS spectra for DMS on Rh/Al2O3/NiAl(100) as-deposited, Rh/Al2O3/NiAl(100) heated at 1000 K, and Al2O3/NiAl(100) surfaces. Rh coverage is 1.0 ML. The samples were treated with O2 gas above 423 K.

**FIG. 4:** Thermal dependence of O 1s XPS spectra for DMS on Rh/Al2O3/NiAl(100) as-deposited, Rh/Al2O3/NiAl(100) heated at 1000 K, and Al2O3/NiAl(100) surfaces. Rh coverage is 1.0 ML. The samples were treated with O2 gas above 423 K.
1000 K, the $\text{Al}_2\text{O}_3$ binding energy returns to a position near that before the deposition of Rh. Therefore, the interaction between the $\text{Al}_2\text{O}_3$ layer and the Rh atoms is lost by heat-treatment. We can consider two possible processes such as the morphological change of Rh layer and the dissolution of Rh into the substrate as shown in Chapter 3. 2. We conclude the dissolution of Rh into the NiAl(100) substrate under high temperature treatments, when DMS molecules adsorb on that surface. The S 2p XPS result shows the charge transfer of between DMS and O$_3$ at elevated temperatures in the case of Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface.

1000 K, the $\text{Al}_2\text{O}_3$ binding energy returns to a position near that before the deposition of Rh. Therefore, the interaction between the $\text{Al}_2\text{O}_3$ layer and the Rh atoms is lost by heat-treatment. We can consider two possible processes such as the morphological change of Rh layer and the dissolution of Rh into the substrate as shown in Chapter 3. 2. We conclude the dissolution of Rh into the NiAl(100) substrate under high temperature treatments, when DMS molecules adsorb on that surface. The S 2p XPS result shows the charge transfer of between DMS and O$_3$ at elevated temperatures in the case of Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface.

D. Surface morphology

Figure 5 shows the AFM images obtained from Al$_2$O$_3$/NiAl(100), Rh/Al$_2$O$_3$/NiAl(100) as-deposited and Rh/Al$_2$O$_3$/NiAl(100) heated at 1000 K. We can see a lot of stripe structures on the Al$_2$O$_3$/NiAl(100) surface growing preferentially along the crystal directions, consistent with the other reports [13, 20, 21]. These stripes disappear when the surface covered with Rh layer. The deposited Rh on Al$_2$O$_3$/NiAl(100) has a protruded structures with the height of 3-7 Å. Thereby, it can be speculated that nanoclusters consisted of 1-3 Rh layer formed on the Al$_2$O$_3$/NiAl(100) surface because the diameter of a Rh atom is estimated to be 2.7 Å. After the heat-treatment at 1000 K, there is no protruded structure but a lot of nano-hole structures as shown in Fig. 5(c). The former XPS results show the absence of Rh atoms on the surface. Thus, it is supposed that this outmost surface is mainly composed with the Al$_2$O$_3$ layer, which undergoes the structural change by the diffusion process of Rh into the NiAl(100) substrate through the Al$_2$O$_3$ layer. In three types of surfaces, only the Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface has the activity for the dissociative reaction of between DMS and O$_3$, because the Rh atoms are exposed on the surface. The proposed mechanism for the interaction of Rh/Al$_2$O$_3$/NiAl(100) with DMS and O$_3$ at elevated temperatures is shown in Fig. 6. The process I shows the initial surface of Rh/Al$_2$O$_3$/NiAl(100). The adsorbed DMS dissociates on the Rh nanocluster surface. The Rh surface is covered with the sulfur atoms in process II. The dissociative adsorption of O$_3$ and the growth of the Al$_2$O$_3$ layer occurs since the Rh layer is lost by heat-treatment with XPS and AFM techniques. Atomic sulfur remains on the Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface at 300 K because of DMS dissociative reaction. The sulfur removal reaction is induced by O$_3$ gas at 523 K with the formation and desorption of SO$_3$. Simultaneously, the growth in the thickness of Al$_2$O$_3$ layer occurs since the Rh layer serves the catalytic effect for the oxidation of aluminum in the NiAl(100) substrate. On the other hand, the Rh/Al$_2$O$_3$/NiAl(100) heat-treated at 1000 K is quite inert against DMS dissociation. The reason for the inertness is confirmed the dissolution of Rh into the NiAl(100) substrate through the Al$_2$O$_3$ layer occurring by the high temperature treatment. The AFM results show the morphological change in these systems; many stripe structures for the Al$_2$O$_3$/NiAl(100), nanoclustered surface that consists of...
of Rh for the Rh/Al$_2$O$_3$/NiAl(100) as-deposited surface, and nano-hole structures formed with Al$_2$O$_3$ layer for the Rh/Al$_2$O$_3$/NiAl(100) heated at 1000 K.

Acknowledgments

The authors are grateful for the financial supported of a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 19008872 and 15360358), 21-Century COE “Isotope Science and Engineering from Basics to Applications” and Innovation Hiroshima/Tokai of JST (Japan Science and Technology Agency). This work was performed under the approval of HSRC Program Advisory Committee (No. 06-A-20 and 06-A-21).

[1] M. Ozawa, M. Kimura, H. Sobukawa, K. Yokota, R& D review of TOYOTA CRDL 27, 43 (1992).
[2] K. Dohmae, R& D review of TOYOTA CRDL 35, 43 (2000).
[3] J. S. Hepburn and H. G. Stenger, Jr., Energy and Fuels. 2, 289 (1988).
[4] S. Yagi, A. Matano, G. Kutluk, N. Shirota, E. Hashimoto, and M. Taniguchi, Surf. Sci. 482, 73 (2001).
[5] S. Yagi, Y. Nakano, E. Ikenaga, S. A. Sardar, J. A. Syed, K. Soda, E. Hashimoto, K. Tanaka, and M. Taniguchi, J. Vac. Sci. Technol. A 20, 1644 (2002).
[6] Z. Paal, K. Matusek, and M. Muhler, Appl. Catal. A: General. 149, 113 (1997).
[7] H. Wakita, Y. Kani, K. Ukai, T. Tomizawa, T. Takeguchi, and W. Ueda, Appl. Catal. A: General. 283, 53 (1997).
[8] T. Nomoto, K. Miura, S. Yagi, G. Kutluk, H. Sumida, K. Soda, E. Hashimoto, H. Namatame, and M. Taniguchi, Surf. Sci. 601, 3784 (2007).
[9] K. Dohmae, Y. Hirose, and M. Kimura, R& D review of TOYOTA CRDL 32, 75 (1997).
[10] T. Nomoto, S. Yagi, G. Kutluk, K. Soda, E. Hashimoto, and M. Taniguchi, J. Surf. Anal. 12, 238 (2005).
[11] T. Nomoto, S. Yagi, K. Soda, G. Kutluk, H. Sumida, E. Hashimoto, and M. Taniguchi, e-J. Surf. Sci. Nanotech. 4, 39 (2006).
[12] T. Nomoto, O. Sumi, S. Yagi, K. Soda, H. Namatame, and M. Taniguchi, Surf. Interface Anal. 40, 391 (2008).
[13] M. S. Zei, C. S. Lin, W. H. Wen, C. I. Chiang, and M. F. Luo, Surf. Sci. 600, 1942 (2006).
[14] N. Ohtsu, M. Oku, T. Shishido, and K. Wagatsuma, Appl. Surf. Sci. 253, 8713 (2007).
[15] M. Yoshitate, T. T. Lay, W. Song, V. Moroz, and Y. Lykhach, Hyoumen Kagaku 8, 458 (2004).
[16] T. L. Barr, J. Phys. Chem. 82, 1801 (1978).
[17] W. Song, M. Yoshitate, and T. T. Lay, Surf. Interface Anal. 36, 1136 (2004).
[18] Sh. Shaikhutdinov, M. Heemeier, J. Hoffmann, I. Meusel, B. Richter, M. Baumer, H. Kuhlenbeck, J. Libuda, H.-J. Freund, R. Oldman, S. D. Jackson, C. Konvicka, M. Schmid, and P. Varga, Surf. Sci. 501, 270 (2002).
[19] J. Libura, F. Winkelmann, M. Baumer, H. J. Freund, Th. Bartrams, H. Neddermeyer, and K. Muller, Surf. Sci. 318, 61 (1994).
[20] N. Fremy, V. Maurice, P. Marcus, J. Am. Ceram. Soc. 86, 669 (2003).
[21] M. F. Luo, C. I. Chiang, H. W. Shiu, S. D. Sartale, C. C. Kuo, Nanotechnology 17, 360 (2006).