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Structure of Rhodium Particles in a Rh/Al_2O_3 Model Catalyst as Studied by X-Ray Photoelectron Diffraction

Since the structure and chemical state of metal particles on an oxide support are known to be important factors for reactivity and selectivity in catalysis, they have been studied by many workers. Yates *et al.* (*1*) have studied Rh/Al_2O_3 by ultrahigh-resolution electron microscopy and found two-dimensional rhodium rafts. Van't Blik *et al.* (*2*) have observed isolated geminal dicarbonyl species on alumina in which the rhodium was present as Rh^+ after CO adsorption.

X-ray photoelectron diffraction (XPED) is based on the diffraction of photoelectrons created by X-ray irradiation and has attracted much interest as a promising surface analytical method (*3*). The information obtained from XPED measurements can be summarized as follows: (i) symmetry and orientation of the crystal are determined; (ii) atomic sites in the crystal are distinguished; (iii) crystal regularity is estimated; (iv) the adsorption site and the direction of the adsorbate molecule are determined.

XPED measurements have been applied to the characterization of metal/semiconductor systems (*4–6*). Kudo *et al.* (*5*) have measured the XPED patterns from gold atoms on a GaAs(110) surface, and it was concluded that the gold grew epitaxially in an island-like fashion after heat treatment. Koshizaki *et al.* (*6*) have measured the angular dependence of gold on a GaSb(110) surface and have shown that gold atoms were incorporated into the GaSb lattice preferentially. XPED measurements have also been applied to Pt/TiO_2 model catalyst and the structure of the platinum particles was clarified (*7, 8*).

The advantages of XPED measurements for the structural analysis of metal particles deposited on an oxide support compared with other surface analytical methods may be summarized as follows. (i) Long-range ordering is not necessary to obtain the diffraction pattern. Thus it is possible to obtain structural information from dispersed particles. (ii) The charging-up problem does not prevent one from obtaining clear diffraction patterns. Thus, structural information is obtained from insulating or poorly conducting supports such as alumina. (iii) Structural information on a particular element can be obtained selectively by discriminating the energy of the photoelectrons. (iv) The damage caused to dispersed small metal particles by the irradiation with X-ray is not very serious compared with that of an electron beam. These advantages make XPED one of the most suitable methods for the structural analysis of supported metal systems.

EXAFS measurements have been applied to the structural analysis of Rh/Al_2O_3 and many other supported metal catalysts. EXAFS also provides structural information such as the number of neighboring atoms and their distance from the emitter atom, information which is complementary to that obtained from XPED. The information obtained from EXAFS, however, is one-dimensional and is insufficient to determine a three-dimensional structural model or the directional relation between metal particles and oxide support.

In the present study, we have studied the Rh/α-Al_2O_3(0001) system by X-ray photoelectron diffraction and have clarified the structure of rhodium particles on the alumina single-crystal support through theoretical calculation.

The equipment for the experiments con-

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sisted of a modified X-ray photoelectron spectrometer equipped with a computer-controlled manipulator which enabled angular dependence measurements of photoelectron intensity and with a multichannel detection system. In order to obtain angular dependence, the acceptance angle of the electrons was restricted. The average divergence of the electron trajectory was calculated as ±1.3° for the horizontal and ±2.0° for the vertical direction. The precision of the manipulator was 1.0° for the horizontal direction and 0.1° for the vertical direction. Aluminum *Kα* radiation was used as the X-ray source.

A clean $Al_2O_3(0001)$ single-crystal surface was created by several cycles of Ar^+ ion bombardment (5×10^{-5} Torr, 1000 eV) and annealing (1023 K). The cleanliness was checked by X-ray photoelectron spectroscopy. After a sufficiently clean surface was obtained, XPED measurements were performed. Rhodium was deposited under vacuum by resistive heating from a pure rhodium ribbon. The amount of rhodium deposited was estimated from the XPS signal intensity ratio (Rh 4*d*/Al 2*s*), assuming layer growth. The base pressure of the system was in the low 10^{-10} Torr range.

It was confirmed that an initially clean $Al_2O_3(0001)$ surface was obtained after the annealing treatment under vacuum. The angular dependence of the photoelectron intensity from a clean $Al_2O_3(0001)$ surface has been reported previously and discussed in detail in connection with the crystal structure (*9*).

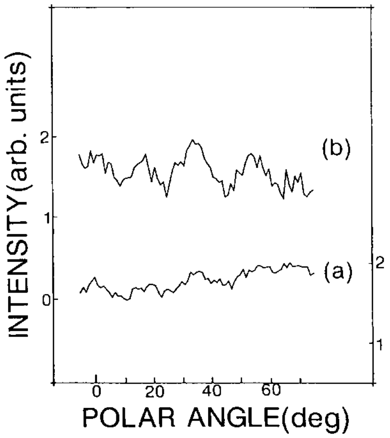

FIG. 1. Polar angle dependence of Rh 4*d* emission from Rh/α-$Al_2O_3(0001)$. (a) After Rh deposition; (b) after vacuum annealing at 823 K for 20 min.

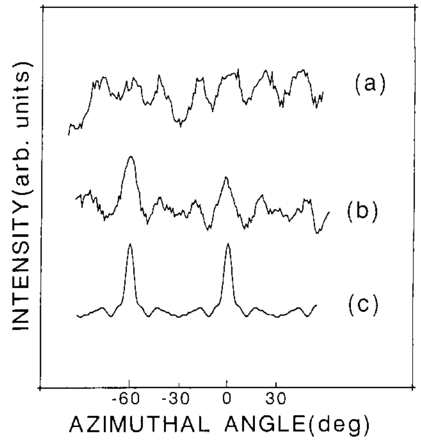

FIG. 2. Azimuthal angle dependence of Rh 4*d* emission from Rh/α-$Al_2O_3(0001)$. Experimental curves at polar angles $\theta = 70°$ (a) and 53° (b), and calculated curve at $\theta = 53°$ (c).

Rhodium was then deposited onto the Al_2O_3 surface under vacuum. The amount of rhodium deposited was equivalent to a layer 12 Å in thickness, assuming that mean free path is 20 Å. The polar angle dependence of the rhodium 4*d* XPS intensity just after deposition is shown in Fig. 1a. This is obtained as the difference between the XPS intensity at the peak energy region and that at the background energy region. Each angular dependence was obtained by a single angular scan at a fixed retarding voltage. In this study, polar angle is defined with respect to the surface normal. The angular distribution curve exhibited weak modulation, which indicates that the rhodium particles already had an epitaxial relation with the substrate after the deposition.

The sample was then annealed under vacuum at 823 K for 20 min. In Fig. 2 the azimuthal dependence of the rhodium 4*d* emission at polar angles $\theta = 70°$ (a) and 53° (b) after annealing is shown, and the polar dependence of the rhodium 4d emission is also shown in Fig. 1b. In these figures, the azimuthal angle $\phi = 0°$ was defined to be on the $(01\bar{1}0)$ plane of α-Al_2O_3. After the heat treatment, the modulation in the angular distribution curve was increased (Fig. 1b) and clear XPED patterns were obtained, which indicated that the degree of crystallization of the rhodium particles and the degree of epitaxial relation with the substrate increased by heat treatment. From these experimental results, both azimuthal patterns were regarded as sixfold symmetry.

As sufficient modulation of photoelectron intensity was obtained, structural analysis of rhodium particles was performed by means of a theoretical calculation which involved double scattering of the photoelectrons. In this calculation, the total photoelectron wave was derived from each scattered wave at surrounding atoms of the electron emitter atom. The details of the calculation are given elsewhere (*8*, *10*). The atomic cluster used in this calculation consisted of a hemispherical rhodium particle 15 Å in radius. The rhodium emitter atom was at the center of the first layer. Considering the experimental results, the structural model of rhodium particles used in the calculation was assumed as shown in Fig. 3. Both rhodium particles have the fcc (111) plane parallel to the substrate (0001) surface with the epitaxial relation shown in the figure. The calculated patterns obtained from each structural model (No. 1 or No. 2) did not agree with the experimental patterns since these structures are threefold symmetry, and experimental patterns were sixfold symmetry. However, when both particles exist on alumina, the correspondent XPED pattern becomes sixfold symmetry. Figure 2c shows the calculated azimuthal dependence for rhodium at polar angle 53°, assuming that both rhodium particles exist with equal probability. Although the relative intensity of the peaks are somewhat different, the calculated pattern reproduced the feature of the experimental pattern as well. This model was examined carefully through the theoretical calculations, and it was found that these structural models could explain all the experimental results including both polar and azimuthal dependences very well, but other models could not reproduce them all. Considering that the XPED pattern is sensitive to the crystal structure, it was concluded from the XPED analysis that the two orientations of rhodium particles based on the fcc structure (Fig. 3) existed with equal probability on the $Al_2O_3(0001)$ surface.

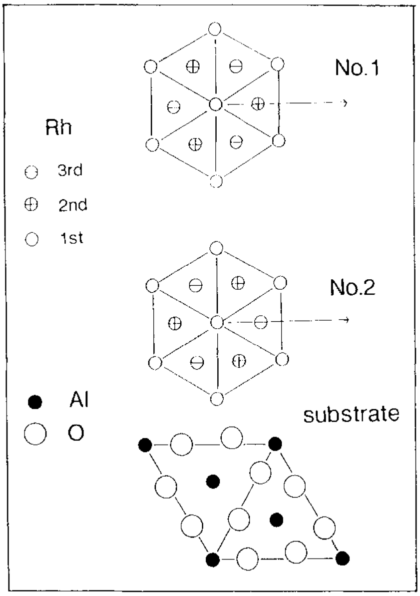

FIG. 3. Structural model of Rh particles on α-$Al_2O_3(0001)$ surface.

Since the (111) surface of fcc metal is thermodynamically the most stable, our results that the Rh(111) surface is parallel to the $Al_2O_3(0001)$ surface is a reasonable one. Moreover, we found that these particles also have azimuthal ordering on Al_2O_3 single crystal. If these particles did not have azimuthal ordering, we would not have observed the intensity modulation in the azimuthal dependence (Figs. 2a and 2b).

Yates *et al.* (*1*) have observed that rhodium on alumina catalyst had all of its rhodium atoms in two-dimensional rafts and its thickness was one monolayer. Our structural model, which explains the experimental results very well, is based on the usual fcc (111) structure and it was not necessary to assume any other particular structures. The strong peaks in the polar angle dependence (Fig. 1b) originate mainly from the forward scattering of photoelectrons (*9*). Thus, a peak at $\theta = 0°$ in polar angle dependences (Figs. 1a and 1b) is created mainly by the forward scattering by the rhodium scatterer atom which is at least three atomic layers over the rhodium emitter atom. Therefore, the fact that a peak at $\theta = 0°$ was observed after deposition and after annealing indicates that the rhodium cluster was at least four monolayers thick. From these considerations, it is concluded that under our experimental conditions, rhodium was not present as rafts but as three-dimensional fcc particles at least several monolayers thick.

The results obtained may therefore be summarized as follows:

(i) rhodium grew epitaxially on the α-$Al_2O_3(0001)$ surface;

(ii) rhodium exists as three-dimensional fcc particles and under our experimental conditions no evidence of rafts was obtained.

Since this information is difficult to obtain by other surface analytical methods, XPED analysis is shown to be a useful technique for the structural analysis of dispersed metal particles on oxides.

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