Comparison of Microstructures in Oxidation and Reduction: Rh and Ir Particles on SiO₂ and Al₂O₃¹

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X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) are used to compare the microstructures and fractions of metal and oxide formed in oxidation and subsequent reduction of ~100-Å particles of Rh and Ir on SiO₂ and Al₂O₃ by treating identically prepared samples under identical conditions in O₂ and H₂. XPS shows that both metals are oxidized at ~200°C higher temperatures on SiO₂ than on Al₂O₃, and reduction in H₂ occurs at a slightly lower temperature on Al₂O₃. For TEM, metal particles are deposited on curved regions of SiO₂ and Al₂O₃ on microscope grids so that particle shapes perpendicular to the substrates can be examined. Rh oxidation occurs largely by film growth and is complete by 600°C, while Ir does not oxidize significantly until 500°C, and complete oxidation does not occur even at 700°C. At higher temperatures the mode of oxide formation changes from film growth to nonuniform oxide penetration into the particles. Oxidation of Ir produces protrusions which grow out from the original metal particles. Subsequent reduction of both oxides produces clusters of 10- to 20-Å particles which only sinter into their original shapes after heating to above 500°C. @ 1989 Academic Press, Inc.

INTRODUCTION

The activity of supported metal catalysts depends strongly on structural properties such as metal dispersion, morphology, and presence of oxides and other phases (1, 2). These properties, in turn, depend sensitively on the preparation, operation, and regeneration environments experienced by the catalyst.

The support can also affect catalyst properties in many ways. One such effect is strong metal-support interaction, which is characterized by strong bonding between the metals and the support (3, 4). This effect is exhibited primarily by supports consisting of reducible oxides of transition metals (notably TiO₂). SiO₂ and Al₂O₃ are generally considered to exhibit only weak metal-support interaction such as charge transfer between metal and support, interfacial compound formation, and support in-

0021-9517/89 \$3.00 Copyright © 1989 by Academic Press, Inc. All rights of reproduction in any form reserved. fluences on oxidation and reduction of particles (4).

Several investigators have examined charge transfer between metal particles and supports using X-ray photoelectron spectroscopy (XPS). Kawai et al. (5) have measured support-dependent charge transfer from Rh and have correlated this with catalytic selectivity. Escard et al. (6) reported that XPS energy shifts of Ir on Al₂O₃ are greater than those on SiO₂ and suggest that charge transfer is due to the formation of a Schottky barrier, as proposed by Solymosi (7). Katrib et al. (8) found similar trends with Ir, but they attributed charge transfer to the formation of an interfacial or surface compound. Horsley and Lytle (9) also found electron transfer from Ir to these supports using EXAFS and suggested the presence of an interfacial species.

Support interactions can also influence the dispersion and oxidation/reduction of supported catalysts. Both Ir and Rh generally exhibit higher dispersions on Al_2O_3 than on SiO₂ for comparable treatments (10, 11). Also, it has been found that $Ir_4(CO)_{12}$ or

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Rh₆(CO)₁₆ impregnation followed by drying yields elemental Ir or Rh on SiO₂ but oxides on Al₂O₃ (5, 12, 13). Several investigators have reported that NiO is more easily reduced on SiO₂ than on Al₂O₃ (14–16).

We have previously studied the oxidation and reduction of catalyst particles using transmission electron microscopy (TEM) and XPS. It was found that Rh and Ir metals sinter into particles when heated in a H_2 atmosphere, but form oxides which then wet and spread on the SiO₂ surface when heated in air (17-19). Low temperature reduction of these oxides creates highly dispersed metal particles, while high temperature treatment in H₂ causes sintering into large particles. Lee and Schmidt (1) monitored oxidation of Rh on SiO₂ using XPS while measuring catalytic activity of alkane hydrogenolysis using gas chromatography and found that oxidation causes large $(\leq 10^3)$ increases in catalytic activity. Exposure of the oxide particles to H₂ at 250°C reduces the oxide to Rh metal particles with high catalytic activity due to slightly higher dispersion and strong morphological effects. Subsequent heating in H₂ at 600°C causes sintering and a decrease in activity by a factor of up to 10^3 .

In this paper we compare the oxidation and reduction of Rh and Ir particles on SiO_2 and Al_2O_3 supports using XPS to monitor the oxidation state of the metal catalysts and TEM to examine structures of metals and oxides.

EXPERIMENTAL

Planar Al₂O₃ supports for XPS analysis were prepared by anodization of aluminum foil in 15 wt% H₂SO₄ at a voltage of 15 v (20), followed by heating in air at 500°C (20). The oxide film thickness was measured gravimetrically to be 13 μ m by etching off the oxide layer of a sample with boiling H₃PO₄/H₂CrO₄ solution (20). Planar SiO₂ supports 1000 Å thick were grown thermally by heating a silicon wafer at 900°C in air for 10 hr. Because Ir samples were heated above the melting point of Al, anodized Al foil supports could not be used. Therefore, to prepare Ir/Al_2O_3 samples, 200 Å of Al was evaporated onto a thermally grown SiO₂ sample prepared as described above. The Al layer was then thermally oxidized in O₂ at 500°C for 72 hr. XPS showed complete coverage of the SiO₂ by Al₂O₃ in that no Si peak could be detected and all Al was in the 3+ state.

Thin Rh and Ir films were then vacuum deposited onto SiO₂ samples. Rh was evaporated from a tungsten basket, while Ir was evaporated directly from a resistively by heating Ir wire. By weighing the evaporation sources, Rh and Ir films were measured to be between 10 and 20 Å for XPS and TEM characterization described here. These films were then sintered into particles by heating in H₂ at 500°C.

XPS was also performed on bulk metal and oxide samples. Rh foil (99.999% purity) and Ir wire (99.999% purity) surfaces were sputtered before analysis. These metals were then thermally oxidized in O_2 at 750°C for 1 hr. After oxidation, the Rh and Ir metals appeared black and gray, respectively.

X-ray photoelectron spectra were obtained using a Perkin–Elmer Physical Electronics Model 5400 with a MgK α anode (h ν = 1253.6 eV). All peaks are referenced to Si (103.4 eV) or Al (74.7 eV) (21).

TEM samples were prepared so that metal particles could be viewed from the side. To accomplish this, Si or Al was vacuum deposited onto a gold grid and SiO₂ or Al_2O_3 was then grown thermally. Because of expansion during oxide growth, portions of the oxide extend beyond the edge of the grid. Rh and Ir were then vacuum deposited as described above and imaged at the edges of the grid. TEM micrographs were taken using a JEOL 100CX STEM after various gas and temperature treatments. We note that, while carbon and oxide may form on particles during ambient exposure to air during transfer from furnace to microscope, this contamination (no more than one to

two monolayers) is removed upon successive heating in O_2 or H_2 in the furnace.

All heat treatments were in a quartz tube furnace at 1 atm for 1 hr unless otherwise indicated. Samples were transferred repeatedly from the furnace to the XPS and TEM instruments so that analysis could be repeated and sequences could be obtained on the same sample for XPS and the same particle for TEM.

RESULTS AND DISCUSSION

XPS Analysis

Figure 1 shows the XPS spectrum of Rh 3d for a clean Rh metal surface (binding energy of 306.7 and 311.5 eV) and thermally grown Rh₂O₃ (binding energy of 307.9 and 312.7 eV). The energy difference between the metal and the oxide of 1.2 eV agrees with that reported by Peuckert (22), who studied the thermal oxidation of the Rh(111) surface. Figure 1 also shows the Ir 4f spectra for a clean Ir surface (60.3 and 63.2 eV) and thermally grown IrO₂ (61.2and 64.1 eV). Note the broad tailing toward higher binding energy for the IrO₂. Peuckert (22) studied thermal oxidation of the Ir(111) surface and also found a 0.9 eV energy difference between the metal and the oxide state, as well as broad tailing from the oxide peaks. Peuckert attributed the broad



FIG. 1. Calibration XPS spectra of bulk metals and oxides. Metals are wire and foil after cleaning by ion bombardment, and oxides are these surfaces after heating in air at atmospheric pressure at 750°C for 1 hr.



FIG. 2. XPS spectra of Rh on SiO₂ and Al₂O₃ following sequential treatment in O_2 and H_2 at temperatures indicated. Metal and oxide peak positions are indicated by vertical lines.

tailing to higher oxidation states of Ir caused by excess surface oxygen as well as Ir deficiency in the thermally grown IrO_2 phase.

Figures 2a and 2b show XPS results for Rh on SiO₂ and Al₂O₃, respectively. The upper spectra show Rh after sintering in H₂ at 500°C for 1 hr. The Rh/SiO₂ spectrum is identical to that obtained from the clean Rh surface, indicating that only Rh⁰ is present. Rh/Al₂O₃ shows a slight shoulder, which is probably due to room temperature oxidation. The Rh⁰ peak positions are at 307.6 and 312.5 eV for both samples as referenced to the Si(2p) peak at 103.4 eV and the C(1s) peak at 284.6 eV. This is a shift of 0.9 eV from the Rh foil peak. Since XPS peak shapes of the supported Rh are very similar to those of the Rh foil, this shift could not be due to oxidation of the supported Rh, and must therefore be due to a difference in charging between the support and the metal. No difference in peak positions existed between the two supports.

After exposure to air at 300°C, significant oxide peaks appear. Rh/Al_2O_3 is oxidized



FIG. 3. Plot of fraction of Rh existing as Rh_2O_3 versus treatment conditions following oxidation and subsequent reduction at temperatures shown for XPS data from Fig. 2. Fractions of metal and oxide were determined by fitting spectra of Fig. 2 to those of pure metal and oxide from Fig. 1. Oxidation occurs much more readily on Al_2O_3 than on SiO₂. Oxide formation is evident at 300°C and is complete by 500°C.

to a much greater degree than Rh/SiO_2 . For Rh/SiO_2 the oxide peak appears as a large shoulder constituting 30% of the Rh spectrum. But for Rh/Al_2O_3 the oxide is the dominant peak, constituting 61% of the spectrum. At 400°C, Rh/Al₂O₃ is nearly completely oxidized because only a small Rh⁰ shoulder, constituting only 10% of the Rh signal, remains (Fig. 2b). For the Rh/ SiO_2 Rh⁰ and Rh³⁺ peaks have similar heights. After exposure to air at 500°C, both spectra are identical to that of a bulk Rh_2O_3 sample, indicating complete oxidation. The difference in binding energy of the oxidized and reduced Rh peaks is 1.2 eV, as for the Rh foil.

After oxidation in air at 500°C, Rh samples were treated in H₂ (lower spectra of Fig. 2). Reduction occurs readily in H₂ for both samples. After exposure to H₂ at 150°C, the Rh₂O₃ peak constitutes only 6% of the Rh/SiO₂ spectrum and is probably due to room temperature oxidation. On Rh/Al₂O₃ the oxide constitutes 10% of the Rh spectrum. After 250°C treatment in H₂, both are nearly completely reduced.

Figure 3 summarizes this oxidation-re-

duction cycle and illustrates the tendency of Al_2O_3 to promote Rh oxidation. The oxide fraction was obtained by measuring the relative peak heights, but deconvolution of spectra gave approximately the same fractions. Since XPS probes only 20–40 Å into the surface, Rh metal may still exist below the oxide layer when none appears on the spectrum.

Figures 4a and 4b show XPS results for Ir/SiO_2 and Ir/Al_2O_3 , respectively. Upper spectra show Ir after treatment in H₂ at 500°C for 7 hr. Ir peaks have oxide shoulders (oxide fractions near 0.10), which are probably due to surface oxidation at room temperature. By referencing to the C and Si or Al peaks, the Ir peaks are positioned at 60.9 and 62.8 on both supports, which is 0.6 eV higher than the position on Ir wire. As with Rh, the Ir peak shapes eliminate the possibility that oxidation caused the shift, and thus the shift is due to a charging difference between the metal and the support. Peak shifts on both supports were identical.

In contrast to Rh, Ir exhibits only minor oxidation (oxide fraction <0.20) up to



FIG. 4. XPS spectra of Ir on SiO_2 and Al_2O_3 following sequential treatment in O_2 and H_2 at temperatures indicated. Metal and oxide peak positions are indicated by vertical lines.



FIG. 5. Plot of fraction of Ir existing as IrO_2 versus treatment conditions following oxidation and subsequent reduction at temperatures shown for XPS data from Fig. 2. Oxidation occurs much more readily on Al_2O_3 than on SiO₂. Oxide formation only begins at 500°C and is not yet complete by 700°C.

500°C in air. At 600°C Ir/Al_2O_3 (Fig. 7e) undergoes significant oxidation, whereas Ir/SiO_2 remains mostly reduced. Thus, as with Rh, the Al_2O_3 support seems to promote oxidation. At 700°C significant oxidation is seen for both cases. At this temperature the Ir peaks are still relatively broad, indicating that some Rh⁰ remains. This oxidation progression is summarized in Fig. 5.

After oxidation in air at 700°C, Ir samples were treated in H₂. Oxidized Ir/SiO₂ and Ir/ Al₂O₃ behave similarly during reduction. Both show significant reduction in H₂ at 150°C (oxide fractions near 0.22). The oxide shoulder remaining indicates that Rh is more easily reduced than Ir during this treatment. The Ir samples are further reduced by H₂ at 250°C to its original state before heat treatment in air.

TEM Analysis

Figures 6 and 7 show TEM micrographs for Rh/SiO₂ and Rh/Al₂O₃ after successive oxidizing and reducing treatments. The dark structures are the metal particles, while the lighter regions are the SiO₂ or Al₂O₃ support.

Figures 6a and 7a show Rh sintered from a 25-Å film in H_2 at 1000°C for 4 hr. Parti-

cles have not reached their equilibrium shape since all are not simple polyhedra, but features such as flat facets and welldefined corners indicate that they are approaching equilibrium shapes.

Figures 6b and 7b show Rh/SiO₂ and Rh/ Al₂O₃ after treatment in air at 300°C. A thin oxide layer about 20 Å thick is evident on Rh/SiO₂ and about 30 Å thick on Rh/Al₂O₃. This oxide layer grows *uniformly* over the metal particles and does not drastically alter their shapes.

Upon treatment in air at 500°C, Rh oxidizes significantly on both supports (Figs. 6c and 7c). The higher contrast regions are metal, whereas the lower contrast regions are metal oxide. In both cases, the metal particles appear to be broken apart by oxide growth. In the case of Rh/SiO_2 the oxygen appears to penetrate into the particles, dividing the remaining metal into small pieces. A likely explanation for this type of growth is that Rh particles crack to accommodate oxide growth. Oxygen then diffuses through the cracks, forming more oxide and creating more cracks. As cracks form throughout the particle, oxide growth separates the metal into several particles. Note also that despite significant oxidation, particles undergo very little shape change. As shown in Figs. 6c and 7c, the particle at the left, although broken up, still maintains a roughly hexagonal shape.

Rh/Al₂O₃ particles appear to be also broken apart by oxide growth, but some differences can be seen between Rh/Al₂O₃ and Rh/SiO₂. Rh/Al₂O₃ particles appear to be broken apart to a lesser extent than Rh/ SiO₂ particles. Rh/Al₂O₃ particles accommodate oxide growth by creating large cracks, which separate large pieces of remaining metal. In addition Rh₂O₃ seems to spread more readily onto Al₂O₃ than on SiO₂. Rh/SiO₂ particles upon oxidation retain their basic shapes and also retain a nearly 90° contact angle with the SiO_2 . However, on Al₂O₃ the oxide appears to move off the particle which suggests more extensive spreading onto the support.



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A number of explanations could account for this structural difference in oxide growth. One possibility is that a stronger interaction between the Rh and the Al₂O₃ prevents the metal particles from breaking apart. As Rh/SiO_2 particles break apart, they maintain their general shape, but swell in order to accommodate the oxide. Stronger interaction between the Rh and the Al₂O₃ may inhibit swelling, thus requiring the particles to accommodate oxide growth in another way. Thus Rh/Al_2O_3 forms a few major fissures which break the particles into a few pieces, rather than forming more, smaller fissures which result in particle swelling. Another possibility is that a stronger Rh₂O₃-Al₂O₃ interaction promotes wetting of the oxide onto the support.

After oxidation in air at 500°C, the particles were reduced in H₂ at 150, 300, and 400°C, as shown in Figs. 6d–6f and 7d–7f. These figures show that the particles are reduced back into the metal state. It is difficult to determine from the micrographs the temperature at which the oxide is completely reduced because, as a result of being broken apart during oxidation, the particles upon reduction form small, highly dispersed particles. Up to 400°C, the metal does not sinter back to its original shape.

 Rh_2O_3/Al_2O_3 also reduces back to Rh upon exposure to H_2 , although redispersion is not as evident, since the Rh/Al_2O_3 did not break apart as readily as the Rh/SiO_2 . Yet the particles still exhibit a rough surface, suggesting that catalytic activity would be enhanced over that of its original annealed state.

Figures 8 and 9 show TEM micrographs of Ir/SiO_2 and Ir/Al_2O_3 . Figures 8a and 9a show Ir/SiO_2 and Ir/Al_2O_3 after sintering a 12-Å film in H₂ at 1000°C for 4 hr. As with Rh, the metal particles have smooth, faceted surfaces, but have not completely reached their equilibrium shape.

Upon treatment in air at 500°C, a 10-Å oxide layer appears on both Ir/SiO_2 and Ir/Al_2O_3 (Figs. 8c and 9c). Recall that after

identical sample preparation, XPS showed that 15-20% of the Ir detected to be IrO_2 on both supports. Thus the two techniques agree up to this point.

After treatment in air at 600°C (Figs. 8d and 9d), a sharp difference between Ir/SiO_2 and Ir/Al_2O_3 is evident. The Ir/Al_2O_3 undergoes significant oxidation, as evidenced by dramatic morphological changes in the Ir particles. In contrast, Ir/SiO_2 undergoes only further film thickening. An increase in the surface oxide thickness is apparent for Ir/SiO_2 , but there are no dramatic morphological changes. These results also corroborate the XPS results.

After treatment in air at 700°C (Fig. 8e), Ir/SiO₂ also undergoes significant oxidation. Pronounced morphological changes are now apparent for Ir/SiO₂ due to oxide growth. Ir/Al₂O₃ particles continue to expand with further oxide growth. Again, XPS and TEM observations agree.

Note that for both Ir/SiO₂ and Ir/Al₂O₃ oxide grows out from the Ir metal in local protrusions. In Fig. 9d, IrO₂ on Ir/Al₂O₃ grows from a few areas of the particles, leaving other portions of the metal relatively unchanged. On the particle at the left in Fig. 9, the oxide grows from the top, leaving the shape unchanged. On the particle at the right in Fig. 9, a large protrusion of oxide forms at the right side of the particle, while the left side maintains its hexagonal shape. In Fig. 8e oxide on Ir/SiO₂ also grows in local protrusions, as indicated by the arrows. These features are similar to those reported by Foger and Jaeger (23) who found that IrO_2 grew in thin blades from SiO₂-supported Ir particles.

This oxide growth structure may also explain why Ir^0 was detected by XPS after significant oxidation. When oxide grows as local protrusions, the unoxidized metal remains exposed and detectable by XPS. The Ir^0 peak will disappear only after complete oxidation. Whereas with Rh, partial oxidation covers the remaining metal. Thus a partially oxidized Rh particle may not exhibit a Rh⁰ peak, whereas a partially oxi-



FIG. 8. Transmission electron micrographs of Ir particles on SiO_2 . An oxide film is evident by 500°C, and complete oxidation does not occur by 700°C. Oxide grows as protrusions which grow out from the original metal particles. Reduction of the oxide forms 10- to 20-Å metal particles which only coalesce after heating to 700°C.



FIG. 9. Transmission electron micrographs of Ir particles on Al_2O_3 . An oxide film is evident by 500°C, and complete oxidation does not occur until 700°C. Oxide grows as protrusions which grow out from the original metal particles. Reduction of the oxide forms 10- to 20-Å metal particles which only coalesce after heating to 600°.

dized Ir sample is likely to exhibit a significant Ir⁰ peak.

After oxidation in air at 700°C, Ir samples were treated in H₂ at 150, 300, and 400°C as shown in Figs. 8f–8h and 9f–9h, respectively. At 150°C, small metal particles appear in the IrO₂. By 300°C, Ir appears to be mostly reduced on both supports. Reduction of the expanded oxide phase on Al₂O₃ creates a large crack in the Ir particles. At 400°C, all particles appear reduced but have not yet sintered into their original shapes. Comparing Ir in Figs. 8h and 9h to the original state in Figs. 8a and 9a, one can see a large increase in surface area and a change from very smooth surfaces to very rough surfaces.

We also note that TEM and XPS measure oxide and metal with different spatial sensitivities. TEM sees through particles while XPS only samples the composition of the top 10–20 Å. XPS is sensitive to the oxidation state near the surface which is more pertinent to the properties of a catalyst. In some cases TEM detects the unoxidized cores in large particles where XPS indicates complete oxidation. Treatment in H₂ rapidly causes complete reduction as indicated by the absence of oxide XPS peaks and the absence of oxide electron diffraction rings.

CONCLUSION

From experiments on samples prepared, treated, and analyzed identically, it is evident that both Rh and Ir particles are oxidized at lower temperatures on Al_2O_3 than on SiO₂. Rh oxidizes between 300 and 400°C on Al_2O_3 and between 400 and 500°C on SiO₂. Ir oxidizes at 500 and 600°C on Al_2O_3 and between 600 and 700°C on SiO₂. No pronounced differences between supports are seen for reduction of Ir or Rh oxides. Rh is nearly completely oxidized in H₂ by 150°C, and Ir is nearly completely oxidized by 250°C.

XPS also shows an energy shift of peaks of supported Ir and Rh particles from those of bulk metal samples which is attributed to charging between the metal and the support. No significant difference in peak position was observed between the two supports.

TEM micrographs corroborate oxidation and reduction trends found using XPS. The occurrence of oxidation of Ir/Al_2O_3 at lower temperatures than Ir/SiO_2 is clear from TEM. The morphological differences between Rh/SiO₂ and Rh/Al₂O₃ are less obvious, but Rh/Al₂O₃ does form a thicker oxide layer than Rh/SiO₂ at 300°C, and Rh₂O₃ appears to spread more readily onto Al₂O₃ than on SiO₂.

TEM also reveals differences in the oxide growth structures on Rh and Ir. Oxygen penetrates the Rh particles, breaking them apart to accommodate oxide growth, while, for Ir, the oxide grows out as protrusions from the particle. Reduction of IrO_2 and Rh_2O_3 breaks metal particles into smaller, more dispersed particles. These dispersion and morphology changes should have a significant role in altering catalytic activity by pretreatment.

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