Accordingly, we propose the following steps for the hydrogen-induced transformation of Rh<sup>1</sup>(CO)<sub>2</sub> into Rh<sub>x</sub>-CO species. At lower temperatures,  $T \le 373$  K

$$Rh^{I} \underbrace{CO}_{CO} + \frac{1}{2}H_{2} \longrightarrow Rh^{I} \underbrace{H}_{CO} + CO_{(g)}$$
 (2)

or

At higher temperatures,  $T \ge 373$  K

R

$$h^{T} \left( \begin{array}{c} H \\ CO \end{array} \right)^{2} \left( \begin{array}{c} - \end{array} \right)^{0} Rh^{0} CO + OH^{-}$$
 (4)

or

$$\operatorname{Rh}^{\mathrm{I}} \underset{\mathrm{H}}{\overset{\mathrm{H}}{\leftarrow}} \operatorname{CO}^{2^{-}} \xrightarrow{\operatorname{Rh}} \operatorname{Rh}^{0} \underset{\mathrm{CO}}{\overset{\mathrm{H}}{\leftarrow}} \operatorname{CO}^{-} \operatorname{OH}^{-}$$
 (5)

$$2Rh^{0}-CO \longrightarrow Rh_{x}-CO + CO_{(g)}$$
 (6)

$$(x = 2)$$

$$y Rh_x - CO \longrightarrow Rh_{xy} - CO + (y - 1) CO_{(a)}$$
(7)

or

$$2Rh^{\circ} \swarrow^{H} \longrightarrow Rh_{x} \xleftarrow^{H}_{H} + CO_{(g)}$$
 (8)

The transformation of  $Rh^{I}(CO)_{2}$  into  $Rh_{x}$ -CO species also occurs in the absence of H<sub>2</sub>, but it requires higher temperatures.<sup>2</sup> This is assumed to be a result of the reduction of Rh<sup>I</sup> by CO and the promotion of subsequent agglomerization of Rh<sup>0</sup>

$$2Rh^{1} CO + O^{2-} - Rh_{x} - CO + CO_{2} + 2CO$$
(9)  
(x = 2)

On the basis of EXAFS data this transformation was observed at 573 K and was attributed to the reductive desorption of CO.<sup>4</sup> Our IR spectroscopic measurements<sup>2</sup> revealed that the re-formation of metallic Rh from isolated Rh<sup>I</sup> occurs in the presence of CO, without any significant desorption, even at 448 K, and goes to completion at 473 K.<sup>2</sup> The fact that the addition of  $H_2$  to CO accelerates this process (Figure 7) is an obvious consequence of the previous considerations. We may add that the surface mobility of Rh is also enhanced in the presence of  $H_2$  at 473 K.<sup>7</sup>

Registry No. Rh, 7440-16-6; CO, 630-08-0; H<sub>2</sub>, 1333-74-0.

# Photoreduction and Reoxidation of Platinum Oxide and Palladium Oxide Surfaces

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Powdered samples of PtO and PdO were found to reduce at room temperature under vacuum upon irradiation with 253.7-nm radiation from a mercury lamp. The reduction of the oxide particle surfaces was followed by X-ray photoelectron spectroscopy (XPS or ESCA). The photoreduction proceeded slowly through the first few monolayers and was 75% completed within the sampling depth (ca. 40 Å) after about 10 h of irradiation. The photoproduced metals, Pt and Pd, were observed to slowly reoxidize upon exposure to the atmosphere. This oxidation of the metals at room temperature is remarkable and suggests a unique nature for the photoproduced metallic crystallites. In contrast, metallic Pt and Pd formed by  $H_2$  reduction of the oxides at room temperature were not oxidized when exposed to air. Powdered samples of ZnO were not reduced under identical conditions. A model has been developed to explain and to predict the reduction of metal oxide surfaces by UV irradiation. The model suggests that complete or partial reduction of many oxides can be achieved, depending upon the band gap of the oxide being irradiated and the chemical stability of the photoproducts.

## Introduction

This research, dealing with the photoreduction of PtO and PdO, is an extension of earlier studies on the interaction of UV light with a number of metal oxide surfaces.<sup>1,2</sup> The photochromism of MoO<sub>3</sub> and WO<sub>3</sub>, i.e., the photoinduced blue color change of these oxides, was found to be related to the formation of +5oxidation state sites which were oxidized back to the +6 oxidation state with the loss of color upon exposure to the atmosphere.<sup>1</sup> Lower oxidation states were not photoproduced. On the other hand, cupric (CuO) and cuprous (Cu<sub>2</sub>O) oxides were reduced to metallic Cu by UV irradiation.<sup>2</sup> Other oxides, such as ZnO, do not show photoreduction at all.<sup>3</sup> Thus, depending upon the oxide system, the consequences of the interaction of UV light with the surface could range from complete reduction to the metallic state to no reduction at all.

A model has been developed that enables us to understand and to predict the extent of photoreduction in these systems. In this model it is postulated that the absorption of a quantum of light by a metal oxide semiconductor promotes an electron from the oxygen ion into the conduction band. While the primary photophysical act is traditionally written as  $O^{2-} + h\nu \rightarrow O^{-} + e^{-}$ , it is now widely recognized that the oxygen atom is only fractionally charged in these oxides,<sup>4</sup> a view which is supported by ab initio molecular orbital studies.<sup>5</sup> The photoproduced electron, which will be thermalized by lattice collisions, can relax a number of ways. It can be captured by the hole,  $k^+$ , which can be represented in the traditional manner as O<sup>-</sup>. It can also be captured by vacant, low-lying metal ion orbitals if any are available. In the latter instance, photoreduction is observed. Thus, whether or not

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photoreduction is observed depends upon whether the energy of the conduction band lies above or below the energy of vacant metal ion orbitals. One can infer the relevant energetics from the knowledge of the optical band gap and the standard enthalpy change for the reduction. Roughly, the relaxation of an electron from the band gap must provide the energy required for the reaction, i.e., the difference in the enthalpies of formation of the reduction products and the enthalpy of formation of the reactant oxide. For example, ZnO has a band gap of 3.2 eV (307 J/mol)<sup>6</sup> and an enthalpy of formation of -320 kJ/mol, and reduction is not predicted by our model and is not observed (vide infra). On the other hand, for Cu<sub>2</sub>O and CuO, the band gaps are 2.67 eV (257 kJ/mol) and 1.95 eV (188 kJ/mol),<sup>8</sup> which exceed the enthalpies of formation<sup>8</sup> of these compounds, -168 and -157kJ/mol, and reduction to metallic copper is expected and found.<sup>2</sup>

The band gaps for  $MoO_3$  and  $WO_3$  are 2.96 eV (285 kJ/mol) and 2.80 eV (270 kJ/mol), respectively, and are larger than the differences in the enthalpies of formation of  $\text{MoO}_2$  and  $\text{MoO}_3$  (156 kJ/mol) and WO<sub>2</sub> and WO<sub>3</sub> (254 kJ/mol), and reduction to the +4 oxidation state should be possible whereas too little energy is available to reduce either oxide to the metallic state. Indeed, no photoreduction to the metallic state is observed; only photoreduction to the +5 state is observed instead of the +4 state. It is not immediately obvious why the expected +4 state is not observed. Many parameters such as kinetics, crystal structure, ion stabilities, etc., have not been included in the model. For example, the +4 state requires two photoproduced electrons to be captured from the conduction band, and this process is almost certainly a two-step process. Capture of a photoelectron by the +5 state probably cannot compete with capture by the +6 state. Considering the simplicity of the model, it works very well at predicting whether or not photoreduction is to be expected. It is not surprising that the simple model suggested will not predict intermediary oxidation states.

Three additional oxides were studied to verify the predictions of the model. The band gap for PdO is reported to be 1.5 eV (144 kJ/mol), more than enough to overcome the enthalpy of formation (85.4 kJ/mol). Photoreduction of PtO was also expected considering its instability and similarity to PdO although neither the band gap nor the enthalpy of formation is available. In addition, these oxides were expected to photoreduce to small clusters of metallic Pd and Pt which are of interest because of their importance in catalysis. On the other hand, ZnO has a reported band gap of 3.2 eV (307 kJ/mol), which is insufficient to overcome the enthalpy of formation (320 kJ/mol) and was not expected to be photoreduced.

#### **Experimental Section**

PdO and ZnO were obtained from Alpha with a reported purity of 99.9%. PtO was obtained from Pfaltz and Bauer. The powders were pressed into 6-mm-diameter pellets with a thickness of approximately 1 mm. Such pellets are routinely prepared to analyze powdered samples in the Hewlett-Packard 5950B electron spectrometer. For the reduction process, each pellet was placed in a simple quartz reaction container described in detail elsewhere.<sup>9</sup> The reaction vessel could be evacuated to  $10^{-6}$  Torr and then sealed off with a Teflon high-vacuum stopcock. After evacuation the vessel was placed in the center of a helically coiled, low-pressure mercury lamp, SC2537, also described previously.<sup>10</sup> The samples were irradiated for up to 16 h. The photons generated by this lamp have a wavelength of 253.7 nm and an energy of 4.8 eV (470 kJ/mol).

Upon completion of the irradiation the samples were transferred to a Hewlett-Packard 5950B ESCA spectrometer. Three pellets at a time could be mounted and introduced into the analysis



Figure 1. Changes in Pd 3d and O 1s/Pd 3p photoelectron spectra of PdO upon reduction by UV irradiation.

chamber under a dry nitrogen atmosphere to avoid exposure to air. Monochromatic Al K $\alpha$  radiation (1486.6 eV) was used for the surface analysis. Line widths of the order of 0.80-eV fwhm were obtained for the Au  $4f_{7/2}$  photoelectron line. The pressure in the spectrometer is typically  $10^{-9}$  Torr. The binding energy scale is calibrated by assigning 284.6 eV to the ubiquitous C 1s signal as suggested by Wagner.<sup>11</sup> The use of a Hewlett-Packard electron flood gun which provided low energy (below 2 eV) electrons to the sample surface during XPS analysis prevented significant sample charging.

The controlled air exposure experiments were performed by withdrawing the sample from the spectrometer into the laboratory air and reinserting it into the analysis chamber after the desired exposure.

The spectrometer is equipped with Hewlett-Packard 21MX and 9845B computers. The software was obtained from Surface Science Laboratories. Data handling consisted of a linear background subtraction followed by a five-point smoothing routine. The spectral areas were determined by computer integration. These areas were corrected for instrumental parameters, photoionization cross sections,<sup>12</sup> and differences in electron mean free path.<sup>13,14</sup> The peak-fitting routine simply provides a least-squares fit of a sum of Gaussian peaks to the experimental XPS spectrum.

#### **Results and Discussion**

ZnO was not photoreduced. The XPS spectra of ZnO before and after irradiation were indistinguishable. PdO and PtO were photoreduced to Pd and Pt. The reduction of PdO was followed by XPS using the  $3d_{5/2}$  line. A binding energy of 336.9 eV, slightly higher than the value reported previously for PdO<sup>15</sup> and for silicaand lanthana-supported PdO, was found for PdO.<sup>16</sup> Upon UV irradiation a new Pd species formed at a lower binding energy, as shown in Figure 1. As the line grew in intensity (with irradiation time) it shifted from a value of 336.1 eV (1-h irradiation) to 335.2 eV (16 h). The latter value is in perfect agreement with the metallic Pd 3d electron binding energy reported by Kumar et al.<sup>17</sup> and is only 0.3 eV higher than another metallic Pd value reported by Wagner.<sup>11</sup> We recently found 335.1 eV for a throughly cleaned Pd foil and for silica-supported Pd.<sup>16</sup> Thus, it is certain that metallic Pd is the end product of the photoreduction. The higher electron binding energy at partial reduction indicates an electronic interaction between the small metallic Pd crystallites and the PdO matrix. Also shown in Figure 1 are the Pd  $3p_{3/2}$  and O 1s spectra. The reduction of PdO to Pd can be

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Figure 2. Typical curve fit of Pd  $3d_{5/2}$  electron peak. PdO: UV irradiation, 6 h.



Figure 3. Changes in Pt 4f photoelectron spectra of PtO upon reduction of UV irradiation.

followed by the changes in the  $3p_{3/2}$  line shifting from 534.2 to 532.6 eV or by the disappearance of the O 1s line.

The Pd 3d electron binding energies and the percent reduction were obtained from a curve fit of the  $3d_{5/2}$  peak, illustrated in Figure 2. The spin-orbit coupling split between the  $3d_{5/2}$  and  $3d_{3/2}$  line is 5.3 eV and permits the fitting of the  $3d_{5/2}$  component, simplifying the curve-fitting process. The fits demonstrated very clearly that there was still 20-25% unreduced Pt<sup>2+</sup> detectable at the end point of the reduction (after very long exposure times). By taking into consideration the exponential decrease of signal intensity with sample depth d, i.e.,  $e^{-d/\lambda \sin \phi}$ , it can be shown that, at an angle  $\phi$  of 38° between the sample surface and the entrance angle of the spectrometer, approximately 95% of the total signal arises from a depth of 2  $\lambda$ . The mean free path,  $\lambda$ , for a Pd 3d electron ejected by Al K $\alpha$  radiation through metallic Pd is about 14 Å.<sup>18</sup> (The kinetic energy of the 3d electron is about 1150 eV.) Thus, it can be concluded that the photoreduction of PdO surfaces proceeds only through the first few atomic layers, the light being unable to penetrate further. The presence of unreduced PdO islands in Pd metal is highly unlikely since the reduction rate dropped to a very low value after 75-80% of the PdO within the analysis volume was reduced.

Irradiation of PtO resulted in the formation of metallic Pt as shown in the 4f core electron spectra compiled in Figure 3. The  $4f_{7/2}$  electron binding energy of PtO was found at 74.4 eV. Small quantities of metallic Pt (<10%) were detected in the untreated PtO of one batch. This observation is not too surprising in view of the instability of PtO. For example, molecular H<sub>2</sub> easily reduces PtO at room temperature. The intensity of the metallic Pt  $4f_{7/2}$ peak near 71.5 eV increases with prolonged irradiation times. After 16 h of irradiation a 72% reduction is observed. The calculation of a percent reduction required the fitting of the 4f envelope with four curves, as demonstrated in Figure 4, since the spin-orbit split is only 3.3 eV. Reasonable fits can only be obtained



Figure 4. Typical curve fit of 4f photoelectron spectrum. PtO: UV irradiation, 6 h.



Figure 5. Changes in Pt valence band and 4f spectra of PtO upon UV irradiation.



Figure 6. Percent reduction as a function of UV radiation time (under vacuum).

with programs that allow the constraining of certain parameters, e.g. the separation and intensity ratio of two peaks. The fit in Figure 4 was generated with a fixed spin-orbit split of 3.3 eV and a theoretical intensity ratio of 4:3 for the  $7/_2$  and  $5/_2$  lines for both the metallic and +2 doublets.

The reduction of PtO to Pt is also reflected in the X-ray-excited valence-band spectra as shown in Figure 5. Platinum oxide exhibits three peaks between the Fermi level and 17 eV. The major peak at about 4.4 eV is associated with Pt 5d emission while the peak at 9.0 eV arises from the O 2p orbitals. Upon photoreduction metallic Pt forms as is evident from the 4f core level spectra also shown for comparison. This formation of Pt results in the filling of the 5d band just below the Fermi level and a simultaneous decrease in the O 2p peak intensity.

The percent reduction as calculated from curve-fitted Pt 4f and Pd  $3d_{5/2}$  is plotted vs. UV exposure time in Figure 6. The photoreductions of PdO and PtO appear to be first-order processes, presumably controlled by the availability of unreacted oxide in the analysis volume. Straight-line relationships are obtained with semilog plots. The small amount of metallic Pt present in PtO prior to irradiation has been subtracted from the total metallic



Figure 7. Reoxidation of photoreduced Pd upon air exposure.

Pt in the data presented in this figure. Thus, the line passes through the origin. The photon cross sections for photoreduction of PdO and PtO are very similar, but a slightly faster photoreduction of PdO is indicated in Figure 6.

Reoxidation of both the photoreduced PdO and PtO surfaces has been observed. This observation is remarkable in that oxidation of these metals at ambient temperatures is not generally found. Apparently, the metallic clusters formed must be sufficiently small to be unstable with respect to oxidation. Small metal particles placed on a support often exhibit a positive shift in binding energy relative to the bulk value. It has been suggested that these shifts are due to differences in the final state, i.e., extraatomic relaxation.<sup>19-22</sup> It is thought that there are not enough metal atoms in the particle to completely screen core holes created by the photoemission and that it is the incomplete screening which gives rise to the positive shift. In the limit of an isolated atom on a support, the positive shift can be as high as 1.6 eV.<sup>23</sup>

In the case of the photoreduced Pd and Pt we find, within experimental error, no difference for the Pd but a 0.5-eV positive shift for the Pt compared to metallic bulk values (Pd 3d, 335.2 eV vs. 335.1 eV for bulk; Pt 4f, 71.6 eV vs. 70.9 eV for bulk). These data suggest that the Pt clusters must be smaller than 20 Å since it has been demonstrated that particles above that size do not show positive shifts.<sup>24</sup> This very small Pt cluster size must be responsible for its reactivity toward oxidation. The oxidation of the larger Pd clusters is not completely unexpected since oxidation of C-, SiO<sub>2</sub>-, and La<sub>2</sub>O<sub>3</sub>-supported Pd crystallites has been observed.2

Figures 7 and 8 contain representative Pd 3d and Pt 4f spectra, which show the reoxidation behavior of the two metals. Palladium exhibits an initially fast and then slow reoxidation. Most of the oxidation takes place during the first day of air exposure with much smaller contributions during the following days. This can be easily understood in terms of successive oxidation from the top protective monolayer into deeper layers of the metallic clusters. The reoxidation of Pt is quite different (Figure 8). No oxidation is observed after minutes or hours of air exposure. Five days were necessary to oxidize the most thoroughly reduced surface. Furthermore, the degree of reduction influences the rate of reoxidation. For instance, the surface which was only photoreduced for 1 h did not have a measurable reoxidation after 6 days of air exposure but was completely reoxidized after 25 days. In general, we observed increasingly faster oxidation with increasing percentages

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Figure 8. Reoxidation of photoreduced Pt upon air exposure.

of reduction. All samples showed an "induction" period of a day or more before they became reoxidized. In contrast to this oxidation of photoreduced crystallites, no oxidation at all was found when the reduction was performed in  $H_2$ . Molecular hydrogen at room temperature quantitatively reduced PtO (and PdO), and the resulting Pt has a binding energy of 70.8 eV, characteristic of bulk Pt.11

We found no other reference to reoxidation of photoproduced Pd and Pt clusters. In previous studies, e.g. those of Chueng<sup>26</sup> involving a careful analysis of line shapes of small clusters of both Pd and Pt, samples were quickly transferred through the atmosphere into the ESCA and no atmospheric oxidation was found. The lack of oxidation is understandable in terms of the short exposure times since the oxidation of Pd clusters was evident only upon exposure to the atmosphere for a few hours and the Pt clusters required more than 5 days. A TEM study of small Pt clusters showed that smaller particles are produced in 100 Pa of O<sub>2</sub> than in a vacuum and that small Pt clusters catalyzed the oxidation of the carbon substrate.<sup>27</sup> This difference in particle growth could be a consequence of the oxidation of small Pt clusters.

Slow electrochemical production of O<sub>2</sub> on Pt clusters is commonly observed. For example, White<sup>28</sup> and others<sup>29</sup> have photoreduced chloroplatinic acid on titania using the method of Kraeutler and Bard<sup>30</sup> and employed the doped titania to study photoassisted chemical reactions involving water. A deficiency in O<sub>2</sub> production is observed. Similar anomalies involving oxygen formation have been found with colloidal platinum.<sup>31</sup> Although apparently not considered, it appears possible that reoxidation of platinum clusters may account for a deficiency of oxygen in these experiments.

## Conclusions

A simple model has been developed to predict the extent of reduction of metal oxide surfaces induced by UV irradiation. As predicted by the model, both PdO and PtO are reduced to the metallic state while ZnO is not. The metallic Pd and Pt crystallites are very small, especially in the case of Pt (< 20 Å). Since the reduction is slow and limited to shallow depths, metal oxide supported metallic crystallites can be formed by this reduction which could have unique applications in catalysis. While Pd and Pt formed by hydrogen reduction of PdO and PtO at room temperature do not reoxidize, the photoproduced metallic clusters do reoxidize on exposure to the atmosphere.

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