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Evidence for Diffusion of a Partially Oxidized Titanium Species into Bulk Platinum

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Auger electron spectroscopy shows that an oxidized titanium species diffuses into a clean Pt foil between 700 and 900 K. This diffusion is reversible and the titania returns to the surface when the sample is cooled. However, when the titania-covered Pt surface is heated in oxygen, the titania desorbs irreversibly from the Pt. Likewise, unoxidized titanium is also removed from the surface irreversibly, indicating that the diffusing species is partially oxidized. This species is found to prevent CO and H_2 chemisorption and may explain the support–metal effects observed on titania-supported Pt. © 1984 Academic Press, Inc.

INTRODUCTION

The changes in chemisorption and reaction properties of transition metals supported on titania are well known. For example, when Pt/TiO_2 catalysts are reduced in H_2 above 750 K, they lose their ability to adsorb H_2 or CO (*1*), but maintain their activity for the methanation reaction. They are actually reported to be 10 times as active as Pt/Al_2O_3 catalysts and 100 times as active as Pt/SiO_2 when compared on a surface area basis (*2, 3*).

Recently, significant evidence has been given that the unusual catalytic properties are due to the migration of titania onto the metal surface. Simoens *et al.* (*4*) have observed titania diffusing through a thin Ni film which had been deposited on titania. Sadeghi and Henrich (*5*) have observed the migration of titania onto Rh particles. Likewise, Belton *et al.* (*6*) have found similar evidence for the diffusion of titania through thin Pt and Rh films. Other workers have also presented evidence that support–metal effects with titania are due to the presence of titania on the metal (*7–11*).

In this paper we will show that a partial oxide of titanium can also diffuse into a bulk metal at temperatures above 700 K. This titania segregates back to the surface at the lower temperatures at which adsorption is measured and is very effective in preventing H_2 and CO adsorption. Finally, we find that flashing this partially reduced titania to high temperatures in oxygen permanently removes the titania from the Pt surface.

EXPERIMENTAL

The temperature-programmed desorption (TPD) and Auger electron spectra (AES) were obtained in an ion-pumped vacuum system with a cylindrical mirror analyzer and a quadrupole mass spectrometer. The AES beam energy was kept at 1500 eV. The back side of our 0.013-cm Pt foil was covered by a Ta foil and could be resistively heated by passing current through 0.025-cm Ta wires spot-welded to the Ta foil. The leads were also passed through a liquid-nitrogen reservoir which allowed the sample to be cooled to approximately 80 K. Temperatures were measured with a chromel–alumel thermocouple spot-welded directly onto the Pt foil. With this sample configuration, we were able to heat the Pt to 1450 K without any observable temperature gradients in the Pt. Heating rates in TPD were kept constant at 7 K/sec by means of a temperature programmer.

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The Pt sample was cleaned by successive oxidation and sputtering cycles until no impurities could be detected by Auger analysis. No strongly bound oxide could be formed on this sample after Si was removed (*12, 13*). Ti was deposited onto the clean Pt by vaporizing a Ti–Ta alloy near the sample. To ensure that the Ti was oxidized, we exposed the sample to 10^{-7} Torr O_2 during deposition. After deposition, the sample was heated to 550 K in 10^{-7} Torr O_2 for 15 min. Following oxidation, the sample was exposed to 10^{-7} Torr of H_2 or CO at 550 K for 10 min. and then flashed to 1300 K.

As we will discuss shortly, flashing the foil to 1300 K caused titania to diffuse into the bulk and cooling the sample forced the titania to segregate to the surface. For multilayer quantities of titania, the high-temperature treatment removed the multilayers. For submonolayer quantities of titania, the quantity of titania returning to the surface after the first flash was always slightly less than was originally deposited on the surface. Some of the diffusing titania remains in the bulk following this first high-temperature flash. While the oxidation and reduction conditions were not critical, this high-temperature treatment was necessary for reproducing the results in this paper.

RESULTS

Auger Spectroscopy

Auger spectra of the clean and titania-covered Pt surfaces are shown in Figs. 1a and b, respectively. The ratio of the Ti(385 eV) peak to the Pt (238 eV) peak, designated Ti(385)/Pt(238), was used as a measure of the titania coverage after subtracting the height of the Pt(390 eV) peak. Detecting the oxygen peak at 508 eV required special attention due to its rapid disappearance in the electron beam. The oxygen peak had a half-life of approximately 100 sec for a beam of 14 μA and could only be detected if the spectrum was taken in this region first. In Fig. 1b, the oxygen peak was scanned first, followed by a complete spectrum from 50 to 550 eV. For all titania coverages, the O(508)/Ti(385) was about 0.6 based on the first scan of the oxygen peak. We found that the damage to the titania could be easily repaired by exposing the sample to 10^{-8} Torr of O_2.

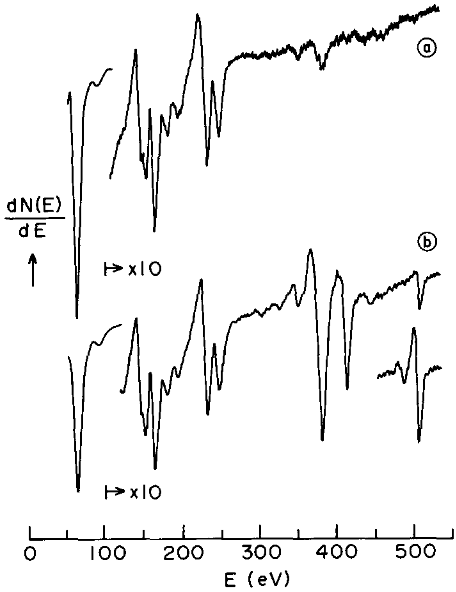

FIG. 1. Auger electron spectra from a clean and a titania-covered Pt surface. In the titania-covered surface, the oxygen was scanned first, followed by a complete spectrum from 50 to 550 eV. The change in the oxygen peak height was due to electron beam damage.

When the sample was heated above 1100 K under vacuum, the Auger spectrum of the sample at that temperature indicated a clean Pt surface. However, when the sample was allowed to cool, the titania returned. Apparently, the titanium oxide diffuses into the bulk Pt at high temperatures and segregates to the surface at low temperatures. This reversible diffusion is shown in Fig. 2 for three different initial coverages of titania. We cycled the sample from 300 to 1100 K as many as 20 times with no visible loss of titania from the surface.

A previous paper also observed the disappearance of titania from Pt above 670 K (*14*). In that paper, results were attributed to the decomposition of the oxide and the dissolution of titanium into the Pt to form an intermetallic compound. However, our

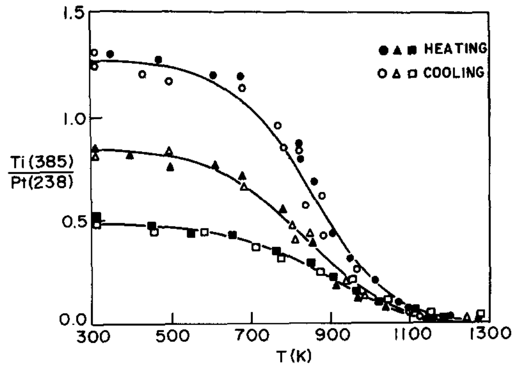

FIG. 2. The equilibrium segregation curves for three different initial coverages of titania on Pt. Closed points are from spectra taken when the surface was being heated from 300 K, and open points are from spectra taken while the surface was cooling from 1300 K.

spectra always indicated that the oxygen and titanium disappeared and reappeared together. We did not observe any evidence for the decomposition of the oxide. In fact, the oxidation state of the titania was very important in this diffusion process. If we allowed the surface to be damaged by the electron beam, the titania in the oxygen-depleted region was irreversibly removed from the surface after heating to 1100 K. The data points shown in Fig. 2 were taken with great care to avoid beam damage effects. In one set of experiments, we took Auger spectra at different positions on the sample at each temperature to avoid looking at a spot previously damaged by the beam. We obtained identical results in another set of experiments in which we maintained a background pressure of 5×10^{-8} Torr O_2 in the vacuum system during the heating and cooling cycles. This oxygen pressure was sufficient to repair the damage done by the electron beam.

We also examined the effect of higher oxygen pressures by flashing the sample from 300 to 1100 K while the surface was placed in front of a directed beam of O_2 with an equivalent pressure of approximately 10^{-5} Torr. This procedure permanently removed all of the titania after three heating cycles. Flashing the sample under vacuum or H_2 or exposing it to O_2 after it had been heated to 1100 K did not remove titania. Apparently, the oxygen prevents titania from diffusing into the bulk and causes it to desorb during the heating cycle.

We attempted to measure the rate of the titania diffusion without success. Even though we were able to quench the sample from 1100 to 300 K in less than 3 min, the equilibrium was always obtained. This indicated that the diffusion rate is very high during the cooling period. However, we did find that the rate was slow at 300 K, as expected. When we sputtered a titania-covered surface clean, residual titania from the bulk would only return to the surface after the sample was heated and allowed to cool. (The O(508)/Ti(385) ratio was again 0.6 for this bulk species.)

One additional interesting feature observed was that the maximum quantity of titania which would segregate to the surface from the bulk corresponded to a Ti(385)/Pt(238) ratio of 1.35. Even though the surface was initially covered with multilayers of titania, the coverage following high-temperature was 1.35.

TPD Results

The TPD spectra for CO from a polycrystalline Pt foil are shown in Fig. 3a. The spectra shown were for adsorption at 300 K, but no additional peaks were observed when adsorption was at 80 K. Desorption occurred in two states centered at 400 and 520 K. The two curves shown correspond to a high and low initial CO coverage and indicate that these two states fill sequentially. These states do not correspond to those observed on simple crystal planes of Pt (*15*), but are similar to states observed on stepped planes (*16*). Since we were concerned that the incorporation of oxide into the surface could change the distribution of exposed crystal planes in the foil and thereby change the desorption temperatures, we investigated the effect of annealing temperature on the foil. High-temperature annealing has been reported to lead to

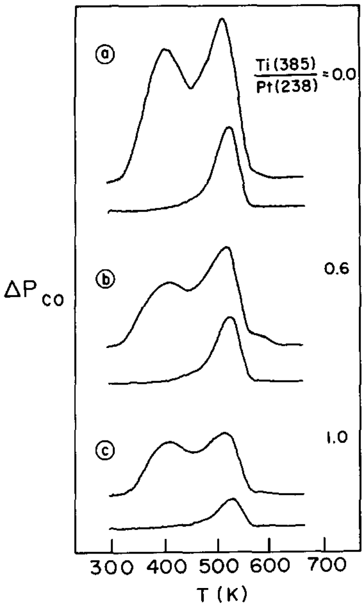

FIG. 3. TPD spectra for CO from Pt. The titania coverages are as shown. The two spectra shown for each titania coverage are for low and high initial CO coverages. Titania prevented the adsorption of CO but did not lead to any new TPD features.

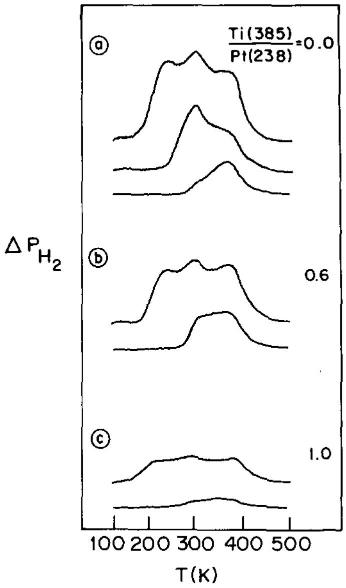

FIG. 4. TPD spectra for H_2 from Pt. The different curves at each titania coverage correspond to different initial H_2 coverages.

predominantly (111) planes on the surface of a foil; however, we observed no difference in the TPD spectra from the foil after argon ion sputtering followed by cleaning at 700 K to those spectra obtained after annealing the foil to over 1400 K.

The effect of titania is shown in Figs. 3b and c. No new desorption states are observed and the peak temperatures remain unchanged. However, titania does prevent adsorption. The total quantity of CO that could adsorb decreased as the titania coverage increased. Similar features were observed for H_2 desorption and these results are given in Fig. 4. Desorption of H_2 from a clean surface occurs in three major desorption states at 220, 300, and 370 K. As with CO, these states fill sequentially and the peak temperatures and shape were unchanged by the presence of titania on the Pt foil. Also, the total amount of H_2 that desorbed decreased with the titania coverage.

The dependence of the saturation coverages for H_2 and CO on the titania coverage is shown in Fig. 5. For both H_2 and CO, the saturation coverage is linearly related to the titania coverage, and adsorption is completely suppressed for Ti(385)/Pt(238) =

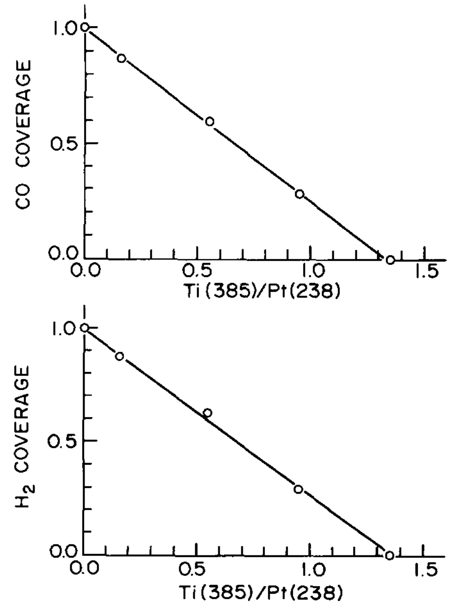

FIG. 5. Plots of saturation coverages of CO and H_2 from Pt as a function of titania coverage.

1.35. As we discussed earlier, a coverage of 1.35 was also the maximum quantity that would diffuse out of the bulk. The linear dependence of CO and H_2 coverage on the titania coverage indicates that the titania species is probably evenly spread over the entire surface. At low titania coverages, parts of the surface are uncovered and the adsorption and desorption properties of that part of the surface are normal. If titania clusters were forming, the coverage dependence should be nonlinear.

DISCUSSION

Application of these results to actual supported catalysts is readily apparent. On TiO_2-supported Pt, the adsorption of H_2 and CO are suppressed when the catalyst is reduced in H_2 above 750 K (*1*). Under these conditions, some of the TiO_2 is almost certainly partially reduced. Our results indicate that some partially reduced titania could diffuse through the metal particles to the surface of the metal. Reoxidation of the catalyst at 750 K restores chemisorption activity by desorbing TiO_2 from the metal surface or by diffusing the partially reduced titania back to the bulk oxide and reoxidizing it. Two very important questions which arise are what is the oxidation state of the diffusing species of titania and what is the coverage of this species when CO and H_2 adsorption is completely suppressed.

Coverages

The coverage of titania necessary to completely prevent CO and H_2 adsorption corresponds to Ti(385)/Pt(238) = 1.35, for which O(508)/Pt(238) = 0.8. For a freshly sputtered Pt_3Ti alloy, the Ti(385)/Pt(238) ratio is 3.8 (*17*). This would indicate that our titania coverages were very low; however, since Auger spectroscopy does sample some distance into the surface, calibrations obtained from alloys are not applicable to surface species. Since the electron beam was able to remove all of the oxygen from the surface, the titania in our experiments was completely on the surface. For bulk titania, we did not observe any beam damage effects.

A more reasonable estimate of coverage could be obtained from the O(508)/Pt(238) ratio. When we saturated our clean Pt foil with oxygen at 300 K, we found this ratio to be 0.3. Gland (*18*) found the same result for Pt(111) and determined that this corresponded to an oxygen atom coverage of $3.8 \times 10^{14}/\text{cm}^2$. These results indicate that an O(508)/Pt(238) = 0.8 corresponds to a coverage of $1.0 \times 10^{15}/\text{cm}^2$. This coverage is high enough so that suppressed adsorption is likely due to physical blocking of the surface.

Chemical State

For all coverages of titania, we observed an O(508)/Ti(385) ratio of 0.6 for the diffusing species. For multilayers of titania, we observed a ratio of 2.2, in reasonable agreement with the 2.5 ratio reported in the literature for TiO_2 (*19*). This same literature reference reported that the Auger ratio is 1.4 for TiO. These results indicate that the diffusing species is Ti_2O, which seems unlikely. As discussed previously, application of Auger spectra from bulk compounds is probably not applicable to a monolayer species. Therefore, it is not possible to determine exactly what the state of the titania is from Auger spectra.

The fact that titania is permanently removed from the surface when the sample is flashed in 10^{-5} Torr of oxygen is evidence that the titania is not TiO_2. Our interpretation of the results is that, in O_2, the titanium is oxidized to TiO_2, which cannot diffuse into the Pt bulk, but is desorbed from the surface when the sample is heated. As we discussed earlier, our results are also not consistent with the formation of an intermetallic, Pt–Ti compound. While thermodynamic calculations show that compound formation is possible, the species we observed was always a partial oxide. When oxygen was removed from the surface with the electron beam, the titanium did not segregate back to the surface following high-temperature treatment.

SUMMARY

We have found direct evidence for the reversible diffusion of a partially oxidized titanium species into the bulk of clean Pt. This species can be removed from Pt metal by flashing the sample in oxygen, but it cannot be removed by heating under vacuum or hydrogen. The adsorption properties of Pt contaminated with this titania correspond very well to those observed on conventional supported catalysts. Therefore, our results indicate that the unusual adsorption and reaction properties of titania-supported catalysts may be due to a similar species on the surface of the metal.

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