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A Study of the Migration and Stability of Titania on a Model Rh Catalyst[1]

We have examined growth and stability of titania overlayers which have been vapor deposited onto a Rh foil. Titania was found to grow layer by layer, with approximately 1 × 10^{15} TiO_x species/cm^2 in the first layer. Submonolayer coverages of titania were unaffected by heating the sample to temperatures as high as 1320 K. However, heating multilayer coverages to 1320 K resulted in one monolayer remaining on the surface, with the rest migrating into the Rh. The migrating titania could be brought back to the surface by removing the top monolayer and heating the sample above 900 K under vacuum. Saturation coverages of CO were found to decrease linearly with surface titania coverage, independent of sample treatment; however, annealing to high temperatures appears to remove defects in the titania overlayer. © 1990 Academic Press, Inc.

INTRODUCTION

Titania-supported Group VII metals have been the focus of considerable investigation due to their unusual chemisorption and reaction properties for CO hydrogenation (*1, 2*). While some questions still remain unanswered, it is now generally accepted that titania is able to migrate onto the metal crystallites under certain pretreatment conditions and that this titania decoration is responsible for at least some of the observed properties (*3–6*). Therefore, a number of investigators have modeled titania support effects by depositing titania onto bulk metals and have shown that suppressed chemisorption and enhanced methanation activities can be duplicated on these model systems (*7–12*). From this work, it appears that adsorption suppression requires a coverage of titania close to a monolayer (*13–15*), although it has been suggested that this monolayer may be "expanded" by high-temperature treatment on some metals (*16*).

Among the remaining questions with titania-supported metals are how is titania able to migrate onto the metal particles and what is the driving force causing this migration. We have examined these questions by studying the growth and stability of titania overlayers on Rh. First, we will show that titania has a strong affinity for the Rh surface and tends to form an even overlayer which is stable to very high temperatures. Second, on Rh, pretreatment conditions do not strongly affect the ability of titania to suppress CO adsorption. Third, titania in excess of one monolayer is able to migrate reversibly into a Rh foil and this process is rapid for temperatures greater than 900 K under ultrahigh vacuum.

EXPERIMENTAL

Details concerning the experimental equipment and procedures have been described elsewhere (*17*). Reproducible coverages of titania were deposited onto a Rh foil by vaporizing a Ti–Ta alloy source under 10^{-7} Torr O_2 in front of a quartz-crystal film thickness monitor and then rotating the Rh in front of the Ti source for a specified time after the flux had been measured. Following titania deposition, the Rh was heated under 10^{-7} Torr O_2 for 10 min at 650 K and then reduced under 5 × 10^{-8} Torr CO for 5 min at 650 K. During AES measurements, care was taken to keep electron exposures

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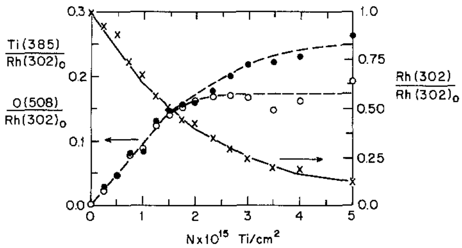

FIG. 1. Auger intensities for Ti (○), O (●), and Rh (×) as a function of the titania coverage measured using the film thickness monitor. The intensities are referenced to the Rh(302 eV) peak for a clean Rh foil. The solid line was calculated assuming layer-by-layer growth using parameters in the text.

low to avoid effects due to beam damage, which had been a problem in past experiments (*13*).

The reproducibility for obtaining a given titania coverage was excellent, and we estimate that absolute masses obtained from the film thickness monitor were probably good to within ~25%. This calibration was determined in separate experiments with Pt overlayers on an α-$Al_2O_3\{0001\}$, crystal in which the Pt fluxes were determined from measurements of metal particle size and density using electron microscopy and compared to coverages obtained with the monitor (*19*). The main uncertainty in calibrating absolute masses in our experiments comes from the fact that the calculated number density of Ti depends on the O/Ti stoichiometry for the film deposited on the monitor. We assumed that the Ti formed TiO_2 on the monitor during deposition, so that we may have underestimated the number density of Ti by as much as 20% if Ti was oxidized to only TiO. Finally, titania coverages obtained from comparison of the O(508 eV) peak intensity at a given titania coverage with that obtained on an O_2-saturated, Rh foil were in excellent agreement with coverages from the monitor. These calculations assumed a saturation coverage of ~0.4 × 10^{15} oxygen/cm^2 on clean Rh (*20*) and an O : Ti stoichiometry of 1, based on the observed O(508 eV)/Ti(385 eV) ratio in the monolayer regime (*21*).

RESULTS AND DISCUSSION

The growth of titania on the Rh foil at 300 K was studied by monitoring the Auger peak intensities as a function of coverage, with the results shown in Fig. 1. All of the AES data were normalized to the intensity of the clean Rh foil peak at 302 eV, Rh(302 eV)$_0$. The Ti(385 eV) and O(508 eV) signals increased and the Rh(302 eV) decreased linearly up to a coverage of ~1 × 10^{15} Ti/cm^2, a coverage close to that expected for one monolayer. For higher coverages, the slope changed. This suggests that the first layer of titania is complete before subsequent layers begin to form. Further evidence that this is the case is given by the solid line drawn through the Rh(302 eV) data, which was calculated for layer-by-layer growth with 1 × 10^{15} Ti/cm^2 in a layer, a titania density of 4.9 g/cm^3 (the density of TiO), and a mean free path of 0.75 nm for the Rh(302 eV) electrons. The numbers used for the calculation are reasonable and fit the data well. Finally, the strongest evidence for 2-D overlayer growth is that the Rh(302 eV) peak is much more strongly attenuated for a given titania coverage than would be expected if 3-D titania particles were formed. That titania overlayers grow in a layer-by-layer manner is consistent with recent single-crystal work for titania on both Ru(0001) (*16*) and Rh(111) (*15*).

The effect of annealing the titania overlayers for 1 min at different temperatures under vacuum is shown in Fig. 2a. For coverages less than 1 × 10^{15} Ti/cm^2, heating the sample to 1370 K had no effect on the Auger spectrum. This is shown by the dashed line through the ◇ points, which show the Ti(385 eV) intensity as a function of temperature following deposition of 0.3 × 10^{15} Ti/cm^2. The O(508 eV) and Rh(302 eV) intensities (not shown) were also unaffected by high temperatures for coverages less than ~1 × 10^{15} Ti/cm^2. However, for titania coverages greater than 1 × 10^{15} Ti/cm^2, thermal treatment did have a significant effect, as shown by the remaining data points which

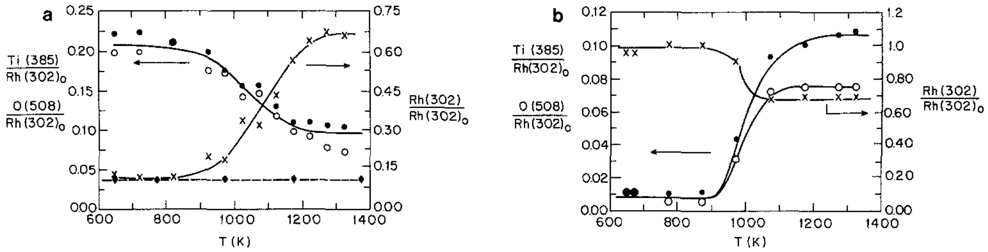

FIG. 2. (a) Auger intensities as a function of heating for titania coverages of 0.3 × 10^{15} Ti/cm^2 (results for Ti shown as ◇) and 5 × 10^{15} Ti/cm^2 (Ti (●), O (○), and Rh (×)). Heating had no effect on the titania overlayers at low coverages, while heating caused migration of multilayered species into the Rh. (b) Auger intensities for Ti (●), O (○), and Rh (×) following deposition of titania to a coverage corresponding to 5 × 10^{15} Ti/cm^2, annealing to 1320 K, sputtering the surface with Ar ions to remove the remaining titania, and heating under vacuum to the indicated temperature. The results show that TiO_x is able to migrate back to the surface from the bulk Rh.

were obtained following deposition of 5 × 10^{15} Ti/cm^2. After heating to temperatures greater than 900 K, there was a significant decrease in the O(508 eV) and Ti(385 eV) peaks and an increase in the Rh(302 eV) peak. Above ~1250 K, the Auger spectrum was close to that obtained following deposition of 1 × 10^{15} Ti/cm^2 at room temperature. While these results would be consistent with agglomeration of the titania overlayers into 3-D particles or desorption of the titania in excess of the first layer, results to be discussed next demonstrate that the excess titania is probably migrating from the surface, leaving one monolayer.

To gain further insight into where the excess titania had gone, the sample which had been heated to 1320 K following deposition of 5 × 10^{15} Ti/cm^2 was bombarded briefly with Ar ions to remove the top layer. The AES and CO TPD results following ion bombardment were very close to those obtained on the clean Rh foil. Auger specra were then taken of the sample after it had been heated under vacuum to various temperatures for 1 min, with the data shown in Fig. 2b. Above 900 K, significant amounts of both Ti and O migrated back to the surface. The Auger spectrum above 1100 K was very similar to that obtained following deposition of 1 × 10^{15} Ti/cm^2 at 300 K. Since the pressure in the vacuum system during these measurements was $<5 \times 10^{-10}$ Torr and the AES measurements were obtained very rapidly, these results cannot be due to oxidation of diffusing Ti. In addition, the O(508 eV)/Ti(385 eV) ratio remained constant at 0.7 as the titania reappeared, a ratio close to that measured after the initial heating of titania to 1320 K. Since this ratio is lower than that for the titania overlayers as deposited, the diffusing species probably has an O/Ti stoichiometry which is lower than that of the species formed in the initial preparation.

It is possible that the migration of titania in our experiments could be occurring along the grain boundaries of our polycrystalline foil; however, we do not believe this is likely. We measured the crystallite size in the foil to be approximately 1–3 μm, which would require the titania to migrate long distances across the surface if the grain boundaries were important. We believe it is much more likely that the titania is forming solutions with the metal near the surface. Further evidence for this comes from the results of Badyal *et al.* (*16*), whose high-temperature annealing results for titania on a Ru(0001) crystal look very similar to our Fig 2a. While they did not look for migration of titania back to the surface, they also observed a special stability for coverages up to 0.68 monolayer and they reported that titania in excess of this coverage disappeared from the surface upon heating.

The amount of titania which can migrate

into the Rh foil appears to be large. In separate experiments, we deposited a coverage of titania corresponding to 35×10^{15} Ti/cm^2, in 5×10^{15} Ti/cm^2 steps with oxidation and high-temperature annealing at each step. The Auger spectrum at the end of this procedure was identical to that obtained after heating with a coverage of titania corresponding to 5×10^{15} Ti/cm^2. This would imply that titania must be migrating deep into the surface.

We also examined the effect of titania on adsorption of CO using TPD. While changes in adsorption properties have been reported for studies of titania on Ru (*16*) and Ni (*11, 12*) we found that the peak temperatures and shapes were unchanged by the presence of titania on Rh, independent of the annealing temperature of the overlayer. Therefore, we observe no evidence for electronic interactions between the CO and the titania. Only saturation coverages were affected. The relative area under the TPD curves declined linearly with titania coverage up to $\sim 1.2 \times 10^{15}$ Ti/cm^2, close to the monolayer coverage. Also, the extent to which submonolayer quantities of titania suppressed adsorption was not changed by annealing. We find no evidence for "expanded" monolayers on Rh such as has been reported for Ru (*16*). These results imply that adsorption suppression is due to steric blocking of the surface. It should be noted, however, that small amounts of CO, ~5 to 10% of clean surface coverages, were able to adsorb on unannealed samples, even after deposition of 5×10^{15} Ti/cm^2. This residual adsorption could be removed by anealing the sample above 900 K, which suggests that the as-deposited overlayer contains defects which are removed by annealing. Apparently high temperatures allow the titania to spread across the surface and form a more uniform overlayer, as well as to migrate from the surface.

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