# ALUMINA AND TITANIA OVERLAYERS ON RHODIUM: A COMPARISON OF THE CHEMISORPTION AND CATALYTIC PROPERTIES

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The effects of submonolayer deposits  $AIO_x$  on the adsorption and hydrogenation of CO on a Rh foil have been investigated and compared with the earlier studied effects of TiO<sub>x</sub> deposits.  $AIO_x$  is found to suppress CO chemisorption in direct proportion to  $AIO_x$  coverage without affecting the energy of adsorption, indicating that the only function of  $AIO_x$  is site blockage. CO hydrogenation activity of Rh decreases in proportion to  $AIO_x$  coverage, but no change is observed in product selectivity or rate parameters for methane synthesis. By contrast, TiO<sub>x</sub> suppresses CO chemisorption to an extent greater than that expected for simple site blockage. With increasing TiO<sub>x</sub> coverage, the CO hydrogenation activity of Rh pastes through a maximum at  $\theta_{TiO_x} = 0.15$  ML. The rate parameters for methane synthesis are affected by TiO<sub>x</sub> coverage: relative to clean Rh, the activation energy is lower and the partial dependences on H<sub>2</sub> and CO are both larger. The unusual effects of TiO<sub>x</sub> are attributed to the formation of Ti<sup>3+</sup> cationic centers at the perimeter of TiO<sub>x</sub> islands present on the Rh surface.

#### 1. Introduction

A growing body of evidence indicates that the effects of support composition on the catalytic properties of small metal particles can be attributed to metal oxide moieties transported from the support onto the surface of the metal particles [1-10]. In an attempt to better understand how metal oxide moieties influence the adsorptive and catalytic properties of metals, several

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groups have begun to study the properties of metal foils and single crystals decorated with small amounts of metal oxide. Takatani and Chung [4] and Raupp and Durnesic [11,12] have found that submonolayer quantities of titania cause a suppression in the CO chemisorption capacity of Ni(111) surfaces. Similar findings were obtained by Dwyer et al. [13] for titania deposited on Pt foil, and by Ko et al. [14,15] for titania deposited on Pt, Pd, and Rh foils. Results from our own laboratory [16] indicate that this suppression is a non-linear function of coverage possibly indicating an interaction between Ti<sup>3+</sup> and adjacent Rh atoms at the titania-rhodium interface. The influence of alumina, silica, and niobia on the CO chemisorption capacity of Pt have also been investigated [17]. These studies show that for a given oxide coverage, niobia suppresses CO chemisorption to a level comparable to that of titania, but silica and alumina have a smaller effect.

Titania deposits have also been found to affect significantly the kinetics of CO hydrogenation on Group VIII metals. Chung et al. (18) observed a five-fold increase in reaction rate over Ni(111) at a titania coverage of 0.075 ML while our own results [19,20] showed a three-fold enhancement on a Rh foil at a coverage of 0.15 ML. Decreases in the activation energy of 7.6 and 10 kcal/mol were also observed for TiO<sub>x</sub> on Rh and Pt foils, respectively [20,21]. The activation energy for a niobia promoted Pt foil was found to be nearly identical to that for a titania-promoted Pt foil [22].

In this paper, we present our findings for CO chemisorption and CO hydrogenation on the  $AlO_x/Rh$  system and compare them to those obtained earlier for the  $TiO_x/Rh$  system. As in our earlier studies, the coverage was determined by plotting the Auger electron spectroscopy (AES) peak intensities as a function of dosing time. In contrast to our results for  $TiO_x$ , temperature programmed desorption (TPD) of CO and atmospheric-pressure hydrogenation of CO on  $AlO_x/Rh$  indicate that alumina overlayers do not modify the chemical properties of the Rh surface and only serve to diminish the number of active sites.

### 2. Experimental

Sample preparation and characterization were performed in a Varian ultrahigh vacuum (UHV) chamber equipped with an Auger electron spectrometer, a quadrupole mass spectrometer, and an atmospheric-pressure isolation cell. This apparatus is identical to that used in our earlier studies of  $TiO_x$  on rhodium [16]. A rhodium foil (99.8% purity) served as the sample substrate. The foil was mounted on 0.020 inch Rh wire for the temperature programmed desorption studies and on 0.020 inch Pt wire for the reaction studies. The foil was heated resistively and the temperature monitored by a thermocouple spot-welded to one face of the foil.

The Rh feil was cleaned by Ar ion bombardment and then annealed at 1273 K. Aluminum was deposited onto the foil by evaporating a small amount of aluminum metal (99.9995% pure) from a heated alumina crucible mounted inside the vacuum chamber. An externally operated shutter located in front of the evaporator was used to control the amount of aluminum deposited. Following the deposition of a desired amount of aluminum, the foil was oxidized at 353 K in 250 Torr of O<sub>2</sub> or at 623 K in 10<sup>-6</sup> Torr of O<sub>2</sub> to produce an AlO<sub>x</sub> overlayer. Identical results were obtained with both methods of oxidation. Oxygen bound to the rhodium was removed by room temperature exposure of the sample to CO followed by heating to 773 K to form CO<sub>2</sub>. The CO exposure step was repeated until no further CO<sub>2</sub> was produced.

The equipment and procedure for the atmospheric-pressure reaction studies was identical to those used in our study of CO hydrogenation on a TiO<sub>x</sub>/Rh catalyst [19,20]. Reactions were carried out in batch mode in the isolation cell at a total pressure of 1 atm. The reaction gas mixture consisted of 0.33 atm CO and 0.67 atm H<sub>2</sub>, except in the partial pressure dependence studies. In the latter case, lower reactant partial pressures were employed and argon was added to bring the total pressure to 1 atm. Circulation of the reaction gas mixture (at 200 cm<sup>3</sup>/min) began 20 min before the sample was heated to reaction temperature. Gas samples were removed periodically and sent to a gas chromatograph for hydrocarbon analysis. Reaction rates were calculated from product accumulation-versus-time plots. The rates usually remained constant during the course of the hour-long reactions.

#### 3. Results and discussion

### 3.1. MO<sub>x</sub> coverage and stoichiometry

The overlayer coverage was determined from a plot of the normalized AES peak intensities as a function of dosing time. Shown in fig. 1 are the effects of aluminum exposure on the intensities of the Rh (302 eV), Al (55 eV), ard O (508 eV) AES peaks, recorded after sample oxidation and CO titration. It is apparent that during the initial five minutes of evaporation, the intensities of all three species change linearly with evaporation time, a pattern indicative of the predominantly two-dimensional expansion of the AlO<sub>x</sub> islands. For larger deposition times, the intensities follow curves of decreasing slope. Monolayer coverage is taken to be the point at which the deviation from linearity begins. This point corresponds to an attenuation of the rhodium signal to  $45 \pm 5\%$  of the value for the bare surface. Attenuations to 50-60% of the bare substrate



Fig. 1. Normalized Auger peak-to-peak heights corresponding to the growth of the  $AlO_x$  overlayer on Rh foil with increasing Al dosage. Solid lines denote trends expected for two-dimensional growth for the first monolayer. Dashed lines show expected behavior for layered growth beyond the first monolayer.

value are typical of monolayer coverage for metal-on-metal growth in the case of substrates for which the AES electrons have energies of 300-400 eV [1-16]. The higher degree of attenuation associated with the AlO<sub>x</sub> monolayer may therefore be due to an overlayer structure that is greater in thickness than a single metallic monolayer [16].

Beyond the point ascribed to monolayer coverage, the AES intensities change more slowly than predicted for layer-by-layer growth (dashed lines in fig. 1). This pattern indicates a progressively larger proportion of multilayer growth. It is also possible that a small amount of multilayer growth occurs before the completion of the first monolayer of oxide.

The stoichiometry of the alumina overlayers was determined by comparing the O/Al AES peak ratio with that of a bulk alumina sample. The recorded AES spectra of the alumina overlayers indicate an O/Al atomic ratio around 1.0. After correction for the differences in Al and O Auger electron escape depths, the O/Al ratio becomes  $1.4 \pm 0.2$ , indicating that the alumina overlayers are nearly stoichiometric. This finding was verified by XPS analysis of an AlO<sub>x</sub>/Rh sample [23].

In our earlier study on the effects of  $\text{TiO}_x$  surface species on the CO chemisorption properties of Rh, we found that titania also grows on Rh through a mechanism similar to that described here for  $\text{AlO}_x$ , and exists as a nearly stoichiometric oxide, approximately  $\text{TiO}_{1.9}$ . The appearance of two-dimensional growth for both oxides on rhodium is consistent with the phe-



Fig. 2. A comparison of the effects of metal oxide overlayers on the CO chemisorption capacity of rhodium (normalized to the value for clean Rh). Solid circles denote the results for  $TiO_x$  overlayers while open squares are those for AlO<sub>x</sub> overlayers. Exposures of 4 L CO were employed.

nomenon of wetting by a low surface energy material of a high surface energy substrate. Beyond monolayer coverage, no exposed patches of the metal substrate exist and so minimization of the oxide surface area becomes a dominant factor in the overlayer growth. This results in increasing three-dimensional clustering, as observed.

#### 3.2. CO chemisorption on $MO_x$ / Rh

Temperature programmed desorption was employed to study CO chemisorption on AlO<sub>x</sub>/Rh. Desorption spectra were taken after exposure to 4 langmuir (L) (1 langmuir =  $1 \times 10^{-6}$  Torr s) of CO at room temperature. This CO exposure corresponds to 75% saturation on the clean Rh surface [16]. Repeated exposures were made to ensure a constant amount of CO desorbing from the surface. Only a single peak was observed in the spectrum for CO desorption from clean Rh and after deposition of alumina. Neither the position nor the shape of the peak was affected significantly by the AlO<sub>x</sub> coverage. The amount of chemisorbed CO, determined from the area of the TPD peaks, is plotted as a function of AlO<sub>x</sub> coverage in fig. 2. A linear decrease in the CO chemisorption capacity as a function of the AlO<sub>x</sub> coverage is observed. A residual amount of CO of about 8% of the clean Rh surface value was seen to adsorb at coverages slightly above one monolayer of alumina suggesting the existence of imperfections in the AlO<sub>x</sub> monolayer. Our results for the CO chemisorption capacity of the  $TiO_x$ -covered Rh surface [16] are also presented in fig. 2, for comparison with those of  $AlO_x$  on Rh. It is evident that the suppression of CO chemisorption is much greater when  $TiO_x$  is present on the surface than  $AlO_x$ . Alumina appears to block CO chemisorption in direct proportion to the coverage while in the case of titania, the attenuation in CO chemisorption capacity is much greater than that expected from mere physical blockage of chemisorption sites.

The suppression of CO chemisorption when titania is present has been identified with an absence of CO chemisorption at Rh sites underneath as well as adjacent to  $TiO_x$  islands [16].  $Ti^{3+}$  species at the perimeter of these islands may interact with neighboring Rh atoms to weaken CO bonding. The differences in the effects of  $TiO_x$  and  $AlO_x$  overlayers on the CO chemisorption capacity of Rh can then be attributed to differences in the degree of interaction between the oxide and neighboring Rh atoms or to differences in the dispersion of the oxides on the surface. In particular, if  $AlO_x$  islands have little or no influence on Rh sites adjacent to the islands, one would anticipate a linear decrease in CO chemisorption capacity with  $AlO_x$  coverage. An identical trend would be observed, though, if  $AlO_x$  and  $TiO_x$  islands altered the properties of Rh sites adjacent to the islands to the same degree but the size of the  $AlO_x$  islands was much larger than that of the  $TiO_x$  islands for the same MO<sub>x</sub> coverage. Unfortunately, the data in fig. 2 do not permit us to decide which of these two possibilities prevails.

#### 3.3. CO hydrogenation over MO<sub>x</sub> / Rh

CO hydrogenation was carried out at 553 K, a total pressure of 1 atm, and a H<sub>2</sub>: CO ratio of 2:1 to assess the effect of AlO<sub>x</sub> on the catalytic activity of Rh. The results of these experiments are displayed in fig. 3 along with those for TiO<sub>x</sub>/Rh [20]. The methanation rates for the Rh foils employed in the studies of the AlO<sub>x</sub>/Rh and TiO<sub>x</sub>/Rh were  $6.1 \times 10^{-11}$  mol/cm<sup>2</sup> s and  $19.4 \times 10^{-11}$  mol/cm<sup>2</sup> s, respectively. Such variations in the absolute rates between two different foil samples was common. Fig. 3 shows that the rate of methane formation decreases linearly with alumina coverage. This trend is in strong contrast to that for TiO<sub>x</sub>/Rh for which the methanation rate passes through a sharp maximum at a TiO<sub>x</sub> coverage of ~ 0.15 ML. Above this value, the methanation rate decreases monotonically and eventually approaches the line characteristic of AlO<sub>x</sub>/Rh.

Ethylene, ethane, and propylene were also observed in the products. As seen in fig. 4a, the product selectivities are invariant with  $AlO_x$  coverage and identical to those for pure Rh. Quite a different trend is seen in fig. 4b for  $TiO_x$  deposition on Rh. In this case the methane selectivity goes to a minimum and the  $C_{2+}$  selectivity goes to a maximum at a  $TiO_x$  coverage of ~ 0.20 M<sup>1</sup>. The



Fig. 3. A comparison of the effects of metal oxide overlayers on the CO hydrogenation rate of rhodium (normalized to the value for clean Rh). Solid circles denote the results for  $TiO_x$  overlayers while open squares are those for  $AIO_x$  overlayers. Reaction conditions are: 1 atm, 553 K, and  $H_2/CO$  ratio of 2:1.

proportion of olefins in the product also goes through a maximum at about the same coverage.

The activation energy and the  $H_2$  and CO partial pressure dependences were determined for an AlO<sub>x</sub> coverage of ~ 0.40 ML. The resulting values are given in table 1. Also given for comparison are the corresponding rate parameters for pure Rh and TiO<sub>x</sub>-covered Rh [19,20]. Clearly, alumina does not affect the kinetics of the CO hydrogenation reaction to any significant extent. However, at a TiO<sub>x</sub> coverage for which the methanation rate is near its maximum, the rate parameters are significantly different from those for pure Rh. The activation energy decreases from 24.4 kcal/mol for clean Rh to 16.8 kcal/mol for 0.24 ML TiO<sub>x</sub> while the hydrogen reaction order increases from 1.0 for clean Rh to 2.6 for 0.10 ML TiO<sub>x</sub>. The CO reaction order also changes from -1.0 for clean Rh to -0.3 for 0.15 ML TiO<sub>x</sub>.

The enhancement in CO hydrogenation activity on rhodium with  $TiO_x$  surface species has been ascribed to the presence of  $Ti^{3+}$  sites at the perimeter of  $TiO_x$  islands [24–31]. It is proposed that these  $Ti^{3+}$  sites interact with the oxygen in CO chemisorbed on nearby Rh atoms and assist in the dissociation of CO. The dissociation of CO is believed to be the rate-determining step in



Fig. 4. Product selectivity for CO hydrogenation as a function of metal oxide coverage. (a) Selectivity as a function of alumina coverage. (b) Selectivity as a function of titania coverage. Reaction conditions are identical to those in fig. 3.

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Catalyst	$E_{\rm a}$ (kcal/mol)	m	n
Clean Rh	24.4	- 1.0	1.0
(0.4 ML)AlO <sub>x</sub> /Rh	24.7	-0.6	1.1
$(0.2 \text{ ML})\text{TiO}_x/\text{Rh}$	19.0	-0.3	2.4

 Table 1

 Rate parameters for methane formation<sup>a)</sup>

<sup>a)</sup> $R_{CH_4} = k_0 \exp(-E_a/RT) P_{H_2}^n P_{CO}^m$ .

this reaction and so the participation of  $Ti^{3+}$  species in the reaction leads to a higher activity.

The linear decline in methanation activity with increasing  $AlO_x$  coverage and the absence of any effect of  $AlO_x$  on the reaction kinetics suggest that the only effect of  $AlO_x$  is to block active Rh sites. As was the case for CO chemisorption, the difference in behavior of  $AlO_x/Rh$  and  $TiO_x/Rh$  can be attributed to two possibilities: differences in metal-metal oxide interaction strength and differences in oxide dispersion. If reduced Al species do participate in the dissociation of CO, then the alumina island size must be sufficiently large so that this contribution is negligible (i.e., the total number of reduced Al species at the island perimeter is small). The absence of any participation by Al would also give the same result.

Although our studies of CO desorption and hydrogenation do not yield information on whether reduced Al species at the perimeter  $AlO_x$  islands play a role in the surface chemistry, thermodynamic considerations reflect the difficulty of forming these species. As shown below, the free energy of reduction of TiO<sub>2</sub> (Ti<sup>4+</sup>) to TiO<sub>2</sub> (Ti<sup>3+</sup>) is considerably lower than the free energy for reducing  $Al_2O_3$  (Al<sup>3+</sup>) to aluminum (Al<sup>0</sup>):

$$TiO_2 + \frac{1}{2}H_2 \rightleftharpoons \frac{1}{2}Ti_2O_3 + \frac{1}{2}H_2O, \quad \Delta G^0 = 3.5 \text{ kcal/mol},$$
  
 $\frac{1}{2}Al_2O_3 + \frac{4}{2}H_1 \rightleftharpoons Al + \frac{3}{2}H_2O, \quad \Delta G^0 = 106.5 \text{ kcal/mol}.$ 

Analyses of TiO<sub>x</sub> and AlO<sub>x</sub> overlayers on rhodium by XPS confirm the predictions of bulk thermodynamics [23]. As deposited TiO<sub>x</sub> overlayers were found to contain from 5–45% of the titanium in the Ti<sup>3+</sup> state, the proportion increasing with decreasing TiO<sub>x</sub> coverage. Since the perimeter-to-area ratio also increases with decreasing TiO<sub>x</sub> coverage, the XPS results suggest an abundance of Ti<sup>3+</sup> species along the perimeter of the TiO<sub>x</sub> islands. Upon reduction in H<sub>2</sub> (50 Torr H<sub>2</sub>, 753 K, 5 min), the proportion of Ti<sup>-+</sup> increased to as much as 65%. A similar analysis of ~ 0.2 ML AlO<sub>x</sub> on Rh showed less than 10% of the aluminum present as Al<sup>0</sup>, after reduction in H<sub>2</sub> (50 Torr H<sub>2</sub>, 753 K, 5 min).

These XPS results correlate with our findings for CO TPD and CO hydrogenation. The presence of reduced Ti species coincides with the additional suppression of CO chemisorption (beyond that due to site blocking) and the enhancement in CO hydrogenation activity. This behavior for CO chemisorption and CO hydrogenation are absent for the  $AlO_x/Rh$  system where reduced species are not present in significant amounts. Thermodynamic arguments would suggest that, even if the alumina island site is identical to that of titania, the formation of reduced Al species is difficult.

#### 4. Conclusions

Submonolayer deposits of  $TiO_x$  and  $AlO_x$  are found to affect the adsorptive and catalytic properties of a Rh foil in a radically different fashion. AlC. suppresses the chemisorption of CO in direct proportion to the AlO, coverage without affecting the energy of adsorption, indicating that the only function of AlO, is site blockage. Likewise, the activity of Rh for CO hydrogenation decreases in proportion to AlO<sub>x</sub> coverage, but no change is observed in product selectivity or rate parameters for methane synthesis. By contrast, TiO, suppresses CO chemisorption to an extent greater than that expected for simple site blockage. With increasing TiO<sub>x</sub> coverage, the CO hydrogenation activity of Rh passes through a maximum at  $\theta_{\text{TiO}} = 0.15$  ML, while the selectivity of C<sub>2+</sub> products passes through a maximum at  $\theta_{\text{TiO}_{2}} = 0.25$  ML. The rate parameters for methane synthesis are affected by TiO, coverage: relative to the parameters observed for clean Rh, the activation energy is lower and the partial pressure dependences on  $H_2$  and CO are both higher. The unusual effects of TiO, are attributed to the formation of Ti<sup>3+</sup> cationic centers at the perimeter of  $TiO_x$  islands present on the Rh surface.

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