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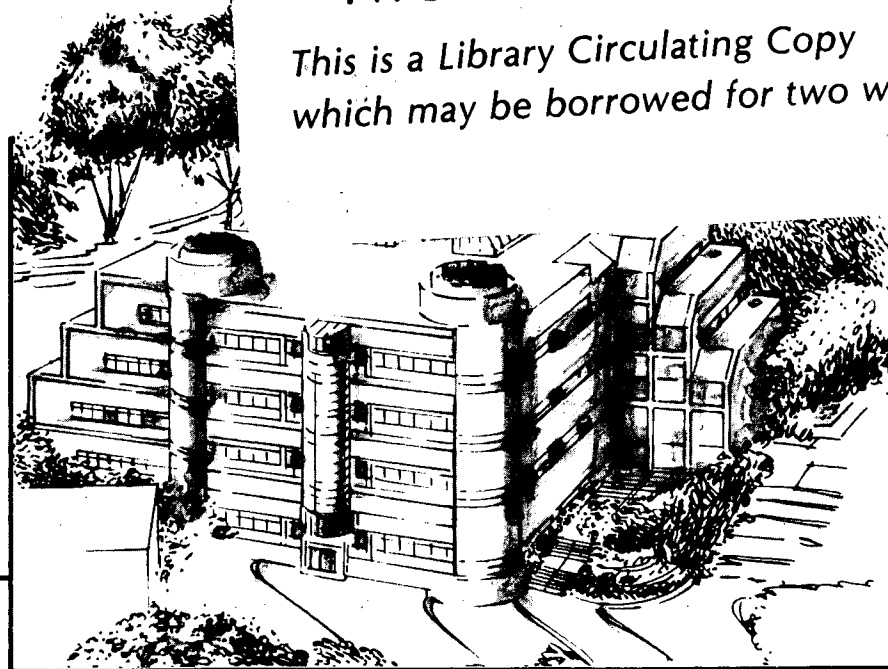Role Characterization in Catalyst Development,
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Introduction

Interest in the composition and structure of submonolayer metal oxide deposits on metals has developed as a consequence of growing evidence that such deposits influence the adsorptive and catalytic properties of the substrate metal [see for example ref. (1)]. In particular, it has been shown that titania deposited on a Ni(111) (2) surface and on the surface of Pt and Rh foils (3,4) will enhance the activity of the metal for CO hydrogenation. Similar results have also been reported for niobia deposited on a Pt foil (5). The present paper discusses the characterization of titania overlayers deposited on the surface of a polycrystalline Rh foil and a Rh(111) surface.

Experimental

Samples were prepared by evaporation of titanium onto a Rh foil or a Rh(111) single crystal. Subsequent oxidation with oxygen at 623 K then produced a titania overlayer on the Rh substrate. Oxygen bound to the Rh was removed as carbon dioxide by repeated exposure of the oxidized sample to 4 L of carbon monoxide followed by flashing to 773 K. The freshly deposited overlayer was then characterized by ISS, AES, and XPS. The effects of the overlayer on the substrate were probed by temperature-programmed desorption of carbon monoxide, by the hydrogenation of carbon monoxide, and by the hydrogenolysis of ethane. All of these experiments were carried out in one of two ultra high vacuum chambers, one of which was equipped with a high pressure cell for carrying out catalytic reactions.

Results

Coverage of the Rh surface by titania was followed by means of ISS and AES. Figures 1 and 2 show the ISS and AES signals for Rh as a function of

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the deposition times for metallic titanium. The ISS signal exhibits a linear decline with the deposition time, and at a time of 150-175 s, the Rh signal goes to zero. The Rh AES signal also follows a linear decrease in intensity for deposition times of less than 175 s. For longer deposition times, the AES signal decreases more slowly. Similar results were obtained with both single crystal and polycrystalline samples.

The linear decline in both the Rh ISS and AES signals for deposition times of less than 175 s, indicates that the first monolayer of titania is deposited as a two-dimensional overlayer. If layer-by-layer growth were sustained beyond the the completion of the first monolayer, then the AES signal would be expected to follow solid line shown in Fig.2. The deviation of the data from the curve for layer-by-layer growth in the time period of 175 to 400 s is indicative of some three-dimensional growth in the second layer. For longer deposition times, however, the data return to the curve predicted for layer-by-layer growth.

Temperature-programed desorption (TPD) spectra of adsorbed carbon monoxide exhibit a single peak for carbon monoxide and no evidence of carbon dioxide formation. Neither the position nor the shape of the carbon monoxide peak is a function of titania coverage. A plot of carbon monoxide chemisorption capacity versus titania coverage is shown in Fig. 3. The CO coverage is observed to decrease linearly with in increasing titania coverage. A similar trend has been observed previously for titania deposited on a Pt foil (6) and on a Ru(0001) single crystal surface (7). The linear relationship between CO chemisorption capacity and titania coverage seen in Fig. 3 contrasts with that reported earlier by Levin et al. (8) for titania deposited on a Rh foil. As discussed by Williams et al. (9), this discrepancy is attributable to an incorrect determination of titania coverage by Levin et al. (8). When correctly interpreted, the data of Levin et al. (8) also show a linear dependence of CO chemisorption capacity on titania coverage. A further consequence of the reanalysis is that the

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titania coverages reported by Levin et al. (8) should be multiplied by a factor of 3.3 (9).

An XPS spectrum of the Ti(2p) core levels for Rh foil covered with 0.3 ML of titania is shown in Fig. 4 (10). Spectrum (1) obtained after oxidation, exhibits two peaks centered at 463.6 and 458.5 eV that can be assigned to the $2p_{1/2}$ and $2p_{3/2}$ core levels of Ti^{4+} (11). A slight assymetry is observed in the $2p_{3/2}$ peak on the low energy side, indicating the presence of a small percentage of Ti^{3+}. CO titration causes an attenuation of the Ti^{4+} peaks and and the appearance of a peak at 455.7 eV that is assigned to Ti^{3+} species (11). A peak at 461.4 eV is assigned to the corresponding Ti^{3+} ($2p_{1/2}$) level. H_2 reduction causes a further decrease of the Ti^{4+} peak intensity and a corresponding increase in the Ti^{3+} peak intensity. Small shifts to higher binding energies of the $2p_{3/2}$ peak of Ti^{4+} are also observed as the degree of reduction increases. In spectrum (3) of Fig. 4, for example, the $Ti^{4+}(2p_{3/2})$ binding energy is 459.0 eV. Reoxidation of the sample returns the titanium to the Ti^{4+} state. Similar changes in the XPS spectrum were observed for all titania coverages studied. The principal difference noted was an increase in the proportion of Ti^{3+} as the coverage of titania decreased. This trend suggests a preferential concentration of Ti^{3+} species at the periphery of the two-dimensional TiO_x islands.

Displayed in Fig. 5 is the methane production rate from CO and H_2 for varying TiO_x coverages (12). Reaction rates were measured at a temperature of 553 K, and at H_2 and CO partial pressures of 0.67 and 0.33 atm, respectively. With the addition of small amounts of TiO_x to the clean Rh surface, a sharp rise in reaction rate is noted. At the maximum corresponding to 0.15 ML [0.50 ML on the corrected scale (9)], a threefold

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increase in the rate is observed. Beyond this coverage, the rate decreases monotonically.

Titania promotion also alters the selctivity of Rh, as may be seen in Fig. 6. The methane content of the hydrocarbon product falls from a value of 94% when no titiania is present to nearly 60% for a titania coverage of 0.20 ML [0.66 ML on the corrected scale (9)]. Ethylene and propylene are the predominant higher hydrocarbon species, comprising roughly 34 mol% of the total hydrocarbon product. At higher titania coverages, the selectivities return to values more charateristic of clean Rh.

XPS characterization of TiO_x/Rh samples after their exposure to synthesis gas under reaction conditions showed that a significant fraction of the titanium ions were still in the Ti^{3+} state. A summary of these observations is given in Table 1. It is evident that sample pretreatment has only a moderate effect on the oxidation state of Ti in the TiO_x overlayer. It would thus appear that during reaction the oxidation state of Ti adjusts to reflect the composition of the gaseous environment. This conclusion concurs with the observation that prereduction of TiO_2-supported and TiO_2-promoted metal catalysts does not significantly change the activity of these catalysts for CO hydrogenation (13-16).

The enhancement in CO hydrogenation activity of Rh is ascribed to the presence of Ti^{3+} sites at the perimeter of TiO_x islands. It is proposed that these sites interact with the oxygen in CO chemisorbed on nearby Rh atoms and assist in the disociation of CO. Since the disociation of CO is believed to be the rate-limiting step in this reaction, the participation of Ti^{3+} in this step leads to a higher activity. The dependence of the methanation rate on TiO_x coverage, seen in Fig. 5, is attributable to the variation in the concentration of Ti^{3+} centers with TiO_x coverage.

The effects of titania deposits on the hydrogenolysis of ethane are quite

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different from those for the hydrogenation of CO. Ethane hydrogenolysis was carried out at 450 K with 25 torr ethane and 25 torr hydrogen. The rate of hydrogenolysis was found to decrease monotonically with increasing titania coverage, the curve exhibiting a shape nearly identical to that observed for CO chemisorption. The presence of titania on the Rh surface was found to have no effect on the activation energy for the reaction. Taken together, these results suggest that hydrogenolysis can occur only on those Rh sites not affected by titania islands.

Conclusions

Submonolayer deposits of titania grow on the surface of Rh in the form of two-dimensional islands until a coverage of nearly a monolayer is achieved, at which point some three-dimensional growth of the islands is observed. The titania islands exclude CO chemisorption on Rh sites covered by the titania. The Ti^{4+} ions in the overlayer are readily reduced to Ti^{3+}. This process begins at the perimeter of the islands and extends inwards as reduction proceeds. Titania promotion of Rh enhances the rate of CO hydrogenation by up to a factor of three and increases the selectivity to C_{2+} hydrocarbons. By contrast, the activity of Rh for the hydrogenolysis of ethane decreases monotonically with increasing titania promotion.

Acknowledgment

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Table 1

Percentage of Ti^{3+} Following CO Hydrogenation

θ_{TiO_x}	After CO Titration	After H_2 Reduction	After CO Hydrogenation
0.50	0.22	--	0.15
0.50	--	0.62	0.26

Figure Captions

Fig. 1 Rh ISS intensity versus titania evaporation time. The substrate is a Rh(111) surface.

Fig. 2 Rh AES intensity versus titania evaporation time. The substrate is a Rh(111) surface.

Fig. 3 CO chemisorption capacity versus titania coverage. The substrate is a Rh(111) surface.

Fig. 4 XPS spectra of the Ti(2p) region for 0.50 ML of TiO_x on a Rh foil. Spectra 1, 2, 3, and 4 were observed after oxidation, CO titration, H_2 reduction, and reoxidation, respectively.

Fig. 5 Methanation rate on TiO_x/Rh foil as a function of TiO_x coverage. Reaction conditions were 553 K, 1 atm total pressure, and a H_2:CO ratio of 2:1 (12). The indicated TiO_x coverages should be multiplied by a factor of 3.3 to account for the corrections recently reported by Williams et al. (9).
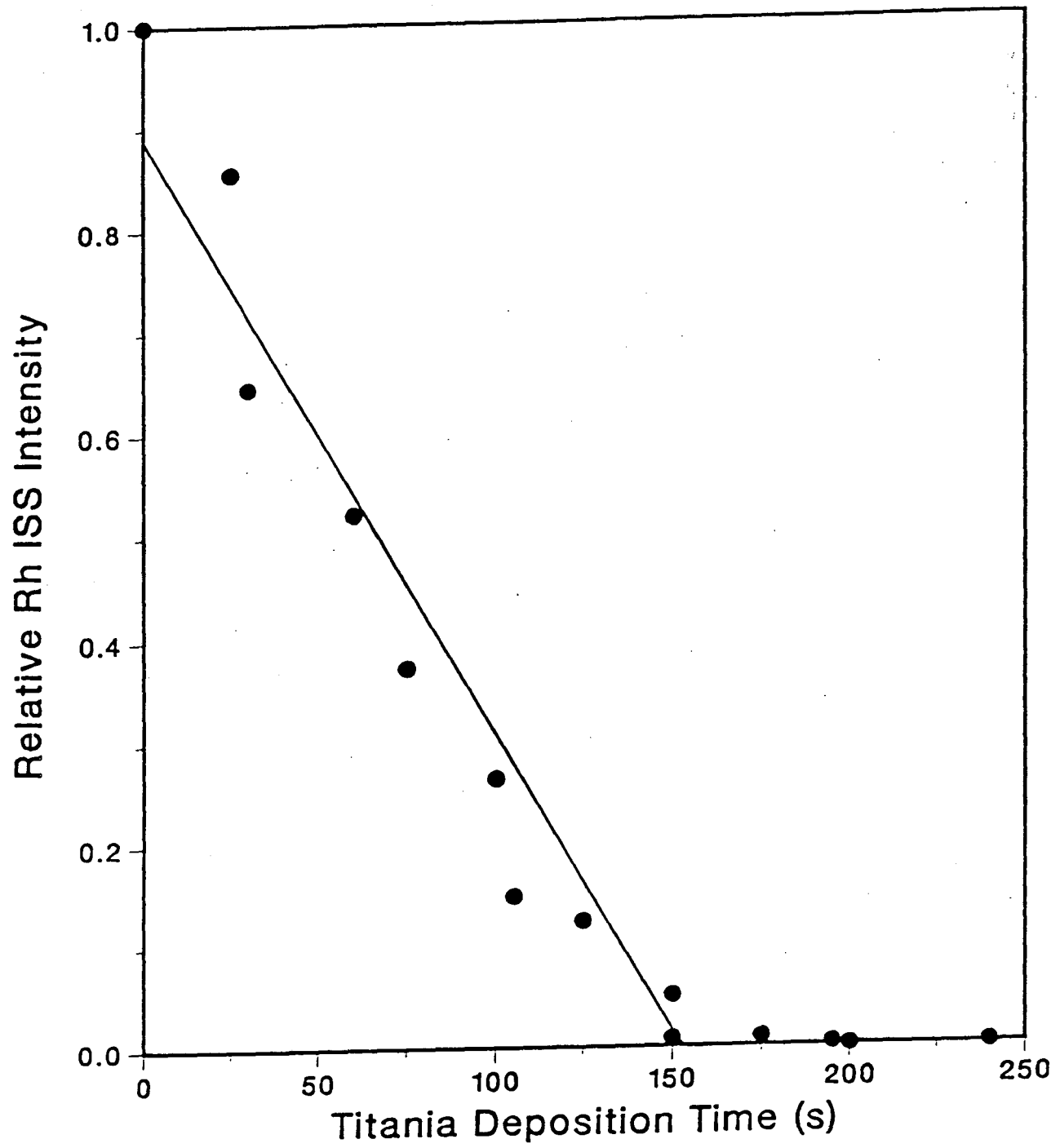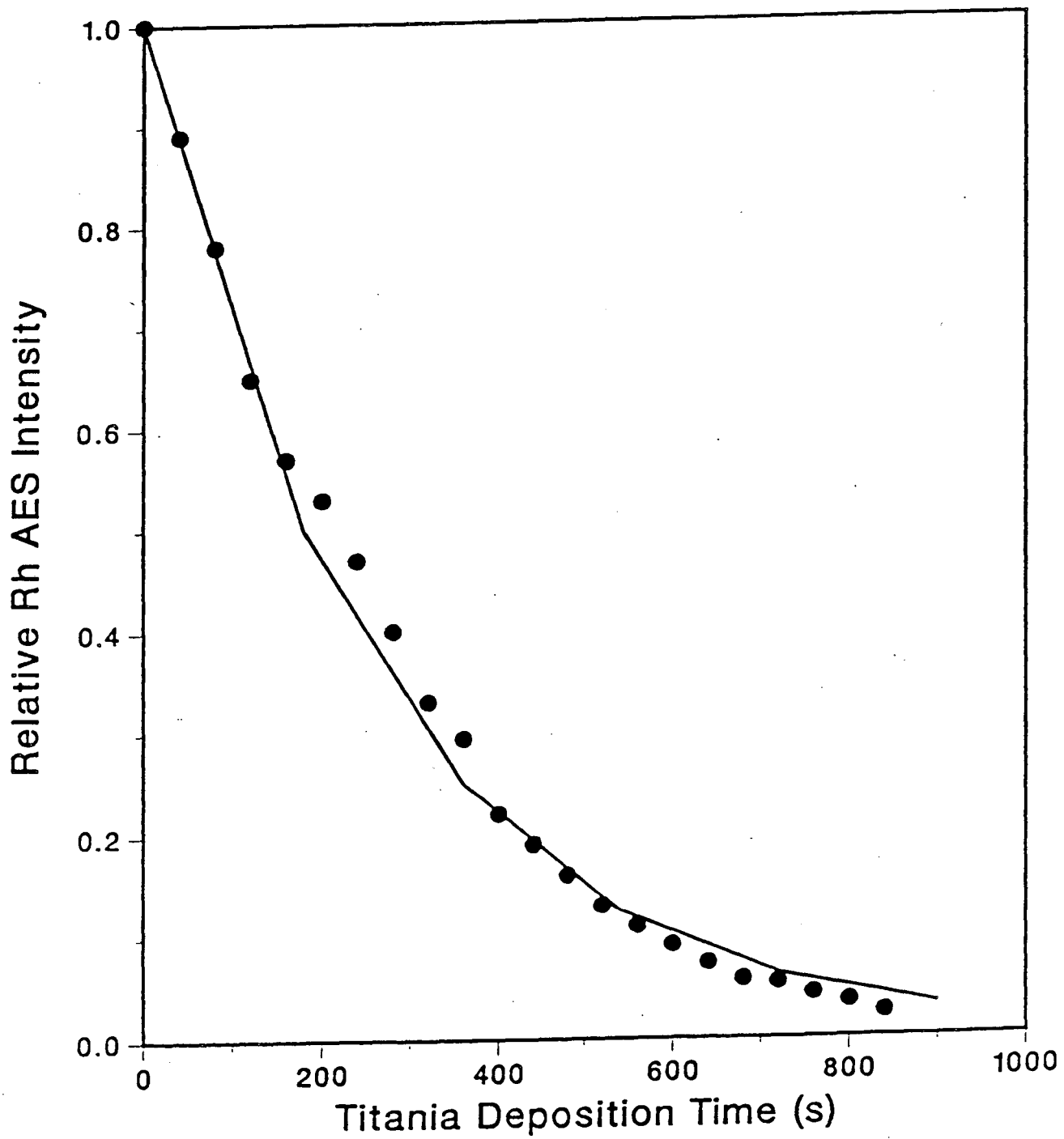
Fig. 6 Hydrocarbon product selectivity as a function of TiO_x coverage on a Rh foil (12). The indicated TiO_x coverages should be multiplied by a factor of 3.3 to account for the corrections recently reported by Williams et al. (9).
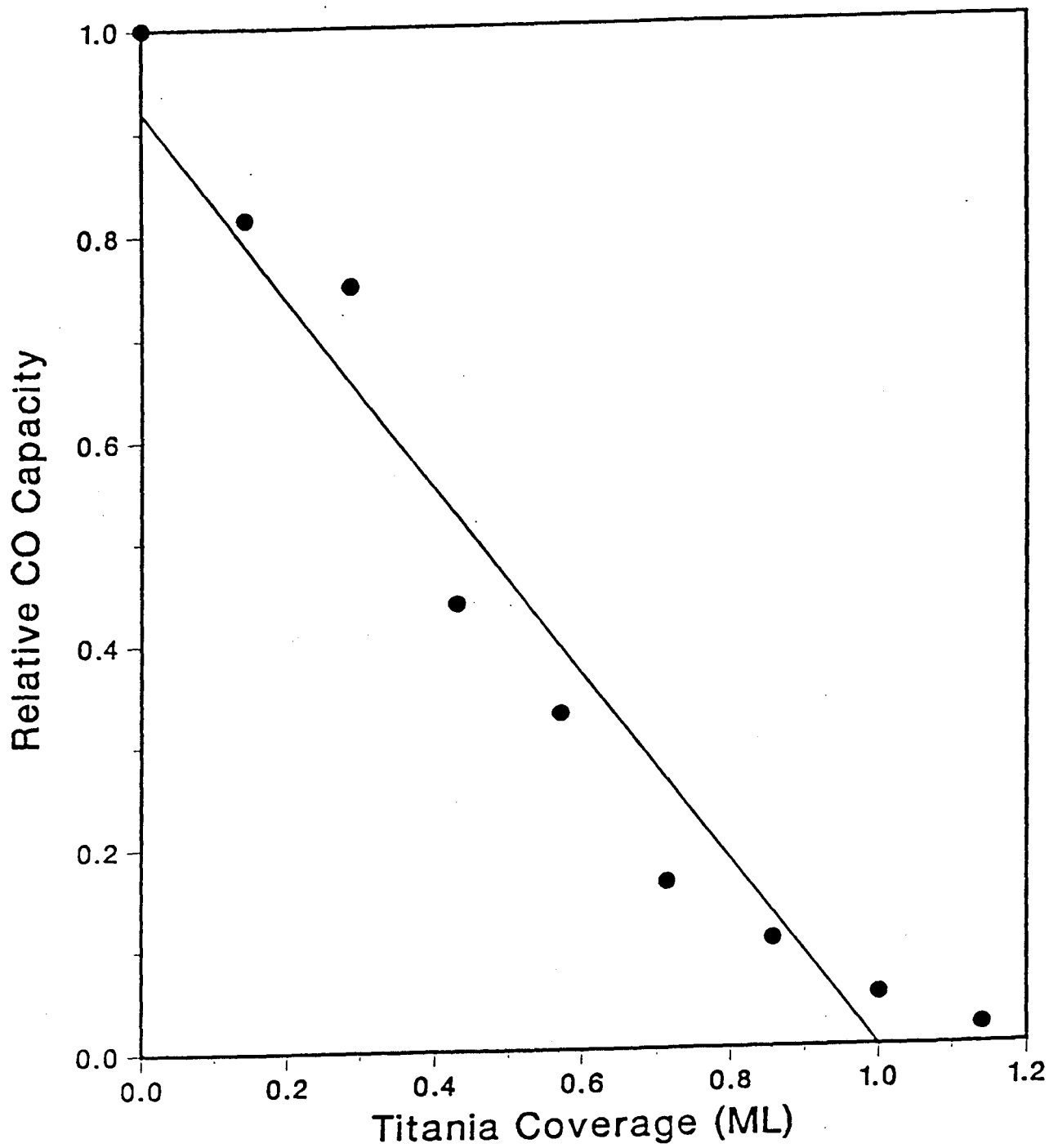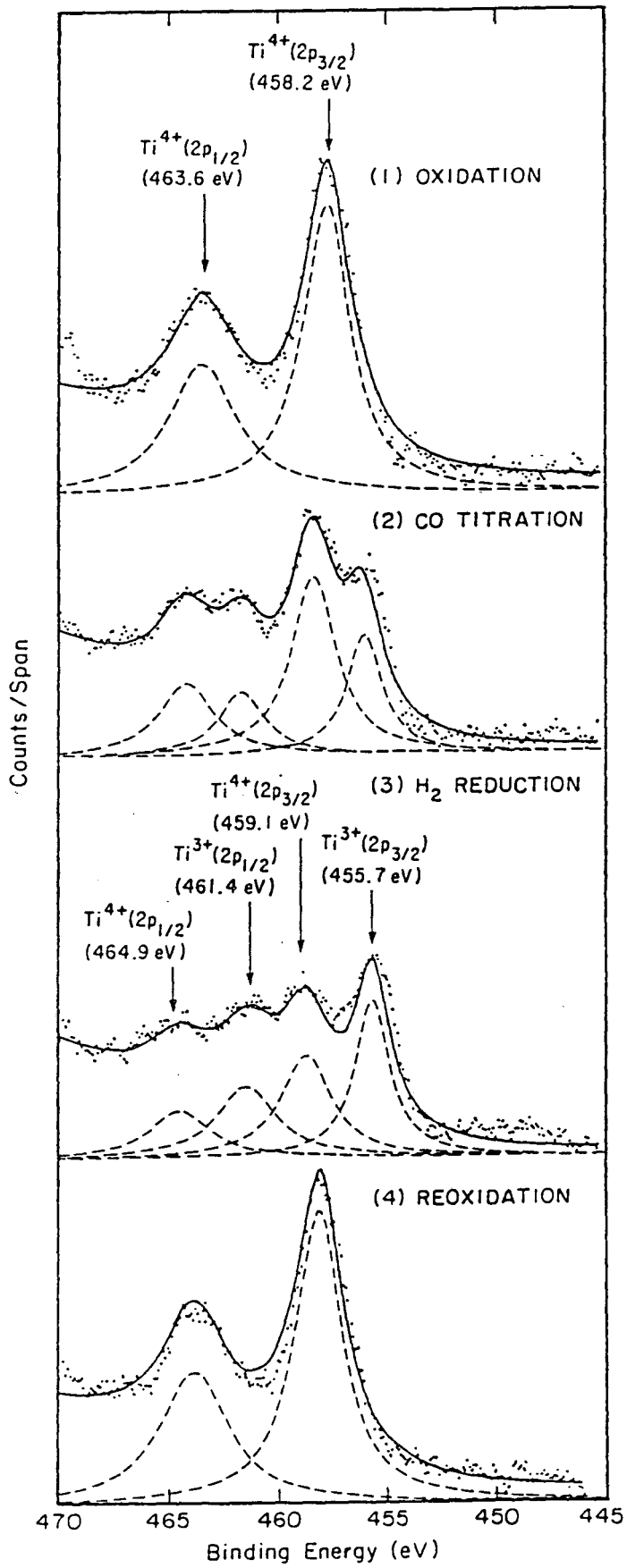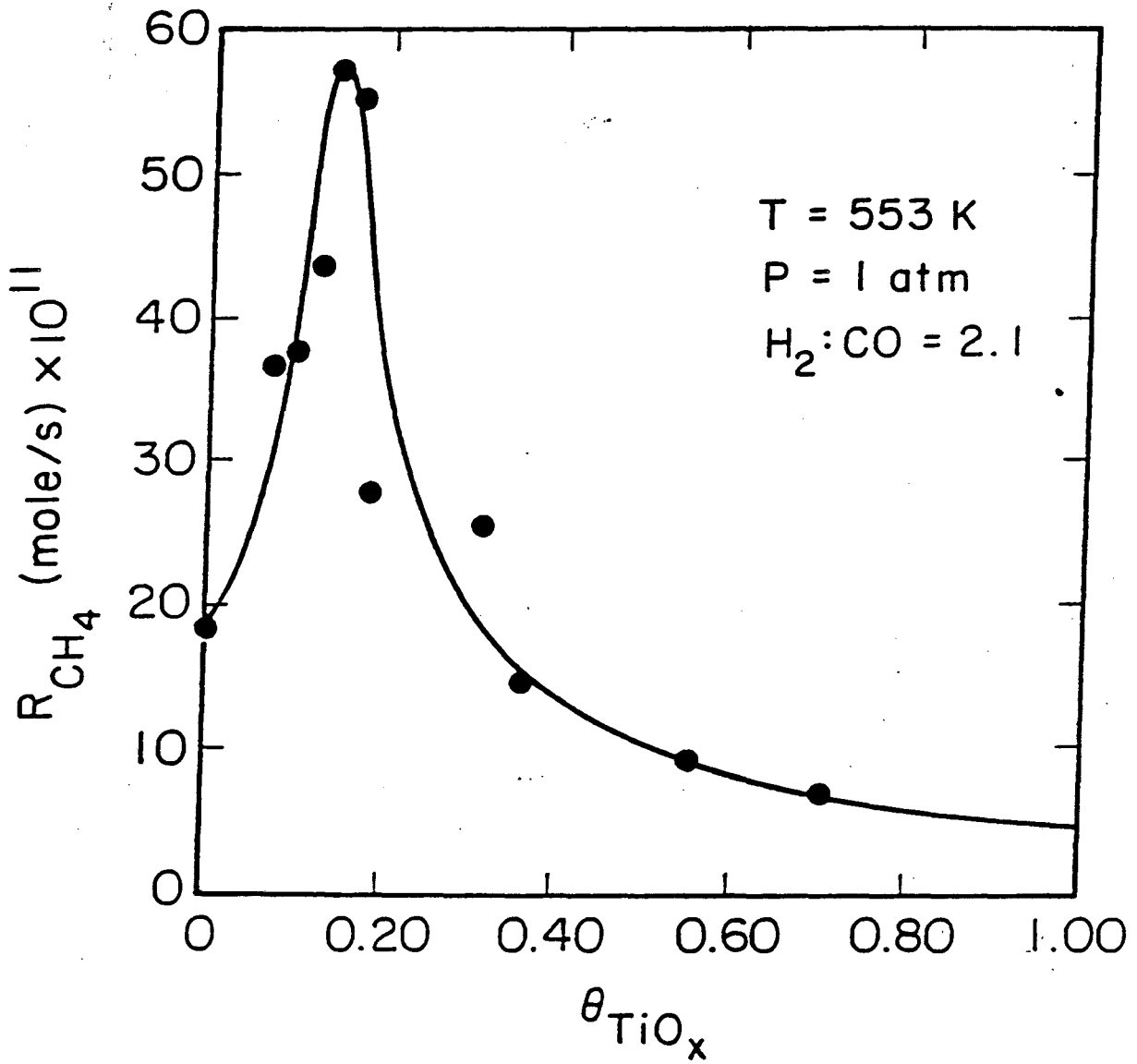
Fig. 1

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Fig. 2

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Fig. 3
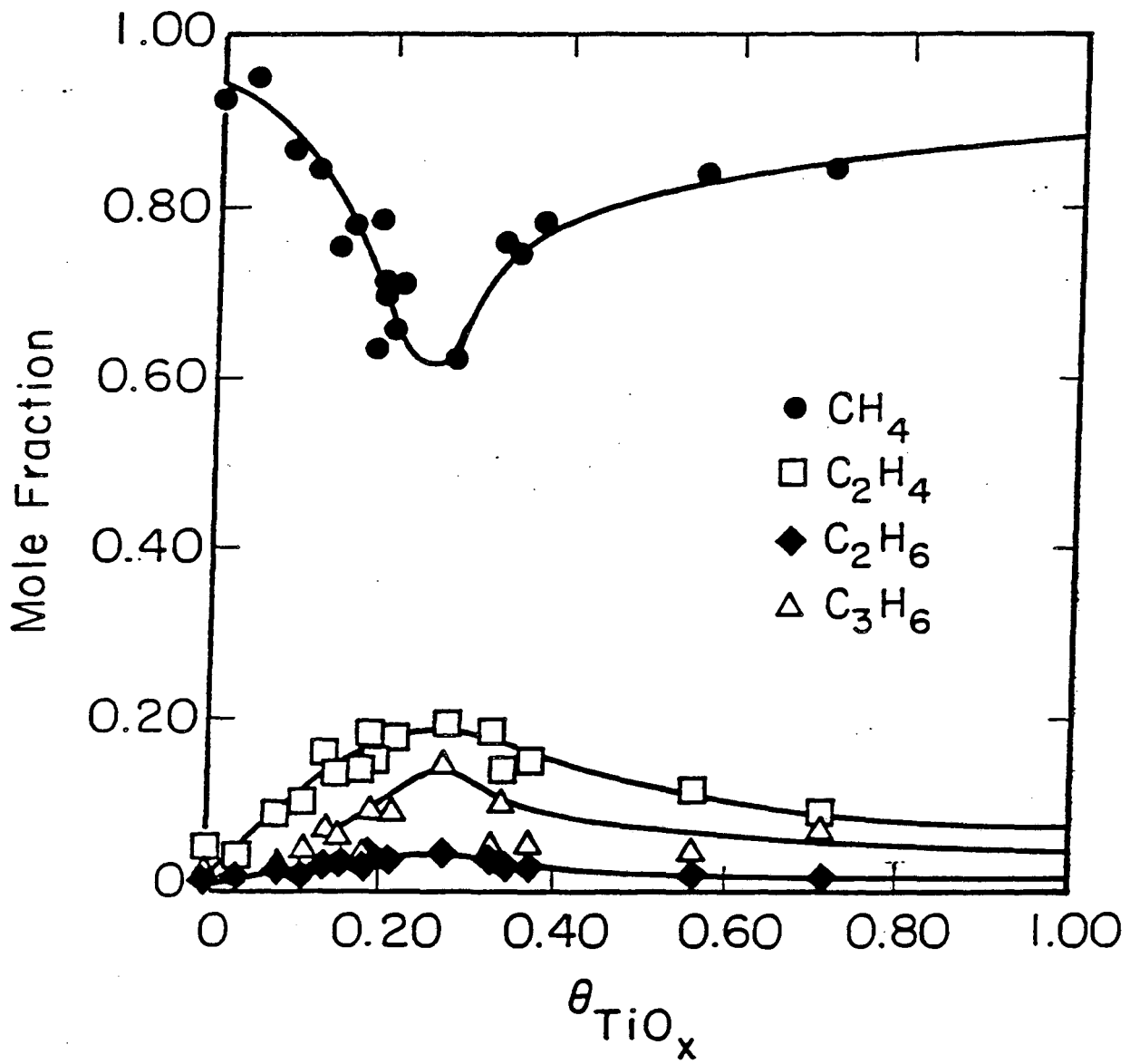
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Fig. 4

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Fig. 5

Fig. 6

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