HYDROGENATION OF CO_2, ACETONE, AND CO ON A Rh FOIL PROMOTED BY TITANIA OVERLAYERS

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The effects of submonolayer deposits of titania on the hydrogenation of CO_2, acetone, and CO on a Rh foil have been investigated. Titania has been found to promote all three of the hydrogenation reactions, with each reaction exhibiting a maximum rate at a titania coverage of 0.5 ML. The maximum rate for CO_2 hydrogenation is 15 times that of the bare Rh surface. Acetone hydrogenation shows a 6-fold rate enhancement, while CO displays a 3-fold increase. Changes in the selectivities for each reaction are also observed upon titania promotion. The effects of titania on these reactions are attributed to an interaction between C–O bonds and Ti^{3+} ions located at the perimeter of titania islands.

1. Introduction

The activation of metals by oxides was first observed by Schwab and Schultes sixty years ago [1]. More recently, numerous studies have shown that the catalytic properties of Group VIII metals can be drastically altered by interaction with reducible oxides such as titania, niobia, and vanadia. Many Group VIII metals, either promoted with or supported on these reducible oxides show much higher CO hydrogenation activities than when supported on silica or alumina (see references [2–4] and references contained therein). Rhodium catalysts promoted with titania and rare earth oxides show increased activity for the reduction of NO by CO and H_2 when compared to the unpromoted catalysts [5–8]. Titania and niobia - supported Rh catalysts also show increased activity for CO_2 hydrogenation relative to silica or alumina - supported Rh [9,10]. In addition, Pt supported

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on titania exhibits higher acetone hydrogenation rates than Pt supported on silica or alumina [11]. The modification of the catalytic properties of the metal in these supported catalysts has been attributed to the decoration of the metal particles by deposits of the oxide.

Similar effects of reducible oxides have been observed by depositing the oxide on an unsupported metal catalyst. Model studies using foils and single crystals of Pt, Pd, Rh, and Ni have shown that submonolayer deposits of titania and niobia can increase the rate of CO hydrogenation [12–17]. In previous studies, we have shown that titania overlayers on a Rh foil promote CO hydrogenation [15,16], while acting purely as a site-blocker in ethylene hydrogenation and ethane hydrogenolysis [18]. In this study, we investigate the effects of titania on a Rh foil during CO_2 hydrogenation and acetone hydrogenation. The results, when compared to those for CO hydrogenation, show that titania possesses a general promotional property for the hydrogenation of C–O bonds, and that the nature of the active sites for each reaction is identical. New sites of high activity appear to reside at the oxide - metal adlineation.

2. Experimental

Experiments were performed in a Varian UHV chamber equipped with an Auger electron spectrometer, a quadrupole mass spectrometer, and an atmospheric - pressure isolation cell. A detailed description of this apparatus is given in ref. [19]. The catalyst was a 1 cm^2 sample of 0.002-in thick Rh foil. For CO and CO_2 hydrogenation, the sample was mounted on 0.020-in Pt support wires; for acetone hydrogenation, 0.030-in Ta support wires were used. The sample was heated resistively and its temperature was measured by a thermocouple spot-welded to the sample. For CO_2 and acetone hydrogenation a chromel/alumel thermocouple was used, while for CO hydrogenation a Pt/Pt-Rh thermocouple was employed to avoid contamination of the sample by Ni due to carbonyl transport from a chromel/alumel thermocouple.

The sample was cleaned using cycles of Ar ion sputtering followed by annealing to 1273 K. Titanium was deposited on the sample by evaporation from a source consisting of a 0.020-in Ti wire wrapped around a resistively heated 0.030-in tungsten filament. A shutter was used to control the deposition times. After deposition the sample was oxidized in 2×10^{-6} Torr O_2 at 623 K to create a titania overlayer. Oxygen bound to Rh was removed as CO_2 by repeated exposure to 4 L of CO at room temperature followed by flashing to 773 K. Titania coverages were measured after preparation using AES. The AES calibration was determined from uptake curves in conjunction with ISS in an earlier study [20].

After characterization, the sample was enclosed in the atmospheric - pressure cell for the catalytic reactions. The reaction gases were measured into the cell and recirculated in a batch reactor system at a total pressure of 1 atm. For acetone hydrogenation, acetone vapor was obtained from a glass bulb containing liquid acetone which had previously been degassed using freeze - thaw cycles. All reactions were run at low conversion. Samples of the reaction mixture were taken periodically and analyzed with a gas chromatograph equipped with a flame ionization detector. A 6-ft × 1/8-in stainless steel column packed with Porapak N was used for the analysis of CO hydrogenation products. For CO_2 and acetone hydrogenation, separation was achieved with a 10-ft × 1/8-in stainless steel column packed with 80/120 Carbopak B coated with 3% SP1500 (obtained from Supelco). Reaction rates were calculated from plots of product accumulation versus time.

3. Results and discussion

Figure 1 shows the effect of titania coverage on the rate of methane formation during the hydrogenation of CO_2 at 523 K. The reactant partial pressures were 570 Torr H_2 and 190 Torr CO_2. The rate increases with the addition of titania up

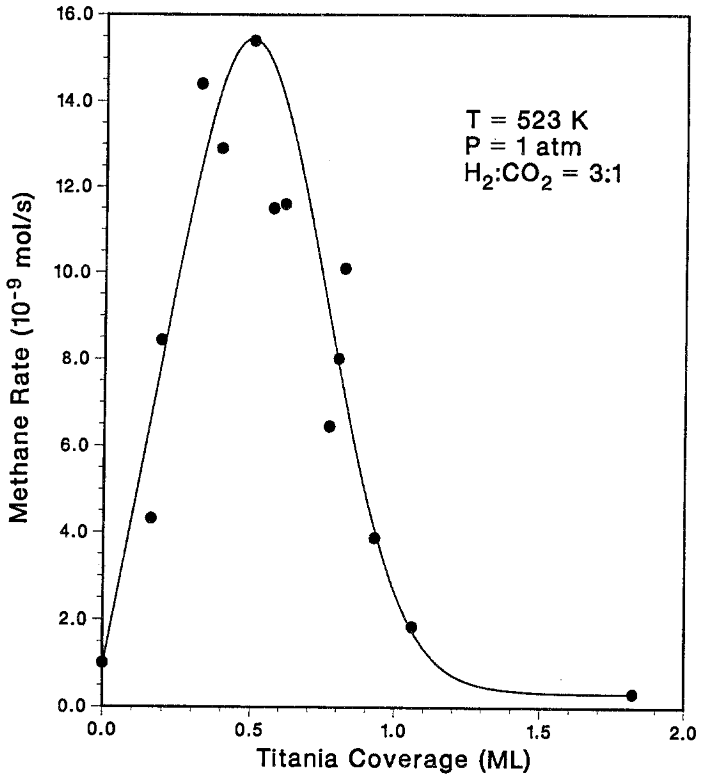

Fig. 1. Rate of methane formation during CO_2 hydrogenation on a Rh foil as a function of titania coverage. Reaction conditions: $T = 523$ K, $P_{H_2} = 570$ Torr, $P_{CO_2} = 190$ Torr.

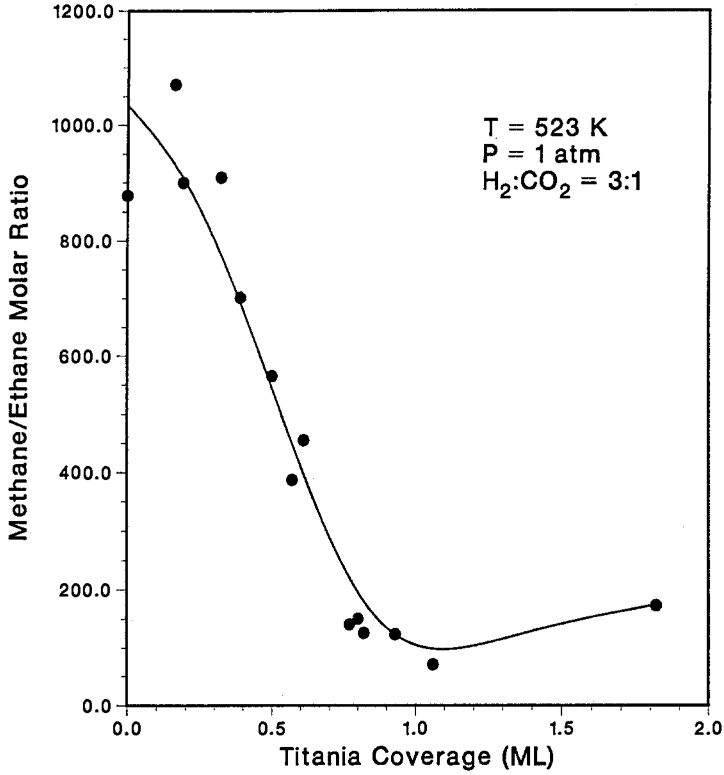

Fig. 2. Product selectivity during CO_2 hydrogenation on a Rh foil as a function of titania coverage. Reaction conditions: $T = 523$ K, $P_{H_2} = 570$ Torr, $P_{CO_2} = 190$ Torr.

to approximately 0.5 ML titania, after which the activity declines. The maximum activity is 15 times that of the bare Rh surface. The methane selectivity exceeds 99% at all coverages. The only other product observed is ethane. As shown in fig 2, the ratio of CH_4/C_2H_6 decreases by a factor of ten as the coverage of titania increases.

The rate of isopropanol formation from the hydrogenation of acetone is shown in fig. 3. The reactions were run at 423 K with partial pressures of 750 Torr H_2 and 10 Torr acetone. Here too, the activity of the catalyst is observed to pass through a maximum at a titania coverage of 0.5 ML. At this coverage, the rate of isopropanol formation is enhanced by a factor of 6 relative to that for the clean surface. Propane is also formed during acetone hydrogenation. On the clean surface, the ratio of isopropanol/propane is 45/1. Figure 4 shows that with increasing titania coverage, the isopropanol/propane ratio passes through a minimum at a titania coverage of about 0.4 ML, at which point the selectivity is 13/1.

The effects of titania coverage on the hydrogenation of CO to methane have been reported previously [15,16]. These results have been replotted in fig. 5 with a correction made to the originally measured coverages of titania, which were in

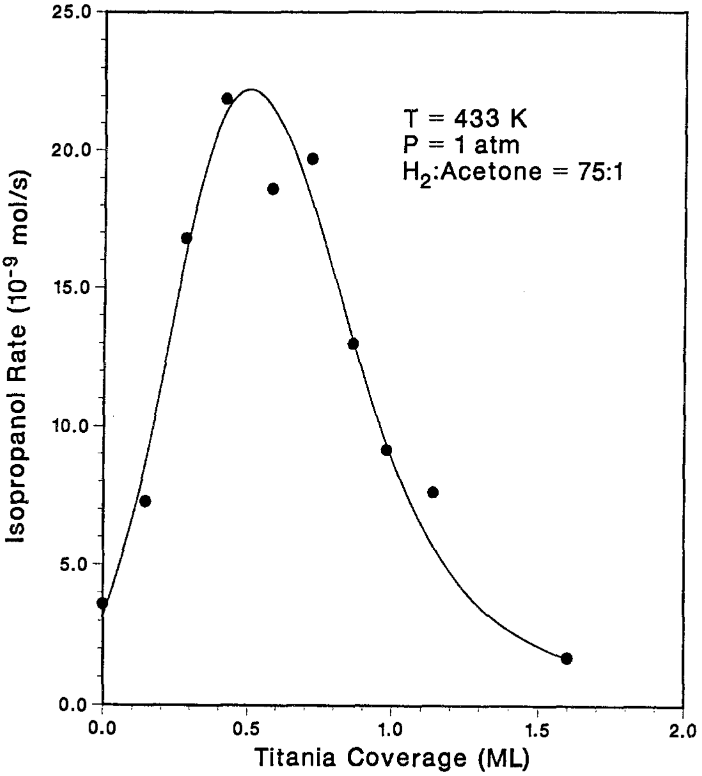

Fig. 3. Rate of isopropanol formation from the hydrogenation of acetone on a Rh foil as a function of titania coverage. Reaction conditions: $T = 423$ K, $P_{H_2} = 750$ Torr, $P_{acetone} = 10$ Torr.

error as a consequence of the method used to determine titania coverage [20]. The rate were obtained at 553 K with partial pressures of 507 Torr H_2 and 253 Torr CO. Figure 5 shows that the rate of methane formation passes through a maximum at a titania coverage of about 0.5 ML. The effect of titania coverage on product selectivity is shown in fig. 6. The selectivity to C_{2+} hydrocarbons passes through a maximum and the selectivity to methane passes through a minimum at a titania coverage of 0.7 ML.

A comparison of the rates for the three reactions on the clean Rh surface is shown in table 1. The rates for CO and CO_2 hydrogenation have been extrapolated to match the temperature and reactant partial pressures used for acetone hydrogenation. The hydrogenation of acetone is more than two orders of magnitude faster than those of CO_2 and CO at these conditions. It is also notable that the rates of CO_2 and CO hydrogenation are similar, with CO_2 hydrogenation being slightly faster.

The dependence of the reaction rate on titania coverage is similar for all three reactions studied: in each case the rate passes through a maximum for a titania coverage of about 0.5 ML. The effects of titania on CO hydrogenation have

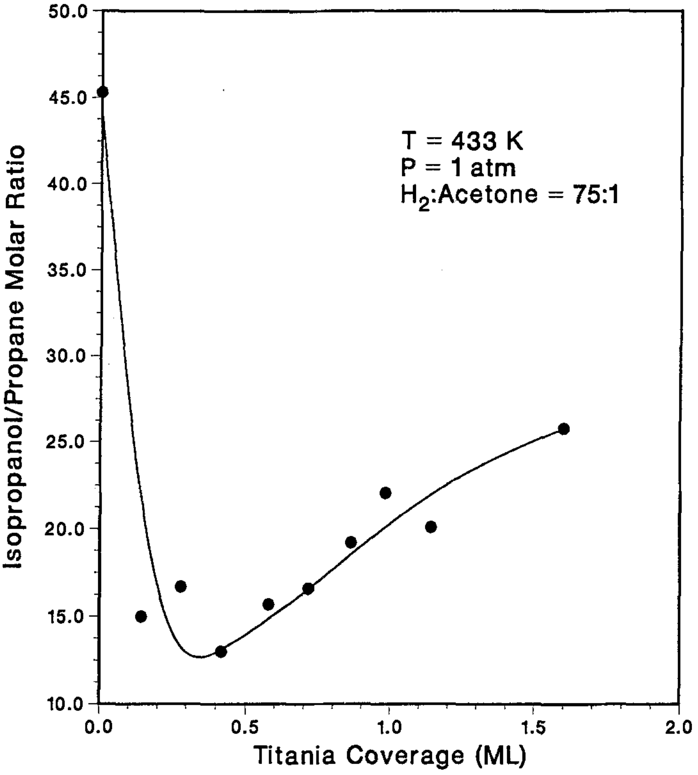

Fig. 4. Product selectivity of acetone hydrogenation on a Rh foil as a function of titania coverage. Reaction conditions: $T = 423$ K, $P_{H_2} = 750$ Torr, $P_{acetone} = 10$ Torr.

previously been ascribed to an interaction between CO chemisorbed on Rh and Ti^{3+} ions located at the perimeter of titania islands [21]. This interaction weakens the C–O bond, facilitating its cleavage and producing an overall increase in the rate at these sites. The results presented here for CO_2 and acetone hydrogenation suggest a general interaction between Ti^{3+} ions and the C–O bonds in all three of these molecules. Furthermore, in considering the promotion of the isopropanol formation rate from acetone hydrogenation, it appears that this interaction can facilitate not only the cleavage but also the hydrogenation of the intact carbonyl bond. Island growth simulations show that the adlineation between titania islands and the exposed Rh surface should maximize near one-half monolayer, which is consistent with the above picture.

The specific activity of the sites located along the oxide - metal adlineation can be estimated from the data presented in figs. 1, 3, and 5. The oxide itself is inactive, and the remaining metal surface has relatively low activity as indicated by the data for the clean surface. Estimates using simple oxide growth models point to a perimeter area which at 0.5 ML titania coverage is only 5–15% of the initially clean metal area. This suggests that the turnover frequencies of the sites

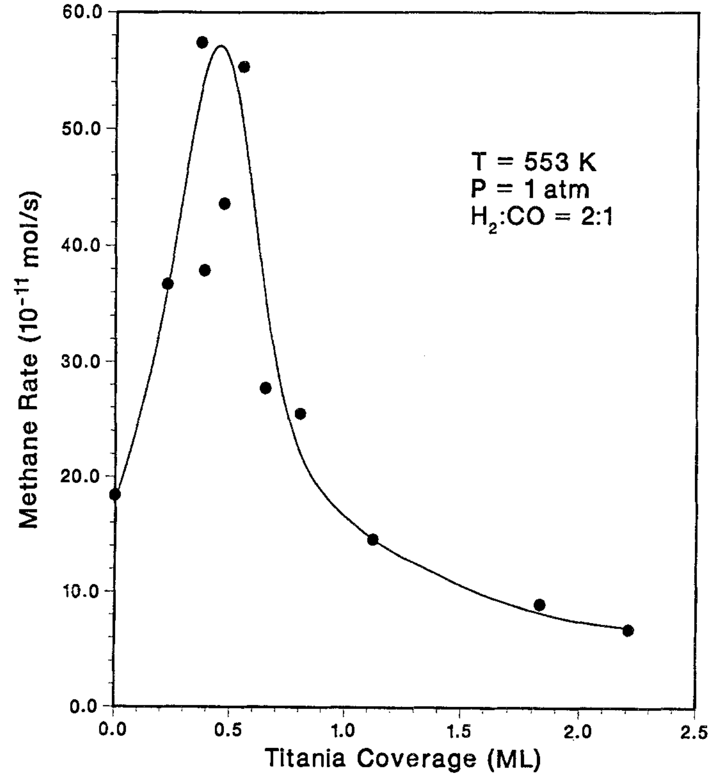

Fig. 5. Rate of methane formation from the hydrogenation of CO on a Rh foil as a function of titania coverage [15]. The indicated titania coverages have been corrected in accordance with results presented by Williams et al. [20] (see text). Reaction conditions: $T = 553$ K, $P_{H_2} = 507$ Torr, $P_{CO} = 253$ Torr.

at the oxide - metal boundary are as much as two orders of magnitude greater than those for metallic Rh sites. The cause of this very significant increase in catalytic activity must be the unique structure and C–O bonding properties of the sites along the oxide - metal boundary. Scanning tunneling microscopy studies of titania deposits on Rh are being made in our laboratory to identify the structure and electronic properties of the region of oxide - metal adlineation.

The promotional effects of titania on the reactions considered in this study are similar to those observed using supported catalysts. Many studies have shown an enhanced CO hydrogenation activity of titania - supported Rh as compared to silica or alumina - supported Rh [2–4]. Additionally, Rh supported on titania is much more active for CO_2 hydrogenation [9,10]. Also relevant are the observations of Sen and Vannice [11] who have reported an increase in the activity of Pt for acetone hydrogenation when titania is used as the support rather than silica or alumina. The effects of titania on the supported metal catalysts have been attributed to a partial coverage of the surfaces of the metal particles by titania.

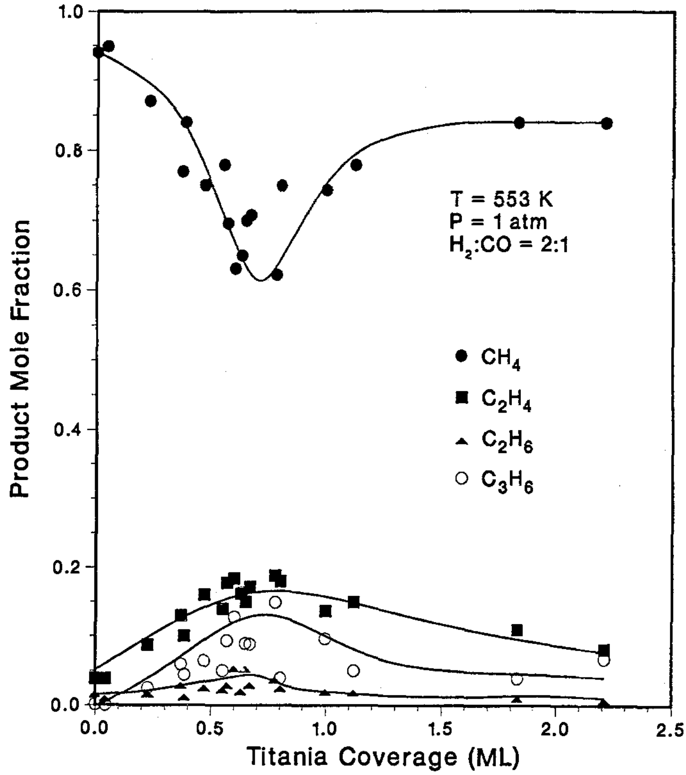

Fig. 6. Product selectivities of CO hydrogenation as a function of titania coverage [15]. The indicated titania coverages have been corrected in accordance with results presented by Williams et al. [20] (see text). Reaction conditions: $T = 553$ K, $P_{H_2} = 507$ Torr, $P_{CO} = 253$ Torr.

An interesting observation in the experiments presented here is that only in CO_2 hydrogenation is a monotonic change in selectivity observed with increasing coverage (fig. 2). For both acetone and CO hydrogenation the selectivities first achieve maxima or minima, then approach the selectivities for clean Rh at higher coverages (figs. 4 and 6). Furthermore, in CO hydrogenation [15,16] the activation energy and the partial pressure dependencies of CO and H_2, which are markedly affected by lower coverages of titania, also revert to the clean Rh values at higher

Table 1
Comparison of hydrogenation rates on clean Rh foil

Reactant	Hydrogenation rate (mol/s)
Acetone	3.60×10^{-9}
CO_2^*	2.14×10^{-11}
CO*	1.62×10^{-11}

Reaction conditions: $T = 433$ K, $P_{H_2} = 750$ Torr, $P_{\text{acetone}, CO_2, \text{or} CO} = 10$ Torr.
* Extrapolated value.

oxide coverages. At coverages nearing 1 ML, the reaction is taking place on relatively small patches of Rh atoms between the titania islands. At coverages beyond 1 ML, the reaction is likely occurring on Rh atoms which are exposed through defects in the titania overlayer. Curiously, the titania appears to have a lesser effect on the molecules reacting on these sites during acetone and CO hydrogenation.

The results for CO_2, acetone, and CO hydrogenation are in contrast to those reported for ethylene hydrogenation and ethane hydrogenolysis on a titania covered Rh foil [18]. For these two hydrocarbon reactions, titania addition resulted in a decrease in catalytic activity which was proportional to the titania coverage. From these observations, it was concluded that the sites occurring at the oxide - metal adlineation played no role in activating either H_2 or the hydrocarbon. This suggests that selective interaction of the adlineation sites with a reactant requires that the reactant contain a nucleophilic group, as is the case for CO, CO_2, and acetone.

4. Conclusions

Submonolayer deposits of titania on a Rh foil have been found to promote the hydrogenation of CO, CO_2, and acetone. The rate enhancement is highest for CO_2, where the maximum rate is a factor of 15 over that of the bare Rh surface. For acetone a 6-fold rate enhancement is observed, while CO shows a 3-fold increase. These rates are based on the total surface area of the sample. In each case, the maximum activity occurs at 0.5 ML titania, indicating that the same sites are responsible for the increased activity for each reaction. For both CO and CO_2 hydrogenation, an increase in the selectivity for higher hydrocarbons is observed in the presence of the oxide. For acetone hydrogenation titania causes a decrease in the isopropanol/propane ratio of the product. The effects of titania on these reactions are attributed to an interaction between C–O bonds and Ti^{3+} ions located at the perimeter of titania islands.

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