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ETHYLENE HYDROGENATION AND ETHANE HYDROGENOLYSIS ON A Rh FOIL WITH TITANIA OVERLAYERS

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The effects of submonolayer deposits of titania on the hydrogenation of ethylene and the hydrogenolysis of ethane on a Rh foil have been investigated. Titania has been found to suppress the activity of Rh for both reactions, and the rate of each reaction is proportional to the exposed Rh area. Titania induces no change in the activation energy of either reaction. Furthermore, high temperature reduction in H_2 does not change the activation energy for ethane hydrogenolysis on a titania-covered Rh foil. It appears that the titania overlayer has no effect on the activation of H_2, ethylene, or ethane, and that the suppression of activity for these reactions is purely the result of titania blocking active sites.

1. Introduction

A growing body of evidence indicates that the catalytic properties of supported metal particles can be altered by metal oxide islands deposited on the surface of the metal particles. The metal oxide islands may be introduced by intentional promotion of the catalyst or by transport of oxidic moieties from the support. Islands of titania, niobia, vanadia, and rare earth oxides have all been found to enhance significantly the rate of CO hydrogenation over Group VIII metals (see references [1–3] and references contained therein) and titania and rare earth oxide promoters have been reported to increase the activity of Rh for NO reduction by CO and H_2 [4–7]. By contrast, high temperature reduction of titania-supported metals, which causes a partial coverage of the metal particles by titania moieties, causes a dramatic decrease in the activity of the metal for alkane hydrogenolysis and a lesser decrease in the activity for olefin hydrogenation [8–12].

Progress towards understanding the effects of metal oxide overlayers on the catalytic properties of metals has been achieved through the use of metal foils and single crystals decorated with small amounts of metal oxide. Titania overlayers have been found to increase the activity of Pt, Pd, and Rh for CO hydrogenation and bring about a reduction in the activation energy [13–16]. These effects are attributed to highly active sites formed at the metal-metal oxide adlineation.

In this paper, we present our findings for ethylene hydrogenation and ethane hydrogenolysis over a Rh foil modified by titania overlayers. The rates of each reaction as a function of titania coverage were measured, as well as the activation energies in the presence and absence of titania. The effects of high temperature H_2 reduction on ethane hydrogenolysis were also examined. The results indicate that ethane hydrogenolysis and ethylene hydrogenation are suppressed due to a loss of active Rh sites, but that there is no significant change in the mechanism of these reactions. Thus the sites present along the boundary between the titania islands and the metal surface appear to have no effect on the activation of either H_2 or hydrocarbons.

2. Experimental

The experiments were performed in a Varian UHV chamber equipped with an Auger electron spectrometer, a quadrupole mass spectrometer, and an atmospheric-pressure isolation cell. Details of this apparatus are given in ref. [17]. The sample substrate was a Rh foil (99.8% purity) mounted on 0.020 in. gold wires for ethylene hydrogenation and 0.020 in. Pt wires for ethane hydrogenolysis reactions. The foil was resistively heated and the temperature was measured by a Pt/Pt-Rh thermocouple spot-welded to the sample.

The Rh foil was cleaned by Ar ion bombardment and then annealed at 1273 K. Titanium was deposited into the Rh foil by resistively heating a Ti-wrapped tungsten filament in a manner identical to that described earlier [17]. Oxidation with 2×10^{-6} torr O_2 at 623 K then produced a titania overlayer on the Rh foil. Oxygen bound to Rh was removed as CO_2 by repeated exposure of the oxidized sample to 4 L of CO followed by flashing to 773 K. Titania coverage was determined from AES Rh, Ti, and O peak heights, a procedure which has been verified by ISS [18]. For several experiments the freshly prepared sample was reduced prior to use. Reduction was carried out by heating the sample in 50 torr of H_2 at 773 K for 5 min.

Reactions were carried out in batch mode in the isolation cell at a total pressure of 1 atm. For the ethylene hydrogenation reactions, the reaction gas consisted of 25 torr ethylene, 25 torr H_2, and 710 torr Ar. For the ethane hydrogenolysis reactions, the reaction gas was 25 torr ethane, 25 torr H_2, and 710 torr Ar. Gas samples were removed periodically and sent to a gas chromatograph equipped with a flame ionization detector for hydrocarbon analysis. 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 ethylene hydrogenation at 323 K. Ethane was the only product observed. One can see that the rate of ethane formation is suppressed when titania is added. As the titania coverage increases, the rate declines linearly until nearly one monolayer, after which the rate begins to level off to a value less than 8% of the bare surface activity. The temperature dependence of the reaction between 293 K and 343 K is shown in fig. 2 for the clean Rh foil and for a titania coverage of 0.71 ML. The Arrhenius plots for the bare and partially covered foil are virtually identical. For temperatures below 323 K, the activation energy is slightly above 6 kcal/mol. At higher temperatures the Arrhenius plots exhibit a smaller slope, possibly indicative of increasing external mass transfer resistance, or a change in the reaction mechanism. The activation energy determined for temperatures below 323 K is in good agreement with that measured by Kemball [19], 7 kcal/mol, for a Rh film, and that measured by Bent [20], 7.5 kcal/mol, for a Rh(111) surface.

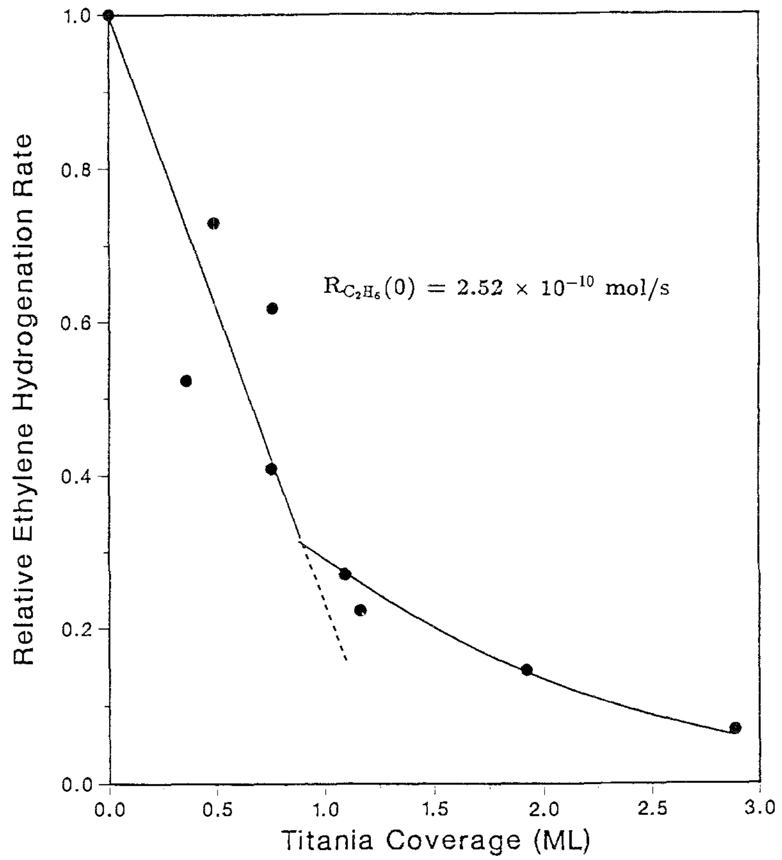

Fig. 1. Rate of ethylene hydrogenation on a Rh foil as a function of titania coverage. Rates are normalized to the value for zero coverage. $T = 323$ K, $P_{H_2} = 25$ torr, $P_{C_2H_4} = 25$ torr.

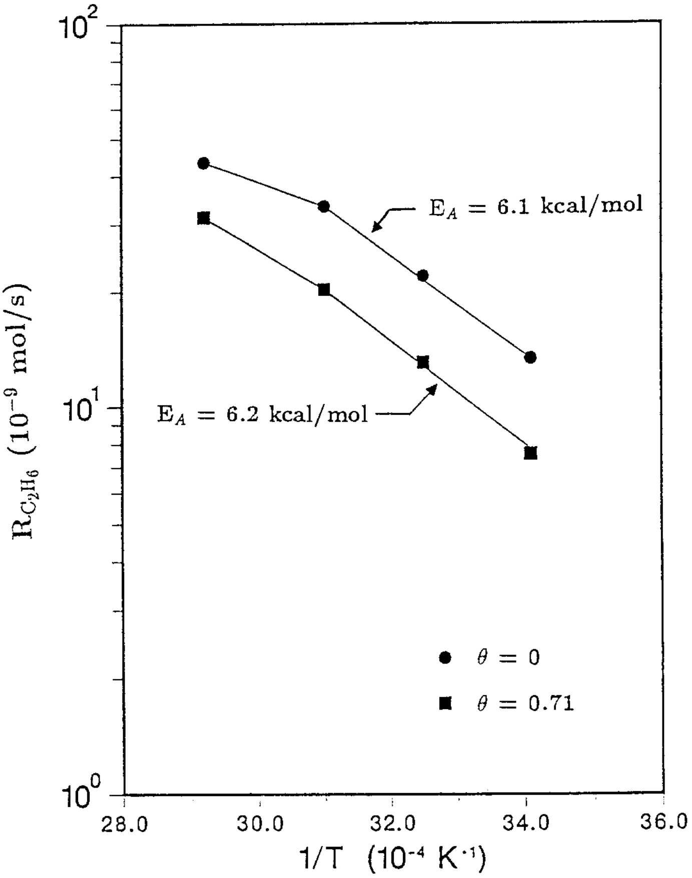

Fig. 2. Temperature dependence of ethylene hydrogenation between 293 K and 343 K for a clean Rh foil and for a coverage of 0.71 ML titania. Activation energies shown are calculated from the slope of the lines through the three lowest temperature points. P_{H_2} = 25 torr, $P_{C_2H_4}$ = 25 torr.

The relative rate of ethane hydrogenolysis at 443 K as a function of titania coverage is shown in fig. 3. The rate of methane formation is suppressed by the addition of titania, in a manner similar to that observed for ethylene hydrogenation. Again, the rate declines linearly with titania coverage until nearly one monolayer, and with higher coverage the rate levels off quickly; by 1.5 monolayers, the rate has decreased to a value which is only 5% of the bare Rh activity. The temperature dependence of the reaction between 408 K and 473 K is shown in fig. 4, for the clean Rh foil and for a coverage of 0.95 ML TiO_2 with no prereduction. Although the rates are lower for the titania-covered surface, the activation energy obtained from both slopes is about 33 kcal/mole, which is close to the value of 36 kcal/mole obtained by Ko and Garten [8] for 2 wt.% Rh/TiO_2.

Table 1 lists the rates of ethane hydrogenolysis for a sample with 0.95 ML titania after three different pretreatment conditions: a) freshly prepared and oxidized, b) prereduced, and c) re-oxidized. As can be seen, the prereduction of

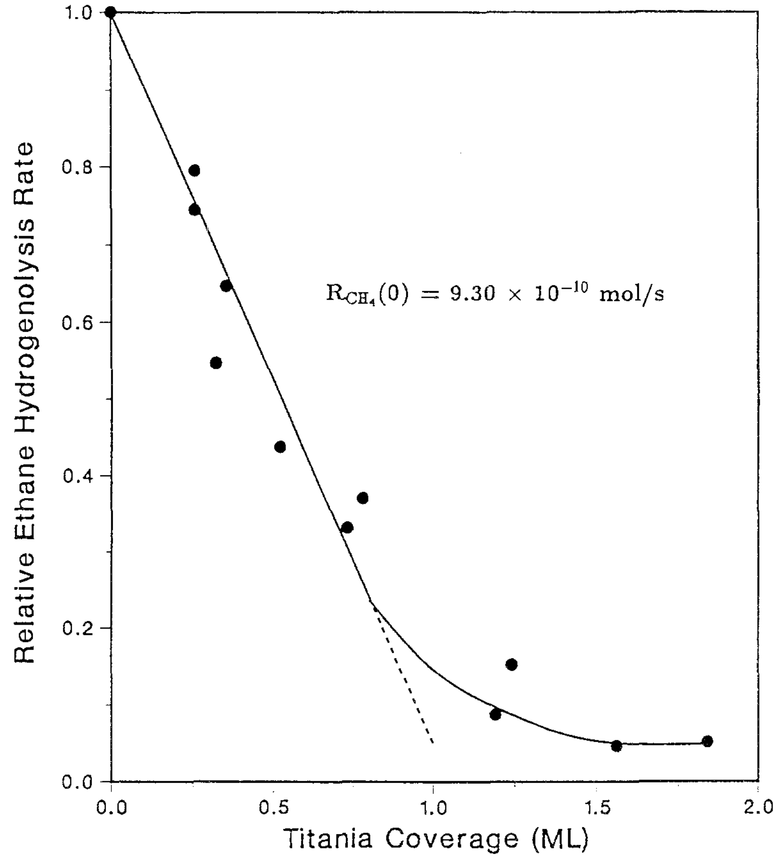

Fig. 3. Rate of ethane hydrogenolysis on a Rh foil as a function of titania coverage. Rates are normalized to the value for zero coverage. $T = 443$ K, $P_{H_2} = 25$ torr, $P_{C_2H_6} = 25$ torr.

the titania overlayer causes further suppression in the hydrogenolysis rate, and this rate is about half of the sample without prereduction. However, if the sample is reoxidized with 5×10^{-6} torr O_2 at 623 K for 15 min., the activity is restored to its previous level. Figure 4 shows that the effect of prereduction is the same at all reaction temperatures and that as a consequence prereduction has no significant effect on the activation energy.

The data presented here indicate that for both reactions, the titania causes a linear decrease in reaction rate in the submonolayer region. Also, the activation energies for both reactions remain unaffected by the presence of titania. It appears that each reaction occurs only on Rh sites which are uninfluenced by the titania.

In previous work [18], we have characterized the growth of titania on a Rh foil and a Rh(111) surface using Auger electron spectroscopy and ion-scattering spectroscopy. In that study we concluded that the titania overlayer grows two-dimensionally in the first monolayer, and that subsequent growth is nearly layer-

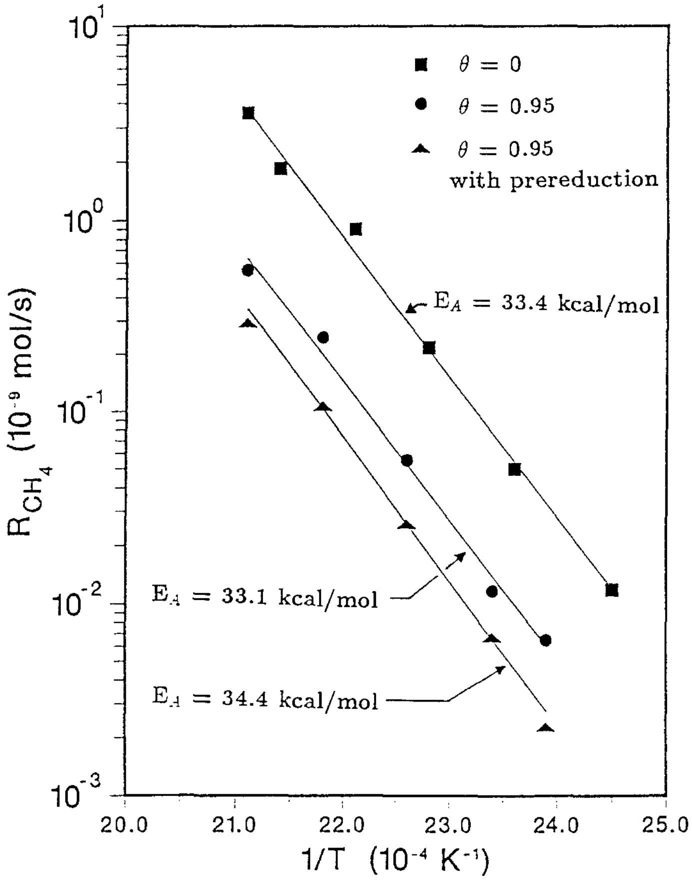

Fig. 4. Temperature dependence of ethane hydrogenolysis rate between 408 K and 473 K. Data are presented for a clean Rh foil, a coverage of 0.95 ML titania with no prereduction, and for a coverage of 0.95 ML titania with prereduction. $P_{H_2} = 25$ torr, $P_{C_2H_6} = 25$ torr.

by-layer. In addition there was evidence to indicate that the second layer grows on a slightly defective first layer, such that a few Rh sites remain exposed even as the second layer begins to grow.

Table 1
Effect of sample pretreatment on the rate of ethane hydrogenolysis

Sample pretreatment	Ethane hydrogenolysis rate (10^{-11} moles CH_4/s)
Oxidized [a]	5.58
Prereduced [b]	2.77
Reoxidized [c]	5.62

Sample is Rh foil with 0.95 ML titania deposited.

[a] Freshly prepared and oxidized with 2×10^{-6} torr O_2 at 623 K.

[b] Prereduced in 50 torr H_2 at 773 K.

[c] Reoxidized with 2×10^{-6} torr O_2 at 623 K.

The capacity of these surfaces for the chemisorption of CO [18] closely resembles the activity behavior presented here in figs. 1 and 3. There is an initial linear decline in the capacity with coverage, but there is not a sharp linear decline to zero adsorption at the monolayer. Rather, there is some tailing beginning just before the monolayer, continuing a more gradual decline in capacity as more titania is added. This tailing was attributed to adsorption at Rh sites exposed in the "defective" overlayer.

In conjunction with these earlier findings, we can interpret the results presented here for ethylene and ethane reactions. At lower titania coverages, the reactions occur only on the exposed Rh patches, hence the linear decline in activity with increasing coverage. As the coverage nears one monolayer, however, there is a tailing due to reaction at those Rh sites exposed due to defects in the overlayer.

Table 1 shows that for a titania coverage of 0.95 ML, the rate of ethane hydrogenolysis can be further suppressed by prereduction of the sample. An almost identical decrease in CO chemisorption capacity at this titania coverage is observed upon prereduction [17]. This behavior can be attributed to a "flattening out" of the overlayer upon prereduction to cover more of the defects in the first layer and hence reduce the number of exposed Rh sites. Evidently this effect is reversible, such that the overlayer reverts to the more defective structure upon re-oxidation and hydrogenolysis activity is completely recovered.

A point of interest in this study is that ethylene hydrogenation and ethane hydrogenolysis are suppressed to the same extent by titania, whereas in studies of titania-supported metals [8–12] hydrogenolysis reactions are suppressed to a much greater degree than hydrogenation reactions. The observations on the supported catalysts may be due to the effects of a distribution of particle sizes in the catalysts. Ethane hydrogenolysis is a structure sensitive reaction which is known to procede at a much higher rate on small metal particles [21,22], and these are likely to be the most efficiently covered by titania species migrating from the support. Ethylene hydrogenation, on the other hand, does not show any pronounced dependence on particle size [23].

It is significant to note that the effects of titania coverage on C_2H_4 hydrogenation and C_2H_6 hydrogenolysis over Rh are markedly different from those observed for CO hydrogenation. For catalyst samples prepared and characterized in a manner identical to that described here, Levin et al. [15,16] observed that the rate of methane formation passed through a maximum value with increasing titania coverage. The maximum rate was threefold greater than that for the clean surface. It was also observed that the activation energy for methane formation passed through a minimum with increasing titania coverage, the minimum value being 9 kcal/mol lower than that for the clean Rh surface. Both of these effects were ascribed to a direct interaction between CO adsorbed on Rh and Ti^{3+} sites present at the perimeter of the titania islands [24]. The present results indicate that these sites have no effect on the activation of H_2, C_2H_4, or C_2H_6.

4. Conclusions

Submonolayer deposits of titania on a Rh foil have been found to suppress the activity for both ethylene hydrogenation and ethane hydrogenolysis. No significant changes are observed in the activation energy of either reaction when titania is added, indicating that the reaction mechanisms are not altered. Thus ethane and ethylene appear to have no special interaction with the titania overlayer. The declines in activity are explained by a blockage of active Rh sites, and each reaction rate is proportional to the exposed Rh area.

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