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The effects of titania overlayers on $C_2H_4/CO/H_2$ reactions over a Rh foil

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The effects of submonolayer deposits of titania on the activity and selectivity of a Rh foil catalyst for $C_2H_4/CO/H_2$ reactions have been investigated. Reactions were carried out at 1 atm total pressure and at temperature of 488 K and 523 K. The addition of titania to the catalyst enhances the total rate of C_3-oxygenate formation. This rate enhancement is due entirely to an increase in the rate of 1-propanol formation, which reaches a maximum at a TiO_x coverage of 0.2 ML. The rate of propanal formation, by contrast, is not enhanced. The rates of formation of methane, ethane, and C_3-hydrocarbons also exhibit rate maxima at a TiO_x coverage of 0.2 ML. The rates of formation of C_4- and C_5-hydrocarbons, on the other hand, are suppressed by titania addition. The higher rate of 1-propanol production in the presence of titania is attributed to an interaction between Ti^{3+} ions at the edge of TiO_x islands and the carbonyl bond of adsorbed C_3-oxygenated species. Such interactions are envisioned to facilitate hydrogenation of the carbonyl bond.

Keywords: Titania-rhodium catalysts; model oxide-metal catalysts; hydroformylation over Rh-TiO_2; combined ethylene and CO hydrogenation over Rh-TiO_2

1. Introduction

Interactions between reducible oxides and Group VIII metal catalysts can greatly enhance the activity of such catalysts and alter their selectivity for certain reactions. A large body of literature on CO hydrogenation shows that many Group VIII metals, supported on oxides such as titania, niobia, and vanadia, show much higher activity than when supported on silica or alumina (see refs. [1–3] and references contained therein). These changes in activity are usually accompanied by shifts in selectivity toward the production of higher hydrocarbons. Similarly, the rate of hydrogenation of CO_2 on Rh is increased by using titania as support [4,5], and the activity as well as the selectivity to higher hydrocarbons can be increased by using niobia as a support [6,7]. In addition, studies using foils and single crystals of Pt, Pd, Rh, and Ni partially covered with deposits of titania or niobia have shown that the rate of CO hydrogenation can be accelerated by promotion with these reducible oxides [8–13].

In recent studies we have shown that titania overlayers on Rh foil are capable of promoting CO hydrogenation and CO_2 hydrogenation [11,12,14]. This promotion was attributed to the creation of sites at the TiO_x-Rh adlineation which facilitate the dissociation of the C–O bond. We have also shown that titania overlayers can promote the hydrogenation of acetone to isopropanol [14]. Here too it was proposed that the rate enhancement can be ascribed to the interaction of the carbonyl in acetone with Ti^{3+} sites at the perimeter of titania islands. Since all three of these reactions exhibit maximum activity at the same titania coverage, 0.5 ML, this suggests that the same type of site is responsible for the promotion of each reaction.

Studies of ethylene addition to CO/H_2 reaction mixtures over supported Ru [15–20], Co [21,22], Fe [23–26], Ni [19,27,28], Rh [19,29–33], and Pd [19,34] indicate that the added ethylene can be converted to higher molecular weight hydrocarbons as well as C_3-oxygenates such as propanal and 1-propanol. Ethylene can undergo reaction in three ways: 1) hydrogenation to form ethane, 2) decomposition to form C_1- and C_2-building units for the formation of higher hydrocarbons, and 3) hydroformylation to form C_3-oxygenates.

There is evidence that ethylene hydroformylation can be promoted by transition metal oxides. Addition of ZnO_x to Rh/SiO_2 [30] has been shown to increase dramatically the rate of hydroformylation, and at the same time suppress the hydrogenation of ethylene to ethane. It was proposed that the ZnO_x promoter enhances the rate of CO insertion into surface alkyl groups. Similarly, Pd catalysts supported on Nb_2O_5 show increased activity for hydroformylation compared to Pd/SiO_2 [34]. In our previous studies of CO/H_2 reactions on the TiO_x/Rh system at 1 atm [11,12], oxygenates were not produced in sufficient quantities to be detected. Thus, it could not be determined from that study what effect titania might have on the production of oxygenates via CO insertion. In the present work, we wish to establish whether the addition of titania to the Rh catalyst might also promote the production of C_3-oxygenates formed from CO insertion into ethylene. As will be shown, the primary function of titania appears to be in facilitating hydrogenation of the carbonyl bond of the C_3-oxygenated species formed from CO insertion.

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. [35]. The catalyst consisted of a 0.003-in thick Rh foil mounted on two 0.020-in Au support wires. The sample was heated resistively and its temperature was measured by a Pt/Pt-Rh (type S) thermocouple spotwelded to the sample.

The Rh catalyst was cleaned using cycles of Ar ion sputtering at 2 keV followed by annealing to 1273 K. Titanium was deposited on the Rh foil by evaporation from a source consisting of a 0.020-in Ti wire wrapped around a 0.030-in tungsten filament. The current necessary to heat the filament during deposition was approximately 34 amps. A shutter on the Ti source 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 chemisorbed on the Rh was removed as CO_2 by repeated exposure to 4 L of CO at room temperature followed by flashing to 773 K. The attenuation of the Rh AES signal was used to determine the TiO_x coverage. A description of this technique and its calibration are given in ref. [36].

To determine the activity and selectivity of the catalyst, it was enclosed in the atmospheric-pressure cell. The reaction gases were introduced into the cell so as to obtain a total pressure of 1 atm and recirculated through the cell at a flowrate of approximately 100 cm^3/min using a metal-bellows pump. For the reaction rate determinations, the gas mixture consisted of 400 Torr H_2, 50 Torr Co, 50 Torr C_2H_4, and 260 Torr Ar. All reactions were run at low conversion ($\leqslant 10\%$). Samples of the reaction mixture were withdrawn periodically and analyzed with a gas chromatograph equipped with a flame-ionization detector. Product separation was achieved using 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

The reaction of $C_2H_4/CO/H_2$ over the Rh catalyst produced ethane as the dominant product. The rates of formation of CH_4 and higher hydrocarbons C_3-C_5 could be measured as well. We were particularly interested in the rates of the C_3-oxygenates propanal and 1-propanol. No other oxygenates were produced in measurable quantities. AES analysis of the surface prior to reaction showed only Rh, Ti, and O. After reaction, C was observed in addition to these elements.

The rate of ethane formation at 488 K is shown in fig. 1 as a function of the titania coverage. The rate increases with titania addition up to a coverage of 0.2 ML TiO_x, and then declines with further addition. The maximum rate is a factor of 1.3 higher than the rate over the clean Rh surface. Fig. 2 shows the rates of CH_4 and the C_3C_5 products. The rate of methane formation also exhibits a

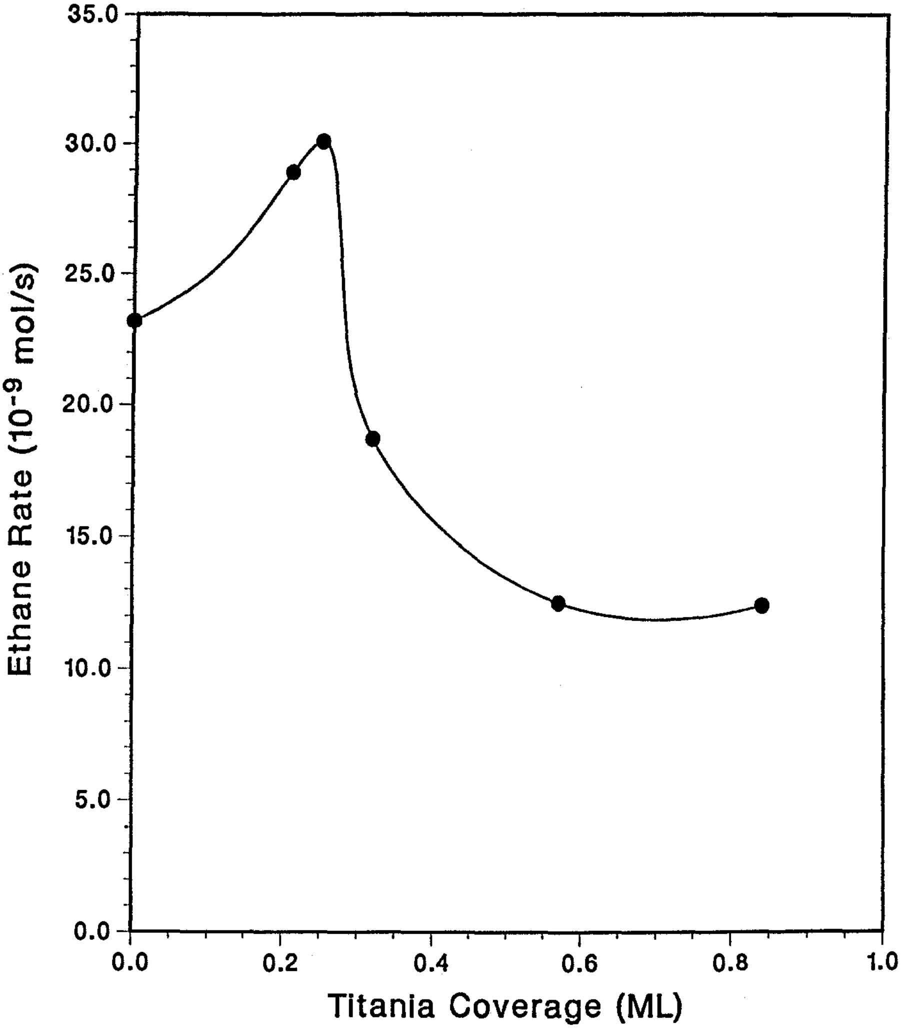

Fig. 1. Rate of C_2H_6 formation from the reaction of C_2H_4, CO, and H_2 on a Rh foil as a function of titania coverage. Reaction conditions: $T = 488$ K, $P_{H_2} = 400$ Torr, $P_{CO} = 50$ Torr, $P_{C_2H_4} = 50$ Torr, $P_{Ar} = 260$ Torr.

maximum at 0.2 ML TiO_x, which was 1.4 times higher than the clean surface rate. The rate of total C_3-production (hydrocarbons + oxygenates) exhibits a maximum at this coverage as well. In this case, the maximum rate is a factor of 1.7 greater than the rate over the bare Rh surface. In contrast, the rates of the C_4- and C_5-products, consisting entirely of hydrocarbons, do not display any rate enhancement due to titania. The rates of these products decline monotonically as titania is added to the catalyst surface.

The C_3-product consists of propylene, propane, propanal, and 1-propanol. Fig. 3 shows that the C_3-hydrocarbons as well as the C_3-oxygenates are pro-

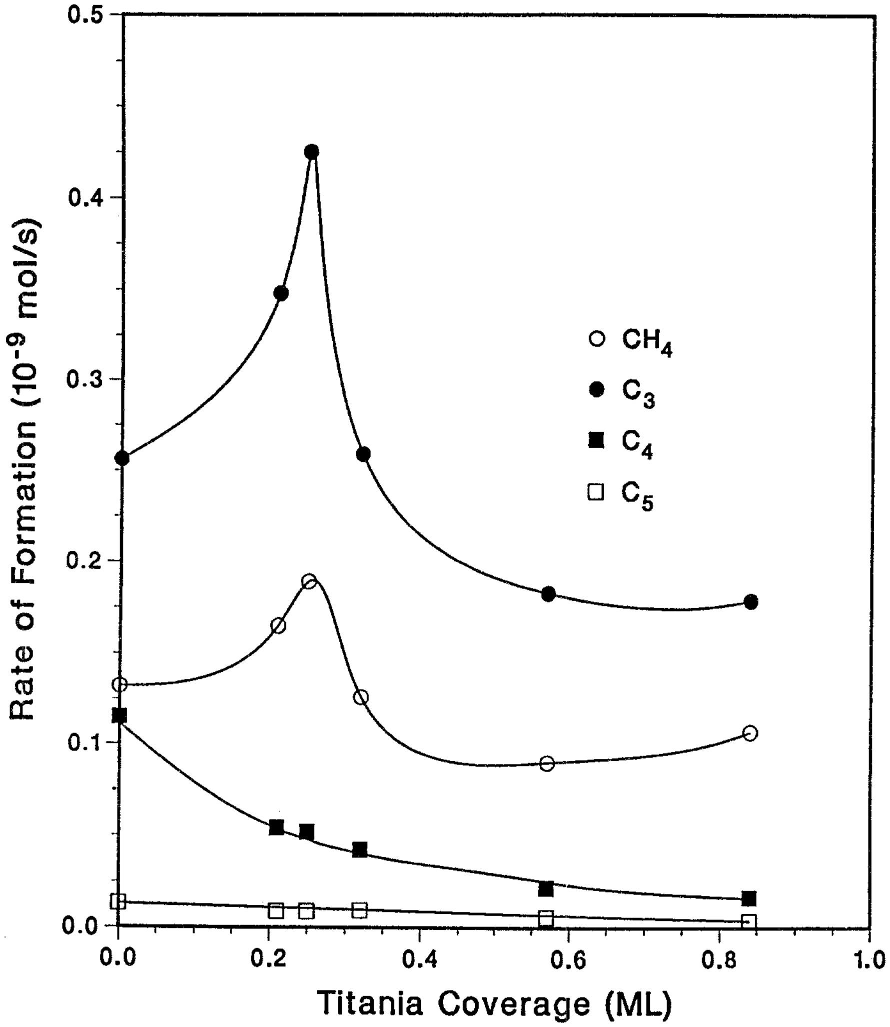

Fig. 2. Rates of formation of CH_4, C_3-, C_4-, and C_5-products from the reaction of C_2H_4, CO, and H_2 on a Rh foil as a function of titania coverage. Reaction conditions: $T = 488$ K, $P_{H_2} = 400$ Torr, $P_{CO} = 50$ Torr, $P_{C_2H_4} = 50$ Torr, $P_{Ar} = 260$ Torr.

moted by titania. Each exhibits a maximum rate at a titania coverage of 0.2 ML. For the hydrocarbons, the enhancement is a factor of 1.6, while for the oxygenates the maximum rate represents a factor of 1.7 increase over the clean surface rate. The rates of the individual C_3-oxygenated products are displayed in fig. 4. Although there is an increase in the total rate of C_3-oxygenates, this is due entirely to the enhancement of 1-propanol formation. The maximum rate of 1-propanol production, which occurs at a TiO_x coverage of 0.2 ML, is a factor of 3.6 higher than for the bare Rh surface. In contrast, the rate of propanal formation declines monotonically with titania addition. Results obtained at 523

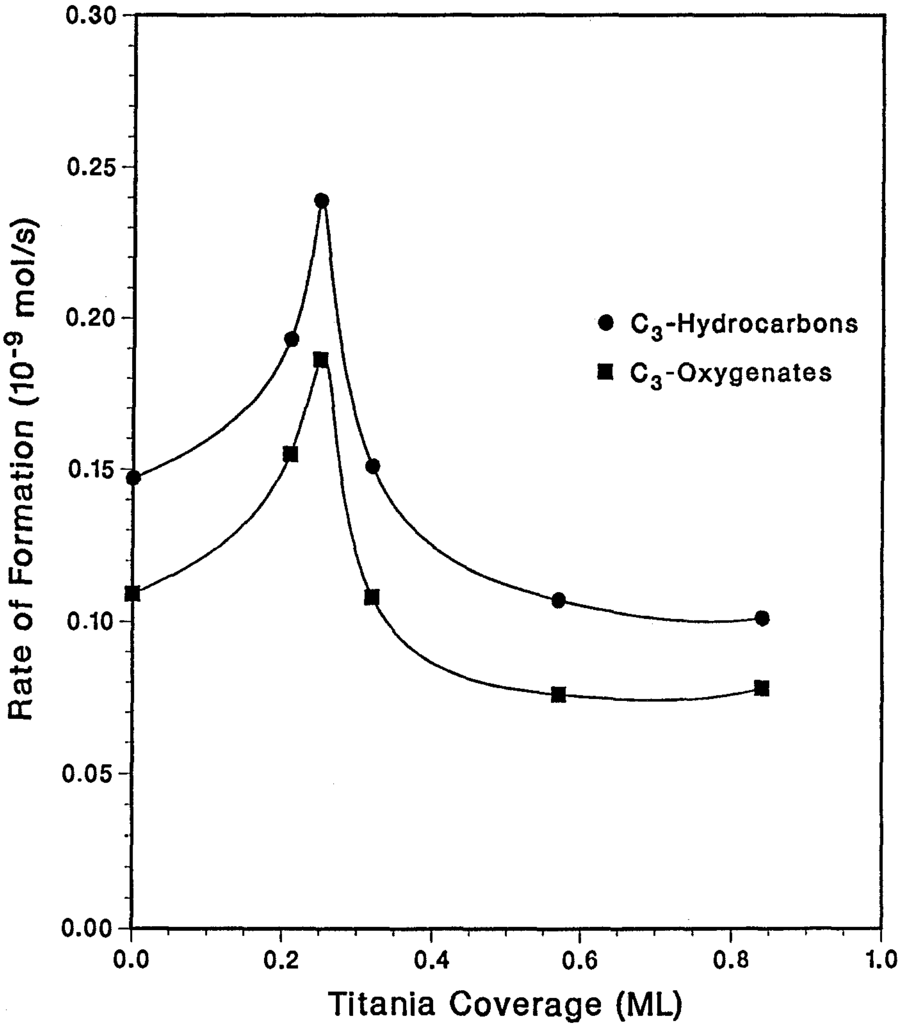

Fig. 3. Individual rates of formation for C_3-hydrocarbons and C_3-oxygenated products. Reaction conditions: $T = 488$ K, $P_{H_2} = 400$ Torr, $P_{CO} = 50$ Torr, $P_{C_2H_4} = 50$ Torr, $P_{Ar} = 260$ Torr.

K show trends identical to those presented here in figs. 1–4. The rates of formation of CH_4, C_2H_6, C_3-hydrocarbons, and 1-propanol all display maxima at a TiO_x coverage of 0.2 ML, while those of propanal, C_4-hydrocarbons, and C_5-hydrocarbons decline monotonically with increasing TiO_x coverage.

4. Discussion

The results presented in figs. 1–4 demonstrate that the promotion of Rh by TiO_x affects the activity and selectivity of the catalyst in a complex manner. Two

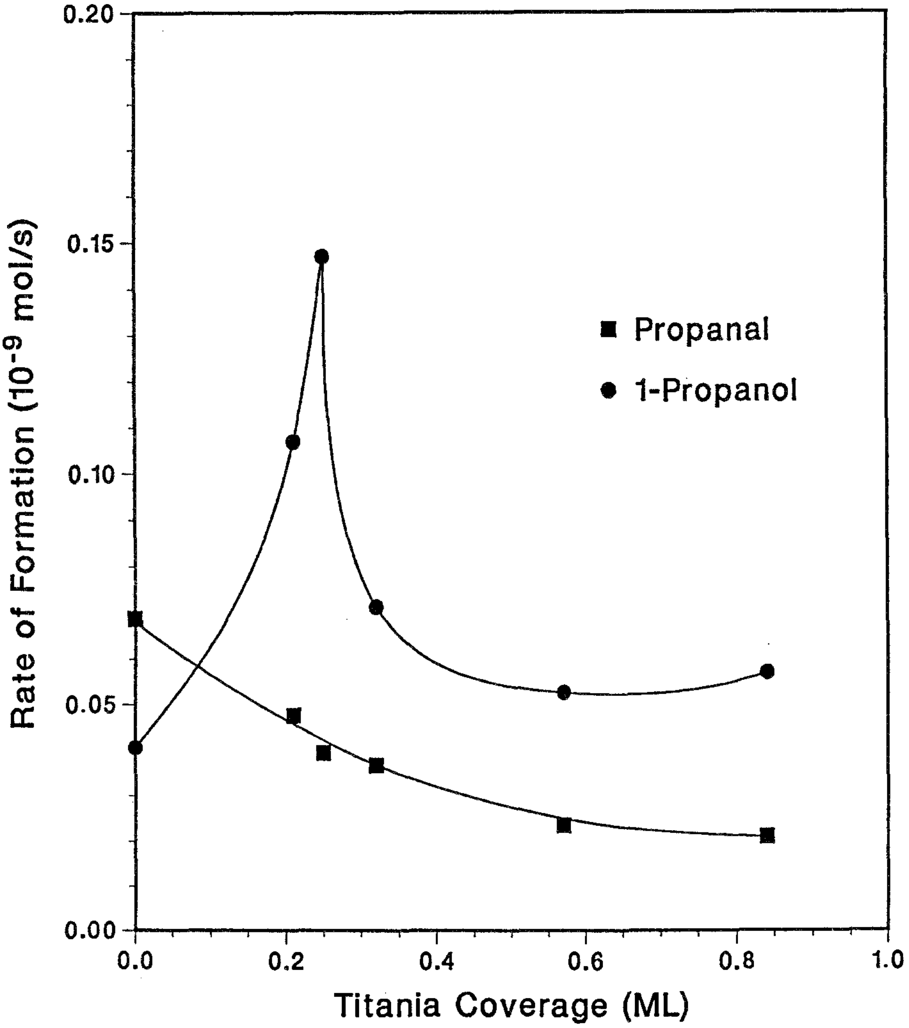

Fig. 4. Individual rates of formation of propanal and 1-propanol. Reaction conditions: $T = 488$ K, $P_{H_2} = 400$ Torr, $P_{CO} = 50$ Torr, $P_{C_2H_4} = 50$ Torr, $P_{Ar} = 260$ Torr.

basic trends with increasing TiO_x coverage are observed. The first is an increase in activity with increasing TiO_x coverage up to a maximum activity at a coverage of 0.2 ML, followed by a decrease in activity as the TiO_x coverage is further increased. This behavior is observed for C_2H_6, CH_4, C_3-hydrocarbons, and C_3H_7OH. The second type of response is a monotonic decrease in activity with increasing TiO_x coverage, as is seen for C_4- and C_5-hydrocarbons, and C_2H_5CHO. The extent to which C_2H_4 and CO contribute to each reaction product and the dependence of the rate of formation of each product on TiO_x coverage can be explained in terms of the hydrogenation of C_2H_4, CO, and C_2H_5CO, and the hydrogenolysis of C_2H_4.

The rate of C_2H_6 formation on unpromoted Rh is six orders of magnitude higher than that deduced from the kinetics of CO hydrogenation [12], but significantly lower than the rate observed for ethylene hydrogenation in the absence of CO [37]. This suggests that all of the C_2H_6 produced from a feed containing CO, C_2H_4, and H_2 derives from the hydrogenation of C_2H_4. The decrease in the rate of C_2H_4 hydrogenation over that observed in the absence of CO can be attributed to the inhibiting effect of CO adsorption [20,38]. Consistent with this is the fact that the heat of adsorption of CO (29–32 kcal/mol [39–42]) is higher than that for C_2H_4 (12 kcal/mol [38]) or H_2 (18.6 kcal/mol [43]).

In the absence of CO, C_2H_4 hydrogenation is inhibited by the addition of TiO_x to Rh [37]. On this basis, one would expect to see a monotonic decrease in the rate of C_2H_6 formation with increasing TiO_x coverage. What is found instead (see fig. 1) is an increase in the rate of C_2H_6 formation up to a maximum rate at a titania coverage of 0.2 ML. This unexpected behavior can be ascribed to a promotion in the rate of CO consumption to products other than C_2H_6, with the consequence that the surface coverage by CO decreases and with it the inhibiting effect of adsorbed CO on C_2H_4 hydrogenation. Such an interpretation leads to the conclusion that C_2H_4 hydrogenation occurs on the open portions of the Rh surface, and that the influence of the TiO_x promoter on the rate of C_2H_6 formation is a consequence of its influence on the inhibiting effects of CO, rather than a positive effect of TiO_x on C_2H_4 hydrogenation.

The rate of methane formation on unpromoted Rh is of the same order of magnitude as that deduced from the kinetics of CO hydrogenation [12]. An alternative path to CH_4 is through hydrogenolysis of ethylene. We have shown in previous studies that the hydrogenation of CO to form methane is promoted by titania addition [11,12], while in the hydrogenolysis of ethane, titania serves only to block active Rh sites [37]. The enhancement in the methane formation rate in the present study by low coverages of titania suggests that a significant portion of the methane is derived from CO.

The rates of formation of C_4- and C_5-hydrocarbons over unpromoted Rh are significantly greater than those observed for CO hydrogenation [11,12]. This suggests that C_4- and C_5-hydrocarbons are formed by hydropolymerization of C_2H_4. Such products have been observed previously when mixtures of C_2H_4, CO, and H_2 were passed over supported Ru [20] and Co [21] catalysts. The C_4-products are attributed to the dimerization of C_2H_4, whereas C_5-products are due to the reaction of C_4-olefin units with CH_2 groups produced by the partial hydrogenolysis of C_2H_4 or the hydrogenation of CO. Studies conducted with Ru/SiO_2 by Jordan and Bell [20] indicate that the extent of C_2H_4 hydropolymerization relative to C_2H_4 hydrogenation is enhanced by the presence of CO. The monotonic decrease in the rates of formation of C_4- and C_5-hydrocarbon formation with increasing TiO_x coverage suggests that hydropolymerization occurs exclusively on the portions of the Rh surface not covered by TiO_x.

Neither propanal nor 1-propanol is observed when CO is hydrogenated over TiO_x-promoted Rh [11,12]. The appearance of these products when both CO and C_2H_4 are present in the feed suggests that both oxygenates are formed by hydroformylation. The simplest mechanism for this is as follows:

1. $C_2H_{4(g)} \rightleftarrows C_2H_{4(a)}$
2. $C_2H_{4(a)} + H_{(a)} \rightleftarrows C_2H_{5(a)}$
3. $C_2H_{5(a)} + CO_{(a)} \rightleftarrows C_2H_5CO_{(a)}$
4. $C_2H_5CO_{(a)} + H_{(a)} \rightarrow C_2H_5CHO_{(g)}$
5. $C_2H_5CO_{(a)} + 3H_{(a)} \rightarrow C_3H_7OH_{(g)}$.

This scheme is consistent with studies conducted using $^{12}C_2H_4/^{13}CO$ over Ru/SiO_2 [20] and $^{12}C_2H_4/^{14}CO$ over Co catalysts [22]. In situ infrared studies of ethylene hydroformylation on Rh/SiO_2 [33] and Ni/SiO_2 [27] also support the CO insertion mechanism.

Fig. 4 shows that the effects of TiO_x coverage on propanal and 1-propanol are quite different. In the case of propanal, the rate decreases monotonically, whereas for 1-propanol, the rate passes through a maximum. The observed patterns can be explained by proposing that propanal and 1-propanol can be formed *both* on exposed Rh and at the adlineation of TiO_x and Rh. Reaction on the first type of site would be inhibited by increasing TiO_x coverage, whereas reaction on the second type of site would be expected to increase and pass through a maximum as a consequence of the variation in the concentration of perimeter sites present at the adlineation between TiO_x islands and the surface of the Rh foil [14,44]. The higher selectivity to 1-propanol over propanal formed at the adlineation sites is consistent with the high activity of such sites for hydrogenation of acetone to 2-propanol [14].

As shown in fig. 3, the production of C_3-hydrocarbons closely parallels the formation of C_3-oxygenates. This strongly suggests that C_3-hydrocarbons are formed via the hydrogenolysis of the C–O bond in the C_3-oxygenate precursor. Such an interpretation would be totally consistent with the observed formation of propane during the hydrogenation of acetone over TiO_x-promoted Rh [14]. In that case, the activity of the catalyst for the conversion of acetone to 2-propanol and propane passes through a maximum with increasing TiO_x coverage.

The effects induced by titania on the reaction of C_2H_4, CO, and H_2 over Rh differ significantly from those observed by Ichikawa et al. [30] for ZnO_x-promoted Rh/SiO_2 catalysts. In that study, the rate of *propanal* formation was enhanced 15-fold at low Zn/Rh ratios, with a simultaneous decrease in the rate of ethane production. The authors attributed their results to a combination of two factors: 1) ZnO_x blocking sites for CO dissociation and ethylene hydrogenation, and 2) acceleration of the CO insertion step by interaction of CO with ZnO_x. The difference between TiO_x and ZnO_x promotion of Rh for $C_2H_4/CO/H_2$ reactions is not surprising, however, in light of the marked difference between the interactions of TiO_x and ZnO_x with CO. While TiO_x facilitates CO dissociation on Rh, ZnO_x inhibits CO dissociation [31].

5. Conclusions

The addition of TiO_x overlayers to a Rh foil catalyst has been found to affect the activity and selectivity for the reaction of C_2H_4, CO, and H_2. The primary function of titania in the production of C_3-oxygenates is to facilitate the hydrogenation of the carbonyl bond in the species formed from CO insertion. The rate of 1-propanol formation reaches a maximum at a titania coverage of 0.2 ML. The rates of CH_4 and C_3-hydrocarbons also achieve maxima at this coverage. In contrast, the titania is of no assistance in C–C bond formation between adsorbed hydrocarbon fragments as evidenced by decline in activity for C_4- and C_5-hydrocarbon production upon the addition of titania. The results are consistent with our previous hypothesis that an interaction between Ti^{3+} ions and C–O bonds assists in the dissociation of CO and the hydrogenation of carbonyl functional groups [14].

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References

[1] S.J. Tauster, Acc. Chem. Res. 20 (1987) 389.
[2] A.T. Bell, Supports and metal-support interaction in catalyst design, in: *Catalyst Design - Progress and Perspectives*, ed. L.L. Hegedus (Wiley, New York, 1987).
[3] G.L. Haller and D.E. Resasco, Adv. Catal. 36 (1989) 173.
[4] F. Solymosi, A. Erdöhelyi and T. Bansagi, J. Catal. 68 (1981) 371.
[5] M.A. Henderson and S.D. Worley, J. Phys. Chem. 89 (1985) 1417.
[6] T. Iizuka, Y. Tanaka and K. Tanabe, J. Molec. Catal. 17 (1982) 381.
[7] F. Nozaki, T. Sodesawa, S. Satoh and K. Kimura, J. Catal. 104 (1987) 339.
[8] Y.-W. Chung, G. Xiong and C.C. Kao, J. Catal. 85 (1984) 237.
[9] R.A. Demmin, C.S. Ko and R.J. Gorte, J. Phys. Chem. 89 (1985) 1151.
[10] R.A. Demmin and R.J. Gorte, J. Catal. 98 (1986) 577.
[11] M.E. Levin, M. Salmeron, A.T. Bell and G.A. Somorjai, J. Catal. 106 (1987) 401.

[12] M.E. Levin, M. Salmeron, A.T. Bell and G.A. Somorjai, J. Chem. Soc., Faraday Trans. 1, 83 (1987) 2061.
[13] R.A. Demmin and R.J. Gorte, J. Catal. 105 (1987) 373.
[14] K.J. Williams, A.B. Boffa, J. Lahtinen, M. Salmeron, A.T. Bell and G.A. Somorjai, Catal. Lett. 5 (1990) 385.
[15] J.G. Eckerdt and A.T. Bell, J. Catal. 62 (1980) 19.
[16] C.S. Kellner and A.T. Bell, J. Catal. 70 (1981) 418.
[17] Y. Kobori, H. Yamasaki, S. Naito, T. Onishi and K. Tamaru, J. Chem. Soc., Faraday Trans. 1, 78 (1982) 1473.
[18] S.R. Morris, R.B. Moyes, P.B. Wells and R. Whyman, J. Catal. 96 (1985) 23.
[19] S.S.C. Chuang, Y.H. Tian, J.G. Goodwin, Jr., and I. Wender, J. Catal. 96 (1985) 396.
[20] D.S. Jordan and A.T. Bell, J. Phys. Chem. 90 (1986) 4797.
[21] Ya.T. Eidus, Russ. Chem. Rev. (Engl. Trans.) 36 (1967) 338.
[22] E.J. Gibson and R.W. Clarke, J. Appl. Chem. 11 (1961) 293.
[23] W.K. Hall, R.J. Kokes and P.H. Emmett, J. Am. Chem. Soc. 82 (1960) 1027.
[24] D.J. Dwyer and G.A. Somorjai, J. Catal. 56 (1979) 249.
[25] W. Molina, V. Perrichon, R.P.A. Sneeden and P. Turlier, React. Kinet. Catal. Lett. 13 (1980) 69.
[26] J. Barrault, C. Forquy and V. Perrichon, J. Mole. Catal. 17 (1982) 195.
[27] S.S.C. Chuang and S.I. Pien, Catal. Lett. 3 (1989) 323.
[28] S.S.C. Chuang and S.I. Pien, Catal. Lett. 6 (1989) 389.
[29] D.G. Castner, R.L. Blackadar and G.A. Somorjai, J. Catal. 66 (1980) 257.
[30] M. Ichikawa, A.J. Lang, D.F. Shriver and W.M.H. Sachtler, J. Am. Chem. Soc. 107 (1985) 7216.
[31] W.M.H. Sachtler and M. Ichikawa, J. Phys. Chem. 90 (1986) 4752.
[32] Y. Konishi, M. Ichikawa and W.M.H. Sachtler, J. Phys. Chem. 91 (1987) 6286.
[33] S.S.C. Chuang and S.I. Pien, J. Molec. Catal. 55 (1989) 12.
[34] A. Maeda, F. Yamakawa, K. Kunimori and T. Uchijima, Catal. Lett. 4 (1990) 107.
[35] M.E. Levin, M. Salmeron, A.T. Bell and G.A. Somorjai, Surf. Sci. 169 (1986) 123.
[36] K.J. Williams, M. Salmeron, A.T. Bell and G.A. Somorjai, Surf. Sci. 204 (1988) L745.
[37] K.J. Williams, M.E. Levin, M. Salmeron, A.T. Bell and G.A. Somorjai, Catal. Lett. 1 (1988) 331.
[38] B.E. Bent, Ph.D. Thesis, Dept. of Chem., Univ. of Calif., Berkeley, 1986.
[39] D.G. Castner, B.A. Sexton and G.A. Somorjai, Surf. Sci. 71 (1978) 519.
[40] D.W. McKee., J. Catal. 8 (1967) 240.
[41] B.E. Koel, D.E. Peebles and J.M. White, Surf. Sci. 107 (1981) L367.
[42] B.E. Koel, D.E. Peebles and J.M. White, Surf. Sci. 125 (1983) 709.
[43] Y.T. Yates., Jr., P.A. Thiel and W.H. Weinberg, Surf. Sci. 84 (1979) 427.
[44] M.E. Levin, M. Salmeron, A.T. Bell and G.A. Somorjai, Surf. Sci. 195 (1988) 429.