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THE KINETICS OF CO_2 HYDROGENATION ON A Rh FOIL PROMOTED BY TITANIA OVERLAYERS

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Submonolayer deposits of titania on a Rh foil have been found to increase the rate of CO_2 hydrogenation. The primary product, methane, exhibits a maximum rate at a TiO_x coverage of 0.5 ML which is a factor of 15 higher than that over the clean Rh surface. The rate of ethane formation displays a maximum which is 70 times that over the unpromoted Rh foil; however, the selectivity for methane remains in excess of 99%. The apparent activation energy for methane formation and the dependence of the rate on H_2 and CO_2 partial pressure have been determined both for the bare Rh surface and the titania-promoted surface. These rate parameters show very small variations as titania is added to the Rh catalyst. The methanation of CO_2 is proposed to start with the dissociation of CO_2 into $CO_{(a)}$ and $O_{(a)}$, and then proceed through steps which are identical to those for the hydrogenation of CO. The increase in the rate of CO_2 hydrogenation in the presence of titania is attributed to an interaction between the adsorbed CO, released by CO_2 dissociation, and Ti^{3+} ions located at the edge of TiO_x islands covering the surface. Differences in the effects of titania promotion on the methanation of CO_2 and CO are discussed in terms of the mechanisms that have been proposed for these two reactions.

Keywords: CO_2 hydrogenation, TiO_2 promoted rhodium, kinetics of CO_2 and CO hydrogenation

1. Introduction

There is now a large body of evidence in the literature which demonstrates that interactions between oxides and metal catalysts can lead to promotional effects which greatly enhance the catalyst activity and alter its selectivity. In particular, many Group VIII metals, when supported on reducible oxides such as titania, niobia, and vanadia, show much higher CO hydrogenation activities than when supported on silica or alumina (see references [1-3] and references contained therein). These changes in activity are accompanied by shifts in selectivity as well. Titania-supported Rh catalysts also show increased activity for the hydrogenation of CO_2 relative to silica- or alumina-supported Rh [4,5], while both the activity and the selectivity to higher hydrocarbons are increased when niobia is used as the support [6,7]. The modification of the catalytic properties of these supported metals has been attributed to a decoration of the metal particles by deposits of the oxide. However, little is known about the mechanism by which the oxide-metal interaction affects the catalytic activity.

The interactions between oxide promoters and metals can best be studied in model catalyst systems, where the surface composition and structure of the catalyst can be measured and modified in a controlled fashion. Low surface area (~ 1 cm^2) metal foils and single crystals can be decorated with submonolayer quantities of oxide promoters. The catalyst surfaces can be analyzed using ultra-high vacuum surface analysis techniques, and the resulting catalytic properties can be measured. In this way, a relationship can be established between the catalytic properties and the surface structure which allows greater elucidation of the action of the promoter. Such model systems have been found to exhibit many of the catalytic properties of supported catalysts. Studies using foils and single crystals of Pt, Pd, Rh, and Ni have shown that sub-monolayer deposits of titania or niobia can increase the rate of CO hydrogenation [8–13].

In contrast to CO hydrogenation, much less is known about CO_2 hydrogenation and the effects of titania promotion on this reaction. Studies conducted with silica- and alumina-supported Rh [4,5,14] and polycrystalline Rh foil [15] have shown that CO_2 hydrogenation proceeds at a higher rate than CO hydrogenation. Henderson and Worley [5] have compared CO and CO_2 hydrogenation on supported Rh and found that the hydrogenation of CO_2 was enhanced to a greater degree by using titania as the support than was the hydrogenation of CO. In this paper we combine UHV surface analysis and atmospheric-pressure reactions to observe the effects of titania overlayers on the kinetics of CO_2 hydrogenation on Rh. When compared to our earlier results for CO hydrogenation [11,12], we find similarities in the promotion of the rates and selectivity shifts. However, differences are apparent in the effect of titania on the activation energy and reactant partial pressure dependence for each reaction.

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. [16]. The catalyst consisted of a 0.002-in thick Rh foil mounted on two 0.020-in Pt support wires. The sample was heated resistively and its temperature was measured by a chromel/alumel (type K) 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 of the sample to 4 L of CO at room temperature and subsequent flashing to 773 K. The decrease in the intensity of the Rh AES signal was used to determine the titania coverage. A description of this technique and its calibration are given in ref. [17].

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-versus-coverage experiments as well as the activation energy determinations, the partial pressures were 570 Torr H_2 and 190 Torr CO_2. For the partial pressure dependence studies, the H_2 or CO_2 partial pressure was decreased and Ar was added to make up the total pressure of 1 atm. All reactions were run at low conversion ($\leqslant 5\%$). 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

Fig. 1 shows the effect of titania coverage on the rate of methane formation from the hydrogenation of CO_2 at 523 K. The rate of CH_4 formation increases up to a titania coverage of 0.5 ML, whereafter the rate declines. The maximum in the rate of CH_4 production is 15 times that measured for the bare Rh surface. The magnitude of the rate increase is similar to that observed by Solymosi et al. [4] and by Henderson and Worley [5] for titania-supported Rh relative to silica- and alumina-supported Rh.

Ethane is formed in the reaction to a minor extent. The ethane rate is shown as a function of titania coverage in fig. 2. In this case, the maximum rate of ethane formation, which occurs at a titania coverage of 0.8 ML, is 70 times that of the bare Rh surface. Even though the rate of ethane production is promoted to a much greater degree than that of methane, the selectivity to methane remains in excess of 99% at all titania coverages. Fig. 3 shows the ratio of methane to ethane in the product as a function of titania coverage. On the clean surface, the ratio is approximately 1100 : 1. As the titania coverage increases, there is a sharp decrease

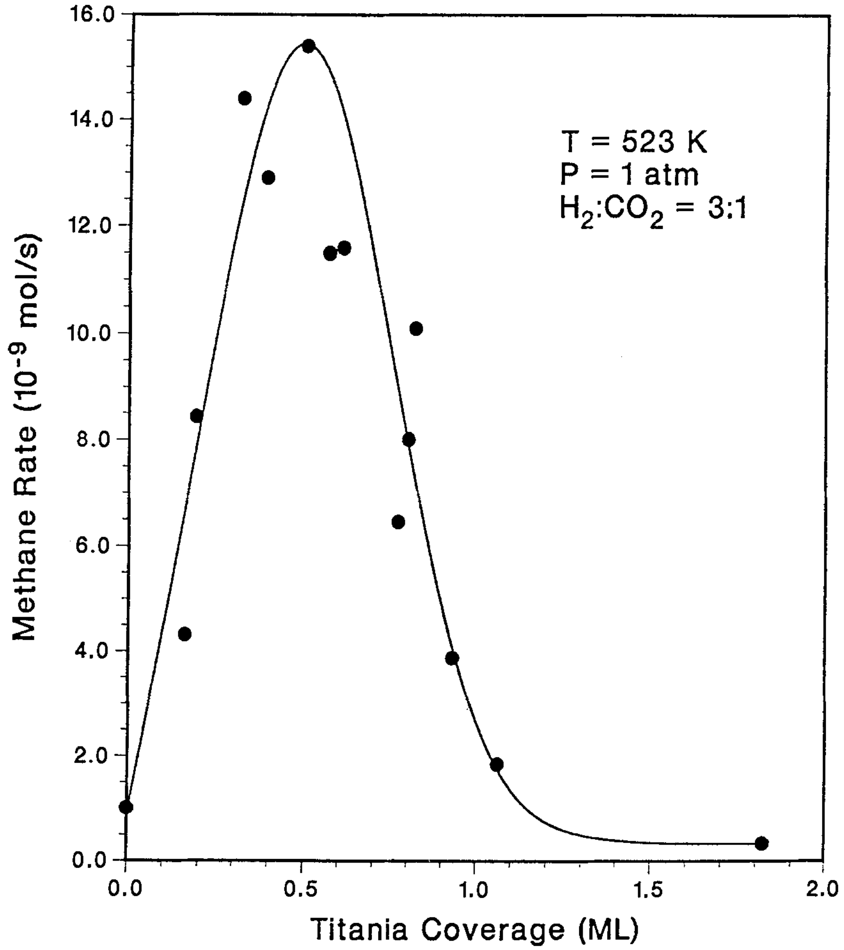

Fig. 1. Rate of CH_4 formation from the hydrogenation of CO_2 on a Rh foil as a function of titania coverage. Reaction conditions: $T = 523$ K, $P_{H_2} = 570$ Torr, $P_{CO_2} = 190$ Torr.

in the $CH_4 : C_2H_6$ ratio, and at a titania coverage of 1 ML, the ratio is only 100 : 1.

Fig. 4 shows the dependence of the apparent activation energy for methane formation on the titania coverage. For bare Rh, $E_a = 16.7$ kcal/mol, in close agreement with that reported by Sexton and Somorjai [15] for a polycrystalline Rh foil (16 ± 2 kcal/mol), and that reported by Solymosi et al. [4] for Rh supported on Al_2O_3 (16.2 ± 0.4 kcal/mol) and SiO_2 (17.3 ± 0.6 kcal/mol). With increasing titania coverage, E_a decreases to a minimum of 15.8 kcal/mol at a titania coverage of 0.3 ML, and then rises progressively with further increase in titania coverage. At a TiO_x coverage of 0.85 ML, $E_a = 18$ kcal/mol.

The effect of titania on the partial pressure dependencies is quite modest. On the clean surface, the methane rate is 0.5 order in the H_2 partial pressure and 0.2 order in the CO_2 partial pressure. These values are close to those reported by

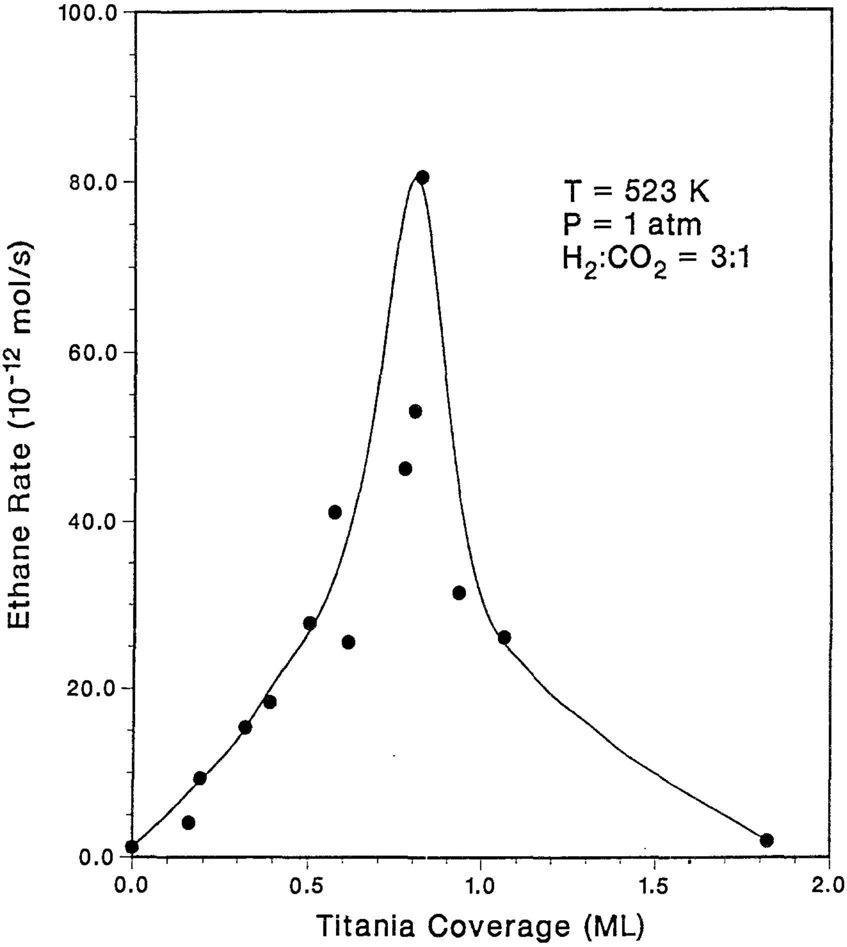

Fig. 2. Rate of C_2H_6 formation from the hydrogenation of CO_2 on a Rh foil as a function of titania coverage. Reaction conditions: $T = 523$ K, $P_{H_2} = 570$ Torr, $P_{CO_2} = 190$ Torr.

Solymosi et al. [4], who observed orders of 0.6 for H_2 and 0.3 for CO_2 for alumina-supported Rh. At a titania coverage of 0.5 ML, where the methane activity reaches a maximum, the rate is still 0.5 order in H_2 while the CO_2 order has increased slightly to 0.3.

A comparison between the hydrogenation of CO and CO_2 is shown in table 1. The data for CO hydrogenation are taken from ref. [12]. Rate parameters are shown for each reaction for the bare Rh surface as well as for a titania coverage of 0.5 ML, the titania coverage at which the rate of methanation is a maximum for both reactions. At 523 K, the rate of CO_2 methanation is 20 times higher than the rate of CO methanation. This pattern is consistent with that reported previously for both polycrystalline Rh foil [15], and silica- and alumina-supported Rh [4,5,14]. Titania enhances the rate of methanation to a greater extent for CO_2

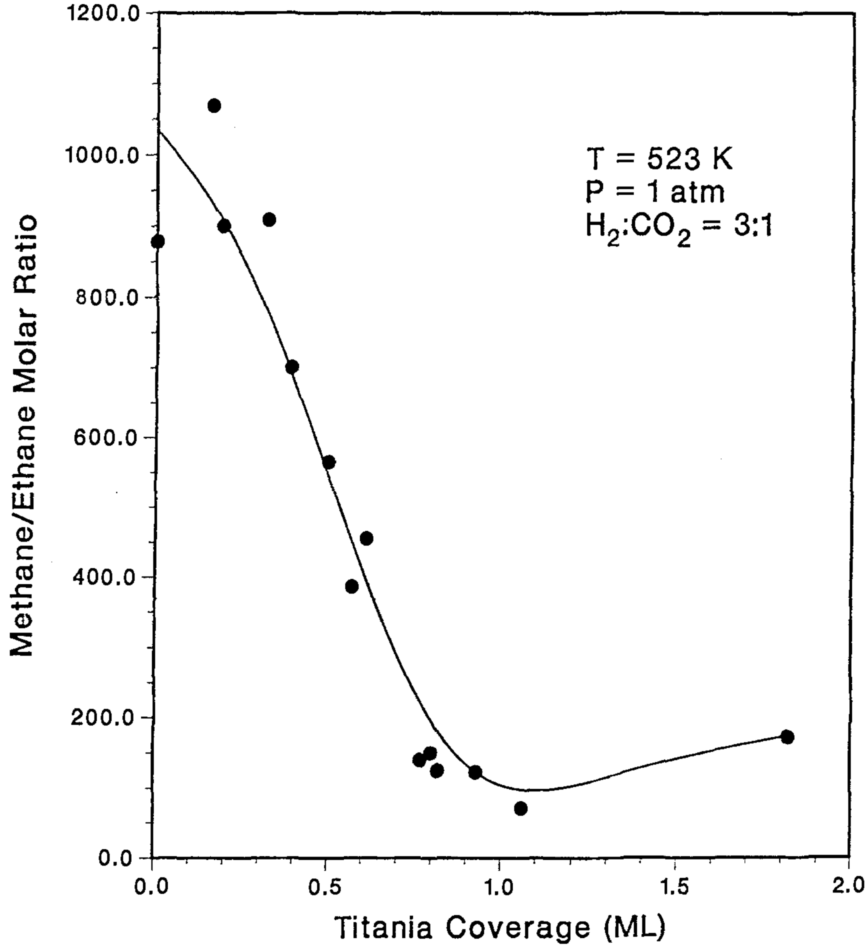

Fig. 3. Product selectivity during CO_2 hydrogenation as a function of titania coverage. Reaction conditions: $T = 523$ K, $P_{H_2} = 570$ Torr, $P_{CO_2} = 190$ Torr.

Table 1
Comparison between CO and CO_2 hydrogenation kinetics

	Co + H_2 (553 K) [a]		CO_2 + H_2 (523 K)	
	Clean Rh	0.5 ML TiO_x	Clean Rh	0.5 ML TiO_x
CH_4 turnover freq. (s^{-1}) [b]	0.034 [c] (0.0096)	0.11 [c] (0.045)	0.19	2.9
CH_4 act. energy (kcal/mole)	24	17	17	17
Hydrogen pressure exponent	1.0	2.5	0.5	0.5
CO/CO_2 pressure exponent	−1.0	−0.3	0.2	0.3
Selectivity to CH_4 (%)	90	60	99+	99+

Reaction conditions: $P = 1$ atm, $H_2/CO = 2$, $H_2/CO_2 = 3$.

[a] From ref. [12].

[b] Based on the number of sites present on a clean Rh surface.

[c] Projected values for 523 K using activation energies shown.

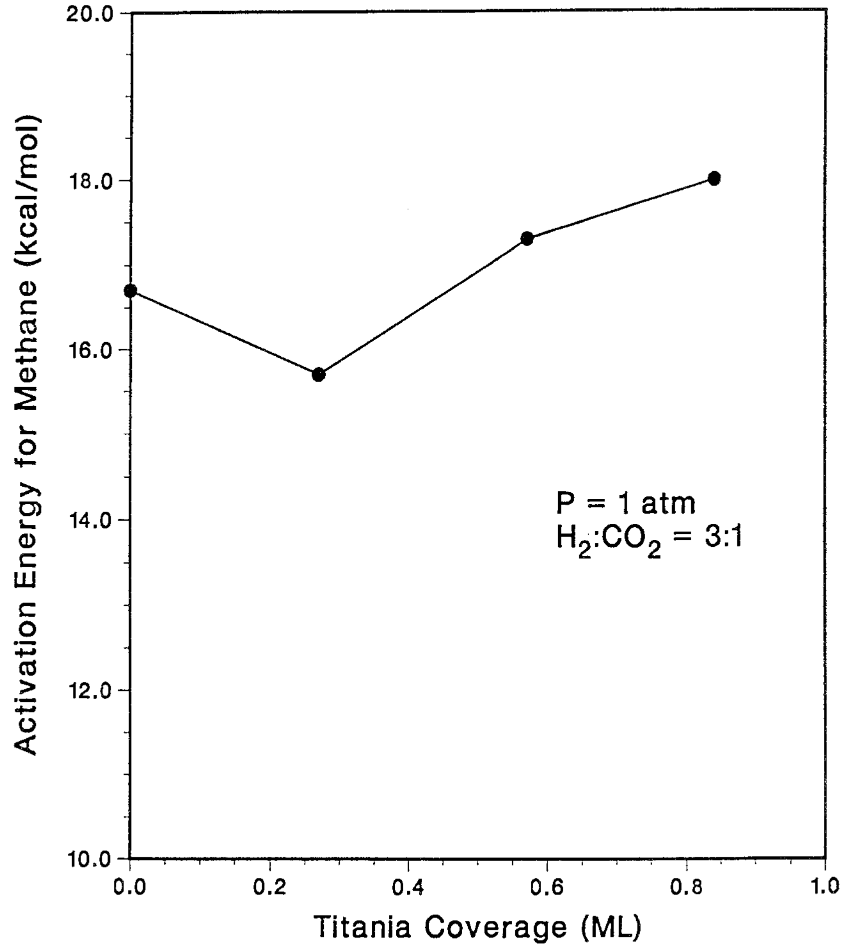

Fig. 4. Activation energy for methane formation from CO_2 hydrogenation as a function of titania coverage. Reaction conditions: $pP_{H_2} = 570$ Torr, $P_{CO_2} = 190$ Torr, $T = 448$–573 K.

than for CO. Table 1 shows that the methane turnover frequency is only enhanced by a factor of 3 for CO, while for CO_2 it is increased by a factor of 15.

Table 1 also shows a sharp contrast between the effects of titania on the rate parameters for the two reactions. Titania has only a modest effect on the activation energy for methanation of CO_2 as well as the orders in CO_2 and H_2 partial pressure. On the other hand, for CO hydrogenation, the CH_4 activation energy decreases from 24 kcal/mol on clean Rh to 17 kcal/mol for a titania coverage of 0.5 ML, and the H_2 partial pressure dependence increases from 1.0 to 2.5 while the CO partial pressure dependence increases from -1.0 to -0.3.

4. Discussion

Before interpreting the present results, it is useful to review what is known about the mechanisms of CO and CO_2 hydrogenation on Rh. For the case of CO hydrogenation, studies by Sachtler and Ichikawa [18] suggest that the rate limiting step in the formation of methane is the rupture of the C–O bond. In support of this conclusion, it was reported that room-temperature adsorption of CO on a Rh/SiO_2 catalyst and subsequent temperature-programmed reduction (TPR) in pure H_2 resulted in the concurrent production of CH_4 and H_2O. Promotion of the catalyst with TiO_x or MnO_x decreased the product peak temperatures, but the peak temperatures for CH_4 and H_2O remained identical. These observations indicate that TiO_x and MnO_x-promotion of Rh/SiO_2 facilitates the cleavage of the C–O bond during CO hydrogenation. While the rupture of the C–O bond appears to be the rate-limiting step, it seems unlikely that this occurs via the dissociation of molecularly adsorbed CO, since the hydrogenation of CO is observed to occur at a lower temperature than that required for CO dissociation in the absence of H_2 [18]. As an alternative, experiments by Mori et al. [19–21] and Rieck and Bell [22] suggest that C–O bond cleavage during CO hydrogenation may occur from a partially hydrogenated species, e.g., $HCO_{(a)}$, $H_2CO_{(a)}$, or $CH_3O_{(a)}$. Theoretical support for such a process is provided by BOC-MP (bond-order-conservation-Morse-potential) calculations reported recently by Shustorovich and Bell [23].

A plausible mechanism for the hydrogenation of CO on metallic Rh is shown in fig. 5. This scheme is consistent with the discussion presented above and assumes that the rate-limiting step is the dissociation of $H_2CO_{(a)}$ [24]. Under reaction conditions, the most abundant surface species is expected to be CO, since the heat of CO chemisorption ($\Delta H = 29$–32 kcal/mol [25–28]) is greater than that of H_2 ($\Delta H = 18.6$ kcal/mol [29]). If it is further assumed that the surface coverage of CO is close to unity, the rate of CH_4 formation can be shown [24] to be proportional to $P_{H_2}^{+1}P_{CO}^{-1}$, in agreement with what is observed experimentally (see table 1).

The hydrogenation of CO_2 over Group VIII metals is thought to proceed via the dissociative adsorption of CO_2 to form $CO_{(a)}$ and $O_{(a)}$, whereafter the adsorbed CO undergoes hydrogenation according to the scheme shown in fig. 5. This mechanism of CO_2 hydrogenation is supported by the studies of Amariglio et al. [30] on Rh powder. Carbon dioxide was adsorbed at room temperature. Upon subsequent passage of H_2 at room temperature, H_2O was observed to form in the amount of one molecule of H_2O per molecule of CO_2 adsorbed. TPR of the residually adsorbed CO resulted in the formation of CH_4 and H_2O in a 1 : 1 ratio with identical peak temperatures, suggesting that, as in the case of CO hydrogenation, rupture of the C–O bond in a species such as $H_2CO_{(a)}$ is the rate-limiting step.

A plausible mechanism for CO_2 hydrogenation which is consistent with these

Proposed Mechanism of CO Hydrogenation

1. $CO_{(g)} + S \rightleftharpoons CO_{(a)}$
2. $H_2 + 2\,S \rightleftharpoons 2\,H_{(a)}$
3. $2\,H_{(a)} + CO_{(a)} \rightleftharpoons H_2CO_{(a)} + 2\,S$
4. $H_2CO_{(a)} + S \rightarrow CH_{2(a)} + H_{(a)}$
5. $O_{(a)} + H_{(a)} \rightleftharpoons OH_{(a)} + S$
6. $OH_{(a)} + H_{(a)} \rightarrow H_2O_{(g)} + 2\,S$
7. $CH_{2(a)} + H_{(a)} \rightleftharpoons CH_{3(a)} + S$
8. $CH_{3(a)} + H_{(a)} \rightarrow CH_{4(g)} + 2\,S$

Rate Expression:

$$R_{CH_4} = \frac{k_4 K_1 K_2 K_3}{[1 + K_2^{1/2} P_{H_2}^{1/2} + K_1 P_{CO}]^2} P_{H_2} P_{CO}$$

Fig. 5. Proposed mechanism of CO hydrogenation and rate expression for methanation. In the rate expression, k_i is the forward rate constant for reaction i and K_i is the equilibrium constant for reaction i.

observations and is analogous to that for CO hydrogenation is shown in fig. 6, along with the rate expression derived using Langmuir-Hinshelwood kinetics [24]. The rate expression shows that the "effective" partial pressure dependence of H_2 can range from 0 to 1.0 order, while that of CO_2 can range from -0.5 to 0.5 order. The observed partial pressure dependencies listed in table 1 for H_2 (0.5) and CO_2 (0.2–0.3) can be reconciled with a particular set of constants for the denominator terms [24] which gives roughly equal importance to the coverages of $H_{(a)}$ and $CO_{(a)}$, and leads to the conclusion that the surface coverages of both $H_{(a)}$ and $CO_{(a)}$ are significant. The heat of dissociative adsorption of CO_2, which can be estimated using the heats of adsorption of CO and dissociative adsorption of O_2 (85 kcal/mol [31]), may be as low as 6 kcal/mol, and hence $CO_{(a)}$ would not be expected to dominate the catalyst surface during CO_2 hydrogenation. Although the rapid removal of $O_{(a)}$ as H_2O would tend to increase the coverage of $CO_{(a)}$ over that predicted on the basis of the heat of adsorption, the low H_2 partial pressure dependence and the small, positive CO_2 partial pressure dependence are indicative of a lower coverage of $CO_{(a)}$ than that produced from CO in the gas phase. We therefore expect the $H_{(a)}/CO_{(a)}$ ratio on the catalyst surface to be much higher during CO_2 hydrogenation than during CO hydrogenation.

We believe that the promotion of CO and CO_2 hydrogenation by titania is due to an interaction between the titania and the adsorbed CO, which facilitates the rate of C–O bond cleavage. Evidence from XPS [32] and STM [33] suggest that at

Proposed Mechanism of CO_2 Hydrogenation

1. $CO_{2(g)} + 2\,S \rightleftharpoons CO_{(a)} + O_{(a)}$
2. $H_{2(g)} + 2\,S \rightleftharpoons 2\,H_{(a)}$
3. $2\,H_{(a)} + CO_{(a)} \rightleftharpoons H_2CO_{(a)} + 2\,S$
4. $H_2CO_{(a)} + S \rightarrow CH_{2(a)} + O_{(a)}$
5. $O_{(a)} + H_{(a)} \rightleftharpoons OH_{(a)} + S$
6. $OH_{(a)} + H_{(a)} \rightarrow H_2O_{(g)} + 2\,S$
7. $CH_{2(a)} + H_{(a)} \rightleftharpoons CH_{3(a)} + S$
8. $CH_{3(a)} + H_{(a)} \rightarrow CH_{4(g)} + 2\,S$

Rate Expression:

$$R_{CH_4} = \frac{(k_4 k_6 K_1 K_3 K_5/2)^{1/2} K_2}{[1 + K_2^{1/2} P_{H_2}^{1/2} + (k_6 K_1 K_5/2k_4 K_3)^{1/2} P_{CO_2}^{1/2}]^2} P_{H_2} P_{CO_2}^{1/2}$$

Fig. 6. Proposed mechanism of CO_2 hydrogenation and rate expression for methanation. In the rate expression, k_i is the forward rate constant for reaction i and K_i is the equilibrium constant for reaction i.

submonolayer coverages, titania covers the Rh surface in the form of islands. The oxidation state of Ti in the interior of the islands is mainly Ti^{4+}, while Ti^{3+} ions are located at the island perimeter. CO molecules adsorbed on Rh sites lying at the adlineation between the Rh surface and the titania islands can interact with the exposed Ti^{3+} ions via a Lewis acid-base interaction (e.g., $Ti^{3+} \leftarrow O{\equiv}C$). This mechanism of interaction has been proposed by Sachtler and Ichikawa [18] and Levin et al. [12] to explain the the promotion of Rh catalysts by TiO_x for CO hydrogenation. The proposed model for the effects of TiO_x promotion is also consistent with the observation of a maximum rate in methane formation at a TiO_x coverage of 0.5 ML, since a simple island growth model shows that the number of oxide-metal adlineation sites should maximize at this titania coverage [24].

The difference in the effect of titania on the kinetic parameters can be understood in terms of the hydrogen surface coverages during each reaction. During CO hydrogenation, the surface coverage of CO is high and the concentration of H atoms is low. It is possible that the addition of titania may so enhance the rate of CO dissociation that the rate-limiting step for methane formation shifts to the hydrogenation of the carbonaceeus fragments on the relatively hydrogen-poor surface. The change in the H_2 partial pressure dependence from 1.0 to 2.5 order is consistent with this view [24].

During CO_2 hydrogenation on the other hand, the surface coverage of hydrogen is expected to be higher than that occurring during CO hydrogenation, for the reasons cited above. Thus, as the titania increases the rate of C–O bond rupture, this step remains rate-limiting, since the hydrogenation of surface carbon remains facile because of the relatively high H atom coverage. This might explain the absence of significant changes in the rate parameters for CO_2 hydrogenation upon TiO_x promotion. The larger enhancement with TiO_x promotion observed for CO_2 hydrogenation relative to CO hydrogenation might also be explained by the same arguments. While the hydrogenation of surface carbon may limit the rate of methanation in the presence of titania, no such limitation occurs for CO_2 hydrogenation.

There is a shift in selectivity toward higher hydrocarbons when titania is present for the hydrogenation of both CO and CO_2. As stated above, we believe that the role of the titania is to accelerate the rate of C–O bond cleavage. This would increase the surface coverage of carbonaceous species during the reaction and, hence, favor C–C bond formation.

5. Conclusions

The addition of titania deposits to the surface of a Rh foil has been shown to have a large impact on the rate of CO_2 hydrogenation. The rate of methane formation displays a maximum at a TiO_x coverage of 0.5 ML which is 15 times that over the unpromoted Rh foil. The rate of ethane formation is enhanced by a factor of 70 over the clean surface rate, although ethane constitutes less than 1% of the product. Although a large promotional effect is observed, the activation energy for methane formation varies only slightly with titania addition, and the dependence of the rate on the partial pressures of H_2 and CO_2 remains virtually unchanged.

The methanation of CO_2 is envisioned to start with the dissociation of CO_2 into $CO_{(a)}$ and $O_{(a)}$, and then proceed through steps which are identical to those for the hydrogenation of CO. The increase in the rate of CO_2 hydrogenation in the presence of titania is attributed to an interaction between the adsorbed CO, released by CO_2 dissociation, and Ti^{3+} ions located at the edge of TiO_x islands covering the Rh surface. This interaction facilitates the rate of C–O bond cleavage, thereby providing a source of carbon atoms which rapidly undergo hydrogenation to form methane and a small amount of ethane. The observation of a maximum rate of methane formation at a TiO_x coverage of 0.5 ML is ascribed to the occurrence of a maximum in the number of oxide-metal adlineation sites.

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