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A Study of Methanation Kinetics on a Clean and a Titania-Covered Platinum Foil*

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We have investigated the detailed methanation kinetics for a clean and a titania-covered Pt foil. Pressure dependences for H_2 and CO were measured between 0.01 and 100 Torr, and Auger electron spectra (AES) were taken of the surfaces following reaction. For the foil not covered by titania, AES indicated that there is no carbon on the surface following reaction, even for H_2/CO pressure ratios as low as 0.03. Kinetic measurements indicated that the reaction order for CO changed from first order at low pressures to zero order at higher pressures, while the reaction was always first order for H_2 except for low CO pressures. The methanation kinetics could be modeled by a Langmuir–Hinshelwood rate expression in which CO and hydrogen are competitively adsorbed. The adsorption equilibrium constants in the rate expression for both CO and H_2 were identical to those obtained from adsorption and desorption measurements in ultrahigh vacuum experiments, indicating that the dominant adsorbed species during reaction are likely the same as those species measured in adsorption. The results for the titania-covered foil showed that methanation on this surface is very different. AES indicated that significant quantities of a reactive carbon were present on the surface at low H_2/CO pressure ratios. The reaction was again zero order in CO at high CO pressures; however, the reaction became half order rather than first order at low CO pressures. The reasons for the enhanced methanation activity of titania-supported catalysts are discussed in terms of these results.

INTRODUCTION

It has long been known that unusual adsorption and reaction properties can be observed for titania-supported, Group VIII metals when they are reduced in H_2 at temperatures above 750 K (*1–3*). Adsorption of CO and H_2 is suppressed on these catalysts but they remain active methanation catalysts. For example, methanation rates based on metal surface areas on Pt/TiO_2 are reported to be 10 times higher than those on Pt/Al_2O_3 and 100 times higher than those on Pt/SiO_2, even though little adsorption of CO or H_2 is observed on the Pt/TiO_2 catalyst (*4, 5*). While a number of mechanisms have been proposed for the cause of these titania-support effects (*1, 2, 6–13*), several recent studies have demonstrated that suppressed adsorption and enhanced reaction properties can be duplicated by depositing titania onto the catalytic metal (*14–22*). It has been shown that titania can migrate onto the metal catalyst and form an even overlayer which can completely prevent the adsorption of CO and H_2 (*14–16*). In addition, a Pt foil with a titania overlayer has been shown to exhibit identical methanation rates to those observed on actual Pt/TiO_2 catalysts (*17*). These results suggest that the metal with a titania overlayer provides a good model for what is happening on normal supported catalysts.

While the results with titania overlayers on bulk metals may explain what is physically happening on the catalyst, they do not explain why the presence of titania should prevent adsorption but enhance activity. One reason that has been suggested is that the role of titania involves an interaction between CO and a Ti^{3+} cation (*23–25*);

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however, no direct evidence for any interactions between the titania and the reacting CO has been observed.

An inherent difficulty in studying how titania affects the reaction is that adsorption is not observed, at least not in significant quantities, under conditions where one can easily examine the surface spectroscopically. There is also the question of whether spectroscopically observed species are relevant to the reaction, even on the clean surface where adsorption is observed. Therefore, in order to probe the surface under the temperature and pressure conditions relevant to reaction, we have measured the detailed methanation kinetics for both a clean Pt foil and a Pt foil with a titania overlayer. As discussed, the foil with the titania overlayer appears to provide an adequate model for the actual, titania-supported catalysts. The advantage to studying this type of sample was that we were able to measure kinetics over a much wider temperature and pressure range than would have been possible on more conventional catalysts. Also, we were able to measure surface coverages easily following reaction using Auger electron spectroscopy.

In this paper, we will show that the kinetics for methanation change dramatically in the presence of titania overlayers and that titania apparently assists in the dissociation of CO. We will also show for the clean surface that H_2 and CO adsorb competitively and that the parameters determined from adsorption experiments can be used to predict transitions in reaction orders.

EXPERIMENTAL

The experimental apparatus has been described previously (*17*). Reactions were performed over a polycrystalline, Pt foil with an area of approximately 1.4 cm^2 in a high-pressure chamber which was attached to an ultrahigh vacuum system. The high-pressure chamber consisted of a magnetically manipulated, linear-motion feedthrough which allowed the sample to be transferred to the vacuum system for Auger analysis. The vacuum system was also used to clean the foil by Ar ion bombardment and to deposit titania. The sample was heated resistively and its temperature was measured using a chromel–alumel thermocouple. Particular care was taken in the design to ensure that only the sample itself was heated and that temperature gradients along the sample were minimized (*17*).

The CO and H_2 reactant gases were of 99.99 and 99.999% purity, respectively, and were further purified by passing them through an activated carbon trap and a liquid N_2 trap before introducing them to the system. In addition, the reaction chamber was carefully baked to prevent contamination from the walls. These purification procedures allowed the sample to be exposed to the reactant gases at near atmospheric pressures at 295 K without causing any carbon or other contamination on the surface. This was an important consideration in our experiments since we wished to look for the presence of carbon or other impurities on the surface following reaction.

The partial pressures of each reactant gas were determined by measuring the increase in the pressure of the chamber with a capacitance manometer. Reactions were run in the batch mode at conversions which were generally much less than 1% and the reaction rates were monitored by measuring the concentration of methane using a gas chromatograph. Gas samples were removed from the chamber by expansion into an evacuated gas-sampling valve, and concentrations were calibrated with known standards. Under all reaction conditions, methane was the predominant hydrocarbon product formed and we never observed a conversion to ethylene and ethane of more than 3% of the methane conversion.

Initial treatment of the sample consisted of cycles of Ar ion sputtering and annealing to remove Si and Ca impurities which segregated to the surface. No stable surface oxides could be formed after these impurities had been eliminated (*51*). Small amounts of carbon were cleaned by heating the sample to 800 K in 10^{-7} Torr O_2. After all impurities had been removed, the foil was heated to 973 K in 400 Torr H_2 and 100 Torr CO for at least one hour. Although this treatment in the reaction environment resulted in no visible changes in the Auger spectrum of the surface, it led to higher methanation rates which were very reproducible, as discussed previously (*17*). These increased methanation rates were not due to changes in surface area since no substantial increases were observed in the amounts of CO or H_2 which could adsorb on the foil.

Titania overlayers were deposited onto the sample by heating a Ti–Ta alloy wire near the surface in 10^{-7} Torr O_2. After several layers of TiO_2 had been deposited, the sample was flashed to above 1300 K to remove the excess titania and give a reproducibly even overlayer on the Pt foil. Previous characterization of these overlayers has shown that the coverage is approximately 10^{15} oxygen atoms/cm^2 with a stoichiometry close to that of TiO (*14, 26*). The titanium in this overlayer is Ti^{3+}, indicating that it is probably bound to the metal surface (*26*). No adsorption of CO or H_2 was observed on these surfaces in temperature-programmed desorption experiments (TPD), even for adsorption at 80 K (*14*).

RESULTS

Clean Pt

Surface analysis. One of the principal objectives of this work was to determine whether carbonaceous deposits are present on the surface during reaction. Figure 1 gives the Auger spectra for a Pt foil following reaction for 3 hr at 770 K in 3 Torr H_2 and 100 Torr CO. Under these conditions, the quantity of methane produced was 4.7×10^{16} molecules/cm^2. In the upper spectrum, the sample was cooled to 295 K in the reaction environment, followed by evacuation and Auger analysis. The spectrum is identical to that of a surface saturated with CO (*27*). The O(508 eV) peak is not observed due to electron beam desorption and the C(272 eV) peak is the height expected for a monolayer of CO. Further evidence that the only carbonaceous species on the surface after reaction is molecular CO was obtained by flashing the sample to 770 K. Only CO and H_2 were observed desorbing from the sample and the spectrum returned to that of the clean Pt surface shown in the lower spectrum. We found no evidence for the presence of hydrocarbons in the desorbing gases.

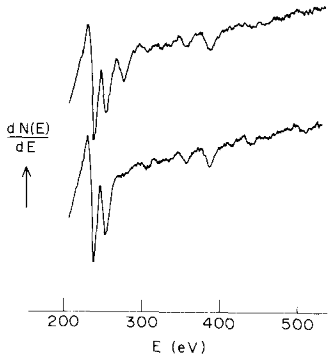

FIG. 1. Auger electron spectra of the clean Pt foil following reaction at 770 K for 3 hr in 3 Torr H_2 and 100 Torr CO. The upper spectrum was taken after the sample had been cooled in the reaction environment and is identical to that of Pt with a monolayer of CO. The bottom spectrum is that of the same sample after heating in vacuo to 770 K and is indicative to uncontaminated Pt.

We believe that it is unlikely that hydrocarbon intermediates would be removed from the sample by cooling in the reaction environment or during evacuation at 295 K; therefore, this result shows that the dominant species on the surface during methanation on a Pt foil, even for very low H_2/CO ratios, are the reactants CO and H_2. Any dissociated CO or CH_x species present during reaction must have a very short lifetime on this surface. This is consistent with surface science studies of CO adsorption on Pt (*27, 28*) and with *in situ* infrared studies carried out on supported Pt catalysts, where the primary adsorbate observed was also CO (*4, 29*).

This lack of carbonaceous materials on Pt is very different from results reported on more active catalytic metals. Goodman and co-workers used AES to show that a carbide species is formed on Ni and Ru crystals under reaction conditions and they demonstrated that reaction rates can be correlated to the carbide levels (*30, 31*). In addition, CH_x species have been detected following reaction on the surface of an Fe(110) crystal with high-resolution electron energy loss spectroscopy (HREELS) (*32*) and on Ni(111) with secondary ion mass spectroscopy (SIMS) (*33*). These surface species were not observed in our experiments on Pt.

In order to determine whether this absence of carbon could be due to rapid removal of a carbide by H_2, we also performed a study of CO dissociation on the clean Pt foil by heating the foil in 10 Torr CO. After 120 sec at 570 K, we examined the sample by AES for any sign of carbon which could be due to dissociated CO. However, the Auger results were the same as shown above, indicating that only CO was present on the surface following this high-temperature treatment. Since this exposure of CO in the presence of 400 Torr H_2 would have produced 10^{14} molecules of CH_4/cm^2, these experiments show that the dissociation rate for CO in the absence of H_2 is not rapid compared to the rate of methanation. A coverage of 10^{14} C atoms/cm^2 corresponds to approximately 20% of a monolayer of CO (*28*) and should have been easily detected by Auger spectroscopy.

Methanation kinetics. To get a better understanding of the methanation reaction on the clean Pt foil, we have measured rates over a wide range of reactant pressures and temperatures. Figure 2 shows the methanation rates as a function of CO pressure at 400 Torr H_2 for three different temperatures. At high CO pressures near the stoichiometric ratio for methanation, the CO pressure dependence is approximately zero order, in agreement with observations on supported Pt catalysts (*34*). At low CO pressures, however, we observe a transition to a first-order regime. This transition between a first-order and a zero-order regime is consistent with a simple, Langmuir–Hinshelwood rate expression and is the expected result for a surface reaction with molecular CO. This pressure dependence has not been observed previously due to the fact that most studies have concentrated on a much more limited pressure range.

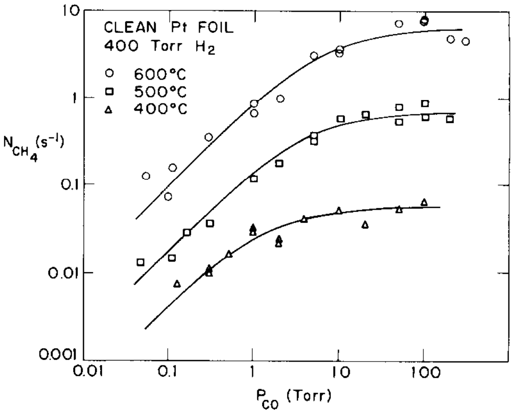

FIG. 2. Methanation rates (molecules CH_4/site sec) over a clean Pt foil as a function of CO pressure at three temperatures in 400 Torr H_2. Reaction rates were first order in CO at low pressures and zero order at higher pressures.

The results for the pressure dependence of H_2 on the methanation rates over our Pt foil are plotted in Fig. 3. Pressure dependence studies were carried out at 770 K with CO pressures of 100 and 0.1 Torr. These CO pressures were chosen since they represent the zero- and first-order regimes for the methanation reaction. At 100 Torr CO, the reaction rate was first order in H_2 pressure, consistent with observations on supported Pt (*34*). At the lower CO pressure, the reaction rate was also first order at low H_2 pressures but the order decreased for H_2 pressures above 100 Torr. Because H_2 adsorbs dissociatively on Pt, the first-order dependence implies that two adsorbed hydrogen atoms are involved in the reaction in the steps leading up to and including the rate-determining step (*35*). The

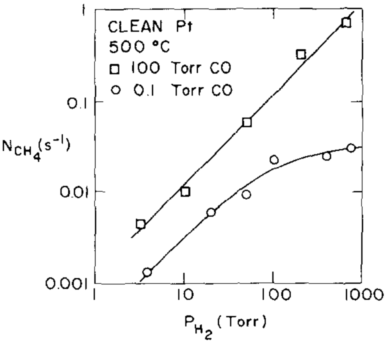

FIG. 3. Methanation rates over a clean Pt foil at 770 K as a function of H_2 pressure for CO pressures of 100 and 0.1 Torr.

fact that the H_2 pressure dependence decreases for low CO pressures which give a first-order CO dependence, and not for the higher CO pressures, implies that there is competition for adsorption sites between the adsorbed CO and hydrogen.

While there are a number of different mechanisms which can lead to rate expressions consistent with the measurements we have made, the saturation effects which we observe in the reaction order are due to adsorption equilibria for H_2 and CO and are common to each of those mechanisms. Therefore, it is informative to examine one possible mechanism in order to discuss the relationship between adsorption measurements and reaction kinetics. For illustration, we have chosen a mechanism in which the rate-limiting step is the hydrogen-assisted dissociation of CO. We assume that a CH_2O complex is formed in small quantities on the surface and that the rate-limiting step is the dissociation of this complex. The mechanistic steps can then be written as follows:

$$\mathrm{CO} + \mathrm{S} \overset{K_{\mathrm{CO}}}{\rightleftharpoons} \mathrm{CO_{ad}}$$

$$\mathrm{H_2} + 2\mathrm{S} \overset{K_{\mathrm{H_2}}}{\rightleftharpoons} 2\mathrm{H_{ad}}$$

$$\mathrm{CO_{ad}} + 2\mathrm{H_{ad}} \overset{K_e}{\rightleftharpoons} \mathrm{CH_2O_{ad}} + 2\mathrm{S}$$

$$\mathrm{CH_2O_{ad}} \xrightarrow{k_r} \text{Products}$$

The rate expression for this mechanism is

$$r = \frac{k_r K_e K_{\mathrm{CO}} K_{\mathrm{H_2}} P_{\mathrm{CO}} P_{\mathrm{H_2}}}{[1 + (K_{\mathrm{H_2}} P_{\mathrm{H_2}})^{1/2} + K_{\mathrm{CO}} P_{\mathrm{CO}}]}.$$

This expression predicts the proper pressure dependence for CO with a fixed H_2 pressure and also predicts that the H_2 pressure necessary to saturate the reaction rate will be dependent on the CO pressure.

Since K_{CO} and $K_{\mathrm{H_2}}$ are adsorption equilibrium constants, these can be calculated independently from adsorption experiments assuming that there are no energetic interactions between the H_2 and CO. While the adsorption of CO on Pt is strongly crystal plane dependent (*36*), the temperature-programmed desorption curves for CO from a Pt foil (*14*) are essentially identical to those reported by Fair and Madix for CO from a Pt(110) crystal (*37*). On both surfaces, two desorption states are observed at 400 and 520 K. Fair and Madix calculated that the first-order desorption preexponential for CO was 6 × 10^{14}/sec, making the activation energies for these two peaks be 27.4 and 35.9 kcal/mol, respectively, assuming that the two peaks correspond to two adsorption states. Fair and Madix also determined that the sticking coefficient for CO on Pt(110) was 0.7 and was approximately temperature independent, at least up to 625 K. We have used this data to calculate the equilibrium constants for the high-temperature state and have listed these in Table 1 for the three temperatures of interest.

TABLE 1

	400°C	500°C	600°C
$K_{\mathrm{CO}}{}^{a}$ (Torr $^{-1}$)	220	6.9	0.48
$K_{\mathrm{H_2}}{}^{b}$ (Torr $^{-1}$)	1.0	0.12	0.022

[a] Calculated assuming adsorption and desorption rate constants obtained from Fair and Madix (*37*) with an adsorption energy of 35.9 kcal/mol.

[b] Calculated assuming an adsorption energy of 22.4 kcal/mol and using adsorption and desorption rate parameters obtained from the literature (*38, 40*).

For H_2 desorption from a Pt foil, there are three peaks in the TPD curve at 220, 300, and 370 K (*14*). Using a second-order, desorption preexponential of 0.01 cm^2/sec (*38*), we calculate that these peaks correspond to adsorption energies of 13.1, 18.1, and 22.4 kcal/mol, again assuming that each peak corresponds to a different adsorption state. The sticking coefficient for H_2 on Pt is reported to be strongly crystal plane dependent and increases significantly with surface roughness (*39, 40*). Using a value of 0.35 determined for a Pt(997) (*39*), we were able to calculate the equilibrium constants listed in Table 1.

It is very interesting to compare these numbers to the pressures at which we observe a change in the order of the reaction. For the H_2 data in Fig. 3, the low CO pressure, 0.1 Torr, corresponds to low coverages of CO at 770 K since the reaction is first order in CO at these pressures. The break in the reaction order for H_2, where $(K_{H_2}P_{H_2})^{1/2}$ should be of order one, occurs at a pressure of approximately 100 Torr. Using the equilibrium constants from Table 1, we find that the most strongly adsorbed state with an activation energy of 22.4 kcal/mol has a value for $(K_{H_2}P_{H_2})^{1/2}$ of approximately 3 at this pressure and the second state has a value of approximately one. The fact that the size of the equilibrium constant from reaction kinetics is in the same range as that from adsorption measurements implies that the species observed in adsorption are probably the important species saturating the surface during reaction. At the higher CO pressure, the break in reaction order should not occur until $(K_{H_2}P_{H_2})^{1/2}$ is greater than $K_{CO}P_{CO}$ and we were unable to raise our pressure enough to observe the transition.

One can examine the CO dependences in Fig. 2 in a similar way. At 870 K and 400 Torr H_2, $(K_{H_2}P_{H_2})^{1/2}$ is of order 3 for even the most strongly adsorbed state and the break in the reaction order for CO from first order to zero order occurs at a pressure when $K_{CO}P_{CO}$ is also approximately 3. At 670 K, the value for $(K_{H_2}P_{H_2})^{1/2}$ for the most strongly adsorbed state is 20, while the value for $K_{CO}P_{CO}$ for the strongly adsorbed state is approximately 200 at a CO pressure of 1 Torr, the approximate break point in the reaction order. While this agreement is not perfect, this difference is only one order of magnitude and could be easily due to the extrapolation of the adsorption and desorption parameters used to calculate the equilibrium constants or to molecular interactions between the adsorbed CO and hydrogen (*41*). Considering the difference in the temperatures and pressures used in the adsorption experiments and the reaction experiments, we believe this is excellent agreement for these adsorption parameters.

Finally, it is interesting to notice that the pressure dependence for CO in Fig. 2, like those results for H_2 in Fig. 3, are inconsistent with noncompetitive adsorption. For noncompetitive adsorption and a constant H_2 pressure, the CO pressure dependence would be given by an expression like

$$r = \frac{kP_{CO}}{1 + KP_{CO}}.$$

For this pressure dependence, the data in Fig. 2 allows K to be evaluated at three temperatures and gives an exponential temperature dependence for K with ΔH_{ads} equal to 9.7 kcal/mol. No adsorption states are observed on a clean Pt foil with an energy close to 9.7 kcal/mol (*14*). In addition, an adsorption state with this low an energy should not be populated at the pressures and temperatures of our experiments. In order for a state with this low an energy to be populated, it would be necessary to have an unusually low desorption preexponential, even with a sticking coefficient of one. Therefore, our rate measurements indicate that H_2 and CO compete for sites on Pt during the methanation reaction.

Titania-Covered Pt

Surface analysis. As with the clean surface, we performed AES measurements on

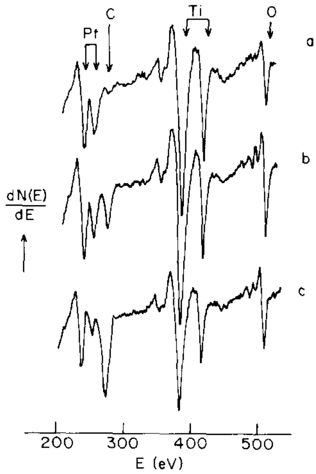

FIG. 4. Auger electron spectra for the titania-covered Pt surface following reaction at 670 K in 10 Torr CO for H_2/CO pressure ratios of (a) 10, (b) 2, and (c) 0.4. The samples were cooled in the reaction environment and flashed in vacuo to 670 K before the spectra were taken. Unlike the results for the clean Pt surface, significant quantities of carbon were present on the titania-covered surface following reaction.

the titania-covered surface following rate measurements to determine whether any carbonaceous materials are present during reaction. The results were very different from those on the clean surface in that we did observe significant quantities of carbon and those quantities were strongly dependent on the H_2/CO pressure ratio. In Fig. 4, AES results are given for several reaction environments after methanation at 670 K, followed by flashing to 670 K in vacuo. For a high H_2/CO ratio of 10, essentially no C(272 eV) peak is observed; however, for pressure ratios of 2.0 and 0.4, we observed quantities of carbon remaining on the surface which were significantly greater than the value of C(272 eV)/Pt(238 eV) of 0.25 observed for a monolayer of CO on clean Pt. For still lower H_2/CO ratios, the surface became completely covered with carbon and the methanation reaction stopped after a short time.

While the carbon deposits formed by very low H_2/CO ratios were apparently graphitic, the deposits formed at moderate pressure ratios on surfaces which remained active did not appear to be graphitic. All of the carbon on the active surfaces, such as those shown in Fig. 3, could be removed by heating the sample very briefly to 1300 K. For graphitic carbon on Pt, this temperature treatment is not sufficient to remove the carbon from the surface. There was also an indication that this active carbon was interacting with the titania. Following high-temperature treatment, some of the titania was removed from the surface along with the carbon. Titania was not removed by high-temperature treatment when no carbon was present.

We also examined the titania-covered surface after heating in 1.0 Torr of pure CO at 670 K for 1000 sec. In 400 Torr H_2, these conditions would have produced 10^{17} molecules of CH_4/cm^2. As we found with the clean Pt surface, we observed no carbon following this treatment, indicating that the rate of CO dissociation was again slow compared to the methanation rate. While dissociation of CO appears to be important when titania is present, the dissociation process must involve H_2.

Methanation kinetics. The effect of CO pressure on the reaction rate at 400 Torr H_2 is shown in Fig. 5 for three different temperatures. At high CO pressures, the reaction rate is approximately independent of CO pressure, consistent with observations

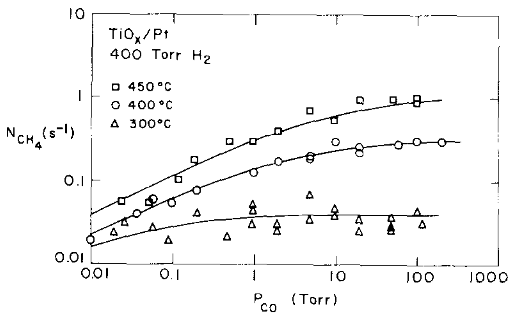

FIG. 5. Methanation rates over a titania-covered Pt foil as a function of CO pressure for three different temperatures at 400 Torr H_2. Reaction rates were half order in CO at low CO pressures.

on supported catalysts (*5*). At lower CO pressures, however, the rate approaches one-half order. This is different from the zero-order to first-order transition observed for the clean Pt surface. The CO pressure at which the transition in reaction order occurs is also much more strongly temperature dependent on the titania-covered surface than we observed for the clean Pt foil. Only at 670 K were we able to observe the entire transition from half order to zero order in the accessible pressure range.

The H_2 pressure dependence is shown in Fig. 6 for two different CO pressures. The two CO pressures were again chosen to be from the zero-order and half-order regimes of Fig. 5. For the experiments carried out at 100 Torr CO, it was necessary to limit experiments to those with H_2 pressures greater than 10 Torr to prevent the surface from being completely covered with graphite. Therefore, the fact that methanation rates for H_2 pressures below approximately 30 Torr were higher for the lower CO pressures may be indicative of surface coking and not to negative reaction orders in CO. As with the clean surface, we again observe a first-order to zero-order transition in the H_2 reaction order for the lower CO pressures. At the higher CO pressures, the reaction was first order in H_2 over the entire pressure range.

The kinetics are considerably harder to interpret on the titania-covered surface than they are on the clean surface for several reasons. First, it is clear that one must take into account coverages of carbonaceous materials on the titania-covered surface which were not present in significant quantities on the clean surface. Second, at low temperatures, the titania-covered surface does not exhibit adsorption of CO or H_2. While the kinetics appear to fit a Langmuir–Hinshelwood rate expression, the equilibrium constants in this rate expression are probably not adsorption constants as with the clean surface but equilibrium constants for an intermediate surface reaction. For intermediate surface reactions, it is difficult to determine reasonable parameters to estimate what is present on the surface.

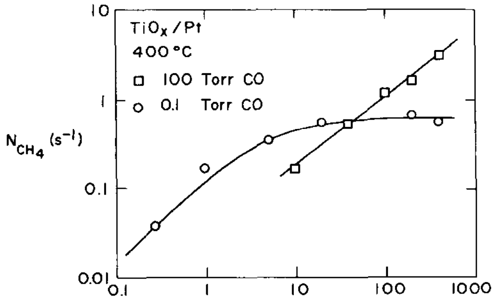

FIG. 6. Methanation rates over a titania-covered Pt foil as a function of H_2 pressure at 670 K for CO pressures of 100 and 0.1 Torr.

However, these measurements do allow us to make some statements about the reaction on the titania-covered surface. As with the clean surface, the reaction is first order in H_2 except for very high H_2/CO ratios. Since metals which do not dissociate H_2, like Cu and Ag, are not active hydrogenation catalysts, we believe that H_2 must be adsorbed dissociatively. This implies that, as with the clean surface, two hydrogen atoms must be involved in the steps leading up to and including the rate-limiting step. The half-order kinetics for CO at low temperatures appear to point toward a dissociatively adsorbed state for CO on the surface in equilibrium with the gas phase. This dissociation is probably hydrogen assisted since the Auger spectra taken after high-temperature exposure to pure CO indicated that dissociation in the absence of H_2 is not as rapid as reaction. The Auger results for the surface after reaction also indicate that a reactive form of carbon can form on this surface.

These measurements also allow us to rule out some proposed mechanisms. For example, some of the first interpretations of the unusual kinetics associated with titania-supported metals were that a weakly adsorbed species, which could not be observed in adsorption, was active in the reaction. We feel that our results rule out the importance of a weakly adsorbed species since this would require that the zero-order regime for CO be due to this species being saturated on the surface. For saturation of a low-energy state to occur at the temperatures and pressures used in our experiments, it would be necessary for this state to have a high sticking coefficient and a low desorption preexponential. This should have been observed during adsorption at low temperatures but was not (*14*). In addition, we should have observed a first-order regime rather than a half-order regime at low CO pressures. Finally, if one assumes noncompetitive adsorption between CO and H_2, the rate should be of the form

$$r = \frac{kP_{CO}^{1/2}}{1 + K_{CO}P_{CO}^{1/2}}.$$

A best fit of the data in Fig. 5 for the activation energy for K_{CO} in this expression is approximately 30 kcal/mol, a value much too large for a weakly interacting state. Assuming competitive adsorption between hydrogen and CO will only make this equilibrium constant even more strongly temperature dependent.

DISCUSSION

There are several interesting conclusions which can be made from our kinetic measurements for both the clean Pt foil and for the effect of titania on the foil. We will discuss these two different catalysts separately.

Methanation on Clean Pt

First, the Auger results show clearly that the concentration of carbide species on the Pt foil under reaction conditions is very low, even at very low H_2/CO ratios. This indicates that the surface is not modified by these species during the reaction and the gas-phase reactants "see" a surface that is clean except for adsorbed molecular CO and dissociated H_2. This is probably not true for all group VIII metals. For metals like Ni, which is much more active for methanation, there does appear to be a substantial quantity of a carbide present on the surface following reaction (*30*, *31*). While this difference between Pt and Ni could indicate a difference in mechanism or in the rate-limiting step, it does not necessarily imply that a carbide intermediate is not important on Pt. It simply implies that any carbon on the Pt surface has a very short lifetime before reacting.

Even though a carbide may be present on the surface during reaction, it is apparent that the dissociation of CO is either not the rate-limiting step or is assisted by adsorbed hydrogen. The dependence of H_2 pressure on the reaction is clear proof of this. Our Auger measurements following high-temperature exposure of CO to the surface also show that the dissociation of CO is not rapid on a clean Pt foil in the absence of hydrogen, implying that the rate-limiting step contains an oxygenated species, either CO or some CH_xO entity. On Ni, the dissociation of CO occurs much more readily (*42*), although the importance of a high dissociation activity is questionable since there is some indication that certain crystal planes of Ni may actually be inactive toward methanation due to coke formation (*43*).

A second important conclusion of this work is that the reaction rate expression could be modeled very well by the competitive adsorption of CO and H_2 using adsorption parameters obtained in ultrahigh vacuum experiments. In that reaction model, we assumed that there were no interactions between the coadsorbed CO and hydrogen and we considered only the most strongly adsorbed states. While interactions have been observed in studies of coadsorbed CO and hydrogen on various metal surfaces, these effects do not seem to be as important on Pt as they are on Ni (*41*). However, we did observe some differences between the adsorption parameters predicted from rate measurements and those measured in adsorption and desorption rate experiments.

These differences may have been due to molecular interactions.

The relationship between reaction and adsorption equilibrium constants has interesting implications. The adsorption of CO and H_2 is strongly crystal plane dependent, with the heat of adsorption of CO and H_2 changing by more than 9 kcal/mol in going from the Pt(111) to the Pt(100) surfaces (*44, 45*). It has also been shown that heats of adsorption are a function of both particle size (*46*) and support (*47*). Since the rate expression when the reaction is zero order in CO and first order in H_2 is proportional to K_{H_2}, this could account for the variations in the rates measured on different Pt catalysts. If heats of adsorption are affected by support, it should not be surprising that silica-supported Pt exhibits an activity approximately one-tenth that of alumina-supported Pt (*5*). Differences in the heats of adsorption may also explain why the activation energy that we measured for methanation on a Pt foil in 400 Torr H_2 and 100 Torr CO was significantly higher than is usually measured on supported catalysts. While our rates were between those of the silica- and alumina-supported catalysts at the temperatures used for the kinetic measurements on the supported catalysts, we observed an activation energy of 30 kcal/mol on the foil compared to 19 kcal/mol usually reported for Pt (*17, 18*).

The Effect of Titania

There has been considerable speculation on the reasons behind the unusual properties observed on titania-supported catalysts. Since the titania-covered Pt foil displays identical reaction and adsorption properties to those observed on actual titania-supported Pt (*5, 17*), we believe that the results reported in this paper apply to these more conventional catalysts as well.

The first important question concerns the role of the titania in enhancing methanation. Long-range electronic effects appear to be ruled out by the fact that the catalytic properties for Pt/TiO_2 can be duplicated by these model catalysts (*14, 17, 18*). A thin layer of oxide should not be able to donate or accept a significant number of electrons to a bulk metal. This implies that the role of the titania must be localized; however, we cannot distinguish between mechanisms for this enhancement based on the experiments in this paper.

The second important question regards the structure and coverage of the oxide layer. In previous papers, it has been shown that titania tends to "wet" the metal surface, forming a bond between the oxide and the metal (*14–16*). Spectroscopic characterization of the oxide indicates that the layer has a stoichiometry approximately that of TiO, with the titanium in the Ti^{3+} oxidation state (*26*). The coverage of the titania corresponds to 1×10^{15} oxygen atoms/cm^2, a coverage high enough to prevent adsorption by sterically blocking the surface (*14*). Further support for the picture that complete adsorption suppression occurs only when the metal is completely covered is obtained from ion scattering results (*22*) and from the fact that other reactions like ethane hydrogenolysis are completely suppressed when titania is used as a support (*48*).

One explanation proposed for the increased methanation rates on these catalysts is that titania forms three-dimensional clusters on the metal surface and that reaction occurs at the oxide–metal interface by an interaction between an adsorbed CO molecule and a Ti^{3+} ion (*23–25, 49, 50*). While the role of the titania in this mechanism may be correct, the idea that reaction occurs at the edges of clusters appears to be ruled out based on the following: (1) Adsorption experiments indicate that the oxide forms a two-dimensional layer and complete adsorption suppression occurs only for a completely covered surface (*14*). (2) There is no maximum in the methanation activity with oxide coverage; the maximum rate occurs on a completely covered surface despite the fact that this should not give the maximum interfacial area (*17, 18*).

(3) The reaction rates on the model catalysts agree with those of actual supported catalysts, even though the gross geometric differences between these samples should give different interfacial areas.

We should point out that the coverage calibrations by Ko and Gorte (*14–16*) have recently been disputed by Levin *et al.* (*52*), who claim that the actual coverage of titania used in our studies corresponds to only one-third monolayer. According to their model, each region of titanium oxide effects the metal sites adjacent to it. These metal sites apparently bind CO more weakly than unaffected metal sites and are responsible for the increased reaction rates. However, we disagree with the coverage calibrations obtained by Levin and co-workers; and the model of weakly adsorbing, active sites is inconsistent with our reaction results. First, it should be noticed that the coverages reported by Levin and co-workers disagree not only with the AES calibrations of Ko and Gorte but also with the Low-Energy Ion Scattering results of Dwyer *et al.* (*22*). Dwyer and co-workers showed that the amount of CO and H_2 which could adsorb on a Pt foil decreased linearly with the amount of exposed Pt on the surface. Complete adsorption suppression only occurred when the surface was geometrically blocked by titania. Second, methanation through a more weakly adsorbed species cannot explain the reaction results. At 300°C, we calculate that a transition in the CO pressure dependence from zero order to first order will occur between 0.1 and 1.0 Torr. On the titania-covered surface at this temperature, we were unable to observe any substantial deviation from zero order in the reaction rate for pressures down to 0.01 Torr, even though the transition to a different pressure dependence should occur at higher pressures for a weakly adsorbed species. Our observations are in agreement with *in situ* infrared spectroscopy studies which were unable to observe substantial quantities of adsorbed CO, even when the reaction rates were zero order (*4*). These observations are inconsistent with a weakly adsorbed species existing at saturation coverages at reaction conditions and being the important intermediate in the reaction.

While it is likely that the important sites for reaction are, indeed, adjacent to both oxide and metal entities, we believe that these sites are constantly evolving under reaction conditions. Although titania forms a two-dimensional overlayer on the surface that prevents adsorption at low temperatures, it has been demonstrated that this overlayer is extremely mobile, even at moderate temperatures (*14–16, 53–55*). Since the oxide is two-dimensional, only a small mobility is necessary to allow the reactant gases access to the metal atoms of the catalyst. We picture the surface as being predominantly covered by the oxide, with an equilibrium fraction of "holes" in the oxide layer. The CO molecules adsorbed on the metal at these sites could donate their oxygen to neighboring, partially reduced titania, resulting in a surface species containing titanium, oxygen, and carbon. Such a species is suggested by our finding that high-temperature annealing of the titania-covered surface following reaction when carbon was present resulted in the removal of both titania and carbon. Presumably, some of the carbon desorbed as CO, reducing the titania to titanium which would be expected to migrate into the bulk of the Pt (*14, 17*). The role of H_2, which appears to be necessary for the dissociation of CO, may be to create oxygen vacancies in the titania layer. These vacancies could then accommodate the oxygen from a CO molecule. This is obviously very speculative and more work is required to verify or refute this possibility.

CONCLUSIONS

These results show clearly that the kinetics for methanation are significantly different on the clean and the titania-covered Pt surfaces. For the clean surface, the agreement between the adsorption equilibrium constants obtained from the Langmuir–

Hinshelwood rate expression and from adsorption and desorption rates measured in ultrahigh vacuum indicate that the predominant species present under reaction conditions are the same as those measured in adsorption. In the presence of titania, however, it appears that the dissociation of CO is enhanced and the methanation reaction becomes half order at low CO pressures, indicating that the main species on the surface during reaction may be a dissociated species.

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