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Studies of the Interactions of H_2 and CO with Pd/TiO_2 and TiO_2-Promoted Pd/SiO_2

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The interactions of H_2 and CO with Pd/SiO_2, Pd/TiO_2, and titania-promoted Pd/SiO_2 have been investigated using temperature-programmed desorption and temperature-programmed surface reaction. In the presence of TiO_2, as a support or promoter, a portion of the TiO_2 is reduced to TiO_x moieties which decorate the surfaces of the Pd particles. These species cause a suppression in chemisorption of H_2 and CO, the magnitude of which is a function of the catalyst reduction temperature. The TiO_x moieties have little influence on distribution of H_2 adstates but cause a noticeable change in CO adstates. Decoration of Pd by TiO_x moieties also aids the dissociation of CO, and raises thereby the activity for CH_4 synthesis relative to that for Pd/SiO_2.

INTRODUCTION

Support composition has a large effect on the activity and selectivity of supported Pd catalysts for CO hydrogenation (*1–19*). It has been found that both lanthana and titania dramatically alter the catalytic properties of Pd (*7–19*). Pd supported on lanthana displays a high selectivity and specific activity for methanol synthesis, whereas Pd supported on titania displays an enhanced activity toward methanation. In both cases, the influence of the support is attributed to the decoration of the supported Pd particles by metal oxide moieties derived from the support itself. This interpretation is strongly supported by recent results showing that the chemisorption and catalytic properties of Pd/La_2O_3 can be closely approximated by promoting Pd/SiO_2 with lanthana (*19*).

The present studies were undertaken to further investigate the manner in which titania alters the catalytic properties of Pd. Experiments were carried out to characterize the strengths of H_2 and CO chemisorption on Pd/TiO_2 and titania-promoted Pd/SiO_2. The influence of the support composition on CO dissociation and hydrogenation was also investigated. The principal techniques used in this study were temperature-programmed desorption (TPD), temperature-programmed reduction (TPR), and temperature-programmed surface reaction (TPSR).

EXPERIMENTAL

Apparatus

The apparatus used for the present study has been described previously (*19–22*). The catalysts were placed in a quartz microreactor which could be heated at up to 1 K/s. The desorbing gas was swept from the microreactor by a continuous flow of carrier gas. Analysis of the effluent flow was performed with a quadrupole mass spectrometer. The transfer time from the microreactor to the mass spectrometer was less than 1.5 s. A microprocessor-based data acquisition system was used to direct the mass spectrometer to a series of preselected masses and to record the signal intensity at each mass setting. The catalyst temperature was also recorded by the data acquisition system.

Materials

The methods of catalyst preparation and characterization employed have been described previously (*19, 23, 24*). The 2% Pd/SiO_2 and 1.7% Pd/TiO_2 were obtained by

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incipient wetness impregnation of the support with a solution of H_2PdCl_4 dissolved in 1 *N* HCl. The supports employed were Cab-O-Sil HS-5 silica and Degussa P-25 titania. The catalysts were dried, calcined in a 21% O_2/He mixture at 623 K for 2 h, and reduced in H_2 at the desired reduction temperature prior to use. These catalysts were characterized by H_2–O_2 titration.

The titania-promoted Pd/SiO_2 catalysts were prepared in a manner similar to that used previously to prepare lanthana-promoted Pd/SiO_2 (*19*). A portion of the calcined 2% Pd/SiO_2 catalyst was impregnated with a solution of $Ti(OCH_3)_4$ in 1 *N* HCl and dried. The catalyst was calcined again to decompose the titania precursor and reduced in H_2 at the desired reduction temperature. The Ti loadings of 0.16, 0.31, and 1.6% correspond to a ratio of Ti to surface Pd of 0.5, 1.0, and 5.0, respectively. These catalysts were also characterized using H_2–O_2 titration.

Helium and H_2 were purified to remove O_2 and water; and CO was purified to remove metal carbonyls, water, and CO_2. Details of the purification procedures are given in Ref. (*19*). The absence of impurities in these gases was established by mass spectrometry.

Experimental Procedure

Temperature-programmed desorption (TPD). The following procedure was used for the TPD experiments. A mass of catalyst corresponding to 3.8×10^{-6} mol of surface palladium atoms based on H_2–O_2 titration was placed in the microreactor. The mass and the particle size were selected to avoid transport effects (*25*). The catalyst was reduced for 4 h in 200 cm^3/min of H_2 at temperatures ranging from 423 to 773 K. Following reduction, the microreactor was evacuated at the reduction temperature for 30 min. The reactor was cooled to room temperature while still under vacuum and then repressurized with He.

Adsorption was carried out by passing pulses of the pure adsorbate through the catalyst bed to ensure saturation. After the adsorption of H_2, the catalysts were evacuated for 30 min to ensure complete removal of the hydride. For CO adsorption, the catalysts were evacuated for 10 min to remove the adsorbate remaining in the gas phase. The reactor was then repressurized with He and the He flow rate was set to 50 cm^3/min. Heating of the catalyst was now commenced at 1 K/s, and the data acquisition system was activated, to initiate analysis of the desorbing gas. Following each experiment, the mass spectrometer was calibrated against He mixtures containing specified concentrations of H_2 and CO.

Temperature-programmed surface reaction (TPSR). The procedure for the TPSR experiments was identical to that of the TPD experiments up to the adsorption step. After pretreatment, a flow of 100 cm^3/min of the desired adsorption mixture—either pure CO or a H_2/CO mixture—was passed through the microreactor. The microreactor was ramped at 1 K/s to the desired adsorption temperature and held at that temperature for 10 min. The catalyst was then evacuated at the elevated temperature for 5 min, cooled to room temperature, and evacuated for 10 min. The catalyst was pressurized with He, and a flow of 50 cm^3/min of H_2 was passed through the catalyst bed as the temperature was ramped at 1 K/s.

The relative activities of the catalysts for CO hydrogenation were determined by ramping the catalyst temperature at 1 K/s in a flow of 75 cm^3/min of H_2 and 25 cm^3/min of CO. The temperature at which the methanation rate began to increase rapidly served as a basis for comparison of the catalyst activities.

Temperature-programmed reduction and oxidation. Temperature-programmed reduction (TPR) experiments were conducted to compare the reducibility of the supports. The catalysts were calcined at 623 K for 2 h in 200 cm^3/min of the 21% O_2/He mixture and then cooled to room temperature in the O_2/He mixture. Next, the microreactor was

TABLE 1

Pd Dispersion of Pd/SiO_2, Titania-Promoted Pd/SiO_2, and Pd/TiO_2

Catalyst	Dispersion[a] (%)				
	T_{red} = 423 K	573 K	623 K	673 K	773 K
2% Pd/SiO_2	—	35	—	34	25
0.16% Ti/(2% Pd/SiO_2)	—	34	—	32	26
0.31% Ti/(2% Pd/SiO_2)	—	34	—	35	26
1.6% Ti/(2% Pd/SiO_2)	—	37	—	35	28
1.7% Pd/TiO_2	51	51	50	50	39

[a] Based on H_2–O_2 titration.

evacuated to remove gas-phase O_2, and a flow of 1000 ppm H_2 in He was passed through the bed. The temperature was ramped at 0.25 K/s and the hydrogen consumption monitored.

Temperature-programmed oxidation (TPO) experiments were conducted to gain further information regarding how the support composition may change depending on its environment. The catalysts were reduced at 573 K for 4 h in 200 cm³/min of pure H_2 and cooled to room temperature in H_2, after which the microreactor was evacuated to remove adsorbed and gas-phase H_2. Next, a flow of 200 cm³/min of 1000 ppm O_2 in He was passed through the bed, and the O_2 consumption was monitored as the catalyst temperature was ramped at 0.25 K/s.

Calibration and data analysis. The absolute rate of desorption in all experiments was determined in the following manner. To correct for mass spectrometer baseline drift, the observed intensity for each mass was normalized with respect to the intensity of the carrier, either He or H_2. The absolute rate of desorption of species i per Pd surface site r_i, was then determined from

$$r_i = \frac{(I_i^{obs} - I_i^{bg})}{S_i N_T} \frac{Q}{273\,R} \qquad (1)$$

where I_i^{obs} and I_i^{bg} are the normalized intensities for the experiment and background, respectively; S_i is the calibration factor for species i; N_T is the total number of surface Pd sites on the sample; Q is the flow rate of the carrier at STP; and R is the gas constant.

The moles of gas desorbing during an experiment were calculated by integration of the spectra to find the peak areas, A_i. The number of moles was calculated from

$$N_i = \frac{A_i}{S_i \beta} \frac{Q}{273\,R} \qquad (2)$$

where β is the heating rate. The initial coverages were found by dividing the number of moles desorbed by the moles of surface Pd present based on H_2–O_2 titration.

RESULTS

H_2–O_2 Titration

The dispersions of the catalysts based on H_2–O_2 titration are given in Table 1. For 2% Pd/SiO_2, this value is in good agreement with that determined previously (*23*) by H_2 or CO chemisorption. No change in the dispersion of this catalyst was observed for reduction temperatures in the range of 473 to 673 K. The TiO_2-promoted Pd/SiO_2 catalysts exhibited the same dispersion based on H_2–O_2 titration as Pd/SiO_2, independent of the reduction temperature. When the reduction temperature was raised to 773 K, though, a decrease in the dispersion was observed for all catalysts.

Temperature-Programmed Reduction and Oxidation

TPR and TPO experiments were performed to characterize the reducibility of

TABLE 2

H_2 and O_2 Uptakes Observed during TPR and TPO

Characteristic	2% Pd/SiO_2	1.7% Pd/TiO_2
H_2 uptake (mol × 10^6)[a]	13.0	14.9
O_2 uptake (mol × 10^6)[b]	2.7	6.9
Pd total (mol × 10^6)	10.9	7.5
Pd surface (mol × 10^6)	3.8	3.8

[a] Following calcination at 623 K.

[b] Following reduction at 573 K.

2% Pd/SiO_2 and 1.7% Pd/TiO_2. The results are summarized in Table 2. Also, shown are the total amount of Pd in each sample and the amount of surface Pd, the latter quantity being determined by H_2–O_2 titration. It is apparent that while the amount of H_2 consumed during the reduction of the calcined catalyst is roughly the same for both silica- and titania-supported Pd, the amount of O_2 taken up by the reduced catalyst is not. The O_2 uptake for 1.7% Pd/TiO_2 is more than twice as great as that for 2% Pd/SiO_2.

H_2 and CO TPD

The TPD spectra for H_2 desorption from 1.7% Pd/TiO_2 for varying reduction temperatures are shown in Fig. 1. The initial coverage by adsorbed H atoms, θ_H^0, is based on the amount of H_2 seen to desorb up to 873 K. As shown by the figure, the chemisorption capacity of the catalyst decreases greatly as the reduction temperature increases. For a reduction temperature of 423 K, the initial coverage is 1.01, in good agreement with the H_2–O_2 titration. As the reduction temperature is increased to 773 K, the saturation coverage drops to 0.23.

In addition to the decrease in chemisorption capacity, the spectra reveal that there is a drastic change in the distribution of adstates for H_2 chemisorption as the reduction temperature is increased. For a reduction temperature of 423 K, a single peak is present at 425 K. As the reduction temperature is increased to 473 K, this peak shifts to 455 K, and a second peak appears at around 575 K. As the reduction temperature is increased further, both peaks broaden and shift to higher temperatures. For a reduction temprature of 773 K, the area of the low-temperature peak is $\theta_H^0 = 0.08$, and the high-temperature peak appears as a tail.

The CO desorption spectra for 1.7% Pd/TiO_2 are shown in Fig. 2. Spectra are only presented for reduction temperatures of 573

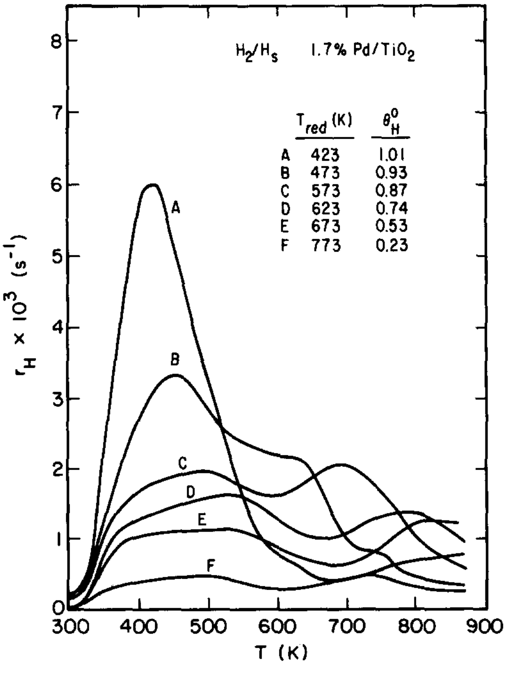


FIG. 1. Effect of reduction temperature on the H_2 TPD spectra for 1.7% Pd/TiO_2.

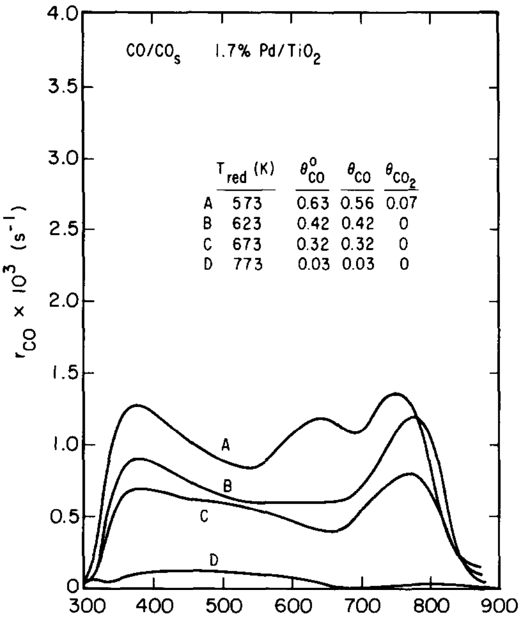


FIG. 2. Effect of reduction temperature on the CO TPD spectra for 1.7% Pd/TiO$_2$.

K or greater. For reduction temperatures less than 573 K, a significant amount of CO_2 was observed during the temperature ramp. Since H_2 was evolved with the CO_2, the formation of this CO_2 was attributed to the reaction of adsorbed CO with H_2O remaining on the support after reduction. Assuming this to be the source of the CO_2, the initial coverage by CO was determined to be 0.94 for a reduction temperature of 423 K. CO_2 was also evolved during CO desorption following reduction at 573 K. However, since no H_2 was observed in this case, the source of this CO_2 is attributed to the disproportionation of CO. The initial coverage of CO, θ^0_{CO}, is given in Fig. 2 and is taken to be the amount of CO desorbed, θ_{CO}, plus twice the amount of CO_2 produced. The equivalent coverage of CO converted to CO_2 is given by θ_{CO_2} based on the stoichiometry: $2\ CO_{ads} \rightarrow C_{ads} + CO_2$.

For a reduction temperature of 573 K, three peaks are evident in Fig. 2. A low-temperature peak is seen at 375 K, and two high-temperature peaks at 645 and 750 K. These peak locations are in good agreement with those observed for Pd/SiO$_2$ (*19*). As the reduction temperature is increased to 623 K, the uptake of CO is suppressed from 0.63 to 0.42. In addition, there appears to be a preferential suppression of the peak at 645 K. The location of the low-temperature peak increases to 385 K, and the high-temperature peak shifts to 780 K. Increasing the reduction temperature to 673 K results in further suppression of all adstates. Finally, for a reduction temperature of 773 K, a single broad low-temperature peak is observed corresponding to an uptake of 0.03. In contrast to Pd/SiO$_2$ (*19*), no CO_2 is seen to form during CO desorption from catalysts reduced at higher temperatures.

In order to gain further insight into the nature of the suppression in H_2 and CO uptakes with reduction temperature observed with Pd/TiO$_2$, TPD experiments were performed on samples of Pd/SiO$_2$ promoted with TiO$_2$. The H_2 TPD spectra for desorption from 2% Pd/SiO$_2$ and the three TiO$_2$-promoted catalysts are given in Fig. 3 for a constant reduction temperature of 673 K. As the degree of TiO$_2$ promotion in-

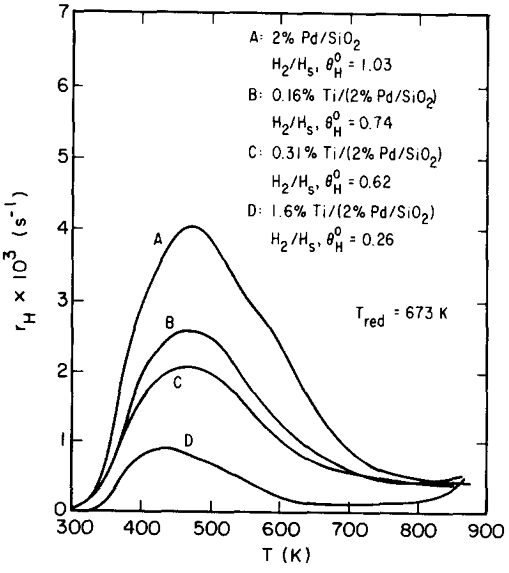


FIG. 3. Effect of titania promotion on the H_2 TPD spectra for 2% Pd/SiO$_2$.

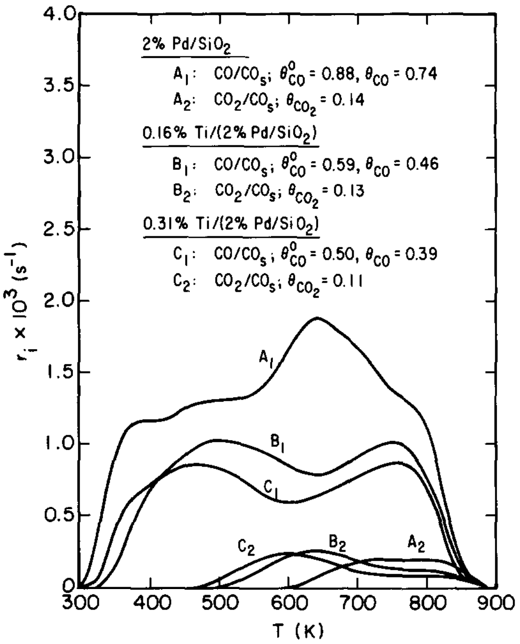


FIG. 4. Effect of titania promotion on the desorption products observed during CO TPD from 2% Pd/SiO$_2$. Curves A$_1$, B$_1$, and C$_1$ represent the rate of CO desorption, while curves A$_2$, B$_2$, and C$_2$ represent the rate of CO$_2$ formation.

creases, the degree of suppression increases, but the general location and shape of the H_2 TPD spectrum is not significantly altered. Since, as shown in Table 1, the dispersion of Pd is unaltered by TiO$_2$ promotion, the suppression in H_2 chemisorption must be attributed to a partial blockage of surface Pd atoms by the promoter.

The TPD spectra for CO desorption from Pd/SiO$_2$ and the three promoted samples are shown in Fig. 4. For the 2% Pd/SiO$_2$, four CO peaks are present at 400, 488, 638, and 773 K. CO$_2$ formation is observed above 620 K and reaches a maximum rate at 473 K. The total amount of CO$_2$ produced corresponds to disproportionation of 0.07 monolayers of adsorbed CO. Promotion with TiO$_2$ results in suppression of the initial CO uptake in a manner similar to that observed for H_2. However, unlike the TPD spectra for H_2, the spectra for CO desorption show that TiO$_2$ promotion causes a redistribution in the forms of adsorbed CO, and in particular a preferential suppression of the peak at 638 K. This effect is similar to that seen with increasing reduction temperatures for Pd/TiO$_2$. However, TiO$_2$ promotion does not significantly alter the location of the peak at 750 K, and causes only a slight shift in the low-temperature peaks to higher temperatures. The amount of CO$_2$ produced is not significantly altered by TiO$_2$ promotion, but the location of the CO$_2$ peak is shifted. For the 0.16% Ti/(2% Pd/SiO$_2$) sample, the onset of CO$_2$ desorption occurs at 500 K, and the peak temperature occurs at 635 K. Further promotion shifts the onset of CO$_2$ production to 475 K and the peak temperature to 605 K, as shown for 0.31% Ti/(2% Pd/SiO$_2$). Thus, TiO$_2$ addition to Pd/SiO$_2$ causes CO to dissociate at lower temperatures. However, the fraction of the initially adsorbed CO which dissociates does not increase.

TPSR of H_2 and CO

TPSR experiments were performed to investigate the interactions between CO and H_2 on the surface of Pd. The spectra for methane formation during the TPSR of CO adsorbed on 1.7% Pd/TiO$_2$ at room temperature are shown in Fig. 5A, as a function of reduction temperature. The CO spectra observed during TPSR are given in Fig. 5B. No other carbon-containing species were formed during TPSR. For a reduction temperature of 473 K, the peak temperature for methane formation occurs at 515 K. This is much lower than the location of the peak for TPSR of CO on Pd/SiO$_2$, 635 K (*19*). The fraction of CO which reacts with H_2 to give methane during the temperature ramp is given by $X_{CH_4/CO}$. As the reduction temperature increases the temperature of maximum methane formation rate shifts to higher temperatures and the total amount of CO removed as methane and CO decreases in a manner consistent with the data shown in Fig. 2. The fraction of CO which reacts to give methane, however, does not vary greatly with reduction temperature.

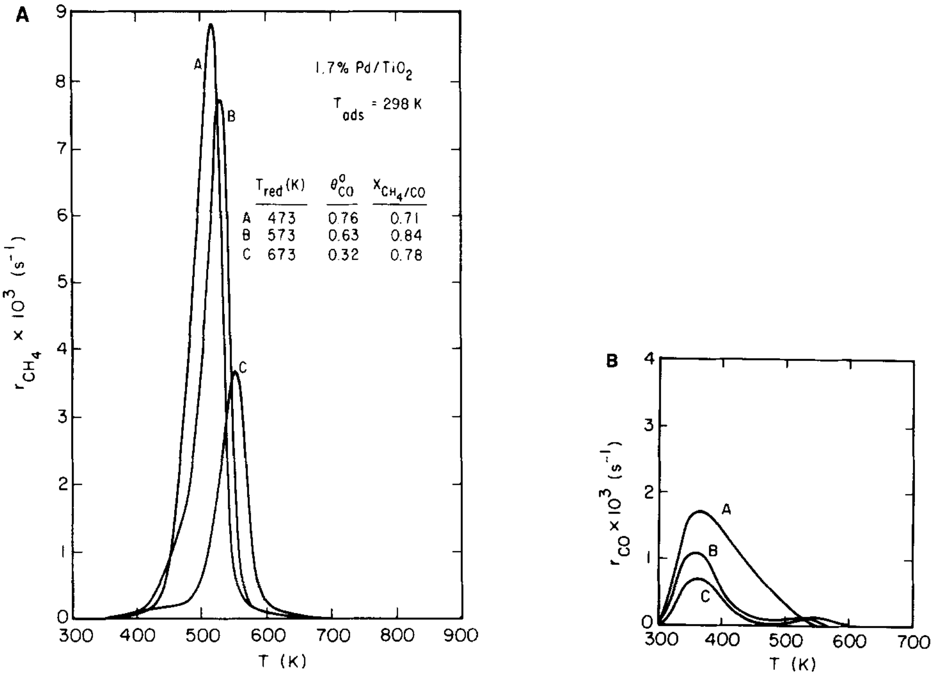


FIG. 5. Effect of reduction temperature on the products formed during TPSR of CO adsorbed on 1.7% Pd/TiO_2: (A) CH_4; (B) CO.

The influence of CO adsorption temperature on the formation of methane during TPSR is shown in Fig. 6 for 1.7% Pd/TiO_2 reduced at 573 K. Raising the adsorption temperature from 298 to 523 K causes a shift in the position of the spectrum to lower temperatures and the appearance of a second, low-temperature peak. The changes in the TPSR spectrum for 1.7% Pd/TiO_2 observed in Fig. 6 are quite similar to those reported by Rieck and Bell (*19*) for 2% Pd/SiO_2. In that study it was concluded that the low-temperature methane peak could be assigned to the hydrogenation of surface carbon deposited during the high-temperature adsorption of CO, and that the high-temperature methane peak is due to hydrogenation of adsorbed CO. Adopting this interpretation, it is observed, in Fig. 6, that the proportion of methane derived from the hydrogenation of surface carbon increases with increasing CO adsorption temperature. However, the initial coverage of the surface by CO and carbon is not

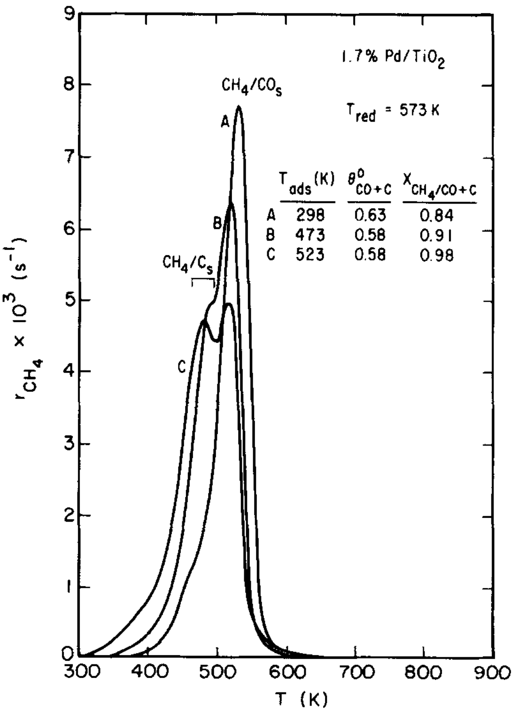


FIG. 6. Effect of CO adsorption temperature on CH_4 formation during TPSR of CO adsorbed on 1.7% Pd/TiO_2.

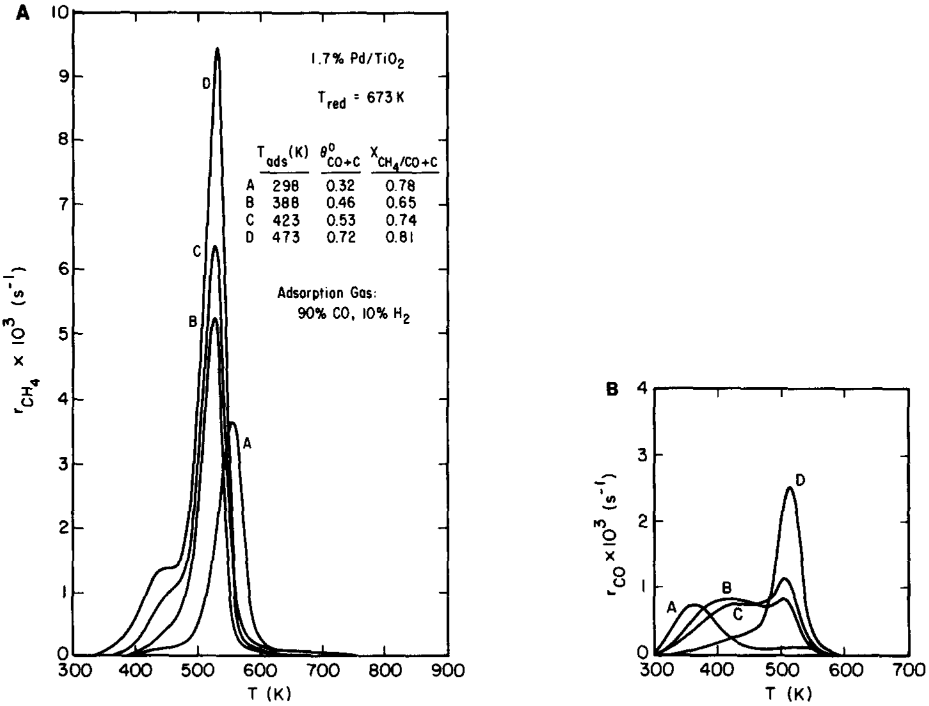


FIG. 7. Effects of the presence of H_2 during CO adsorption on the products formed during TPSR for 1.7% Pd/TIO$_2$: (A) CH_4; (B) CO.

strongly affected by the adsorption temperature.

The effects of the presence of H_2 on the adsorption and dissociation of CO were studied by adsorbing CO in the presence of 10% H_2. The features for methane formation during TPSR following such an adsorption step are given in Fig. 7A for 1.7% Pd/TiO$_2$ reduced at 673 K. The spectra for all three adsorption temperatures exhibit a peak at 530 K which does not vary in location with adsorption temperature. In addition, as the adsorption temperature is increased, a low-temperature shoulder appears on the methane feature at around 455 K. In contrast to adsorption in the absence of H_2, the peak at 530 K increases greatly in magnitude as the adsorption temperature increases. The CO desorption spectra for these experiments are given in Fig. 7B. Two peaks are observed, one located at 460 K, and the second at 510 K. While the CO peak at 460 K decreases in magnitude as the reduction temperature is increased, the height of the peak at 510 K increases.

The TPSR experiments were performed on the titania-promoted catalysts to gain further information regarding the influence of titania on the interactions of CO with H_2. The methane features for TPSR of CO following adsorption at room temperature are given in Fig. 8A for 2% Pd/SiO$_2$ and three titania-promoted Pd/SiO$_2$ catalysts for a constant reduction temperature of 473 K. The corresponding spectra for CO desorption are given in Fig. 8B. The methane spectrum for 2% Pd/SiO$_2$ exhibits a peak at 620 K. Promotion with 0.16% Ti causes a shift in the location of this peak to 550 K and an increase in the amount of CO being converted to methane, but does not alter the initial coverage of CO. Raising the promoter level to 0.31% Ti shifts the methane peak to 535 K. The initial uptake of CO is now reduced to 0.85 of a monolayer, from

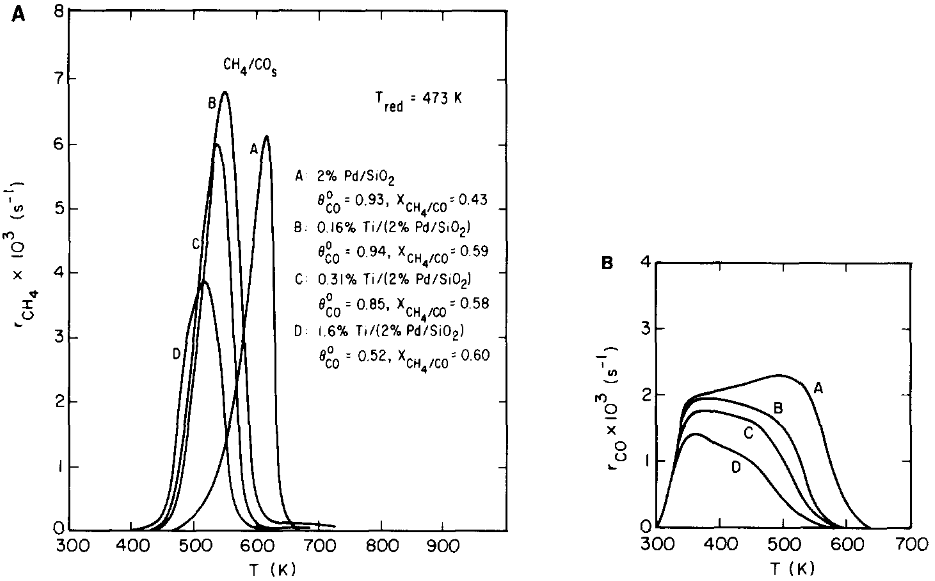


FIG. 8. Effects of titania promotion on the desorption products observed during TPSR of CO adsorbed on 2% Pd/SiO$_2$: (A) CH$_4$; (B) CO.

0.93, but the fraction of the initially adsorbed CO that reacts to give methane remains the same as for 0.16% Ti/(2% Pd/SiO$_2$). When the promoter level is raised to 1.6% Ti, the methane peak shifts to 518 K and the initial uptake of CO decreases to 0.52 of a monolayer. Here again, though, the fraction of CO that reacts to give methane remains the same as for the other TiO$_2$-promoted catalysts. Thus, it is seen that TiO$_2$ promotion significantly increases the activity of Pd/SiO$_2$ for the hydrogenation of molecular CO.

Only a limited examination was made of the effects of reduction temperature on the TPSR of CO over TiO$_2$-promoted Pd/SiO$_2$. Spectrum A in Fig. 9 shows the methane response observed for CO adsorbed at 298 K on 0.16% Ti/(2% Pd/SiO$_2$) reduced at 673 K. Comparison of this spectrum with that taken following reduction at 473 K (spectrum B in Fig. 8A) reveals that for the higher reduction temperature, the methane peak occurs at a higher temperature and the initial coverage by CO is lower. This trend is identical to that observed in Fig. 5A for Pd/TiO$_2$.

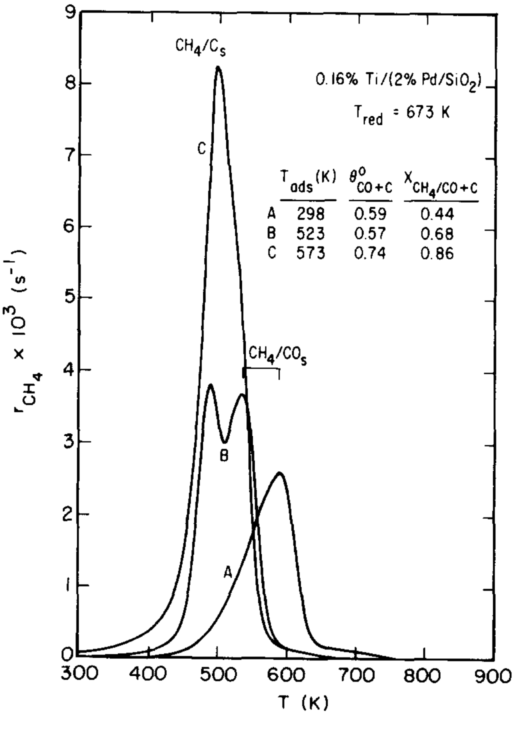


FIG. 9. Effect of CO adsorption temperature on CH$_4$ formation during TPSR of CO adsorbed on 0.16% Ti/(2% Pd/SiO$_2$).

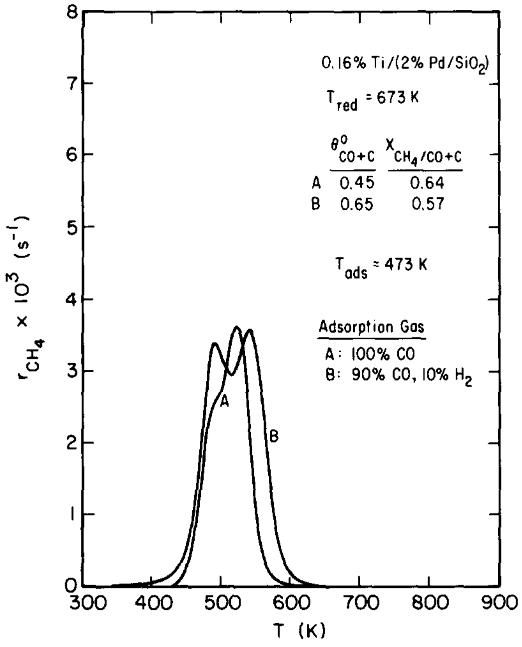


FIG. 10. Effect of the presence of H_2 during CO adsorption on CH_4 formation during TPSR of CO adsorbed on 0.16% Ti/(2% Pd/SiO_2).

The effect of CO adsorption temperature on the methanation of adsorbed CO on the 0.16% Ti/(2% Pd/SiO_2) catalyst is shown in Fig. 9. Raising the adsorption temperatures from 298 to 523 K results in a shift in the methanation peak from 590 to 535 K, and the appearance of a second peak at 490 K. This peak is attributed to the hydrogenation of surface carbon. A further increase in the adsorption temperature to 573 K results in a large increase in the magnitude of this peak, while the peak for methanation of molecular CO becomes a shoulder. Comparison of these results with those of 2% Pd/SiO_2 (*19*) reveals that the promoted sample has a much greater activity for CO dissociation. For an adsorption temperature of 673 K on 2% Pd/SiO_2, 0.63 of a monolayer of surface carbon was deposited. As seen in Fig. 9, a similar amount of carbon is deposited on 0.16% Ti/(2% Pd/SiO_2) for adsorption at 573 K. It should be noted, though, that the carbon formed on the TiO_2-promoted catalyst is slightly less reactive to H_2 than that on unpromoted Pd/SiO_2; for 0.16% Ti/(2% Pd/SiO_2) the peak temperature for methane formation from carbon is 495 K, while for 2% Pd/SiO_2 it is 473 K.

Figure 10 shows the effect of the presence of H_2 in the adsorption stream on the dissociation of CO on 0.16% Ti/(2% Pd/SiO_2) for reduction at 673 K and CO adsorption at 473 K. For the adsorption of CO alone, a peak from the hydrogenation of molecular CO is present at 525 K and a shoulder from the hydrogenation of surface carbon is present at 490 K. The presence of H_2 results in the shift of the molecular CO hydrogenation peak to 540 K, and an increase in the magnitude of the peak from methanation of surface carbon. Thus, the presence of H_2 aids the dissociation of CO as seen previously for Pd/SiO_2. The presence of H_2 results in an increase in the initial coverage by carbon and CO from 0.45 to 0.65, but the amount of unreacted CO which desorbs also increases. In contrast to the results for 1.7% Pd/TiO_2, there is no buildup in the magnitude of the peak associated with the hydrogenation of adsorbed CO.

Comparison of Activities for CO Methanation

The dependence of the methanation activity of each catalyst on temperature was determined by ramping the catalyst temperature at 1 K/s in a flowing mixture of synthesis gas. In all cases, the maximum conversion was kept below 1%. Figure 11 shows an Arrhenius plot for four of the five catalysts examined. The data for 0.31% Ti/(2% Pd/SiO_2) were virtually identical to those for 1.6% Ti/(2% Pd/SiO_2) and hence are not shown for clarity. The catalyst activities increase in the following order: 2% Pd/SiO_2 < 0.16% Ti/(2% Pd/SiO_2) < 0.31% Ti/(2% Pd/SiO_2) = 1.6% Ti/(2% Pd/SiO_2) < 1.7% Pd/TiO_2. The activation energy for methanation is also given in Fig. 11. The highest value of E_a is for 2% Pd/SiO_2, 27.5 kcal/mol, and the lowest value of E_a is for 1.7% Pd/TiO_2, 22.7 kcal/mol. The other cat-

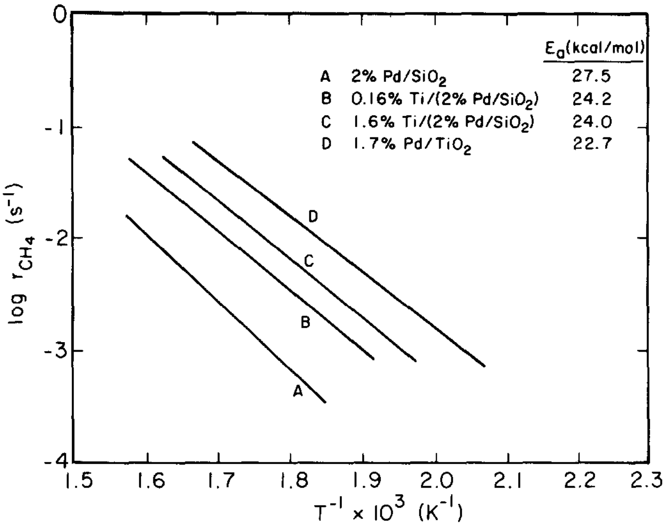


FIG. 11. Comparison of the methanation activities for Pd/SiO$_2$, Pd/TiO$_2$, and titania-promoted Pd/SiO$_2$: P = 1 atm, H_2/CO = 3/1.

alysts exhibit activation energies which fall between these limits.

DISCUSSION

H_2–O_2 Titration

The suppression of H_2 and CO chemisorption following high-temperature reduction of TiO_2-supported metal catalysts has been attributed to decoration of the supported metal particles by partially reduced titania moieties, TiO_x (*26–41*). A similar model has been proposed by Hicks *et al.* (*23*) to explain the chemisorption characteristics of Pd/La_2O_3 catalysts. An important finding in the studies of Hicks *et al.* (*23*) was the observation that the surface area of Pd particles, both covered and uncovered by LaO_x moieties, could be measured accurately by H_2–O_2 titration. The results presented here indicate that H_2–O_2 titration can also be used to measure the total surface area of Pd particles supported on TiO_2. This conclusion is supported by the observation (see Table 1) that the Pd dispersion for Pd/TiO_2 shows no change with increasing reduction temperatures, up to a level of 673 K, even though the Pd surface area capable of H_2 and CO chemisorption steadily decreases. Likewise, it is noted that the Pd dispersion of 2% Pd/SiO_2 is not altered by promotion with TiO_2.

TPR and TPO

The results of TPR and TPO experiments provide an indication of the amounts of hydrogen consumed during catalyst reduction and oxygen consumed during catalyst oxidation. For 2% Pd/SiO_2, the sample contains 1.09×10^{-5} mol of total Pd and 3.81×10^{-6} mol of surface Pd. During the reduction of this sample following calcination, 1.3×10^{-5} mol of H_2 is consumed. This uptake corresponds to the reduction of bulk PdO plus a smaller amount of surface adsorbed oxygen. The uptake of O_2 during TPO is 2.7×10^{-6} mol. This amount can be attributed to the following stoichiometry

$$Pd_s\text{—}H + \tfrac{3}{4}\,O_2 \rightarrow Pd_s\text{—}O + \tfrac{1}{2}\,H_2O$$

Because of the low concentration of O_2 in the oxidizing stream (1000 ppm of O_2), bulk oxidation of Pd does not occur. Thus for Pd/SiO_2, only the Pd crystallites undergo oxidation and reduction.

For 1.7% Pd/TiO_2, the sample contains 7.51×10^{-6} mol of total Pd and 3.81×10^{-6}

mol of surface Pd. Reduction of this sample following calcination involves the consumption of 1.49×10^{-5} mol of H_2. This is twice the amount of total Pd. The excess amount of H_2 consumption is attributed to the reduction of portions of the TiO_2 support adjacent to the supported Pd particles. Evidence for such a reaction has been reported by Huizinga *et al.* (*42*) for Pt/TiO_2. During TPO, the O_2 consumption is 6.91×10^{-6} mol. In this case, the amount of oxygen taken up is more than twice that required for the reaction of Pd_s–H. Presumably, the excess oxygen is used to reoxidize the portions of the support that are reduced.

H_2 TPD

The TPD spectra shown in Fig. 3 clearly demonstrate that the promotion of Pd/SiO_2 with titania causes a suppression in the H_2 chemisorption capacity of the catalyst but does not strongly influence the shape or position of the TPD spectrum. This indicates that titania promotion blocks sites for H_2 adsorption but does not alter the energetics of the remaining exposed sites. A similar effect has been observed when Pd/SiO_2 is promoted by lanthana (*19*).

The TPD spectrum for H_2 desorption from Pd/TiO_2 reduced at 423 K resembles that for Pd/SiO_2 in both peak position and shape, leading to the conclusion that the peak centered at 425 K is due to H_2 desorption from Pd. With increasing reduction temperature the intensity of this peak diminishes substantially, and a new peak appears above 500 K. The presence of a similar high-temperature peak has also been reported by Dybowski and co-workers (*43, 44*) in studies of Rh/TiO_2 reduced at 573 K. With the aid of NMR spectroscopy these authors were able to assign the high-temperature H_2 peak to the decomposition of surface hydroxyl groups on the titania support. Beck and White (*45*) have also presented definitive evidence of hydrogen adsorption on TiO_x systems. It appears reasonable, therefore, to attribute the portions of the TPD spectra occurring above 550 K, shown in Fig. 1, to H_2 desorption from the support.

The reduction in H_2 chemisorption on Pd sites with increasing temperature seen in Fig. 1 is attributed to a progressive coverage of the Pd particles by TiO_x moieties derived from the support. In contrast to the behavior seen in Fig. 3 for titania-promoted Pd/SiO_2, it appears that the coverage of Pd particles supported on TiO_2 by TiO_x structures does cause some changes in the energetics of H_2 adsorption. Quite possibly this is due to an alteration in the stoichiometry and/or structure of the TiO_x species as the reduction temperature is increased. Evidence for a decrease in the O/Ti ratio of TiO_x deposited on polycrystalline Rh with increasing reduction temperature has been observed in experiments conducted by Levin *et al.* (*46*).

CO TPD

The TPD spectrum for CO desorption from Pd/SiO_2 is comprised of four peaks located at 400, 488, 638, and 773 K. As discussed recently by Rieck and Bell (*19*), the peaks at 638 and 773 K can be attributed to CO adsorption in bridge bonding sites on Pd(100) and Pd(111) planes, respectively. The two low-temperature peaks were attributed to linearly adsorbed CO, but with no specification of the Pd planes.

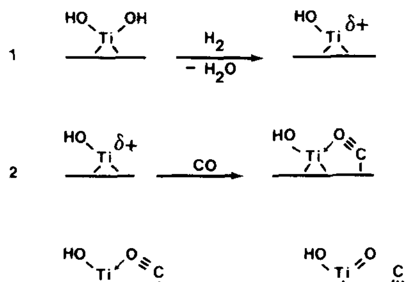
Promotion of Pd/SiO_2 with titania causes a suppression of CO chemisorption and a significant change in the distribution of adstates. As seen in Fig. 4, the intensity of the peak at 638 K is much more strongly attenuated relative to the other peaks, suggesting that the promoter preferentially blocks CO chemisorption in bridging sites on Pd(100) planes. This behavior contrasts with that observed for Pd/SiO_2 promoted with lanthana where the promoter is found to block bridge-bonded CO on both Pd(100) and Pd(111) planes (*19*).

The shape of the spectra for CO desorption from Pd/TiO_2 closely resemble those for CO desorption from TiO_2-promoted Pd/

SiO_2. As in the case of H_2, the suppression in CO adsorption capacity with increasing reduction temperature is attributed to progressive coverage of the Pd particles by TiO_x moieties. The trends suggest that as the reduction temperature increases bridge-bonding sites on Pd(100) planes are lost first, followed by the loss of similar sites on Pd(111) planes.

The disproportionation of CO to carbon and CO_2 was observed for Pd/SiO_2 and all three samples of TiO_2-promoted Pd/SiO_2. While the data in Fig. 6 clearly demonstrate that CO dissociates at elevated temperatures on Pd/TiO_2, no CO_2 was detected in the TPD spectrum of adsorbed CO. We assume that this was due to the strong retention of the oxygen atom released upon CO dissociation by the partially reduced support.

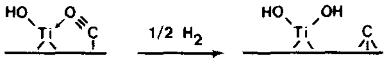
From the CO_2 spectra shown in Fig. 4, it is evident that TiO_2 promotion of Pd/SiO_2 facilitates the disproportionation of CO. Since the enregetically demanding step in this process is the dissociation of CO, we infer that the addition of TiO_2 reduces the activation energy for this step, and/or increases the number of sites capable of dissociating CO. The means by which TiO_2 addition promote CO dissociation cannot be determined definitely from the present experiments. A possible interpretation is that oxygen-deficient TiO_x moieties residing on the surface of the Pd crystallites contribute to CO dissociation. Such a mechanism of CO activation has been proposed by several authors recently (*12, 17, 47–49*) and could be envisioned to occur via the following sequence of steps.



TPSR of Adsorbed CO

The formation of methane from CO over Pd is believed to proceed via the dissociation of CO to form adsorbed carbon and the subsequent hydrogenation of this species (*8, 19*). The results of this study and those previously reported by Rieck and Bell (*19*) for Pd/SiO_2 support this picture, in that carbon formed by the predissociation of CO reacts more readily with hydrogen than adsorbed CO. As noted above, TiO_2 promotion of Pd/SiO_2 facilitates the dissociation of CO. In the absence of H_2, this process might occur via Reaction 3. When H_2 is present the dissociation of CO appears to proceed more readily, both over Pd/SiO_2 (*19*) and TiO_2-promoted Pd/SiO_2 (see Fig. 10). A similar effect of H_2 has also been reported for Pd/Al_2O_3 (*50, 51*). Reaction 4 illustrates how hydrogen might assist in the CO dissociation process.

4



With the preceding ideas in mind, it is possible to interpret the TPSR spectra presented in Fig. 8. As the level of promotion increases, the fraction of the particle surface covered by TiO_x increases causing a reduction in the total amount of CO chemisorbed. The concurrent lowering of the temperature at which methane is formed is ascribed to the promotion of CO dissociation.

As the reduction temperature increases, the coverage of the Pd particles by TiO_x moieties increases, and it would be expected that the effectiveness of TiO_x moieties on the surface of Pd in promoting the dissociation of CO (and hence the rate of methanation) would also increase. The TPSR spectra in Fig. 5A, however, show that the peak temperature for methane synthesis shifts upscale as the reduction temperature increases. This trend may be explained in the following manner. As the reduction temperature increases, two changes in the state of the catalyst might be expected to occur. The first is an increase in the concentration of TiO_x moieties on the surface of Pd particles and the second is an agglomeration of the TiO_x patches. Since it is proposed that the interfacial sites between the Pd and the TiO_x moieties are very active for CO dissociation, the first effect should result in a higher activity for methanation, while the second effect should result in a decrease due to a reduction in the number of interfacial sites. Apparently, the second effect is more significant, since the CH_4 peak in the TPSR spectrum shifts to higher temperatures with increasing reduction temperature. It is interesting to observe that the same trend with reduction temperature seen in Fig. 5A for Pd/TiO_2 is also observed for TiO_2-promoted Pd/SiO_2 (compare spectrum B in Fig. 8A and spectrum A in Fig. 9).

In addition to affecting CO dissociation, the TiO_x species on Pd also influence the reactivity of adsorbed carbon. For CO adsorption at 573 K on 2% Pd/SiO_2, Rieck and Bell (*19*) reported a carbon coverage of 0.08 Pd monolayer equivalents and a maximum rate of methane formation from carbon at 473 K. The results of this study show that when the same catalyst is promoted with TiO_2 at the level of 0.16% Ti, the carbon coverage increases to nearly unity (see spectrum C in Fig. 9) and the peak temperature shifts to 495 K. Since the kinetics of carbon hydrogenation are first order in carbon coverage [see, for example, Refs. (*52*, *53*)], the small upscale shift in the peak temperature suggests that the carbon deposited in the presence of the promoter is slightly less reactive than that deposited in the absence of the promoter. It is interesting to note that a similar trend is observed when Pd/SiO_2 is promoted with lanthana (*19*). Thus, it is concluded that while titania promotion enhances the dissociation of CO to carbon, the nascent carbon is slightly less reactive than that formed in the absence of promotion. The higher steady-state activity of the promoted catalyst (see Fig. 11) indicates that the first of these effects is much more significant than the latter.

While several recent papers (*54–56*) have demonstrated that Pd dispersion can influence the turnover frequency for CO methanation over Pd, the influence of such effects on the present results should be quite small. The data in Table 1 show that the dispersions of all five catalysts are comparable, and that the dispersions of Pd/SiO_2 and the TiO_2-promoted Pd/SiO_2 catalysts are virtually identical. This then leads to the conclusion that the higher steady-state activities for the TiO_2-containing catalysts, seen in Fig. 11, are attributable solely to the effects of the interactions of Pd with TiO_2.

The activation energies for methanation given in Fig. 11 for 2% Pd/SiO_2 and 1.7% Pd/TiO_2 are in good agreement with those reported previously for SiO_2- and TiO_2-supported Pd (*7*, *8*, *15*). The observed decrease in E_a in proceeding from Pd/SiO_2 to TiO_2-promoted Pd/SiO_2 to Pd/TiO_2 coincides with an increase in methanation activity. Ryndin *et al.* (*7*) and Wang *et al.* (*8*) also observed a lower activation energy for methanation over Pd/TiO_2 than Pd/SiO_2. While not proven by the present results, it seems reasonable to propose that the lower activation energies for the TiO_2-containing catalysts are due to the participation of TiO_x moieties in the dissociation of adsorbed CO (Reactions 3 and 4 discussed above).

Inspection of Fig. 11 shows that the specific of Pd/TiO_2 is virtually the same whether the catalyst is reduced at 473 or 673 K. While this observation appears to differ from that reported previously for Wang *et al.* (*8*) for Pd/TiO_2, there is, in fact, no contradiction. To begin with, it must be recalled that the surface area used in the calculation of specific activity is that obtained by H_2–O_2 titration which includes portions of Pd particles covered by TiO_x moieties. Table 1 shows that this measure of Pd surface area (or dispersion) is unaffected by reduction temperatures up to 673 K. The use of total metal surface area (i.e., that covered and uncovered by TiO_x moieties) differs from previous practice which based specific activities on either H_2 or CO chemisorption (*8*) measured following reduction. As is clearly evident from Figs. 1 and 2, the uncovered surface area decreases with increasing reduction temperature. If the uncovered Pd surface area on the freshly reduced catalyst had been used, then the apparent specific activity following reduction at 673 K would have been significantly higher than that following reduction at 473 K, in agreement with the observations of Wang *et al.* (*8*). The absence of a significant influence of reduction temperature on the performance of Pd/TiO_2 suggests that, under reaction conditions, the distribution of TiO_x moieties on the Pd particles changes, and eventually reaches a distribution which is independent of the initial reduction temperature. A similar observation has also been made recently by Anderson *et al.* (*17*) and Kunimori *et al.* (*18*). The driving force for the change in the coverage of Pd by TiO_x is believed to be oxidation of the TiO_x moieties by water vapor produced as a byproduct of CO hydrogenation. This interpretation seem quite reasonable since it is well known that O_2 exposure will restore the H_2 and CO chemisorption capacities of TiO_2-supported metals (*57*, *58*), and that H_2O can act as an oxidizing agent.

CONCLUSIONS

The present studies demonstrate that the adsorptive and catalytic properties of TiO_2-promoted Pd/SiO_2 more closely resemble those of Pd/TiO_2 than Pd/SiO_2. These differences are attributed to the decoration of the supported Pd particles by partially reduced TiO_x moieties. These species suppress the chemisorption of both H_2 and CO. While the TiO_x moieties do not significantly alter the distribution of H_2 adstates, the distribution of CO adstates is affected. The TiO_x moieties also facilitate the dissociation of CO to carbon and oxygen. The higher specific activity of Pd/TiO_2 and TiO_2-promoted Pd/SiO_2 for methanation, compared to Pd/SiO_2, is attributed to this effect. It is also concluded that the dissociation of adsorbed CO proceeds more readily in the presence of H_2. A mechanism is proposed for the means by which TiO_x moieties facilitate CO dissociation. The central idea is that the oxygen atom of adsorbed CO interacts with anionic vacancies in the TiO_x deposit.

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