

# The Effect of SMSI (Strong Metal-Support Interaction) Behavior on CO Adsorption and Hydrogenation on Pd Catalysts

## I. IR Spectra of Adsorbed CO Prior to and during Reaction Conditions

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An infrared cell was designed and operated as a differential, plug-flow reactor so that its spectra and kinetic data could be obtained simultaneously under well-defined, steady-state conditions. In agreement with results from other reactor systems, turnover frequencies varied over two orders of magnitude from the most active catalysts, TiO<sub>2</sub>-supported Pd in the SMSI state, to the least active, Pd/SiO<sub>2</sub>. Infrared spectra of CO adsorbed on Pd/TiO<sub>2</sub> and Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were recorded for the first time, and spectra for Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/SiO<sub>2</sub> were also obtained. The effects of temperature and hydrogen on the spectra were studied, and spectra were obtained under reaction conditions for five different catalysts. In the absence of H<sub>2</sub>, a high-frequency band above 2080 cm<sup>-1</sup> and a broader, dominant low-frequency band below 2000 cm<sup>-1</sup> were present on all catalysts. Hydrogen had little influence on the CO spectra on the typical Pd catalysts, but it markedly reduced the CO band intensities on the Pd/TiO<sub>2</sub> catalysts, even at 300 K. The effect was most pronounced for the Pd/TiO<sub>2</sub> (SMSI) catalyst, and under reaction conditions no CO bands were detected whereas all other Pd catalysts had observable IR bands. Primarily for this reason, no obvious correlation was found between observed IR-active CO species and specific activity. However, these results strongly indicate that only a small fraction of the Pd surface atoms constitute active sites, and the large surface concentrations of CO detected by IR are not directly involved in the rate-determining step for methanation.

### INTRODUCTION

Supported palladium catalysts have proven to be of interest in CO hydrogenation reactions for both fundamental and practical reasons. First, a large increase in specific activity for methanation occurs which is dependent upon the type of support utilized, with turnover frequencies over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts being one to two orders of magnitude greater than those over Pd/SiO<sub>2</sub> catalysts and nearly 100-fold greater than those over Pd black (1). Second, palladium is a metal whose adsorption properties can be influenced markedly by the support upon which it is dispersed, and

Tauster *et al.* (2) have clearly shown that SMSI (strong metal-support interaction) behavior exists in Pd/TiO<sub>2</sub> catalysts. One consequence of this SMSI effect is a severe inhibition of CO and H<sub>2</sub> chemisorption on well-dispersed Pd particles. Third, CO adsorbed on both supported and unsupported Pd has been studied by infrared spectroscopy, and at least two general forms of adsorbed CO have been identified on Pd, with both crystallite size and the support appearing to influence the adsorbed state of CO (3). Finally, the capability to prepare highly dispersed Pd on supports which greatly enhance specific activity allows serious consideration of Pd as a commercial methanation catalyst (4). In addition, Poutsma *et al.* (5) have found that supported Pd catalysts can produce methanol quite selectively under appropriate conditions of temperature and pressure.

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For these reasons, an *in situ* infrared study of Pd dispersed on various supports seemed very appropriate. Metal-support interactions are presently not well understood, and the effect of the support upon the infrared spectra of the adsorbed CO could yield important information about metal-support interactions. The design and use of an ir cell doubling as a single-pass, plug-flow reactor would provide information about the state of CO adsorption on a working catalyst surface under well-defined, differential reaction conditions. Obtaining simultaneous kinetic and ir results would allow one to determine if any correlation exists between the range of specific activities and the surface concentrations of the different adsorbed states of CO as identified by ir spectroscopy. This is the first of two papers which describe the properties of palladium supported on silica, alumina, silica-alumina, and titania as characterized by H<sub>2</sub> and CO chemisorption, X-ray diffraction, infrared spectroscopy, and kinetic behavior for CO hydrogenation (6). The first two supports have frequently been studied, whereas results for Pd dispersed on silica-alumina or titania have not been reported. Titania-supported palladium is of particular interest because of its SMSI properties.

#### EXPERIMENTAL

*Materials.* All palladium catalysts prepared in this laboratory used PdCl<sub>2</sub> obtained from the Ventron Corporation. The support materials used were:  $\eta$ -Al<sub>2</sub>O<sub>3</sub> prepared at the Exxon Research and Engineering Company following previously described procedures (7), Grade 57 SiO<sub>2</sub> and Grade 979 SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> from the Davison Chemical Co., and P-25 TiO<sub>2</sub> from the Degussa Co. The reported surface areas for each material are 245, 220, 400, and 50 m<sup>2</sup> g<sup>-1</sup>, respectively (2, 7, 8).

Hydrogen (99.999% from Linde) was further purified by flowing it through a Deoxo unit (Englehard Ind.), an alumina trap, and

an Oxytrap (Alltech Assoc. Inc.). The CO (99.99% from Linde) was passed through a molecular sieve trap while the helium (99.9999% from Linde) was flowed through a Dryrite-molecular sieve trap and an Oxytrap, both from Alltech Assoc. Inc.

*Catalyst preparation.* Six different catalysts were studied by ir spectroscopy—five of these consisted of a nominal 2 wt% Pd on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, while the last consisted of a 10.3% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalyst. All were prepared from 40/80 mesh powders using an aqueous incipient wetness technique except for the 1.98% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, which was prepared using excess water (8). The PdCl<sub>2</sub> was dissolved in concentrated HCl and evaporated twice to near dryness before diluting with deionized, distilled water. After impregnation all catalysts were dried in air for 16 hr, bottled, and stored in a desiccator. The 10.28% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was calcined in flowing air at 773 K then sintered in flowing H<sub>2</sub> at 973 K.

Actual weight loadings are reported for the fresh, unreduced catalysts, and were determined by neutron activation analysis by comparison to a standard solution of PdCl<sub>2</sub> in concentrated HCl.

*Apparatus—(A) chemisorption.* Hydrogen and CO adsorption measurements were performed in a conventional, mercury-free, glass vacuum system capable of an ultimate vacuum of about  $4 \times 10^{-7}$  Torr ( $5.3 \times 10^{-5}$  Pa). Pressures during adsorption measurements were determined using a Texas Instrument Precision Pressure Gage. A detailed description of the system is given elsewhere (8).

*(B) X-ray diffraction (XRD).* X-Ray line-broadening experiments were conducted with a Rigaku Geigerflex Model 4036-Al diffractometer using CuK $\alpha$  radiation passed through a diffraction monochromator. A fast scan of 4° min<sup>-1</sup> was used for the  $2\theta$  range of 20 to 90° while a slower scan of 1° min<sup>-1</sup> was carried out for  $2\theta$  between 42 and 55° because the (111) Pd peak was used in line-broadening calculations. All XRD runs

were carried out on used catalyst powder samples.

(C) *Infrared reactor system.* A unique infrared reactor cell was designed and constructed for this study. Techniques were developed, which are described elsewhere in detail (9), to press a 50–60 mg wafer (5/8 in. diameter) into a stainless-steel cylinder, which produced a thin, fixed catalyst bed fulfilling the requirements of an ideal, single-pass, plug-flow reactor. Both the ir beam and the gas flow passed perpendicularly through the wafer thereby achieving high space velocities (5,000–15,000 hr<sup>-1</sup>) and eliminating the concern expressed by others regarding stagnant films created by low-velocity flows parallel to the catalyst surface (9). The cell design allowed *in situ* pretreatment and reaction studies at temperatures above 700 K, if desired. Accurate gas flow rates were measured with Hastings-Raydist mass flowmeters, and product analyses were determined using a P-E Data Analyzer and a Perkin-Elmer Sigma 3 gas chromatograph with Chromosorb 102 columns and subambient temperature programming. A Perkin-Elmer 580 dual-beam spectrophotometer was incorporated into the system. A cell with the catalyst wafer was placed on the sample side and an identical cell with an equal weight of pure support material was placed on the reference side. The same gas mixture was flowed through both cells and all spectra obtained represent the difference in transmittance (or absorbance) between the two wafers. Details of the ir reactor cell and a more complete description of the ir system are reported elsewhere (10, 11). The only change has been a switch to a stainless-steel cylinder from an aluminum cylinder to enhance leak-free operation.

(D) *Steady-state microreactor.* All kinetic results obtained in the ir reactor cell were checked using a separate steady-state microreactor system which utilized 10–20 times the amount of catalyst (i.e., 0.5–1 g), lower space velocities (1–4 × 10<sup>3</sup> hr<sup>-1</sup>) and provided greater sensitivity and accuracy in

kinetic measurements. Differential operation was maintained, mass flowmeters again measured flow rates, and a P-E Sigma 3 with a Data Analyzer again was used for analysis. The system was very similar to that described earlier (12).

*Procedure.* All fresh, unreduced catalysts were given the same pretreatment except for the Pd/TiO<sub>2</sub> samples. This pretreatment consisted of: heating to 393 K in 50 cm<sup>3</sup> H<sub>2</sub> min<sup>-1</sup> and holding 30 min at this temperature, heating to 533 K and holding for 30 min, and heating to 673 K and holding for 1 hr. At this point, if chemisorption experiments were to be conducted, the sample was cooled to 648 K, H<sub>2</sub> flow was terminated, and the sample was evacuated for 30 min at 648 K before cooling under dynamic vacuum over a 25-min period to 300 K for adsorption measurements. This same procedure was employed for used samples prior to chemisorption measurements. If kinetic studies were desired, the sample was cooled under flowing H<sub>2</sub> to the desired temperature before CO was introduced. Two Pd/TiO<sub>2</sub> catalysts were prepared—one which was reduced at only 448 K and did not show SMSI adsorption behavior, and one reduced at 773 K which did and is designated SMSI (2). In each case, the pretreatment procedure was that described by Tauster *et al.* (2). The same pretreatment was utilized for the used SMSI sample as for the fresh sample.

All ir wafers, with one exception, were pressed in air from catalyst powders that had previously been reduced in the chemisorption unit and then passivated in air. The exception was a second 1.86% Pd/TiO<sub>2</sub> wafer (sample 2), which was pressed from the fresh unreduced catalyst and reduced *in situ* at 448 K following the procedure of Tauster *et al.* (2) before the ir spectra were obtained. Following this study, the wafer was reduced at 773 K for 1 hr to induce the SMSI state before another set of spectra was obtained. With this exception, all wafers in the ir cell were reduced in flowing H<sub>2</sub> at only 548 K for 1 hr

because of the previous reduction step in the chemisorption unit. When runs in He were desired, the H<sub>2</sub> flow was stopped at 548 K and He was passed through the cell until no H<sub>2</sub> was detected by gc analysis, the cell was cooled to the desired temperature, and the CO flow was started. All ir spectra were recorded with a CO/He or a CO/H<sub>2</sub> mixture flowing through the cells.

Two isotherms were measured for H<sub>2</sub> sorption at 300 K and the technique of Benson *et al.* (13) was used to determine irreversible hydrogen adsorption on the Pd surface. This method allows separate determination of both absorbed hydrogen in bulk Pd and chemisorbed hydrogen on the Pd surface. Two CO isotherms were also measured at 300 K using the technique of Yates and Sinfelt (14), with the difference between the two isotherms at 100 Torr (13.3 kPa) chosen to represent irreversible CO adsorption. Details of the techniques are contained in these two references.

#### RESULTS

The amounts of hydrogen and CO irreversibly chemisorbed on the five fresh samples and on the samples after use in the microreactor are given in Table 1. Uptakes were not measured on the used wafers from the ir studies because of the small amounts, and uptakes per gram were assumed to be the same as those measured on the used samples in Table 1.

When possible, the Scherrer equation was used to calculate average Pd particle sizes using a value of  $b = 0.26$  in Warren's correction for instrumental line broadening (15). In three cases, the lines were so broad that they could not be distinguished from the background of the support material indicating average particle sizes below 3–4 nm. These values are listed in Table 2 and compared to Pd particle sizes calculated from the H<sub>2</sub> and CO uptakes in Table 1 assuming an adsorption stoichiometry of 1 H atom or 1 CO molecule per surface Pd atom.

Kinetic results from the ir cell and the microreactor system are given in Table 3 and compared to previous results. Both turnover frequencies (molecules CH<sub>4</sub> site<sup>-1</sup> sec<sup>-1</sup>) and activation energies for the methanation reaction were determined. This was the predominant reaction with only trace amounts of higher hydrocarbons detectable at times. Results for the calcined and sintered 10.28% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> wafer are also included although no ir spectra could be obtained for this sample because of minimal transmission. Conversions in the ir cell were 1% or less while conversions ranged from 0.01 to 7% in the microreactor.

The ir spectra of CO adsorbed at different temperatures on these five 2% Pd catalysts in the presence of helium are shown in Figs. 1–5. Unless otherwise noted, spectra are plotted as transmittance,  $T$ , versus

TABLE 1  
Chemisorption on Palladium Catalysts<sup>a</sup> ( $\mu\text{mole g}^{-1}$ )

Catalyst	Fresh sample				Used sample			
	H <sub>2</sub>	CO	H/Pd <sub>t</sub>	CO/Pd <sub>t</sub>	H <sub>2</sub>	CO	H/Pd <sub>t</sub>	CO/Pd <sub>t</sub>
1.98% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	38	83	0.41	0.44	19.2	22.6	0.20	0.12
Calcined and sintered 10.28% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	13	16.4	0.027	0.017	20.4	17.4	0.043	0.018
1.93% Pd/SiO <sub>2</sub>	18	26	0.20	0.14	5.7	11	0.063	0.061
2.12% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	26.5	59	0.26	0.30	16.2	27.1	0.162	0.136
1.86% Pd/TiO <sub>2</sub>	16	41	0.18	0.23	—	—	—	—
1.86% Pd/TiO <sub>2</sub> (SMSI)	3	13	0.03	0.07	2	7	0.023	0.04

<sup>a</sup> Micromoles per gram. Based on gram fresh, unreduced catalyst.

TABLE 2  
Calculated Average Pd Particle Sizes for Catalysts

Catalyst	Used sample diameter (nm) calculated from			Fresh sample diameter (nm) calculated from	
	XRD	H <sub>(ad)</sub>	CO <sub>(ad)</sub> <sup>a</sup>	H <sub>(ad)</sub>	CO <sub>(ad)</sub> <sup>a</sup>
1.98% Pd/Al <sub>2</sub> O <sub>3</sub> Calcined and sintered	ND <sup>b</sup>	5.7	9.4	2.8	2.6
10.28% Pd/Al <sub>2</sub> O <sub>3</sub>	23.0	26.3	62.8	41.0	64.0
1.93% Pd/SiO <sub>2</sub>	16.0	18.0	18.9	5.7	7.6
2.12% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	7.2	7.0	8.3	4.2	3.8
1.86% Pd/TiO <sub>2</sub>	—	—	—	6.2	4.8
1.86% Pd/TiO <sub>2</sub> (SMSI)	ND	—	—	—	—

<sup>a</sup> Assuming CO/Pd<sub>s</sub> = 1.

<sup>b</sup> ND, not detectable.

wavenumber,  $\nu$ , in cm<sup>-1</sup>. CO partial pressures were nearly always 0.25 atm (25 kPa) because this was the pressure under reac-

tion conditions; however, the spectra were essentially unchanged when CO pressures were varied from 50 to 185 Torr on Pd/Al<sub>2</sub>O<sub>3</sub>. The spectra recorded at different temperatures in the presence of hydrogen (H<sub>2</sub>/CO = 3) are shown in Figs. 4–8. Al-

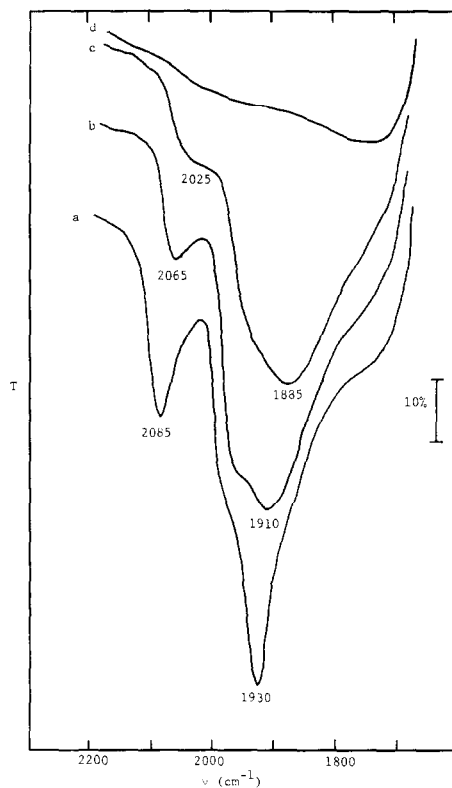


FIG. 1. Spectra of CO adsorbed on 1.98% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>;  $P_{CO}$  = 6.6 kPa,  $P_{He}$  = 92 kPa: (a) 300 K, (b) 428 K, (c) 548 K, (d) baseline in He at 300 K.

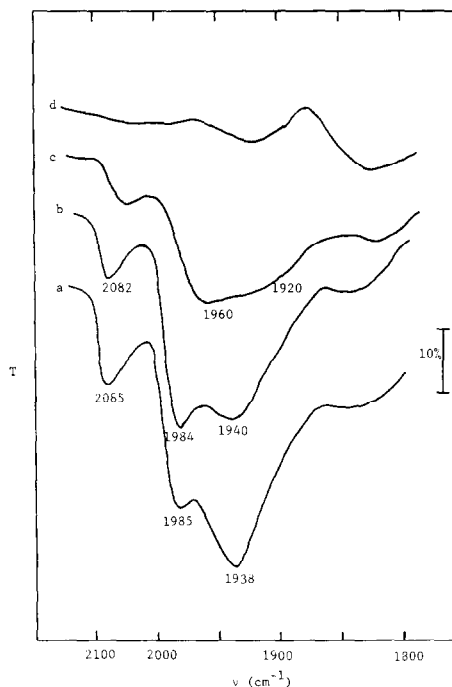


FIG. 2. Spectra of CO adsorbed on 1.93% Pd/SiO<sub>2</sub>;  $P_{CO}$  = 25 kPa,  $P_{He}$  = 75 kPa: (a) 300 K, (b) 373 K, (c) 548 K, (d) baseline in He at 300 K.

TABLE 3  
Specific Activities and Activation Energies for Methanation over Pd Catalysts<sup>a,b</sup>

Catalyst	ir cell		Microreactor		Previous work <sup>c</sup>	
	$N_{\text{CH}_4}$ ( $\text{s}^{-1} \times 10^3$ )	$E_a$ (kcal/mole)	$N_{\text{CH}_4} \times 10^3$	$E_a$	$N_{\text{CH}_4} \times 10^3$	$E_a$
1.98% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub> Calcined and sintered	3.3	10.3 ± 1.8	4.8	19.7 ± 1.3	9.7(ave)	21.7(ave)
10.28% Pd/ $\eta$ -Al <sub>2</sub> O <sub>3</sub>	6.4	20 ± 1.8	5.1	22.8 ± 0.7	10	21.0
1.93% Pd/SiO <sub>2</sub>	ND	—	0.12	27.7 ± 2.6	0.32	26.9 ± 1.8
2.12% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	1.8	21.3 ± 0.03	4.1	19.9 ± 0.3	—	—
1.86% Pd/TiO <sub>2</sub>	2.0 <sup>d</sup>	22.1 ± 0.7	4.1	19.7 ± 1.2	—	—
1.86% Pd/TiO <sub>2</sub> (SMSI) (sample 1)	10 (1.8) <sup>d</sup>	27.8 ± 0.6	4.5	22.4 ± 0.6	—	—
1.86% Pd/TiO <sub>2</sub> (SMSI) (sample 2)	40 (7.4) <sup>d</sup>	—	18 (3.1) <sup>d</sup>	24.3 ± 1.9	50 <sup>e</sup>	22.3 ± 1.2 <sup>e</sup>
			27 (4.6) <sup>d</sup>	23.6 ± 0.7		

<sup>a</sup>  $P = 1$  atm,  $T = 548$  K,  $\text{H}_2/\text{CO} = 3$ .

<sup>b</sup> Based on  $\text{CO}_{(\text{cat})}$  on used catalyst (from Table 1).

<sup>c</sup> Reference (1).

<sup>d</sup> Based on  $\text{CO}_{(\text{cat})}$  on fresh catalyst reduced at 448 K (from Table 1).

<sup>e</sup> Vannice, M. A., Symp. honoring A. G. Oblad, Adv. in Catalytic Chem., Snowbird, UT, Oct., 1979.

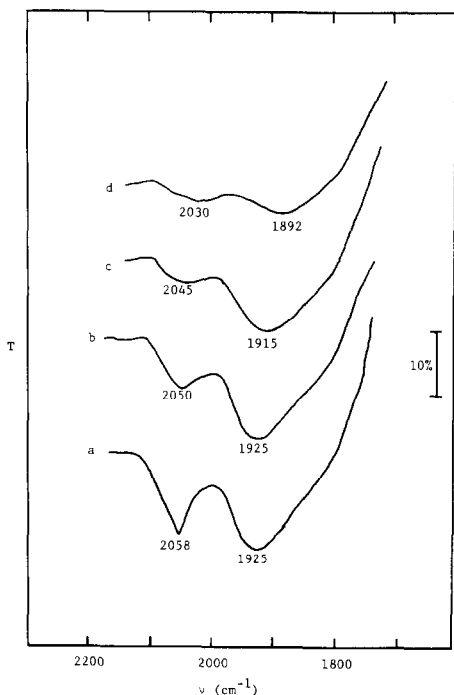


FIG. 3. Spectra of CO adsorbed on 1.86% Pd/TiO<sub>2</sub> (SMSI) (sample 2);  $P_{\text{CO}} = 25$  kPa,  $P_{\text{He}} = 75$  kPa: (a) 300 K, (b) 373 K, (c) 453 K, (d) 548 K.

though the bands were usually asymmetric and broad, this appearance was accentuated in Figs. 2 and 7 because of an automatic change in scale at  $\nu = 1980$  cm<sup>-1</sup>. The vertical scale in the figures represents 10% relative transmittance; absolute transmittance (single beam) ranged from less than 1% for the alumina and silica-alumina wafers to 7% for the titania wafer.

The wavenumber region between 4000 and 1500 cm<sup>-1</sup> was always scanned; however, no bands attributable to CH<sub>x</sub> stretching frequencies were observed, with one exception. The 1.93% Pd/SiO<sub>2</sub> wafer gave two very large bands between 2800 and 3000 cm<sup>-1</sup> after reduction in H<sub>2</sub> and before exposure to CO. These surface species were attributed to hydrocarbon impurities adsorbed on the SiO<sub>2</sub> prior to wafer preparation. The intensities of these bands were sharply reduced after a 30-min burnoff at 623 K in flowing air (11).

Experiments showed that essentially

identical ir spectra were obtained that were independent of the order in which experiments were conducted. For example, Fig. 5 shows a CO spectrum obtained in He at 300 K followed by one obtained in H<sub>2</sub> after replacing the He with H<sub>2</sub> at 300 K. A spectrum of CO in H<sub>2</sub> at 300 K was also obtained by cooling the wafer in a H<sub>2</sub>/CO mixture from 548 to 300 K and the similarity is apparent. Similar experiments on other wafers also showed that spectra at a given set of conditions could be reproduced after several heating and cooling steps, indicating that no major changes in the Pd surfaces occurred (11).

#### DISCUSSION

The chemisorption results in Table 1 show that the initial dispersions (fractions exposed) of the 2% Pd catalysts are similar on all four supports regardless of the choice of adsorbate. However, hydrogen adsorp-

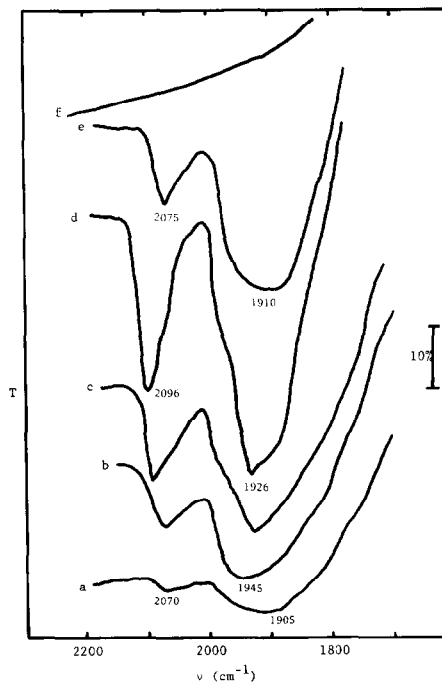


FIG. 4. Spectra of CO adsorbed on 1.86% Pd/TiO<sub>2</sub> (448 K);  $P_{\text{CO}} = 25$  kPa,  $P_{\text{He}} = P_{\text{H}_2} = 75$  kPa: (a) in H<sub>2</sub> at 548 K, (b) in H<sub>2</sub> at 448 K, (c) in H<sub>2</sub> at 300 K, (d) in He at 448 K, (e) in He at 448 K, (f) baseline in He at 300 K.

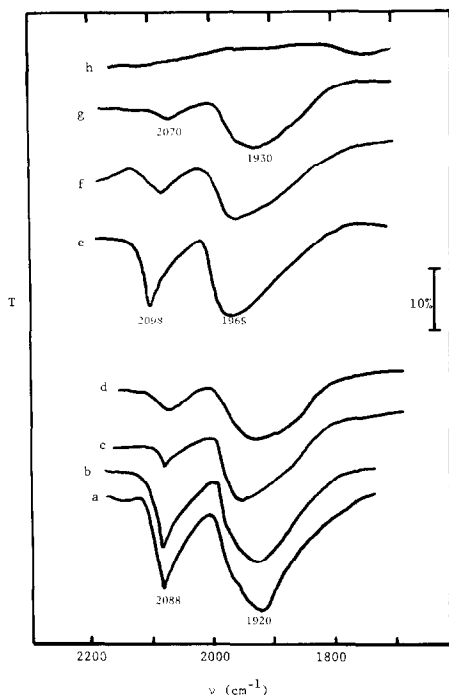


FIG. 5. Spectra of CO adsorbed on 2.12% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>;  $P_{\text{CO}} = 25$  kPa,  $P_{\text{H}_2}$  or  $P_{\text{He}} = 75$  kPa: (a) in H<sub>2</sub> at 300 K—cooling from 548 K, (b) in H<sub>2</sub> at 300 K—replacing He with H<sub>2</sub> at 300 K, (c) in H<sub>2</sub> at 473 K, (d) in H<sub>2</sub> at 548 K, (e) in He at 300 K, (f) in He at 473 K, (g) in He at 548 K, (h) baseline in He at 300 K.

tion is somewhat preferred for Pd surface area measurements because of the uncertainty of the CO adsorption stoichiometry. The uptakes on Pd/TiO<sub>2</sub> after reduction at 448 K are expected to represent normal adsorption behavior (2); however, the suppression of both hydrogen and CO adsorption after the SMSI state is induced at 773 K negates the use of chemisorption as an accurate technique to determine dispersion (2, 15). Tauster *et al.* found no indication that significant sintering occurred during the 773 K reduction; therefore, a reasonable estimate of Pd surface area in the SMSI state is that measured on the 448 K reduced catalyst. Although the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst had the highest initial dispersion, all used 2% catalysts had values of 0.2 or lower, which correspond to Pd crystallites 5 nm or larger, as indicated in Table 2. Because of the limited range of crystallite

size and the fact that average sizes are greater than 5 nm, the significant variations in ir spectra or kinetic properties cannot be attributed to a Pd crystallite size effect.

Kinetic parameters obtained in the ir reactor cell agreed very well with those determined in larger reactor systems as shown in Table 3. The agreement in both activation energies and turnover frequencies demonstrates that accurate kinetic measurements can be made with this cell design and confirms the kinetic data from these *in situ* ir studies. The low activation energy for the 1.98% Pd/Al<sub>2</sub>O<sub>3</sub> wafer is unusual as only one other Pd catalyst in our study exhibited  $E_a$  values below 19 kcal mol<sup>-1</sup>, and activation energies for Pd/Al<sub>2</sub>O<sub>3</sub> catalysts are typically near 20 kcal mol<sup>-1</sup> (6). Results for the 10.28% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst are included even though transmission was too low to provide ir spectra. These data indicate that crystallite size does not appear to be an important factor in deter-

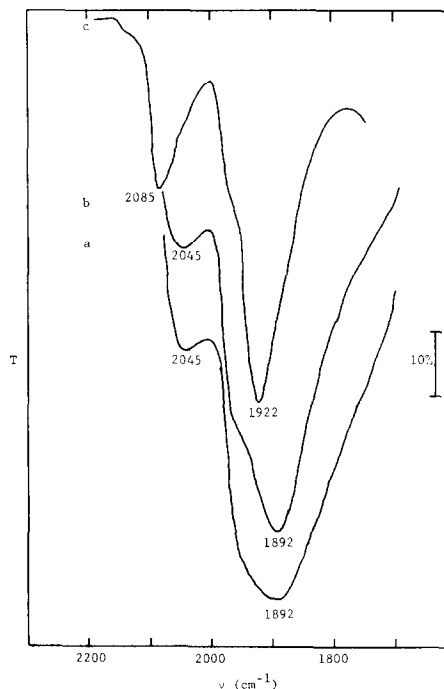


FIG. 6. Spectra of CO adsorbed on 1.98% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>;  $P_{\text{CO}} = 25$  kPa,  $P_{\text{H}_2} = 75$  kPa: (a) 548 K, (b) 423 K, (c) 300 K.



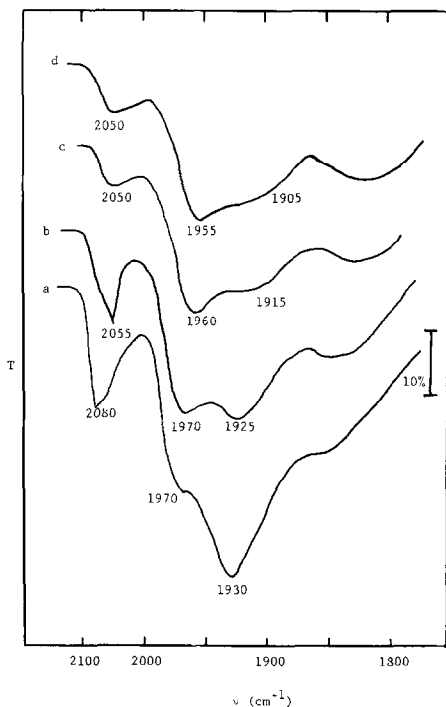


FIG. 7. Spectra of CO adsorbed on 1.93% Pd/SiO<sub>2</sub>;  $P_{\text{CO}} = 25$  kPa,  $P_{\text{H}_2} = 75$  kPa: (a) 300 K, (b) 373 K, (c) 473 K, (d) 548 K.

mining specific activity, and this is confirmed elsewhere (6, 11).

The high methane turnover frequencies,  $N$ , on alumina-supported Pd and the much lower values on silica-supported Pd which have been previously reported (1) were clearly confirmed in this study. The Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst exhibited  $N$  values very similar to those of Al<sub>2</sub>O<sub>3</sub>-supported Pd as did both TiO<sub>2</sub>-supported Pd catalysts, if adsorption on the fresh 448 K reduced sample is chosen in both cases to count surface sites. If, however, adsorption on the SMSI sample is used to count surface sites, much higher turnover frequencies are obtained, as indicated in Table 3. On a relative basis, the choice of an H atom or a CO molecule to count sites on either the fresh or the used sample is immaterial—identical trends in specific activity were observed in each of the four cases (11). For comparison purposes here, CO adsorption on the used sample is chosen to account for

any loss of Pd surface area and to allow direct comparison with previous results (1). However, the choice of H<sub>(ad)</sub> on the used samples provides  $N$  values which are very similar, as illustrated elsewhere (6, 11). The low CO conversion levels provided kinetic data free from mass transfer effects as verified by independent checks for diffusional limitations (11). This behavior, along with similar results found for Pt catalysts (16, 17), appears to represent one of the best-defined metal-support effects reported to date. The ir spectra will be discussed in regard to this catalytic behavior.

Many infrared studies have been devoted to the investigation of CO adsorbed on palladium, beginning with the pioneering work of Eischens and co-workers on supported metals (18, 19). Although these studies have covered a wide range of CO pressures ( $10^{-5}$  to 45 Torr), two CO bands have nearly always been found, and band

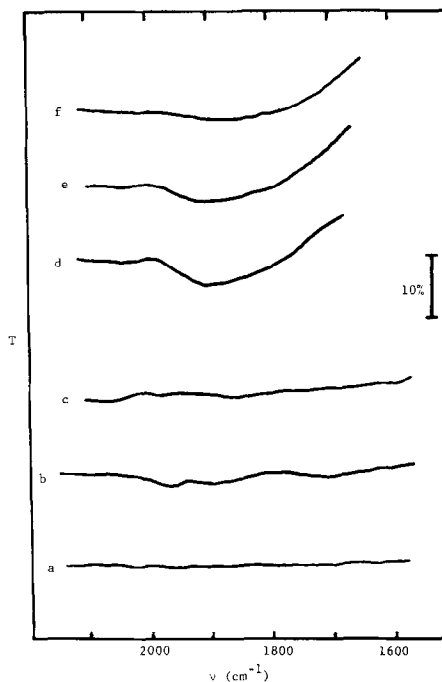


FIG. 8. Spectra of CO adsorbed on 1.86% Pd/TiO<sub>2</sub> (SMSI);  $P_{\text{CO}} = 25$  kPa,  $P_{\text{H}_2} = 75$  kPa: sample 1: (a) 548 K, (b) 300 K, (c) baseline in He at 300 K; sample 2: (d) 300 K, (e) 373 K, (f) 548 K.

TABLE 4  
 Reported CO Bands on Pd at 300 K

Reference	Catalyst	Bandwidth (cm <sup>-1</sup> )		Frequency (cm <sup>-1</sup> )				<i>P</i> <sub>CO</sub> (Torr)
		HF	LF	2100	2000	1900	1800	
(20)	Pd/SiO <sub>2</sub>	60	140					10 <sup>-5</sup>
(21)	9% Pd/SiO <sub>2</sub>	60	130					45
(22)	10% Pd/SiO <sub>2</sub>	70	125					1.5
(18)	8% Pd/SiO <sub>2</sub>	60	105					0.1
(23)	10% Pd/SiO <sub>2</sub>	65	95					30
(24)	3.6% Pd/SiO <sub>2</sub>	15	40					—
(24)	13.7% Pd/SiO <sub>2</sub>	35	100					—
(25)	Pd/SiO <sub>2</sub> (A)	55	75					1.3
	Pd/SiO <sub>2</sub> (B)	55	105					0.1
(3)	Pd/SiO <sub>2</sub>	60	95					1
(3)	Pd/Al <sub>2</sub> O <sub>3</sub>	43	65					1
(3)	Pd/Al <sub>2</sub> O <sub>3</sub>	40	144					1
(26)	Pd film	30	45					5.5
(27)	Pd film	30	90					9
(28)	5% Pd/SiO <sub>2</sub>	50	130					10
(29)	Pd (100)	—	16					< 10 <sup>-9</sup>
(29)	—	—	24					3 × 10 <sup>-7</sup>
(29)	Pd (111)	—	35					10 <sup>-5</sup>

maxima from these earlier results are depicted in Table 4 to facilitate comparison. A relatively narrow high-frequency (HF) band is usually observed between 2050 and 2100 cm<sup>-1</sup> and is typically associated with a linearly adsorbed CO molecule. A much broader, low-frequency (LF) band, which frequently consists of more than one peak, lies between 2000 and 1800 cm<sup>-1</sup>, and is attributed to multiply coordinated CO, such as bridged-bonded CO. These two bands have always been observed on supported Pd catalysts and Pd films; only on two Pd single-crystal surfaces at very low pressures has a single CO band been observed. On Pd catalysts, the LF band is usually the more dominant of the two bands, in contrast to the relative intensities of these two bands on Pt catalysts (16, 17).

The presence of these HF and LF bands

on Pd, and the observed changes in relative intensities as a consequence of different supports and Pd crystallite size, such as those reported by Van Hardeveld and Hartog (3), raised the question of whether the wide range of specific activity for Pd could be due to changes in the relative surface concentration of these two adsorbed CO species (1). The possibility of correlating activity with these ir-active adsorbed CO species was a principal driving force behind this study. In addition, effects of the presence of hydrogen on CO adsorption had not been reported, and ir spectra obtained in H<sub>2</sub>/CO mixtures were desired, especially under reaction conditions.

The peak positions and half-widths of CO bands obtained in He/CO mixtures in this study are very similar to those reported previously for CO adsorbed on Pd, as

TABLE 5  
Peak Position and Bandwidth of CO Bands on Supported Pd Catalysts (CO/He Mixture)<sup>a</sup>

Catalyst	Temperature (°K)	Bandwidth (cm <sup>-1</sup> )		Frequency (cm <sup>-1</sup> )			
		HF	LF	2100	2000	1900	1800
1.98% Pd/η-Al <sub>2</sub> O <sub>3</sub>	300	60	120				
	548	70	180				
1.93% Pd/SiO <sub>2</sub>	300	40	100				
	548	60	140				
2.12% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	300	35	120				
	548	40	130				
1.86% Pd/TiO <sub>2</sub>	300	50	115				
	448	55	140				
1.86% Pd/TiO <sub>2</sub> (SMSI)	300	60	105				
	548	55	75				
Bradshaw and Hoffmann adsorption model							

<sup>a</sup>  $P_{CO} = 190$  Torr.

shown in Figs. 1–5 and Table 5, which summarizes some characteristics of the ir bands obtained in this study. Both a broad LF band and a narrower HF band are observed on all catalysts, and the LF band is always the more dominant band. The irregular baseline for the 1.93% Pd/SiO<sub>2</sub> wafer complicates somewhat the spectra obtained for adsorbed CO. With the exception of Sample 1 of the 1.86% Pd/TiO<sub>2</sub> (SMSI) catalyst, all five 2% Pd catalysts exhibited ir bands which were very similar to those reported in earlier studies although some variation occurred in relative band intensities. However, the first 1.86% Pd/TiO<sub>2</sub> (SMSI) wafer (Sample 1) showed *no detectable adsorbed CO*, as shown in Fig. 8, despite the fact that these TiO<sub>2</sub> wafers had the highest absolute transmittance.

The presence of hydrogen had almost no influence on the ir spectra of CO adsorbed at 300 K on the Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub>, and Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. Even at higher temperatures, effects were not pronounced for these three catalysts, and band intensities under reaction conditions were similar

to those occurring at 300 K. The principal effect was a downshift of 3–25 cm<sup>-1</sup> in the HF band and 0–40 cm<sup>-1</sup> in the LF band compared to CO in helium. These results are listed in Table 6. The most probable explanation is that little hydrogen adsorbs on Pd in the presence of CO, which would not be surprising because of the much higher heat of adsorption for CO (~36 kcal mol<sup>-1</sup>) compared to H<sub>2</sub> (~23 kcal mol<sup>-1</sup>) (30). If significant H<sub>2</sub> adsorption does occur, there is little interaction with, or displacement of, adsorbed CO. Although conducted at much lower pressures, an earlier study by Conrad *et al.* (31) has shown that CO displaces hydrogen from a Pd surface and that little interaction occurs between adsorbed CO and hydrogen. The results of Rabo *et al.* (32) would also tend to support the latter possibility. The fact that high surface coverages of CO exist under reaction conditions is in agreement with partial pressure dependencies which are near zero for CO and unity for H<sub>2</sub> (6, 11, 12).

However, the Pd/TiO<sub>2</sub> (SMSI) catalyst exhibited markedly different behavior as

TABLE 6  
 CO Bands in He and in H<sub>2</sub> at Different Temperatures<sup>a,b</sup>

T(°K)	HF (cm <sup>-1</sup> )		LF (cm <sup>-1</sup> )			
	in He	in H <sub>2</sub>	in He		in H <sub>2</sub>	
			1.98% Pd/Al <sub>2</sub> O <sub>3</sub>			
298	2085	2083	1970	1930	1970	1930
423–428	2065*	2050	1960(s)*	1910*	1960(s)	1910
473	2050*	2045	1960(s)*	1905*	1955(s)	1890
548	2045	2045	a	1890	1950(s)	1890
			1.93% Pd/SiO <sub>2</sub>			
298	2085	2080	1985	1938	1970(s)	1930
373	2082	2055	1984	1940	1970	1925
473	2075	2050	1975	1925	1960	1915
548	2050	2050	1960	1920	1955	1905
			2.12% Pd/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>			
298	2098	2088	1965			1920
373	2092	a	1960			1940
473	2085	2075	1965			1960
548	2070	2070	1930			1930
			1.86% Pd/TiO <sub>2</sub>			
298	2096	2089	1926	1890		1920
448	2075	2070		1910		1945
548	—	2070		—		1905

<sup>a</sup>  $P_{\text{CO}} = 185$  Torr,  $P_{\text{H}_2}$  or  $P_{\text{He}} = 555$  Torr.

<sup>b</sup> (s), shoulder; a, could not be accurately determined; \*, measured at  $P_{\text{CO}} = 50$  Torr.

shown by Figs. 3 and 8 and, to a smaller degree, the 448 K reduced Pd/TiO<sub>2</sub> wafer also exhibited these trends. *In particular, on Pd/TiO<sub>2</sub> (SMSI) catalysts, the presence of hydrogen significantly reduced the band intensities even at 300 K, and no ir-detectable CO was observed under reaction conditions.* Sample 1 of the Pd/TiO<sub>2</sub> SMSI catalyst showed no ir-detectable CO under any experimental conditions as shown in Fig. 8. This pronounced effect of hydrogen on the band intensity is attributed to hydrogen competing successfully with CO for adsorption sites thereby displacing (desorbing) CO and reducing CO surface concentrations. Although the SMSI state decreases both H<sub>2</sub> and CO adsorption, this result infers that the effect is more pronounced for CO adsorption than for H<sub>2</sub> adsorption in CO-H<sub>2</sub> mixtures. The removal of CO as a consequence of CH<sub>4</sub>

formation cannot be completely discounted at this time; however, predicted rates at 300 K are too low to support this possibility (6, 32). One other explanation which cannot be eliminated is that adsorbed hydrogen converts adsorbed CO into a species not detectable by ir spectroscopy. Such forms of ir-inactive CO on Pd surfaces have been suggested by Rice and Haller (26). Regardless, the behavior on the Pd/TiO<sub>2</sub> (SMSI) catalyst is clearly different from the other Pd catalysts, and this effect of hydrogen on the ir band intensities coupled with the absence of ir-active CO under reaction conditions, compared to its obvious presence on the other Pd catalysts, are two of the most important results of this study.

The effects of increasing temperature and of hydrogen on peak positions were similar on all catalysts—a small downward shift occurred in band maxima. The small shifts

which occurred are not considered to be significant, and can be attributed to changes in CO surface concentration, which affect intermolecular interactions within the CO overlayer. At high coverages this interaction is repulsive (33), and increasing coverages are expected to increase the C–O stretching frequency. At the high CO pressures used in this study, the Pd surface is saturated with CO. Hoffmann and Bradshaw (34, 35) indeed found that strong shifts in band frequencies to higher values occurred as CO coverage was increased on Pd (100), (111), and (211) single-crystal surfaces. Calculated band shifts with increasing coverage are consistent with such a dipole–dipole coupling mechanism (36). Either an increase in temperature or the substitution of H<sub>2</sub> for He would be expected to decrease CO coverages thereby shifting the CO bands to lower frequencies, and this is the consistent pattern exhibited by all the catalysts. Bradshaw and Hoffmann (29) have proposed a localized site adsorption model for CO on Pd surfaces, with different spectral regions representing CO adsorbed at sites of one-, two-, three-, and possibly fourfold symmetry. These regions are designated in Tables 4 and 5. Employing this model, the assumption of only linear and bridged (one- and two-site) CO adsorption occurring on these Pd catalysts seems justified. It also indicates the surface heterogeneity of these supported Pd catalysts.

The absence of any detectable frequencies other than C–O stretching indicates that other adsorbed species or intermediates in the methanation reaction either (1) have lifetimes too short to allow measurement by ir spectroscopy or (2) their surface concentrations are too low for detection, or (3) they exist in an ir-inactive state. It seems clear that high-surface coverages of CH<sub>x</sub> or CHO species do not exist under the steady-state reaction conditions employed here.

The ir spectra obtained for these five catalysts under reaction conditions, which

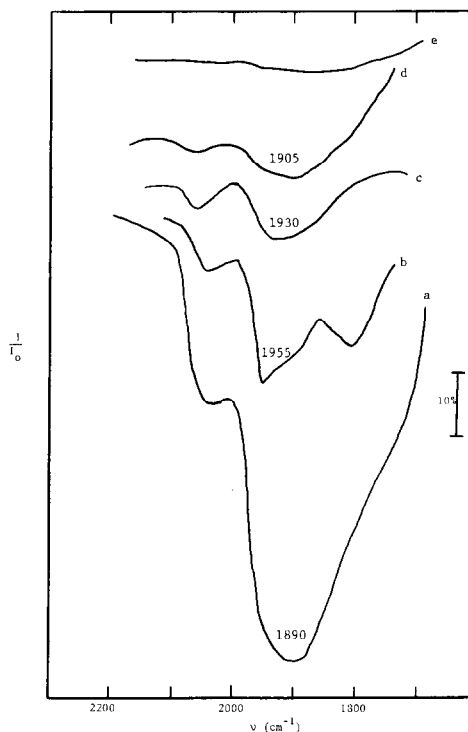


FIG. 9. Relative intensities of CO adsorbed under reaction conditions;  $P_{\text{Total}} = 1$  atm,  $\text{H}_2/\text{CO} = 3$ ,  $T = 548$  K.  $I_0$  is the baseline intensity in pure H<sub>2</sub> at 548 K. (a) 1.98% Pd/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, (b) 1.93% Pd/SiO<sub>2</sub>, (c) 2.12% Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, (d) 1.86% Pd/TiO<sub>2</sub> (448 K), (e) 1.86% Pd/TiO<sub>2</sub> (SMSI).

are compared in Fig. 9, do not provide an obvious correlation between the ir-active forms of CO observed and specific activity. Figure 9 shows the bands after correction for the baseline. Again, an irregular baseline complicated the spectrum for Pd/SiO<sub>2</sub> and the unusual shape of the LF band may well be due to this factor. The similarities among these catalysts under reaction conditions, excluding the Pd/TiO<sub>2</sub> samples, can be noted: Band intensities remain high, both HF and LF bands are evident, and the LF band is dominant. However, the intensity of neither the HF nor the LF band correlates with specific activity. The most active catalyst, Pd/TiO<sub>2</sub> (SMSI), exhibits no ir bands during methane formation whereas the other four catalysts, with a 40-fold range of  $N$ , show the presence of both

HF and LF CO bands. In addition, these four catalysts with high activity and similar  $N$  values have widely varying band intensities, while the least active catalyst has the second strongest band intensity.

If similar chemistry is assumed to govern the methanation reaction on Pd surfaces, these results indicate that only a small fraction of the Pd surface atoms constitute "active sites" although all, or nearly all, of the Pd surface atoms in typical supported Pd catalysts chemisorb CO. This conclusion is reached because the rates per surface area of Pd in the SMSI state on  $\text{TiO}_2$  are equal to or greater than those for the other Pd catalysts, yet surface concentrations of CO are so low that no CO species are detectable by infrared spectroscopy. The large surface reservoirs of adsorbed CO detected by ir are not directly involved in the rate determining step—band intensities do not correlate with activity and the elimination of this ir-active CO by inducing the SMSI state does not hinder specific activity. In fact, turnover frequencies appear to increase. Extinction coefficients calculated for both the HF and LF forms of CO adsorbed on Pd have been reported elsewhere (37), and they indicate that maximum coverages of CO under reaction conditions on SMSI  $\text{TiO}_2$ -supported Pd are less than 1% of a monolayer. The higher activity of Pd/ $\text{TiO}_2$  may be due to more equal surface coverages of CO and hydrogen, a conclusion which is consistent with reaction modeling (6). If adsorbed CO is involved in the RDS over these Pd catalysts, then it does not appear to be the CO species associated with the two major ir bands which are most readily observed. It may be a form adsorbed on sites of higher coordination number which constitute only a small fraction of the surface, or, alternatively, the RDS step may involve a carbon-containing species other than CO. For example, the hydrogenation of surface carbon may be the slow step, as mentioned in the recent review by Biloen (38). However, on Pd surfaces carbon is quite reactive and CO

dissociation does not occur readily, as shown by Rabo *et al.* (32). This behavior would strongly support the former possibility, and such a model is discussed elsewhere (6).

#### SUMMARY

A new design of an ir reactor cell, which was operated as a differential, plug-flow reactor, allowed ir spectra and kinetic data to be obtained simultaneously under well-defined, steady-state conditions. These kinetic data agreed very well with independent results obtained in a separate reactor system using much larger catalyst loadings. The turnover frequencies for methanation varied by two orders of magnitude and are very dependent upon the support utilized, with Pd/ $\text{SiO}_2$  being the least active, in confirmation of earlier results (1).

IR spectra of CO adsorbed on Pd/ $\text{TiO}_2$  and Pd/ $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  were recorded for the first time as well as spectra of CO on Pd/ $\text{Al}_2\text{O}_3$  and Pd/ $\text{SiO}_2$ . The effects of temperature and the presence of  $\text{H}_2$  on the state of CO adsorption were studied, and spectra were obtained for five catalysts under reaction conditions, including a Pd/ $\text{TiO}_2$  (SMSI) catalyst. Infrared spectra for CO adsorbed at 300 K in the absence of  $\text{H}_2$  were very consistent with earlier results, with both a high-frequency band and a broader, dominant, low-frequency band existing on all samples. The presence of hydrogen had little effect on the CO spectra obtained for all catalysts except the  $\text{TiO}_2$ -supported Pd. *For the Pd/ $\text{TiO}_2$  (SMSI) catalyst in particular, CO band intensities in  $\text{CO}/\text{H}_2$  mixtures were markedly reduced, even at 300 K, and on one Pd/ $\text{TiO}_2$  (SMSI) wafer no ir bands were detected under any experimental conditions.*

*Under reaction conditions, detectable CO bands were present on all catalysts except the Pd/ $\text{TiO}_2$  (SMSI) catalysts yet this catalyst had the highest turnover frequency. Primarily for this reason, no obvious correlation exists between the observed ir-active CO species and specific*

activity. However, these results have allowed us to propose that only a small fraction of the Pd surface atoms constitute active sites, and the large surface concentrations of CO detected by ir spectroscopy are not involved in the rate determining step (RDS) for methanation. This reaction model is discussed in more detail elsewhere (6).

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