

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

II. Kinetic Behavior in the Methanation Reaction

S-Y. WANG,¹ S. H. MOON,² AND M. ALBERT VANNICE

*Department of Chemical Engineering, The Pennsylvania State University,
University Park, Pennsylvania 16802*

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The specific activity of Pd in the methanation reaction can show a 200-fold variation depending upon the support used. In contrast, the CH₄ turnover frequency is independent of Pd crystallite size, at least over the range of 3-30 nm particles. The most active catalyst is TiO₂-supported Pd in which an SMSI state has been induced, and silica-supported Pd is the least active. Turnover numbers increase in the following order: Pd/SiO₂ ≪ Pd/SiO₂-Al₂O₃, Pd/Al₂O₃ ≈ Pd/TiO₂ (448 K) < Pd/TiO₂ (SMSI). All CO partial pressure dependencies were near zero, while H₂ partial pressure dependencies shifted from unity to near one-half for the TiO₂-supported catalysts. A reaction model for Pd is proposed which is consistent with this behavior, with ir spectra of CO adsorbed on these Pd surfaces, and with recent results in the literature on CO hydrogenation. This model involves no assumptions regarding CO coverage, and assumes CH₄ forms from surface carbon produced by a hydrogen-assisted CO dissociation step. The higher *N* values for Pd/TiO₂ in the SMSI state are consistent with this model and appear to be a consequence of much higher surface concentrations of hydrogen compensating for markedly reduced CO coverages, thereby resulting in a rate enhancement.

INTRODUCTION

Although early studies of palladium as a CO hydrogenation catalyst found this metal to have very low activity (1-3), more recent results show that Pd dispersed on the appropriate support can have quite high specific activities (4, 5). For example, Pd/Al₂O₃ catalysts had turnover frequencies for methanation (molecules sec⁻¹ site⁻¹) which approached those on nickel; however, Pd black and Pd/SiO₂ catalysts were nearly two orders of magnitude less active than Pd/Al₂O₃ (4). In addition to this contrast in behavior, new interest also exists in palladium catalysts because of their capability to selectively produce methanol under the appropriate reaction conditions (6).

This variation in specific activity has been attributed to a support effect rather than to a palladium crystallite size effect. In this investigation, we wished to see if the independence of activity on crystallite size could be verified and to examine further the role of the support. By studying the ir spectra of CO adsorbed on Pd under reaction conditions, earlier assumptions regarding the methanation reaction could be tested and additional insight into the molecular pathway for CH₄ formation could possibly be obtained. Two new supports were used in this study, silica-alumina and titania, with particular interest residing in the latter because of its capability to induce SMSI (strong metal-support interaction) behavior (7). The significant influence TiO₂ has on both the CH₄ turnover frequency on Pd and the ir spectra of CO adsorbed on Pd/TiO₂ catalysts was reported in the first paper of this series (8). This second paper deals with the consideration of crystallite

¹ Present address: CSIST, Lung Tan P. O. Box 1-4, Tao-Yuan, Taiwan, R. O. C.

² Present address: KIST, P.O. Box 131, Dong Dae Mun, Seoul, Korea.

size effects and discusses a model for methanation consistent with our recent results and with new results pertaining to this reaction.

EXPERIMENTAL

The materials utilized are described in the previous paper (8). All catalysts but one were prepared from PdCl₂ by an aqueous incipient wetness technique—the 1.98% Pd/ η -Al₂O₃ catalyst was prepared using excess water (8). The sample of 1.98% Pd/ η -Al₂O₃ designated with a "C" was calcined for 3 hr at 773 K in air (200 cm³ min⁻¹). The samples of 8.78% Pd/SiO₂, and 10.28% Pd/ η -Al₂O₃ designated by "C, S" were calcined then sintered for 2 hr at 973 K in flowing hydrogen (50 cm³ min⁻¹). One sample of 10.28% Pd/ η -Al₂O₃, designated with an "S," was sintered without prior calcination. Finally, several of the catalysts noted in the table and designated by F, G, H, J, and K, were prepared and studied previously and have been described elsewhere (4). Neutron activation analysis was used to determine actual metal loadings of catalysts prepared in this laboratory.

The apparatus have been described in the preceding paper (8). All kinetic data were obtained in a differential plug-flow reactor using 0.5–1 g catalyst and a hydrogen bracketing technique (8, 9). All catalysts were pretreated in the same manner (8) with the exception of TiO₂-supported Pd, which was pretreated both at 448 and 773 K following the procedure of Tauster *et al.* (7), as the latter treatment induces an SMSI state. The dual isotherm technique of Benson *et al.* (10) was used to measure irreversibly adsorbed hydrogen, and that of Yates and Sinfelt (11) was used for CO chemisorption. All used samples were reduced in the same manner as the fresh samples prior to chemisorption measurements, and details on adsorption procedures are given in Part I of this study (8).

RESULTS

The CO and hydrogen uptakes on both the fresh reduced catalysts and the rereduced samples which were used in the reactor are listed in Table 1. In nearly all cases, use in the kinetic studies decreased the chemisorption of H₂ and CO on the used samples. Initial dispersions (fractions exposed) were highest for the Al₂O₃-supported samples but still were seldom higher than 0.5, indicating the smallest average crystallite size present in any fresh sample was near 2.0 nm. All used samples were also characterized by X-ray diffraction, and the average crystallite sizes based on line-broadening measurements using the Scherrer equation are listed in Table 2 and compared to those estimated from the chemisorption values assuming spherical particles and a Pd_s site density of 1.3×10^{19} m⁻². An adsorption stoichiometry of 1 was assumed for both H/Pd_s and CO/Pd_s, where Pd_s is a surface Pd atom, although bridged-bonded CO can also occur. The ratio of unity for H/Pd_s is well established and, as a consequence, particle sizes based on H uptakes should be more reliable because particle sizes are expected to be overestimated using CO uptakes. The better agreement with hydrogen is confirmed in Table 2. Overlap of the Pd(111) and (200) peaks with alumina peaks complicated the XRD measurements for the Al₂O₃-supported catalysts. Regardless, quite reasonable agreement was obtained in all cases but the 8.78% Pd/SiO₂ sample, where poor dispersion was clearly evident but both H₂ and CO chemisorption appeared to be markedly lower than expected.

The technique of Benson *et al.* (10) allows the determination of *absorbed* H as well as hydrogen chemisorbed on the Pd surface, and palladium hydride ratios at 300 K and 30 kPa are listed in Table 3 to show that the β -hydride phase expected under these conditions appeared to exist for every catalyst except the 8.78% Pd/SiO₂. The Pd hydride ratios, determined after disregard-

TABLE 1
Adsorption on Palladium Catalysts at 300 K

Catalyst	Fresh sample		Used sample			
	H ₂ (μ mole/g)	CO(μ mole/g)	H ₂ (μ mole/g)	CO(μ mole/g)	H/Pd _t	CO/Pd _t
1.79% Pd/ η -Al ₂ O ₃	41	72	9.2	12.3	0.11	0.073
1.98% Pd/ η -Al ₂ O ₃	38	83	19.2	22.6	0.20	0.12
1.98% Pd/ η -Al ₂ O ₃ (C)	54	87	33.5	43.3	0.36	0.23
(G) 2% Pd/ η -Al ₂ O ₃ ^a	21	32	19.9	40.7	0.21	0.21
(H) 9.5% Pd/ η -Al ₂ O ₃ ^a	—	—	32.4	80.5	0.072	0.09
10.28% Pd/ η -Al ₂ O ₃ (C, S)	13	16	20.4	17.4	0.043	0.018
10.28% Pd/ η -Al ₂ O ₃ (S)	40	36	26.5	29.8	0.056	0.032
1.93% Pd/SiO ₂	18	26	5.7	11	0.063	0.061
8.78% Pd/SiO ₂ (C, S)	1.7	<1	3	<1	0.008	0.00086
2.12% Pd/SiO ₂ -Al ₂ O ₃	26.5	59	16.2	27.1	0.162	0.136
1.86% Pd/TiO ₂ (448 K)	16	41	—	—	—	—
1.86% Pd/TiO ₂ (SMSI) (sample 1)	0	12	—	—	—	—
1.86% Pd/TiO ₂ (SMSI) (sample 2)	3	13	2	7	0.023	0.04
1.86% Pd/TiO ₂ (SMSI) (sample 2)	1.5 ^b	7 ^b	1.5 ^b	5 ^b	0.017	0.028

^a Fresh samples prepared and described in Reference (4).

^b Chemisorption data at 548 K.

ing the surface layer of HPd_s, were consistently near the value of H_{0.55} Pd expected for the β -hydride phase, with the average being 0.56 ± 0.14 . These results indicate the presence of Pd crystallites large enough to

exhibit normal bulk Pd behavior. The unusual behavior of the 8.78% Pd/SiO₂, giving a Pd hydride ratio near that of the α -phase (0.03), cannot be explained at this time. Silicon in Pt has recently been found

TABLE 2

Calculated Average Pd Particle Sizes for Used Catalysts

Catalyst	Diameter (nm) based on		
	XRD	H _(ad)	CO _(ad)
1.79% Pd/Al ₂ O ₃	12.0	10.2	15.5
1.98% Pd/Al ₂ O ₃	NV ^a	5.7	9.4
1.98% Pd/Al ₂ O ₃ (C)	NV	3.2	4.9
(G) 2% Pd/Al ₂ O ₃	NV	5.4	5.4
(H) 9.5% Pd/Al ₂ O ₃	10.0	15.7	12.6
10.28% Pd/Al ₂ O ₃ (C, S)	23.0	26.3	62.8
1.93% Pd/SiO ₂	16.0	18.0	18.9
8.78% Pd/SiO ₂ (C, S)	20.0	153.0	1060.0
2.12% Pd/SiO ₂ -Al ₂ O ₃	7.2	7.0	8.3
1.86% Pd/TiO ₂ (448 K)	—	—	—
1.86% Pd/TiO ₂ (SMSI)	NV	—	—

^a NV; not visible.

TABLE 3

Bulk Pd Hydride Ratios for Hydrogen Absorbed in Fresh, Reduced Catalysts

Catalyst	H _{bulk} /Pd _{bulk}
1.79% Pd/ η -Al ₂ O ₃	0.67
1.98% Pd/ η -Al ₂ O ₃	0.74
1.98% Pd/ η -Al ₂ O ₃ (C)	0.70
(G) 2% Pd/ η -Al ₂ O ₃	0.48
(H) 9.5% Pd/ η -Al ₂ O ₃	—
10.28% Pd/ η -Al ₂ O ₃ (C, S)	0.42
10.28% Pd/ η -Al ₂ O ₃ (S)	0.53
1.93% Pd/SiO ₂ (C, S)	0.52
8.78% Pd/SiO ₂ (C, S)	0.04
2.12% Pd/SiO ₂ -Al ₂ O ₃	0.46
1.86% Pd/TiO ₂ (448 K)	0.62
1.86% Pd/TiO ₂ (SMSI)	0.42
Average ^a	0.56

^a All the catalysts except 8.78% Pd/SiO₂.

to alter the chemisorption behavior of Pt (12), and a similar effect or surface Pd silicide formation represent two possible explanations of this behavior. No X-ray peaks attributable to Pd silicide, Pd₄Si, were observed, thereby eliminating the possibility of bulk silicide formation.

Catalytic activities and activation energies for the methanation reaction at standard conditions are shown in Table 4. Methane was the principal hydrocarbon product formed and no methanol was detected so N_{CH_4} and N_{CO} values were nearly identical and only the former is reported. The temperature range covered for Arrhenius plots was typically between 250 and

300°C. The CO conversions for all runs were between 0.01 and 6.8%, except for the 10.28% Pd/Al₂O₃ where conversions ranged between 2 and 9%. Partial pressure dependencies were determined for Pd/SiO₂-Al₂O₃ and the two titania-supported palladium catalysts, and these values are listed in Table 5 along with previously reported values for alumina- and SiO₂-supported Pd.

DISCUSSION

This study shows that a 100-fold range of turnover frequencies exists for supported Pd catalysts and, in addition, these results clearly reproduce the high specific activities for Pd/Al₂O₃ and the low values for

TABLE 4
Kinetic Properties of Palladium Catalysts^a

Catalyst	Rate ($\mu\text{mole CH}_4/\text{s} \cdot \text{g cat.}$)	N_{CH_4} ($\text{s}^{-1} \times 10^3$)		E_a (kcal mol^{-1})	Average particle size ^c (nm)
		(b)	(c)		
1.98% Pd/ η -Al ₂ O ₃ (C)	0.200	4.6	3.0	13.8 ± 0.6	3.2
(F) 2% Pd/Al ₂ O ₃ ^d	—	12	—	19.7 ± 1.6	4.8 ^e
(G) 2% Pd/ η -Al ₂ O ₃ ^f	0.125	3.1	3.2	19.2 ± 0.8	5.4
1.98% Pd/ η -Al ₂ O ₃	0.108	4.8	2.8	19.7 ± 1.3	5.7
(G) 2% Pd/Al ₂ O ₃ ^d	—	7.4	—	23.6 ± 1.9	8.2 ^e
1.79% Pd/ η -Al ₂ O ₃	0.109	8.8	5.9	19.4 ± 0.7	10.2
(H) 9.5% Pd/Al ₂ O ₃ ^d	—	7.4	—	21.0 ± 0.8	12.0 ^e
(H) 9.5% Pd/ η -Al ₂ O ₃ ^f	0.257	3.2	4.0	24.5 ± 1.1	15.7
10.28% Pd/Al ₂ O ₃ (S)	0.25	8.5	4.7	19.0 ± 1.0	20.0
10.28% Pd/Al ₂ O ₃ (C, S)	0.09	5.1	2.2	22.8 ± 0.6	26.3
2.12% Pd/SiO ₂ -Al ₂ O ₃	0.11	4.1	3.4	19.9 ± 0.3	7.0
(J) 4.75% Pd/SiO ₂ ^d	—	0.32	0.23	26.9 ± 1.8	3.1 ^e
(K) 4.75% Pd/SiO ₂ ^d	—	0.26	—	—	4.9 ^e
1.93% Pd/SiO ₂	0.0013	0.12	0.11	27.7 ± 2.6	18.0
8.78% Pd/SiO ₂ (C, S)	0.00103	1.0	0.34	19.2 ± 1.8	153
1.86% Pd/TiO ₂ (448 K) Sample 1	0.168	4.1 ^g	5.2 ^h	19.7 ± 1.2	6.2 ^g
Sample 2	0.187	4.5 ^g	5.8 ^h	22.4 ± 0.6	—
1.86% Pd/TiO ₂ (SMSI) Sample 1	0.128	18	32	24.3 ± 1.9	—
		3.1 ^g	4.0 ^h		
Sample 2	0.187	27	47	23.6 ± 0.7	—
		4.6 ^g	5.8 ^h		

^a $T = 548 \text{ K}$, $P_T = 1 \text{ atm}$, $\text{H}_2/\text{CO} = 3$.

^b Based on $\text{CO}_{(\text{ad})}$ on used sample.

^c Based on $\text{H}_{(\text{ad})}$ on used sample.

^d Results previously reported in Reference (4).

^e Based on $\text{CO}_{(\text{ad})}$ on used sample assuming $\text{CO}/\text{Pd}_s = 0.5$.

^f Results obtained in this study with fresh catalysts so designated in Reference 4.

^g Based on $\text{CO}_{(\text{ad})}$ on fresh, reduced sample.

^h Based on $\text{H}_{(\text{ad})}$ on fresh, reduced sample.

TABLE 5
Kinetic Parameters on Different Supported Pd Catalysts

Catalyst	N_{CH_4} at 548 K ^a ($\text{s}^{-1} \times 10^3$)	X	Y	A (molecules CH_4 / $\text{s} \cdot \text{Pd}_s \cdot \text{atm}^{X+Y}$)
2.12% Pd/SiO ₂ -Al ₂ O ₃	3.4	0.90 ± 0.11	0.12 ± 0.04	8.8×10^5
1.86% Pd/TiO ₂ (448 K)	5.5 ^b	0.55 ± 0.02	-0.15 ± 0.01	9.0×10^5
1.86% Pd/TiO ₂ (SMSI)	40 ^b	0.55 ± 0.02	-0.03 ± 0.01	1.16×10^5
2% Pd/Al ₂ O ₃ ^c	6 ^d	1.03 ± 0.05	0.03 ± 0.09	6.0×10^5
4.75% Pd/SiO ₂ ^c	0.23	0.71 ± 0.05	0.15 ± 0.07	1.4×10^5

^a From Column 4, Table 4.

^b Average values.

^c Reference (4).

^d Assuming $H_{(\text{ad})}/CO_{(\text{ad})} = 2$.

Pd/SiO₂ which were reported previously (4). The recent work of Fujimoto *et al.* (13) has also indicated that SiO₂-supported Pd is much less active than Al₂O₃-supported Pd for methanation. The 8.78% Pd/SiO₂ sample has very low activity but the turnover frequency for methanation, N , is somewhat higher than those for other Pd/SiO₂ catalysts because of the extraordinarily low chemisorption values. The 2.12% Pd/SiO₂-Al₂O₃ catalyst has N values very similar to Pd/Al₂O₃ while values for the Pd/TiO₂ catalysts are substantially higher. Turnover frequencies show the same trend regardless of the choice of adsorbed H, which defines the number of surface Pd atoms, or adsorbed CO, which only defines a surface "site" because its adsorption stoichiometry can vary. Adsorption values on the used samples were chosen to calculate turnover frequencies because of the noticeable decrease in H₂ and CO chemisorption after usage. This is most likely caused by sintering of the Pd particles. However, *identical trends in activity* and the same range in N values exists if adsorption of H₂ or CO on the fresh samples is chosen as a basis (14). The only significant change is that the turnover frequencies are all decreased by a factor of two or so (14).

The Pd/TiO₂ (SMSI) catalysts clearly have the highest turnover frequencies when these values are based on chemisorption on

Pd in the SMSI state. However, monolayer coverage of CO and hydrogen are greatly suppressed and may not be indicative of the total metal surface area (7). Tauster *et al.* have shown that sintering cannot account for these reduced uptakes, and if it is assumed that the Pd surface area measured on the 448 K reduced sample remains constant during the high-temperature reduction, N values for SMSI Pd based on adsorption on the sample reduced at 448 K are remarkably close to the other Pd catalysts, excluding the SiO₂-supported samples. This choice of Pd surface sites obviously results in lower N values and represents a reasonable lower limit for N . Increasing the adsorption temperature does not increase the uptakes on the Pd/TiO₂ (SMSI) catalyst; in fact, the amounts of H₂ and CO chemisorbed at 548 K are reduced to half the uptakes at 300 K, as shown in Table 1. The activity of Pd in this catalyst remains quite high despite the very small number of adsorption sites present. Such activity enhancement has also been observed for Ni/TiO₂ systems (15, 16).

There is no evidence in the literature that methanation requires a dual functional catalyst and, in fact, earlier runs with physical mixtures of Pt and Al₂O₃ showed no rate enhancements, thereby eliminating this explanation of enhanced activity (4). The range of specific activity existing with Pd

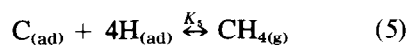
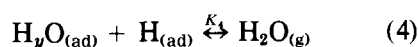
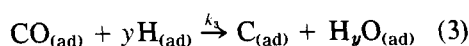
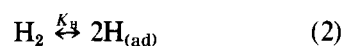
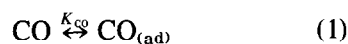
must be attributed to an interaction between the Pd crystallites and the support. Unsupported Pd has turnover frequencies near those on Pd/SiO₂ (4), and this indicates that alumina, silica-alumina, and titania enhance the activity of Pd rather than silica acting to inhibit activity. A similar trend has been found for Pd catalysts in benzene hydrogenation; however, the range of turnover frequencies was much narrower (17).

As shown in Table 4, turnover frequencies can vary by more than two orders of magnitude as a consequence of the support used. Similar dispersions exist on all four supports so that this factor can be eliminated as a variable. In addition, a number of Pd/Al₂O₃ catalysts were prepared with different Pd particle sizes, and a comparison of turnover frequency versus crystallite size clearly shows that no dependency exists in the range of 3 to 30 nm, as less than a random threefold variation in turnover frequency exists. This supports the earlier conclusion that crystallite size cannot account for the low specific activity observed for SiO₂-supported Pd (4). If the anomalous behavior of the 8.78% Pd/SiO₂ sample is excluded, Pd/SiO₂ catalysts also show no trend in *N* values as particle size varies from 3 to 18 nm. Therefore, the methanation reaction appears to be structure-insensitive on Pd catalysts.

A kinetic model for methanation has been proposed for Group VIII metals which assumed that the surface was predominantly covered by CO, which was interacting with adsorbed hydrogen, and that the rate determining step (RDS) was the reaction of this (H₂-CO) complex with hydrogen to form water and a CH_x moiety on the surface (18). The validity of these assumptions must now be reconsidered in light of recent studies of CO hydrogenation reactions and our recent results (8). The preceding paper clearly showed that the assumption of high surface coverages of CO under reaction conditions is justified on all the catalysts except Pd/TiO₂ (SMSI) (8). It also indicated that, excluding the

Pd/TiO₂ (SMSI) catalyst, hydrogen adsorption may not occur to a large extent on these catalysts or, if it does, it does not alter the adsorbed state of CO significantly. Recent studies by Rabo *et al.* have shown that surface carbon produced by CO dissociation is more reactive to hydrogen than molecular CO; however, almost no dissociation occurs at temperatures below 573 K on Pd (19). The formation of CH₄ via dissociative CO adsorption has been shown to occur on other metal surfaces (19-23). Recently, Ho and Harriott have proposed that, in order to achieve the high methanation rates observed, a hydrogen-assisted C-O bond rupture step occurs on Ni to produce a surface carbon species (24).

As a consequence, the following sequence of steps is suggested over Pd, and possibly other Group VIII noble metals which appears realistic in view of these recent results, yet is very similar to that proposed earlier (18):



Step 3 is the RDS with all other steps in quasi-equilibrium, and if *y* is equal to 2, H₂O_(g) can be formed directly. The use of Langmuir-Hinshelwood kinetics in a manner shown earlier (25) produces the following power rate law if the surface coverage of hydrogen is assumed to be low (i.e., $K_{\text{H}}P_{\text{H}_2} \ll 1$):

$$r(\text{molecules sec}^{-1} \text{ cm}^{-2} \cdot \text{Pd}) = (N^*) (\text{Pd site density}) = kP_{\text{H}_2}^{y/2} P_{\text{CO}}^{y(n-1)+n}$$

where $k = (k_3)(K_{\text{CO}})^{y(n-1)+n}(K_{\text{H}})^{y/2}$ and *N** is based on hydrogen adsorption. It should be stressed that this model involves *no* assumptions regarding CO. This derived rate equation can be compared to the experimental rate laws, $N = kP_{\text{H}_2}^x P_{\text{CO}}^y$, whose

parameters are given in Table 5. From this comparison, integral y values are chosen to provide the best fit while the parameter n must be between 0 and 1 (25). The fit obtained by this procedure is shown in Table 6 and appears to be quite adequate.

Although efforts such as this do not prove the proposed mechanism, they can test it for consistency and provide insight regarding the surface reaction if the kinetic parameters and the chemistry seem reasonable. This model is supported by the study of Rabo *et al.* (19), which found that CO dissociation is slow on Pd, and surface carbon which does form is expected to easily hydrogenate. The RDS appears to involve either a hydrogen atom or molecule (2 atoms), with the former species appearing to be favored on the Pd/TiO₂ catalysts. This is consistent with the ir results which showed that hydrogen could adsorb strongly enough to displace CO on Pd/TiO₂ catalysts, but had little effect on CO band intensities for the other three catalysts. Dissociative adsorption of hydrogen would provide this stronger bond and facilitate the competitive adsorption of hydrogen with CO whereas adsorbed CO can prevent hydrogen adsorption, in general, and may prevent dissociative adsorption, in particular. The higher N values on Pd in the SMSI state can also be understood in a qualitative sense because of the more competitive hydrogen chemisorption on the Pd/TiO₂ (SMSI) catalyst. If the RDS is considered a bimolecular reaction involving adsorbed CO and surface hydrogen, then a rate maximum is expected when surface coverages of each reactant are equal. The sensitivity

of methanation rates on low surface concentrations of hydrogen, compared to CO, has been clearly shown by Polizzotti *et al.* (26). If decreased CO band intensities represent hydrogen adsorbing on Pd by displacing CO, then higher surface coverages of hydrogen appear to exist on this Pd SMSI catalyst under reaction conditions. Although surface concentrations of CO decrease significantly, as shown in the preceding paper (8), rates are not decreased and N values actually increase.

Using calculated ir extinction coefficients, we have estimated that the maximum surface coverages of linearly bonded CO and bridged-bonded CO are near 1 and 0.1%, respectively (27). This implies that the density of active sites on TiO₂-supported Pd in the SMSI state is much lower than the Pd_s density, which is $1.27 \times 10^{15} \text{ cm}^{-2}$ assuming equal areas of the three low index planes. If similar surface chemistry is assumed to occur on all these Pd catalysts, which is not unreasonable based on the narrow range of partial pressure dependencies and activation energies in Table 5, then one can conclude that the "active site" densities on "typical" Pd catalysts may also be far lower than the surface atom density. The large surface concentrations of ir-active CO which exist on these Pd catalysts do not represent the form of adsorbed CO participating in the RDS, and if anything, they may impede the reaction by excluding hydrogen from the surface. Therefore, the statement made previously that weakened CO adsorption could result in higher activity is supported (4); however, the route by which the rate enhancement occurs is somewhat different than anticipated, as the two forms of adsorbed CO detectable by ir spectroscopy do not appear to represent species residing on sites which are responsible for catalytic activity. It is suggested that Pd sites of higher coordination, which would be predicted to produce wavenumbers near 1800 cm⁻¹ or lower (28) and to constitute only a small fraction of the surface, may constitute the "active sites" in these catalysts.

TABLE 6

Experimental and Calculated Partial Pressure Dependencies

Catalyst	X_{exp}	Y_{exp}	y	n	$X_{\text{calc.}}$	$Y_{\text{calc.}}$
Pd/Al ₂ O ₃ ^a	1.0	0.03	2	0.68	1.0	0.04
Pd/SiO ₂ ^a	0.7	0.15	2	0.72	1.0	0.16
Pd/SiO ₂ -Al ₂ O ₃	0.94	0.12	2	0.71	1.0	0.13
Pd/TiO ₂	0.55	-0.15	1	0.43	0.5	-0.15
Pd/TiO ₂ (SMSI)	0.55	-0.03	1	0.51	0.5	-0.02

^a From Reference (9).

SUMMARY

The specific activity of Pd in the methanation reaction is strongly dependent upon the support used, and a 200-fold variation exists in turnover frequencies. In contrast, the CH₄ turnover frequency is independent of Pd crystallite size, at least over the range of 3–30 nm particles. The most active catalyst is TiO₂-supported Pd in which an SMSI state has been induced, and silica-supported Pd is the least active. Turnover numbers increase in the following order: Pd/SiO₂ ≪ Pd/SiO₂-Al₂O₃ ≈ Pd/Al₂O₃ ≈ Pd/TiO₂ (448 K) < Pd/TiO₂ (SMSI).

All CO partial pressure dependencies were near zero, while H₂ partial pressure dependencies shifted from unity to near one-half for the TiO₂-supported catalysts. A reaction model is proposed which is consistent with this behavior, with ir spectra of CO adsorbed on these Pd surfaces, and with recent results in the literature. This model involves no assumptions regarding CO coverage and assumes CH₄ formation from surface carbon produced by a hydrogen-assisted CO dissociation step. The higher *N* values for Pd/TiO₂ in the SMSI state are consistent with this model and appear to be a consequence of much higher surface concentrations of hydrogen compensating for markedly reduced CO coverages, thereby resulting in a rate enhancement. Although the influence of the support is clearly evident in this study, a satisfactory explanation of the chemistry involved is difficult to propose. However, the synergistic effects observed in the CO hydrogenation reaction bode well for improved catalyst systems in the future.

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