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SMSI Effects on CO Adsorption and Hydrogenation on Pt Catalysts

Part II. Influence of Support and Crystallite Size on the Kinetics of Methanation

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Platinum was dispersed on η-Al_2O_3, SiO_2, SiO_2–Al_2O_3, and TiO_2, and its fraction exposed was varied from near unity to 0.007. The turnover frequency (TOF) for CO hydrogenation to CH_4 was constant over this range of Pt crystallite size on a given support. However, the support utilized had a major influence on specific activity and TOF values on Pt/TiO_2 catalysts were 10 times greater than those on Pt/Al_2O_3 and Pt/SiO_2–Al_2O_3 and 100-fold higher than the TOF on Pt/SiO_2. A model for methanation invoking H-assisted CO bond rupture as the rate determining step correlated the different kinetic parameters measured over these Pt catalysts. Analysis of this model using transition state theory provided an estimate of the maximum active site density and, in agreement with *in situ* ir spectroscopic studies, indicated that only a small fraction (0.01 or less) of the surface Pt atoms constitute active sites on TiO_2-supported Pt. The alteration in catalytic behavior for TiO_2-supported Pt is attributed to a change in structure of the Pt crystallites caused by a strong interaction with a partially reduced titania surface. The observed enhancement in activity after reduction at only 473 K implies that this effect is localized and not dependent on bulk electronic properties.

INTRODUCTION

Platinum is one Group VIII metal which, when dispersed on titania and reduced under appropriate conditions, exhibits markedly altered chemisorption and catalytic behavior involving CO and hydrogen. High-temperature reduction suppresses or eliminates chemisorption of these two molecules, as first reported by Tauster *et al.* (*1*), yet significantly higher activity occurs for CO hydrogenation, which is essentially methanation at low pressures (*2*, *3*). Although this behavior is very reproducible and has been attributed to SMSI (Strong Metal–Support Interaction) behavior, numerous explanations of this phenomenon have been proposed and the exact nature of this synergistic effect is not presently known.

In order to gain a better understanding of the influence of the support and of crystallite size in this reaction, a family of Pt catalysts utilizing silica, alumina, silica-alumina, and titania and involving a wide range of dispersion (fraction Pt exposed) was examined using chemisorption, X-ray diffraction, and ir spectroscopy, and employing CO methanation as a probe reaction. The *in situ* ir studies were reported in Part I (*3*). This paper discusses the kinetic properties of these catalysts and proposes a modified model for the methanation reaction which is consistent with the kinetic parameters and with other results which have been published in the literature. In an effort to gain insight about the catalytic surface and to determine support effects, transition state theory was applied to this model so that active site densities could be estimated.

EXPERIMENTAL

The glass volumetric adsorption system, the plug-flow, differential microreactor,

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0021-9517/83 $3.00

TABLE 1

Characterization of Pt Catalysts by Chemisorption and X-Ray Diffraction

	Gas uptake (μmole g^{-1})				Dispersion (H/Pt_t)		Final crystallite diameter (nm) from		
	Initial		Final		Initial	Final	$H_{(ad)}$	$CO^{i}_{(ad)}$	XRD
	H_2	CO	H_2	CO					
A. 2.1% Pt/Al_2O_3	51.0	62.5	39.0	38.1	0.95	0.72	1.6	3.2	ND[a]
B. 2.0% Pt/Al_2O_3	8.0	10.5	—	—	0.16	—	4.7[b]	—	ND[b]
C. 2.0% Pt/Al_2O_3(S)[c]	2.0	2.5	0.7	1.1	0.040	0.014	80	100	14
D. 2.0% Pt/Al_2O_3(S)[d]	1.5	2.5	—	—	0.030	—	38[b]	47[b]	17[b]
E. 10.0% Pt/Al_2O_3(S)[e]	37.5	43.0	32.7	38.3	0.15	0.13	8.7	15	27
F. 10.0% Pt/Al_2O_3(S)[f]	2.5	2.5	1.9	2.8	0.010	0.007	160	220	40
G. 1.5% Pt/SiO_2(D)	6.5	13.0	4.1	8.0	0.17	0.11	10	11	ND
H. 1.3% Pt/SiO_2(C)	14.0	—	7.0	12.5	0.42	0.21	5.4	5.9	ND
I. 2% Pt/SiO_2(C)[g]	—	—	10.5	17.0	0.63	0.20	5.6	7.0	21
J. 2% Pt/SiO_2(C)[h]	—	—	30.0	27.0	1.0	0.59	1.9	4.0	13
K. 1.5% Pt/SiO_2-Al_2O_3	33.5	52.0	10.3	18.2	0.87	0.27	4.2	4.7	ND
L. 1.9% Pt/TiO_2(LT)	6.5	9.0	4.8	6.7	0.13	0.10	11	16	20
M. 1.9% Pt/TiO_2(LT)(H_2)	—	—	2.9	2.9	—	0.060	19	38	16
N. 1.9% Pt/TiO_2(LT)(He)	30.0	37.5	24.7	28.0	0.62	0.51	2.2	3.9	ND
O. 1.9% Pt/TiO_2(SMSI)	—	—	1.4	1.4	—	0.029	(39)[j]	(75)[j]	ND
P. 1.9% Pt/TiO_2(SMSI)(He)	3.0	5.0	4.8	4.8	0.062	0.10	(11)[j]	(22)[j]	ND

[a] Not detected.

[b] Initial values.

[c] Sintered in air for 16 hr at 973 K.

[d] Sintered in air for 24 hr at 973 K.

[e] Sintered in H_2 for 16 hr at 1073 K.

[f] Sintered in air for 24 hr at 1073 K.

[g] Catalyst I from Ref. (*6*).

[h] Catalyst E from Ref. (*6*).

[i] Assuming $CO/Pt_s = 1$.

[j] Not representative because of suppressed chemisorption.

and the X-ray diffractometer have been described previously (*3–5*). The catalysts were prepared in this study using aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ or $(NH_3)_4Pt(NO_3)_2$ (Ventron Corp.) with η-Al_2O_3 (Exxon R & E Co.), SiO_2 ((D) Grade 57, Davison Chem. Co. and (C) Cab-O-Sil Grade M5, Cabot Corp.), SiO_2–Al_2O_3 (Grade 979, Davison Chem. Co.), and TiO_2 (P-25, Degussa Co.). Details of catalyst preparation are given elsewhere (*3*, *5*). The gases used were H_2 (99.999%, Linde Co.), CO (99.99%, Linde Co.), and He (99.9999%, Linde Co.) and were subjected to additional purification (*3*, *5*). Platinum loadings were determined using neutron activation analysis.

The Pt/TiO_2 catalysts were pretreated in H_2 either at a low temperature (LT) of 473 K or at a high temperature of 773 K to induce the SMSI state following the procedure of Tauster *et al.* (*1*). All other catalysts were given a standard pretreatment which consisted essentially of stepwise heating in flowing H_2 to 723 K and a 1 hr reduction at this temperature. If kinetic studies were to be conducted, the sample was cooled in flowing H_2 to the desired temperature whereas if adsorption measurements were to be made the sample was evacuated at 698 K for 1 hr prior to cooling in vacuum to 300 K (*3*, *5*). The chemisorption procedures are also described in the previous papers (*3*, *5*). The Pt crystallite size was varied on the η-Al_2O_3 support by the preparation technique and by sintering in flowing H_2 or cylinder

TABLE 2

Kinetic Behavior of Platinum Catalysts[a]

Catalyst[b]	Rate $\left(\frac{\mu\text{mole CH}_4}{\text{s} \cdot \text{g cat}}\right)$	N_{CH_4}($s^{-1} \times 10^3$) (c)	(d)	E_a (kcal $mole^{-1}$)	Diameter (nm) (c)	CO conversion range (%)
Pt/Al_2O_3						
1.75% Pt[h]		1.7		16.7	1.2	
A—2.1%						
I	0.134	1.7	3.5	16.2 ± 0.7	1.6	1.0–3.8
II	0.164	2.1	4.3	—	1.6	0.2–1.0
B—2.0%	0.040	1.6[e]	2.4[e]	16.5 ± 1.2	4.7[e]	0.2–1.0
E—10.0%	0.092	1.4	2.4	16.7 ± 1.0	8.7	0.3–1.3
D—2.0%	—	—	—	—	38	—
C—2.0%	0.0024	1.7	2.3	17.6 ± 0.8	80	0.03–1.0
F—10.0%	0.0028	0.73	1.0	18.6 ± 1.4	160	0.05–0.2
Pt/SiO_2						
J—2%	0.0084	0.14	0.31	—	1.9	<0.01
H—1.3%	0.0024	0.17	0.19	—	5.4	0.01–0.03
I—2%	0.0040	0.19	0.24	—	5.6	<0.01
G—1.5%	0.0016	0.19	0.19	16.8 ± 1.1	10	0.01–0.05
Pt/SiO_2–Al_2O_3						
K—1.5%	0.029	1.4	1.6	16.4 ± 1.0	4.2	0.2–1.0
Pt/TiO_2						
N—1.9% (LT)						
I	0.538	10.9	19	19.1 ± 0.6	2.2	2.6–16
II	0.737	14.9	26	20.3 ± 0.3	2.2	1.8–5.0
L—1.9% (LT)						
I	0.064	6.7	9.6	17.2 ± 0.7	11	0.4–1.8
II	0.081	8.4	12	19.0 ± 1.5	11	0.3–1.7
M—1.9% (LT)	0.084	14.5	29	—	19	—
P—1.9% (SMSI)						
I	0.564	59(11.3)[f]	120	20.6 ± 0.8	(2.2)	3.0–15
II	0.659	66(12.7)[f]	130	19.1 ± 1.6		0.7–4.2
O—1.9% (SMSI)						
I	0.150	54(16)[g]	110	17.7 ± 0.8	(11)	1.8–5.0
II	0.355	127(38)[g]	250	23.3 ± 3.2		0.8–4.9

[a] T = 548.2 K, P_T = 101 kPa, H_2/CO = 3.

[b] Roman numerals indicate different samples.

[c] Based on final $H_{(ad)}$.

[d] Based on final $CO_{(ad)}$.

[e] Based on initial $H_{(ad)}$.

[f] Based on final $H_{(ad)}$ on catalyst N.

[g] Based on final $H_{(ad)}$ on catalyst L.

[h] From Ref. 8.

air at elevated temperatures in a furnace. Conditions for each catalyst are noted in Table 1. For the 1.9% Pt/TiO_2 catalyst, it was found that a 10 hr purge with flowing He at 300 K followed by heating to 423 K before H_2 was substituted for He produced a much more highly dispersed catalyst (62 vs 13%), designated (He). An identical 10 hr purge in H_2 at 300 K prior to the pretreatment resulted in a more poorly dispersed sample, designated (H_2).

RESULTS

Initial chemisorption of H_2 and CO was measured on the fresh reduced samples and final uptakes were measured on the used samples after the kinetic studies. The standard pretreatment was also employed with the used samples. These gas uptakes are listed in Table 1 along with the XRD results on the used samples utilizing the Pt peak at $2\theta = 39.76°$. The Scherrer equation was used with the constant $K = 0.9$ and with Warren's correction for instrumental line broadening which was found to be equal to a 2θ value of 0.29. Two of the Pt/SiO_2 (C) catalysts were the identical samples used in a previous investigation (*6*).

Catalytic activities are listed in Table 2 on both a unit weight basis and as a turnover frequency (N_{CH_4} = molecules CH_4 s^{-1} Pt_s^{-1}). The choice of adsorption measurement to count Pt surface sites is not critical (the only effect is a variation in absolute values within a factor of approximately 2) and the same conclusions are always reached, namely, that Pt crystallite size has essentially no effect on N_{CH_4} and more than a 100-fold variation exists among the least active (Pt/SiO_2) and the most active (Pt/TiO_2) catalysts (*7*). For comparison, N_{CH_4} values based on both $H_{(ad)}$ and $CO_{(ad)}$ on the used catalyst sample are listed. The N_{CH_4} values based on the former may be preferred because one adsorbed H atom is typically associated with one surface Pt atom, Pt_s. Most CO conversions were well below 2%; however, conversions up to 16% with the Pt/TiO_2 catalysts did not induce any changes in kinetic parameters. The apparent activation energies were determined between 520 and 575 K.

Table 3 contains partial pressure dependences measured at 548 K along with *average* values for N_{CH_4} and E_a for the TiO_2-supported catalysts. The results for $Pt/\eta\text{-}Al_2O_3$ have been reported previously (*8*), and the excellent agreement between these parameters and those found in this study is apparent.

DISCUSSION

The influence of the support upon the catalytic behavior of a dispersed metal system has received considerable interest re-

TABLE 3

Kinetic Parameters for Methanation over Supported Platinum[a]

Catalyst	N_{CH_4} at 548.2 K[b] $\left(\frac{\text{molecules}}{s \cdot Pt_s}\right) \times 10^3$	A $\left(\frac{\text{molecules}}{s \cdot \text{site}\,(\text{atm})^{X+Y}}\right)$	E_a^b (kcal/mole)	X (exp)	Y (exp)	X (calc)	Y (calc)	y	n
$Pt/\eta\text{-}Al_2O_3$[b]	1.9	1.8×10^4	17.1	0.83 ± 0.03[c]	0.04 ± 0.01[c]	1.0	0.04	2	0.68
1.9% Pt/TiO_2 (LT)	11.1	5.8×10^5	18.9	0.45 ± 0.02	0.21 ± 0.03	0.5	0.22	1	0.61
1.9% Pt/TiO_2 (SMSI)	76 (19.5)[d]	1.0×10^7	20.2	0.50 ± 0.02	0.01 ± 0.01	0.5	0.01	1	0.50

[a] $N_{CH_4} = Ae^{E_a/RT}P_{H_2}{}^{X}P_{CO}{}^{Y}$.

[b] Average values from Table 2, column 3.

[c] From Ref. (*8*).

[d] Average value based on Pt_s for the (LT) sample.

cently, primarily because of the results found for titania-supported Group VIII metals (*9*). However metal–support effects on catalytic properties are not easy to prove, and all other explanations must be eliminated before support effects can be unambiguously invoked to explain variations in activity and selectivity. Platinum has been one metal which has clearly shown that its catalytic activity for CO hydrogenation can be altered by the choice of support (*2, 3, 6*), and this study provides further justification for this conclusion. Selectivity is not a consideration here because at low pressures and conversions Pt produces essentially methane, with only trace amounts of higher hydrocarbons.

An examination of Table 2 shows that a 100-fold variation in turnover frequency exists for Pt on different supports even if the Pt surface sites after the low-temperature pretreatment are used to determine N_{CH_4} values for the SMSI catalyst. These values (in parentheses in Table 2) for the Pt/TiO_2 (SMSI) catalyst should represent minimum values because an enhancement in dispersion by high-temperature reduction is not expected, yet TiO_2-supported Pt still represents the most active catalyst system reported to date for CO hydrogenation over Pt. Even on a g Pt basis, the Pt/TiO_2 catalysts are much more active, as can be seen by comparing catalysts A, J, N, and P, which have similar Pt loadings and dispersions. The lower activity of SiO_2-supported Pt compared to Al_2O_3-supported Pt has also been confirmed by TPR studies (*10*). It is important to note that the enhanced activity on titania is not dependent on dispersion and occurs *even after reduction at 473 K.* Additional reduction has little effect on activity per g catalyst. No significant bulk reduction of TiO_2 is expected at this temperature for the reduction times involved; however, it is exceedingly possible that hydrogen spillover can occur to provide some reduction of the TiO_2 in the immediate vicinity of the Pt crystallites.

A crystallite size effect cannot explain this variation in activity, and N_{CH_4} values are essentially constant as Pt particle size varies from 1.2 to 160 nm on Al_2O_3, from 1.9 to 10 nm on SiO_2, and from 2.2 to 19 nm on TiO_2, as determined by hydrogen chemisorption. The constant TOF values on a given support indicate no dependence on crystallite size or crystallite size distribution. The XRD results frequently did not give good agreement with the particle sizes calculated from the chemisorption measurements; however, they indicated large Pt crystallites on the poorly dispersed samples and could not detect the small crystallites on the well-dispersed samples. Despite any uncertainty about exact particle sizes in the sintered catalysts, average crystallite sizes vary over the range of principal interest (1–10 nm) regarding changes in structure. The nearly constant values of the apparent activation energy for the three "typical" Pt catalysts using Al_2O_3, SiO_2, and SiO_2–Al_2O_3 supports along with the near constant N_{CH_4} values for each family, i.e., $\sim 1.6 \times 10^{-3}$ s^{-1} for Pt/Al_2O_3 and $\sim 0.17 \times 10^{-3}$ s^{-1} for Pt/SiO_2, show that there are no mass or heat transfer effects in these data (*11*). As a consequence of this study, the possibility of a crystallite size effect previously proposed for Pt can be discounted (*6*). The activity of the Pt black sample employed in that study may have been affected by potassium (sodium) impurities, which can remain in Pt black prepared by potassium (sodium) borohydride reduction and can migrate to the surface during pretreatment in hydrogen (*7, 12*).

Although an effect attributable to the support appears to be the only explanation, the exact nature of this influence is difficult to understand, particularly since it appears to affect large Pt crystallites as well as small ones. The possibility of Si migration to the Pt surface can be considered as an explanation of the low activity of the SiO_2-supported Pt (*13*); however, the chemisorption properties of the Pt/SiO_2 catalysts do not appear unusual and the lower activity *per adsorption site still exists.*

The first paper in this series showed no correlation between activity and either of the two observable ir-active species, the linearly adsorbed species with a band near 2065 cm^{-1} or the bridged-bonded species with a band near 1820 cm^{-1} (*3*). However, the ir study showed that the TiO_2-supported catalysts, particularly the SMSI sample, exhibited two particularly different properties compared to the three "typical" Pt catalysts: hydrogen displaced a large fraction of adsorbed CO on the Pt/TiO_2 catalysts even at 300 K whereas it had essentially no effect on the ir bands of the other three catalysts, and under steady-state reaction conditions the SMSI Pt/TiO_2 catalyst had only a small amount of ir-active CO on the surface while the other catalysts retained strong band intensities.

As a consequence of these results and the different kinetic parameters measured in this study for methanation over Pt/TiO_2 catalysts (Table 3), reaction models for methanation over Pt, and noble metals in general, were re-examined. Although CO dissociation can occur readily over some metals, it does not do so on platinum, even at temperatures up to 575 K (*14*). Further evidence against significant CO dissociation was the fact that CO adsorption at 548 K on Catalyst P equilibrated rapidly, that it was less than that at 300 K, and that it provided an ir extinction coefficient identical to that at 300 K (*15*). Finally, no bands in the C–H stretching regions were observed indicating that any surface species with C–H bonds had very short life-times and/or existed at very low concentrations. As a consequence of these results, the rupture of the C–O bond was assumed to be the rate determining step (RDS) as in a previous model (*8*); however, because of the absence of high concentrations of $CO\text{–}H_x$ species and the high reactivity of the surface carbon once formed (*14*), a small modification is proposed to allow the formation of this surface carbon. The resulting sequence of elementary steps, shown below, assumes that a hydrogen-assisted CO bond rupture (Step 3), is the RDS:

$$H_{2(g)} \overset{K_H}{\longleftrightarrow} 2\,H_{(ad)} \tag{1}$$

$$CO_{(g)} \overset{K_{CO}}{\longleftrightarrow} CO_{(ad)} \tag{2}$$

$$CO_{(ad)} + yH_{(ad)} \xrightarrow{k_3} C_{(ad)} + H_yO_{(ad)} \tag{3}$$

$$C_{(ad)} + 4H_{(ad)} \overset{K_4}{\longleftrightarrow} CH_{4(g)} \tag{4}$$

$$H_yO_{(ad)} + (2 - y)H_{(ad)} \overset{K_5}{\longleftrightarrow} H_2O_{(g)} \tag{5}$$

All steps other than the RDS are assumed to be in quasi-equilibrium; however, steps after the RDS are kinetically unimportant (*16*). Because of the rapidity of steps (4) and (5), H_2O formation is expected to parallel CH_4 formation independently of y, the number of H atoms in the RDS. Assuming the surface concentration of hydrogen is low, the following rate expression can be derived from Langmuir–Hinshelwood kinetics (*17*):

$$r\left(\frac{\text{molecules } CH_4}{\text{s} \cdot \text{cm}^2\text{Pt}}\right) = N_{CH_4}\left(\frac{Pt_s}{cm^2}\right)$$
$$= k_3\theta_{CO}\theta_H{}^y = kP_{H_2}^{y/2}P_{CO}^{y(n-1)+n} \tag{6}$$

where $k = k_3(K_H)^{y/2}(K_{CO})^{y(n-1)+n}$ and N_{CH_4} and Pt_s are based on the final hydrogen adsorption.

Matching this derived equation to the power rate law shown in Table 3 allows determination of the integral values of y giving the best fit subject to the constraint that n, the slope of the Langmuir isotherm, lies between 0 and 1 (*17*). These calculated values are also listed in Table 3, and quite satisfactory agreement can be achieved between experimental and calculated X and Y values. A difference in the RDS on TiO_2-supported Pt is suggested by this approach. Using transition state theory, this derived equation can be analyzed in greater detail because K_H and K_{CO} are adsorption equilibrium constants and can be expressed as:

$$K_H = e^{\Delta S^\circ_H/R}e^{-\Delta H^\circ_H/RT} \tag{7}$$

and

$$K_{CO} = e^{\Delta S^\circ CO/R}e^{-\Delta H^\circ CO/RT} \tag{8}$$

where ΔS_i° and ΔH_i° represent standard entropies and enthalpies of adsorption. In addition, k_3 can be represented as

$$k_3 = \left(\frac{Z}{2}\frac{[S]^2}{L}\right)\left(\frac{kT}{h}\right) e^{S^+/R} e^{-E^+/RT} \qquad (9)$$

where Z is the coordination number of the surface Pt atom, [S] is the vacant site density, L is the Pt_s density (1.24×10^{15} cm^{-2}), k is the Boltzmann constant, h is the Planck constant, and S^+ and E^+ are the entropy of activation and activation energy, respectively, in the RDS. Assuming a bimolecular reaction on neighboring surface atoms, the first term in parentheses is the site pair density, designated as M. Substituting these terms into Eq. (6), it can be shown that:

$$E_a = E^+ + [y(n - 1) + n]\Delta H^\circ_{CO} + y/2\ \Delta H^\circ_H \qquad (10)$$

and

$$\ln A = \ln M + \ln\left(\frac{kT}{h}\right) + S^+/R + [y(n - 1) + n]\Delta S^\circ_{CO}/R + y/2\ \Delta S^\circ_H/R. \qquad (11)$$

Using the derived values for n and y, this allows the estimation of the true activation energy and the site pair density providing that meaningful values of enthalpy and entropy of adsorption can be found for H_2 and CO on Pt surfaces.

This exercise was undertaken for two reasons: (1) the higher activity of the Pt/TiO_2 cannot be attributed to a lower apparent activation energy (in fact it is higher), and (2) the ir study showed that only a very small fraction of the TiO_2-supported Pt surface was covered by adsorbed CO, yet this was the most active catalyst. Recent measurements conducted under UHV conditions indicate that initial ΔH°_i values for H_2 are near 16 kcal/mole and decrease to near 12 kcal/mole at saturation while for CO initial values are near 32 kcal/mole and final values on saturated surfaces can be near 20–22 kcal/mole (*18, 19*). Using the high values and the low values for each molecule, limits for E^+ can be established and these are shown in Table 4. Two conclusions can be drawn: E^+ for a given catalyst does not vary markedly with the choice of ΔH°_i values, and the true activation energy is lowered over Pt/TiO_2 regardless of the choice of ΔH°_i values.

It is clear that the activity enhancement is a consequence of a higher preexponential factor, as shown in Table 3. Now, Eq. (11) can be rearranged to give:

$$M = \frac{A}{(\nu)\ e^{S^+/R} e^{X\Delta S^\circ_H/R} e^{Y\Delta S^\circ_{CO}/R}} \qquad (12)$$

From this, an upper limit for M can be established by determining minimum values for $\nu = (kT/h)$ and S^+ and maximum absolute values for ΔS°_H and ΔS°_{CO}, which must be negative (*20, 21*). From the ΔH°_i values used, upper limits in Langmuir–Hinshelwood rate expressions can be estimated for ΔS°_H and ΔS°_{CO} (*20, 21*) and these values are listed in Table 4. A minimum value for the

TABLE 4

Parameters for H_2 and CO Adsorption and Reaction on Pt[a]

Catalyst	$-\Delta H^\circ_{CO}$ (kcal/mole)	$-\Delta H^\circ_H$ (kcal/mole)	$-\Delta S^\circ_{CO}$ (e.u.)	$-\Delta S^\circ_H$ (e.u.)	E^+ (kcal/mole)	M (cm$^{-2} \times 10^{-15}$)	Turnover frequency $\left(\frac{\text{molecules } CH_4}{s \cdot M}\right)$
Pt/Al_2O_3	32	16	57	35	34	0.23	0.01
	22	12	43	29	30	0.01	0.23
Pt/TiO_2 (LT)	32	16	57	35	33	0.11	0.11
	22	12	43	29	29	0.0069	1.9
Pt/TiO_2 (SMSI)	32	16	57	35	28	0.0087	10
	22	12	43	29	26	0.0021	46

[a] $\nu = 1.14 \times 10^{13}$ s^{-1}, $S^+ \approx 0$, $T = 548.2$ K, $P = 1$ atm, $H_2/CO = 3$.

frequency factor, ν, is 1.14×10^{13} s^{-1} at 548 K, and actual values may be much larger (*22–24*). Finally, from transition state theory S^+ can be related to partition functions in the following way assuming immobile adsorption (*25*):

for $y = 1$:

$$e^{S^+/R} = \frac{Q^+_{CO\text{-}H(a)}}{Q_{CO(a)}Q_{H(a)}} = \frac{q^+_{rot}q^+_{vib}}{q_{vib_{CO}}q_{vib_H}} \quad (13)$$

or

for $y = 2$:

$$e^{S^+/R} = \frac{Q^+_{CO\text{-}H_2}}{Q_{CO(a)}Q^2_{H(a)}} = \frac{q^+_{rot}q^+_{vib}}{q_{vib_{CO}}q^2_{vib_H}} \quad (14)$$

Both of these expressions will be near unity if no rotation of the activated complex occurs and somewhat larger if rotation is allowed; however, a lower limit near 1 is established, i.e., $S^+ \simeq 0$. Substituting the values from Table 4 and using the derived X and Y values, *maximum* values of M can be calculated for the range of ΔH°_{CO} and ΔH°_H expected on Pt surfaces. These are listed in Table 4 along with the turnover frequencies estimated per "active site", M.

This analysis, subject as it is to the choice of values used therein, nevertheless should provide a reasonable range of maximum active site densities on the different Pt surfaces, the bounds of which are determined by the heats of adsorption which actually exist on the working catalyst. The intent of this effort was not to prove the proposed rate equation, but to see if a theoretical approach was consistent with the ir study which indicated that only a small fraction of surface Pt atoms appeared to be active sites, and also to determine if gross differences existed among these catalysts. With this perspective in mind, it is worthwhile to note that the calculated fraction of Pt_s atoms constituting active sites ($2M/Pt_s$) on the SMSI catalyst is ca. 0.01, while ir spectra indicated a fractional coverage of CO also near 0.01 (*3, 15*). Even on the typical Pt/Al_2O_3 catalysts, M values are much smaller than the density of surface Pt atoms. Finally, if this picture is valid, it indicates reasonable turnover frequencies per active site that are two to three orders of magnitude higher on the Pt/TiO_2 (SMSI) catalyst. The assumption of lower values for ΔH°_{CO} and ΔH°_H, which is a possibility in view of the greatly suppressed chemisorption of CO and H_2 on the Pt/TiO_2, further decreases the estimated active site density, M (*7*). Perhaps the greatest uncertainty is the assumption of immobile adsorption of hydrogen; however, treating adsorbed hydrogen as a two-dimensional gas would produce sizable negative values for S^+ resulting in calculated values of M being increased by factors of 10^4, for example, and giving physically meaningless values far greater than 10^{15} cm^{-2}. It may be that the presence of adsorbed CO on the surface greatly hinders surface migration of $H_{(ad)}$ and therefore strengthens the assumption of immobile adsorption.

The *in situ* ir investigation, along with the chemisorption results, led to the conclusion that the most active Pt catalyst, TiO_2-supported Pt, had only a small fraction of the metal surface covered with adsorbed CO, implying that the number of active sites was only a small fraction of the total number of surface Pt atoms (*3*). Similar behavior was observed for Pd (*26*). The kinetic model discussed in this paper supports this conclusion. Apparently, adsorption sites are altered on these TiO_2-supported catalysts to allow hydrogen to compete more favorably with CO, as evidenced by H displacement of CO from the surface at 300 K (*3*). The higher activity can then be attributed, at least partially, to a much higher surface coverage of $H_{(ad)}$ under reaction conditions, as reflected in Eq. (3). Studies have shown that Pt on TiO_2 can form two-dimensional rafts after high-temperature reduction which could alter the structure (i.e., electronic and geometric properties) of the Pt crystallites (*27*). Recent studies on Pt stepped surfaces have identified low concentrations of sites which provided higher

CO binding energies and much lower CO stretching frequencies of 1410 and 1560 cm^{-1} (*28*), and such a CO species would be expected to experience bond rupture more easily. This change in particle morphology may increase the fraction of these surface sites. Were these to be the active sites, the lack of correlation between activity and the linear- and bridged-bonded species would be explained (*3*). Recent UHV studies of metals dispersed on TiO_2 have indicated that some charge transfer from the support to the metal can occur under reduction conditions resulting in a negative charge on the metal crystallites (*29–33*). However, these results are not always achieved (*34*). Although filling of the d-band could explain the greatly reduced chemisorption capacity in the SMSI state, it does not provide a ready explanation of the enhanced activity. An alternative explanation, namely, that special sites are created at the Pt–titania interface, cannot be discounted; however, this model would be expected to be dependent upon dispersion, yet 19-nm particles show the same activity enhancement as 2-nm particles. Only if a homogeneous migration of TiO_x occurred onto the surface of the Pt crystallites would this model be consistent with the results in this study. This migration does not seem likely at 473 K and, in addition, it might be expected to alter the chemisorption properties, but these appear normal at 473 K. At this time, therefore, we conclude that the higher activity of Pt on TiO_2 is a consequence of changes in structure of the Pt particles, created by a strong interaction with a partially reduced titania surface, which alters the intrinsic catalytic properties of the Pt atoms. The activity enhancement by reduction at a low temperature of 473 K strongly implies that the SMSI is localized and that bulk electronic properties are not directly involved.

CONCLUSIONS

Methanation TOF values have been found to be essentially constant on Pt crystallites ranging from 1.2 to over 100 nm as indicated by H_2 chemisorption, CO chemisorption, and XRD measurements. Although independent of Pt crystallite size on a given support, the support itself has a major effect on specific activity, and TOF values on titania-supported Pt are 100-fold higher than on silica-supported Pt and 10-fold higher than on alumina-supported or SiO_2–Al_2O_3-supported Pt. The model proposed for methanation assuming a hydrogen-assisted, CO bond rupture rate determining step is consistent with the kinetic data, previous infrared results (*3*), and transition state theory. It implies that the higher activity on Pt/TiO_2 catalysts may be a consequence of higher surface concentrations of hydrogen under reaction conditions. The previous infrared study indicated that only a small fraction of the TiO_2-supported Pt surface (1–2%) is covered by CO during reaction, in contradistinction to typical Pt catalysts, and transition state theory analysis supported this conclusion assuming immobile hydrogen adsorption. Therefore, one conclusion indicated by this study is that only a small fraction of the surface Pt atoms constitute "active sites."

The exact nature of this activity enhancement is not known; however, it is attributed to a change in Pt structure due to SMSI behavior. Very recent studies strongly support the possibility that electron transfer to the Pt occurs as a consequence of partial reduction of the titania (*29–33*). The short reduction time at 473 K is not expected to cause significant bulk reduction of TiO_2; therefore, we interpret the higher activity after this pretreatment to be strongly suggestive of a more localized interaction at the metal–support interface. The formation of Pt rafts on the titania surface, as found by others (*27*), would facilitate this interaction. Despite this additional insight, however, the precise nature of the surface chemistry involved in creating this enhanced catalytic activity is not known, and further research in this intriguing area is required.

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