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SMSI Effects on CO Adsorption and Hydrogenation on Pt Catalysts

I. Infrared Spectra of Adsorbed CO prior to and during Reaction Conditions

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Infrared spectroscopy has been employed to characterize adsorbed CO species under steady-state reaction conditions in the presence of H_2 and also under equilibrium adsorption conditions in the presence of He. During reaction, kinetic data were obtained simultaneously with ir spectra using a special ir reactor cell. Turnover frequencies on Pt were found to vary more than 100-fold as the support material varied, and the activity ranking of these catalysts was: Pt/TiO_2 (SMSI) $>$ Pt/TiO_2 (LT) $\geq$ $Pt/\eta\text{-}Al_2O_3 \simeq Pt/SiO_2\text{–}Al_2O_3 > Pt/SiO_2$. Two principal ir bands were observed on Pt—a high-frequency band between 2050 and 2080 cm^{-1} and a low-frequency band between 1780 and 1860 cm^{-1}. Except for TiO_2-supported Pt, very similar behavior was observed, i.e., intense ir bands occurred which were nearly insensitive to temperature and the presence of H_2, and these catalysts exhibited strong bands under reaction conditions. In contrast, the Pt/TiO_2 (SMSI) catalyst showed almost no ir-detectable CO during reaction and, even more surprising, CO band intensities were also markedly reduced at 300 K by the presence of H_2. No obvious correlation was found between detectable CO species and specific activity; however, this study strongly infers that only a very small fraction of surface Pt atoms constitute active sites, and the higher activity occurring on the SMSI Pt/TiO_2 catalyst is attributed to a weakened CO–metal bond resulting in more competitive H_2 chemisorption and higher surface concentrations of hydrogen under reaction conditions.

INTRODUCTION

Many examples exist which show that the type of support utilized in a catalyst has little or no effect upon the adsorption and catalytic properties of the dispersed metal. However, Tauster *et al.* found that certain supports can markedly alter the adsorption behavior of hydrogen and carbon monoxide on Group VIII metals (*1*, *2*), and the manifestation of this behavior has been termed SMSI (strong metal–support interaction). Titania is a support which can produce this behavior, and platinum is a metal which exhibits reduced monolayer coverages when dispersed on TiO_2; regardless, it possesses very high activity for the methanation reaction (*3*). In addition, a previous study had indicated that methanation activity over Pt and Pd could be altered by the support (*4*).

The chemisorption behavior of CO and hydrogen is quite well understood on normal Pt surfaces, and numerous infrared studies exist which have characterized CO adsorbed on Pt films and single crystals and on Pt crystallites dispersed on silica and alumina. Infrared spectroscopy has proven to be a powerful tool to characterize surface species of CO, and it can be adapted for *in situ* studies at high pressures which allow the characterization of adsorbed species on the metal surface under well-defined reaction conditions. Such studies had not been conducted on the CO hydrogenation reaction over Pt catalysts although Ru and Pd have recently been examined by this technique (*5–9*).

An ir reactor cell was designed to allow both pretreatment and steady-state reaction

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conditions over a temperature range of 300 to 723 K. It was operated as a fixed-bed, single-pass, differential reactor and provided kinetic data simultaneously with ir spectra obtained under reaction conditions. It was of particular interest to characterize the state of CO adsorption on the TiO_2-supported Pt catalysts before and after the SMSI state had been induced, and to compare these spectra with those obtained under identical conditions for "typical" Pt catalysts; i.e., Pt dispersed on silica, alumina, and silica–alumina. It was of particular interest to determine if any correlation existed between the 100-fold variation in turnover frequency and the different ir-active species of adsorbed CO.

EXPERIMENTAL

All platinum catalysts prepared in this laboratory used $H_2PtCl_6 \cdot 6H_2O$ or $(NH_3)_4Pt(NO_3)_2$ obtained from the Ventron Corporation, and the support materials, preparative techniques, and gases used have been described previously (*9–11*). All catalysts consisted of a nominal 2 wt% Pt on 40/80-mesh powders of Al_2O_3, SiO_2, SiO_2–Al_2O_3 (abbreviated S–A), and TiO_2, with two different Pt dispersions prepared on η-Al_2O_3. Actual weight loadings are reported for the unreduced catalysts after this drying procedure and were determined by neutron activation analysis by comparison to a standard solution of $H_2PtCl_6 \cdot 6H_2O$ dissolved in deionized, distilled water. Hydrogen and CO adsorption measurements were performed in a conventional, mercury-free, glass vacuum system capable of an ultimate vacuum of 4×10^{-7} Torr (5.3×10^{-5} Pa) which is described elsewhere (*11*). The infrared reactor cell designed and constructed for this study and the ir reactor system incorporating a Perkin–Elmer 580 spectrophotometer and a P-E Sigma 3 gas chromatograph have also been described elsewhere (*9*, *12*).

All fresh, unreduced catalysts, except for the Pt/TiO_2 samples, were given the same pretreatment which consisted of: heating to 393 K in 50 cm^3 H_2 min^{-1} and holding 30 min at this temperature, heating to 533 K and holding for 30 min, then heating to 723 K and holding for 1 hr. At this point, if chemisorption experiments were to be conducted, the sample was cooled to 698 K, H_2 flow was terminated, and the sample was evacuated for 30 min at 698 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 from the reactor prior to chemisorption measurements. If kinetic studies were desired, the sample was cooled under flowing H_2 to the desired temperature before CO was introduced. Two Pt/TiO_2 catalysts were prepared—one, designated LT, which was reduced at low temperature (473 K) and did not show SMSI adsorption behavior, and one reduced at 773 K which did and is designated SMSI. The two pretreatment procedures were those described by Tauster *et al.* (*1*).

Irreversible H_2 adsorption on Pt at 300 K was measured by extrapolating the linear isotherm to zero pressure (*14*, *15*). Chemisorption of H_2 on the pure metal was measured with the difference between the two isotherms at 100 Torr (13.3 kPa) chosen to represent irreversible CO adsorption (*16*).

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 the low-temperature reduced 1.9% Pt/TiO_2 wafer, which was pressed from the fresh unreduced catalyst, flushed with He overnight, then reduced *in situ* at 473 K following the procedure of Tauster *et al.* (*1*) before the ir spectra were obtained. Following this ir study, this wafer was further reduced at 723 K to produce the SMSI state for additional study. All other wafers in the ir cell, including a second Pt/TiO_2 (SMSI) wafer, were reduced in flowing H_2 at 548 K for 1 hr because of the previous high-temperature reduction step in the chemisorption unit. All ir spectra were recorded with either a CO/He or a CO/H_2 mixture flowing through the cells.

RESULTS

The amounts of hydrogen and CO chemisorbed on both new and used samples of the six catalysts in this study are listed elsewhere (*17*), and the letter designations used are consistent with the second paper in this series (*17*). Pt dispersions (fractions exposed) are probably best represented by the H/Pt ratios given; however, H_2 and CO uptakes follow the same trend among these catalysts. The H/Pt and CO/Pt ratios on the used samples are listed in Table 1. Results from kinetic measurements made in the ir reactor cell are also listed in Table 1, where they are compared to data obtained in the microreactor and to previous work. Both turnover frequencies (TOF) (molecules $CH_4 \cdot Pt_s^{-1} \cdot s^{-1}$) and activation energies for the methanation reaction were determined, with TOF values based upon Pt surface atoms, Pt_s, using the H/Pt ratios on the used samples. Only trace amounts of hydrocarbons other than methane were detected. Conversions of CO were below 1% in the ir reactor cell and less than 5% in the microreactor system.

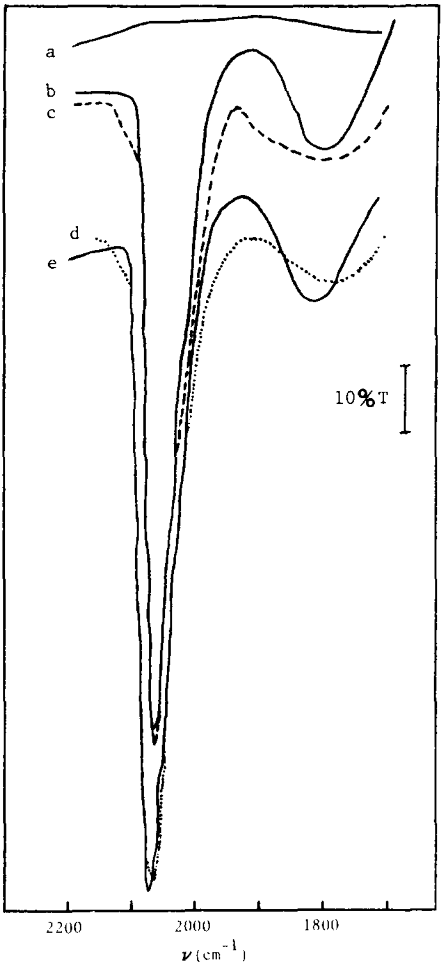

FIG. 1. Infrared spectra of CO adsorbed on 1.5% Pt/SiO_2-Al_2O_3 (P_{CO} = 185 Torr, He/CO or H_2/CO = 3); (a) baseline in He, (b) 3000 K in H_2, (c) 548 K in H_2, (d) 548 K in He, (e) 300 K in He.

Infrared spectra of adsorbed CO at different temperatures on these Pt catalysts were obtained and are shown in detail elsewhere (*3, 18, 19*); however, the band maxima under different conditions are listed in Table 2. The spectra for CO on the Pt/Al_2O_3 and Pt/SiO_2 catalysts were in excellent agreement with previous studies (*20–36*), because the Pt/Al_2O_3 wafers gave two CO bands—a high-frequency (HF) band near 2060 cm^{-1} and a low-frequency (LF) band around 1830 cm^{-1}—while the Pt/SiO_2 wafer produced only one HF band also near 2060 cm^{-1}. CO adsorbed on S–A-supported Pt and TiO_2-supported Pt had not been studied prior to this investigation, and these spectra are shown in Figs. 1 and 2. The CO pressure was usually 0.25 atm (25 kPa); however, spectra from the 2.1% Pt/Al_2O_3 catalyst were nearly unchanged as pressures varied from 50 to 380 Torr indicating, as expected, that saturated CO coverage occurs at these pressures. For all catalysts at temperatures from 300 to 573 K, in the presence of either He or H_2, the HF band maximum was 2065 ± 15 cm^{-1} while the LF band maximum varied between 1780 and 1860 cm^{-1}. Finally, spectra taken under steady-state reaction conditions are shown in Fig. 3.

With the Pt/Al_2O_3 and Pt/SiO_2 catalysts, spectra obtained at all temperatures with H_2/CO mixtures were very similar to those obtained with He/CO mixtures, similar to

TABLE 1

Specific Activities and Activation Energies of Pt Catalysts[a]

Catalyst	$H_{(a)}/Pt$	$CO_{(a)}/Pt$	Infrared reactor cell		Microreactor		Previous work	
			N_{CH_4} ($s^{-1} \times 10^3$)	E_a (kcal/mole)	N_{CH_4} ($s^{-1} \times 10^3$)	E_a (kcal/mole)	N_{CH_4} ($s^{-1} \times 10^3$)	E_a (kcal/mole)
(A) 2.1% Pt/η-Al_2O_3 (C-i)	0.72	0.35	1.1	17.8 ± 1.0	1.7	16.2 ± 0.7	1.7[b]	16.7 ± 0.8[b]
(B) 2.0% Pt/η-Al_2O_3 (A-e)	—	—	1.6[c]	18.0 ± 0.9	1.6[c]	16.5 ± 1.0	—	—
(G) 1.5% Pt/SiO_2 (C-e)	0.11	0.10	Not detectable	—	0.19	16.8 ± 1.1	1.2[b]	—
(K) 1.5% Pt/SiO_2–Al_2O_3 (C-e)	0.27	0.24	2.6	16.1 ± 1.2	1.4	16.4 ± 1.0	—	—
(N) 1.9% Pt/TiO_2 (LT)	0.51	0.29	2.4	20.0 ± 0.8	6.7	17.2 ± 0.7	—	—
					8.4	19.9 ± 1.5	—	—
(O) 1.9% Pt/TiO_2 (SMSI)	0.029	0.015	8.4[d]	19.7 ± 0.9	54	17.7 ± 0.8	130[e]	16.8 ± 3.9
					16.1[d]			

Note. $P = 103$ kPa, $T = 548$ K, $H_2/CO = 3$.

[a] Based on $H_{(ad)}$ on used sample.

[b] Ref. (*13*).

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

[d] Based on H/Pt = 0.10 for used Pt/TiO_2 (473 K) (Sample L, Ref. (*17*)).

[e] Ref. (*51*).

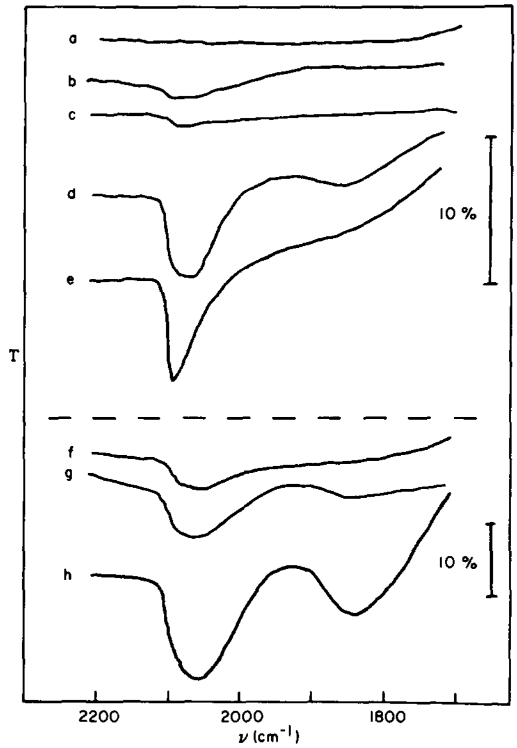

FIG. 2. Infrared spectra of CO adsorbed on 1.9% Pt/ TiO_2 (P_{CO} = 185 Torr, He/CO or H_2CO = 3): Catalyst O (SMSI)—(a) baseline in He at 300 K, (b) 300 K in H_2, (c) 548 K in H_2, (d) 300 K in He, (e) 548 K in He; Catalyst N (LT)—(f) 473 K in H_2, (g) 300 K in H_2, (h) 300 K in He. Note change in transmittance scale.

the behavior indicated in Fig. 1, and the spectra in Fig. 3 are very similar to those attained at 300 K, except that the LF band on Pt/Al_2O_3 is slightly sharper and more intense and the highly dispersed Pt/Al_2O_3 wafer exhibited a small 2120-cm^{-1} band in CO/He mixtures which was attributed to subcarbonyl formation on the small crystallites (*36, 37*). The admittance of H_2 at 300 K resulted in no change or only a small downward shift of 5–10 cm^{-1} in the HF and LF bands. No ir bands in the region 2800–3200 cm^{-1}, which could be attributed to hydrocarbon intermediates, were observed on any catalyst under reaction conditions.

DISCUSSION

Eischens and co-workers were the first to direct ir techniques toward supported catalysts, and their early work on CO chemisorbed on SiO_2-supported Pt showed only one sharp band at 2070 cm^{-1} (*20*). However, in a later study, Eischens and Pliskin clearly showed that two bands, at 2040 and 1810 cm^{-1}, occurred for CO adsorbed on Al_2O_3-supported Pt (*21*). On the basis of metal carbonyl spectra, they assigned the high-frequency (HF) band above 2000 cm^{-1} to a linearly adsorbed CO species while the low-frequency (LF) band was assigned to bridged-bonded CO. It is typically assumed that a stronger carbon–metal interaction produces a weaker C–O bond, thereby causing a decrease in frequency, and a back-bonding model proposed by Blyholder has routinely been used to explain these frequency shifts (*22*).

All subsequent studies have been very consistent with these initial investigations

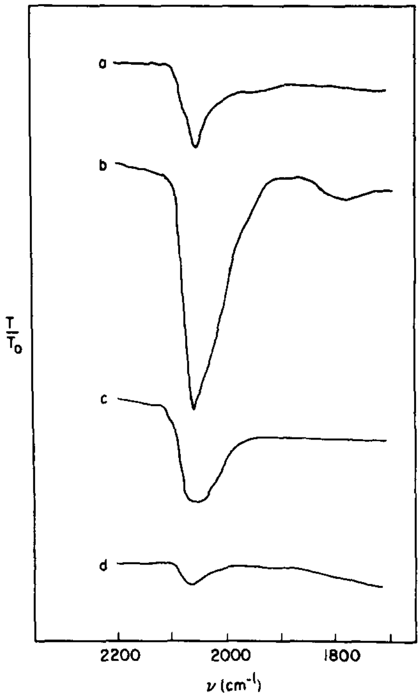

FIG. 3. Infrared spectra of CO adsorbed on Pt catalysts under reaction conditions (T = 548 K, H_2/CO = 3, P_{CO} = 185 (Torr)—(a) 1.5% Pt/SiO_2 (0.66), (b) 2.1% Pt/Al_2O_3 (0.11), (c) 1.9% Pt/TiO_2 (LT) (0.72), (d) 1.9% Pt/TiO_2 (SMSI) (0.98). The number in parentheses represents T/T_0 at the band minimum.

TABLE 2

Band Maxima for Adsorbed CO under Different Experimental Conditions

Catalyst		Temp. (K)	HF (cm^{-1})	LF (cm^{-1})
(A) 2.1% Pt/Al_2O_3				
		300	2120, 2070	1825
	He/CO = 3	548	2060	1805
		300	2065	1820
	$H_2/CO = 3$	548	2055	1790
(B) 2.0% Pt/Al_2O_3				
		300	2065	1845
	He/CO = 3	548	2060	1830
		300	2060	1840
	$H_2/CO = 3$	548	2055	1820
1.5% Pt/SiO_2				
		300	2070	—
	He/CO = 3	548	2060	—
		300	2065	—
	H_2/CO	548	2055	—
1.5% $Pt/SiO_2–Al_2O_3$				
		300	2065	1800
	He/CO = 3	548	2065	1780
		300	2065	1800
	$H_2/CO = 3$	548	2065	1780
1.9% Pt/TiO_2 (LT)				
(H/Pt = 0.62)		300	2050	1830
	He/CO = 3	473	2050	1940(s), 1840
		300	2050	1830
	$H_2/CO = 3$	548	2050	—
1.9% Pt/TiO_2 (SMSI)				
		300	2070	1860
	He/CO = 3	548	2080	—
		300	2080	—
	$H_2/CO = 3$	548	2080	—

Note. (P_{CO} = 183 Torr.)
(s) = shoulder.

in that all Pt/SiO_2 samples have produced only a single strong HF band, and all Pt/Al_2O_3 catalysts but one have exhibited both HF and LF bands (*23–29*). In addition, on all catalysts over a wide range of CO pressure and Pt particle sizes the HF band occurs between 2040 and 2075 cm^{-1} and the LF band lies between 1800 and 1865 cm^{-1}. Spectra obtained on unsupported Pt sometimes show both bands and sometimes only the HF band, but the positions of band maxima are very similar for all Pt surfaces (*30–35*). These data have been tabulated elsewhere (*18*). The fact that the HF band frequencies for these catalysts are typically at the high end of this range is consistent with previous studies which have shown that a band shift to higher frequencies occurs as CO coverage increases (*20, 32, 35*). This is attributed primarily to dipole–dipole interactions among CO molecules (*32, 35, 38*).

The original assignment of the HF band to linearly adsorbed CO and the LF band to bridged-bonded CO was based on metal carbonyl spectra (*20, 21*); however, it has been clearly proven by recent studies (*39–42*). Ibach and co-workers used electron energy loss spectroscopy (EELS) accompanied by low-energy electron diffraction (LEED) to study CO adsorption on Pt (111) single crystals, and concluded that on clean surfaces linear-bonded CO species appear first, and bridged CO is not present until coverages above $\theta = 0.3$ are attained (*39, 40*). Previous experimental and theoretical similarities between CO adsorption on different Group VIII transition metals seemed to favor the picture that more highly coordinated CO (e.g., the bridged structure) would have a higher binding energy on all Group VIII metals. On the basis of these findings by Ibach and co-workers, this picture needs revision, at least for Pt. One result found in this study was in full agreement with those found in previous ir spectra of CO on Pt surfaces; i.e., the band intensity is smaller for bridged-bonded CO species. The study by Norton and co-workers of CO on Pt (111) single crystals gave results in good agreement with those of Ibach and co-workers and showed that bridged-bonded CO had a lower heat of adsorption than linearly adsorbed CO (*42*).

Studies of the coadsorption of H_2 and CO on Pt have generally found that no major change occurred in the ir spectra of adsorbed CO. Eischens reported that the HF band on SiO_2-supported Pt decreased 5–10 cm^{-1} upon the addition of H_2 (*43*), whereas Palozov *et al.* (*25*) and Basset *et al.* (*27*) found no frequency shift in the HF band on Al_2O_3-supported Pt. A 20-cm^{-1} upward shift in the LF band on Pt/Al_2O_3 was produced by hydrogen, but the band was restored to its original position by evacuating the hydrogen (*25*).

The ir spectra of CO adsorbed on Pt/SiO_2, Pt/Al_2O_3, and Pt/S–A obtained in this investigation are extremely consistent with those from earlier studies. At 300 K both HF and LF band maxima fell within previously reported ranges, the HF band was always more intense than the LF band, and the Pt/SiO_2 catalyst exhibited no LF band. All three of these catalysts using "typical" supports produced nearly identical behavior regarding CO adsorption and interaction with hydrogen. First, CO spectra obtained in the presence of H_2 at all temperatures were nearly identical to those measured in helium. Second, in either the presence or absence of H_2, heating from 300 to 548 K produced a 5- to 15-cm^{-1} downshift in the HF band and a 15- to 35-cm^{-1} downshift in the LF band. Third, the intensities and bandwidths of the HF CO species were essentially constant under all conditions, while the LF bands showed some decrease in intensity and some broadening. Spectra for CO adsorbed on Pt/S–A, which have not been reported prior to this study, were particularly intense and narrow, as shown in Fig. 1. However, these spectra along with Table 2 nicely demonstrate the characteristics mentioned above, i.e., the more intense HF band, the insensitivity of the HF band to hydrogen, and the lack of dependence of the HF band on temperature.

The negligible influence of hydrogen on these spectra is most reasonably explained by inhibited H_2 chemisorption in the presence of CO. The higher heat of adsorption for CO on Pt (22–34 kcal/mole) compared to H_2 (15–20 kcal/mole) (*44*) and the partial pressure dependencies for methanation support this hypothesis, as both predict a surface nearly saturated with CO with only very low coverage of hydrogen. The small frequency downshifts that are observed could be due either to electron transfer from adsorbed H to the Pt as proposed by Eischens (*43*), thereby increasing back-donation to the antibonding π^* orbital of CO, or to a small reduction in dipole–dipole interactions between CO molecules because of adsorbed hydrogen. Regardless, the effect of hydrogen is small on these Pt surfaces.

In contrast, the TiO_2-supported catalysts, especially the SMSI catalyst, exhibited markedly different behavior compared to the "typical" Pt catalysts, as shown in Fig. 2. The 1.9% Pt/TiO_2 (LT) sample (Catalyst N) gave both HF and LF bands, but the admission of hydrogen produced a noticeable decrease in band intensity, especially in the LF band, yet the positions of the band maxima were unaffected. Also, at higher temperatures the intensity of the LF band was significantly decreased. Finally, a determination of extinction coefficients and integrated absorption intensities has shown noticeably higher values for CO adsorbed on the TiO_2-supported catalysts compared to CO on the catalysts using typical supports (*19*). These differences were even more apparent in the (SMSI) Pt/TiO_2 sample (Catalyst O). As might be expected from the lower CO chemisorption values, ir band intensities were noticeably lower, as indicated by the expanded scale in Fig. 2. The most striking differences were the pronounced decrease in intensity upon the introduction of hydrogen into the system, which occurred even at 300 K, and the near absence of ir-detectable CO under steady-state reaction conditions. The HF band maximum was essentially unaffected by the presence of hydrogen. The introduction of hydrogen had either no affect on band maxima or it produced a small upshift in peak position.

CO adsorption on typical Pt catalysts is very strong, and intense CO bands remain after long evacuation periods at 300 K. However, desorption experiments on the Pt/TiO_2 catalysts showed all the ir-active CO could be removed in less than 1.5 hr from the Pt/TiO_2 (SMSI) catalyst at 300 K. This behavior strongly infers that CO adsorption is much weaker on this catalyst, a conclusion that is consistent with the marked reduction in intensity observed when hydrogen competes for adsorption sites on this catalyst. CO adsorbed on Catalyst N appeared to be more strongly adsorbed, and 1.5 hr at 437 K was required to remove the ir bands. This decrease in surface coverage on TiO_2-supported Pt results in an increase in both extinction coefficients and integrated absorbances for the HF CO species compared to the values determined for typical Pt catalysts (*19*). This is consistent with previous studies which have shown that such values remain constant at low surface coverages, but decrease as saturation is approached (*35*). In addition, this behavior argues against CO dissociation because dissociative adsorption would produce lower integrated absorbances.

The behavior of CO adsorption on the SMSI Pt/TiO_2 catalyst is attributed to reduced monolayer coverages of CO on the Pt surface, due, at least partially, to a weaker CO–Pt surface bond. The reduced CO uptakes measured in this study are consistent with those of Baker *et al.*, who showed that reduced CO uptakes on Pt in the SMSI state cannot be attributed to sintering (*45*). In addition, increasing the temperature to 548 K resulted in a further decrease in CO adsorption on Catalyst O, which shows that activated adsorption cannot explain the low uptakes at 300 K (*19*). Finally, a decrease in the heat of adsorption of CO would facilitate its displacement by hydrogen. Methanation rates at 300 K are far too low to explain the decrease in band intensity by reaction of hydrogen with CO (*46*), and no evidence exists in the literature to indicate that adsorbed hydrogen and CO interact on Pt at 300 K to produce ir-inactive species (*47, 48*).

As shown in Table 1, methanation TOF values are very dependent upon the support used and vary over two orders of magnitude, with the Pt/TiO_2 (SMSI) catalysts representing the most active Pt catalysts reported to date, while Pt/SiO_2 catalysts are the least active. This trend is identical to that for Pd (*49*), and the lower methanation activity obtained using silica, compared to alumina, has been observed by others (*50*). All catalysts except the most active SMSI catalyst exhibited strong HF bands, and these bands are especially intense and essentially independent of temperature and H_2 pressure on Pt/Al_2O_3, Pt/SiO_2, and Pt/S–A. Catalysts A, B, and K have detectable LF bands during reaction, whereas Catalysts G, N, and O do not. The lack of correlation between activity and these ir-detectable CO species and the observation that the most active methanation catalyst has the lowest surface concentration of CO have led us to conclude that neither the HF nor the LF CO species is directly involved in a rate-determining step in the methanation reaction. This proposition leads to the conclusion that the concentration of "active sites" on the SMSI Pt surface is quite low, based on CO surface coverages under reaction conditions calculated using extinction coefficients for both linear and bridged CO (*19*), and only a very small fraction (1–2%, at most) of the surface Pt atoms constitute active sites for this reaction. A similar conclusion has been reached for Pd catalysts (*49*). Such active sites, which can consist of more than one atom, may be Pt atoms which can provide particularly high coordination with CO, such as step sites or kink sites. Hopster and Ibach examined the stepped 6(111) × (111) Pt surface and found low concentrations of such sites, which gave higher CO binding energies and CO stretching frequencies of 1410 and 1560 cm^{-1} (*41*). Such low frequencies infer a greatly weakened C–O bond, which would lead to a higher probability of bond rupture on these surface sites. This bond rupture is very likely the rate-determining step on metals like Pt and Pd, which do not dissociate CO readily (*17*, *49*). Were this to be the case, the large surface concentrations of CO present under reaction conditions would have essentially no direct effect on reaction rates and, in fact, these species of CO actually inhibit methanation by their preferential adsorption over hydrogen, thereby blocking sites and decreasing surface concentrations of hydrogen. The H_2 partial pressure dependencies for methanation over Pt, which range between $\frac{1}{2}$ and 1, are consistent with this supposition and, in addition, the rate enhancement on TiO_2-supported Pt can be explained by this model, which is discussed in the second paper of this series (*17*).

SUMMARY

Infrared spectroscopy has been employed to characterize adsorbed CO species under steady-state conditions in the presence of He or H_2. Under steady-state reaction conditions, ir spectra and kinetic data were obtained simultaneously using a new design for a combined ir reactor cell. Turnover frequencies on Pt were found to vary more than 100-fold as the support material varied, and the activity ranking of these catalysts was: Pt/TiO_2 (SMSI) > Pt/TiO_2 (LT) ≥ $Pt/\eta\text{-}Al_2O_3 \simeq Pt/SiO_2\text{–}Al_2O_3$ > Pt/SiO_2. Two principal ir bands were observed on Pt—a high-frequency band between 2050 and 2080 cm^{-1} and a low-frequency band between 1780 and 1860 cm^{-1}. Except for TiO_2-supported Pt, very similar behavior was observed—intense ir bands occurred which were nearly insensitive to temperature and the presence of H_2 and these catalysts exhibited strong HF bands under reaction conditions. In contrast, the Pt/TiO_2 (SMSI) catalyst showed almost no ir-detectable CO during reaction and, even more surprising, CO band intensities were markedly reduced at 300 K by the presence of H_2. This represented one of the most unusual findings of this study. No obvious correlation was found between detectable CO species and specific activity; however, this study strongly infers that only a very small fraction of surface Pt atoms constitute active sites, and the higher activity occurring on the SMSI Pt/TiO_2 catalyst is attributed to a weakened CO–metal bond resulting in more competitive H_2 chemisorption and higher surface concentrations of hydrogen under reaction conditions. It is proposed that the active sites occur at step and kink sites which provide higher CO coordination and extremely low C–O stretch frequencies.

ACKNOWLEDGMENTS

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