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Direct Measurements of Heats of Adsorption on Platinum Catalysts

II. CO on Pt Dispersed on SiO_2, Al_2O_3, SiO_2-Al_2O_3, and TiO_2

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Integral, isothermal heats of adsorption of CO on Pt dispersed on SiO_2, η-Al_2O_3, SiO_2-Al_2O_3, and TiO_2 have been measured using a uniquely modified differential scanning calorimeter integrated into a gas handling system. The Pt catalysts which had "normal" adsorption behavior exhibited a range of $\Delta H_{(ad)}$ values at 300 K between 21 and 32 kcal/mole, with the more poorly dispersed Pt/SiO_2 catalysts having the highest values and the very highly dispersed Pt/TiO_2, following a low-temperature reduction at 473 K, having the lowest values. A consistent trend occurred under "normal" adsorption conditions, independent of support, that indicated the presence of a crystallite size effect, with weaker CO–Pt bonding occurring on small crystallites. Only the Pt/TiO_2 samples after a high-temperature reduction, which showed the decreased chemisorption capacity associated with the strong metal–support interaction state, exhibited a pronounced support effect which reduced heats of adsorption at 300 K after repeated high-temperature reduction cycling to values as low as 10 kcal/mole. All $\Delta H_{(ad)}$ values were lower at 215 K, and the range between 15 and 20 kcal/mole on the "normal" catalysts indicated the filling of lower-energy states. The logarithm of the CH_4 turnover frequency correlated almost linearly with the CO heat of adsorption over a 1000-fold variation in activity; however, this enhancement in specific activity cannot be easily explained by considering *only* a decrease in CO $\Delta H_{(ad)}$ values.

INTRODUCTION

Carbon monoxide adsorption on Pt has been a frequently studied system and CO heats of adsorption on films, foils, and single crystals have been calculated based on experiments involving thermal desorption and adsorption isosteres. The direct calorimetric measurement of this property has been reported only in the early study by Brennan and Hayes, which was conducted before the routine use of ultrahigh vacuum (UHV) systems (*1*). No $\Delta H_{(ad)}$ values have been measured on supported Pt using calorimetric techniques, and the only two $\Delta H_{(ad)}$ values on supported Pt have been estimated from infrared data (*2*) and calculated from temperature-programmed desorption (TPD) experiments (*3*).

The need for CO heats of adsorption on supported Pt was perceived not only because of the limited studies to date, but also because recent investigations have indicated that the support can have a significant effect upon the adsorption behavior of CO on noble metals such as Pt. The papers by Tauster and co-workers were the first to demonstrate how TiO_2 and certain other oxide supports can markedly decrease adsorption capacity after a high-temperature reduction (HTR) that does not sinter the metal (*4, 5*). In addition, specific activity, in the form of a turnover frequency (TOF) (molecule CH_4/s/surface site), for methanation from CO and H_2 over the Group VIII metals has been found to correlate with the CO heat of adsorption (*6*), and it was of interest to see if the wide range of TOF values on Pt alone (*7*) were also correlated with surface bond strengths. This paper presents our initial calorimetric study of CO adsorption on Pt dispersed on SiO_2, η-Al_2O_3, SiO_2-Al_2O_3, and TiO_2 using a modified differential scanning calorimeter. This technique, from which integral, isothermal $\Delta H_{(ad)}$ values were obtained, avoids the

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complications presented by diffusion and readsorption processes when TPD methods are used with supported metals. In addition, this calorimeter coupled with our gas handling system provides a rapid method for obtaining reproducible results for many catalyst samples.

EXPERIMENTAL

The preparation of the catalysts—2.1% Pt/SiO_2, 2.1% $Pt/\eta\text{-}Al_2O_3$, 1.5% $Pt/SiO_2\text{-}Al_2O_3$ (1.5% Pt/S-A), 1.5% Pt/TiO_2, and 2.0% Pt/TiO_2—has been described in earlier papers (*7–9*). All catalysts were prepared from a 80/40 mesh powder and pretreated without further sieving.

Chemisorption measurements were conducted in either a glass high-vacuum system capable of vacuum near 4×10^{-7} Torr (1 Torr = 133 Pa) or a stainless-steel system providing a vacuum below 10^{-8} Torr. Pressures in either system were measured using a Texas Instruments Precision Gauge. More detailed descriptions of the systems and gas purification have been given elsewhere (*8, 10*).

The typical catalysts involving SiO_2, $\eta\text{-}Al_2O_3$, and S-A were given pretreatment A (Table 1) utilizing a 1-hr reduction in flowing H_2 at 723 K, whereas the Pt/TiO_2 samples were given either a low-temperature reduction (LTR) at 473 K or a high-temperature reduction at 773 K (see Table 1) following the procedure of Tauster *et al.* (*4*). The gas flow through the cell was always 50 cm^3 (STP)/min and the amount of catalyst was 0.5–0.7 g except for the Pt/TiO_2 (HTR) samples for which 1 g was used. The irreversible CO adsorption at both 215 and 300 K was measured using the procedure of Yates and Sinfelt (*11*), with the difference at 75 Torr representing CO adsorbed on the Pt during the calorimetric measurements. Although no irreversible CO occurred on the pure supports at 300 K (*12*), it was substantial at 215 K on both the LTR and HTR TiO_2 surfaces.

The isothermal energy changes that occurred upon introduction of 10% CO (75 Torr) into a stream of ultrapure Ar flowing over these catalysts were measured using a Perkin–Elmer DSC-2C differential scanning calorimeter (DSC) and a P-E Intracooler II. Under optimum operating conditions with CO, switching occurred between a make-up stream of 4 cm^3/min Ar and a mixture of 4 cm^3/min CO plus 0.6 cm^3/min He to minimize baseline perturbations. This make-up

TABLE 1

Procedure for pretreatment A[a]

1. Heat sample to 393 K in flowing He (or Ar), and hold for 30 min.
2. Switch to flowing H_2 (or 20% H_2, 80% Ar) at 50 cm^3/min, heat to 533 K and hold in flowing H_2 for 30 min.
3. Heat to final temperature of 723 K and maintain for 1 hr in flowing H_2.
4. Cool to 698 K in flowing H_2, evacuate (in adsorption system) or purge in Ar (in DSC system) at 698 K for 1 hr, then cool.

Procedure for (LTR) pretreatment

1. Heat sample to 423 K in flowing He (or Ar), and hold for 30 min.
2. Switch to flowing H_2 (or 20% H_2, 80% Ar) at 50 cm^3/min, heat to 473 K, and hold in flowing H_2 for 2 hr, then cool.
3. Terminate H_2 flow, evacuate at 473 K (or purge in Ar) for 2 hr, then cool.

Procedure for HTR pretreatment

1. Heat sample to 423 K in flowing He (or Ar), and hold for 30 min.
2. Switch to flowing H_2 (or 20% H_2, 80% Ar) at 50 cm^3/min, heat to 773 K, and hold in flowing H_2 for 1 hr.
3. Cool to 723 K in flowing H_2, evacuate (in adsorption system) or purge in Ar (in DSC system) at 723 K for 30 min, then cool.

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[a] All heating rates were 40 K/min, and gas flow rate through the DSC was constant at 40 cm^3/min.

stream was added to a constant Ar flow of 36 cm^3/min. Details of the gas handling system and the modifications to the calorimeter were provided in the first paper in this series (*9*).

As with the experiments involving H_2 adsorption, parallel adsorption and calorimetric measurements were conducted after giving the samples in each system identical pretreatments and pretreatment cycles. This was especially critical for those runs with CO because it appeared that an LTR step was not sufficiently severe to remove all the chemisorbed CO (or carbon) from the Pt surface. Consequently, a treatment in a flowing 20% O_2/80% He stream at 673 K for 30 min followed by rereduction was required to completely clean the Pt surface prior to sequential measurements on the Pt/TiO_2 (LTR) samples.

RESULTS

CO adsorption at 215 and 300 K on the family of Pt catalysts studied is listed in Table 2. As mentioned, the irreversible adsorption at 215 K on pure TiO_2 is large compared to the total adsorption, and the uptake values in column 4 for the Pt/TiO_2 catalysts have been corrected for this uptake on the support. The $CO_{(ad)}$/Pt ratios indicate that some of these catalysts were quite well dispersed, but because of the uncertainty of the adsorption stoichiometry, the crystallite sizes were calculated from H_2 chemisorption values using the equation $d(\text{nm}) = 1.13/(\text{H/Pt})$ (*9*).

In the early part of this study, before all modifications were made to the DSC system, some baseline offset occurred after switching to 10% CO because of the change in thermal conductivity, as shown in Fig. 1a. However, this offset was much smaller than that which occurred with H_2 (*9*). After using the CO/He make-up stream and inserting needle values to control relative flow rates to the sample and reference cavities, a significant improvement in baseline stability was achieved for the typical sup-

TABLE 2

CO Adsorption on Supported Platinum

Catalyst	Sample	Irreversible uptake (μmol/g cat)		CO/Pt[a]	Crystallite size[b] (nm)
		300 K	215 K		
2.1% Pt/η-Al_2O_2		49.0	77.0	0.455	1.5
1.5% Pt/SiO_2-Al_2O_3		26.5	30.0	0.345	2.9
Pure TiO_2 (LTR)		0.0[c]	30.0		
1.5% Pt/TiO_2 (LTR)		52.5	62.0[d]	0.683	1.1
2.0% Pt/TiO_2 (LTR)	I[e]	32.0	—	0.306	2.3
	II[e]	32.8	—	0.314	1.9
	III	74.6	—	0.713	1.2
Pure TiO_2 (HTR)		0.0[c]	49.0		
1.5% Pt/TiO_2 (HTR)		4.5	5.0[d]	[0.059]	1.1
2.0% Pt/TiO_2 (HTR)	I[e]	2.4	—	0.023	2.3
	II[e]	2.5	—	0.029	1.9
2.1% Pt/SiO_2	I	12.0	13.5	0.111	14.8
	II	24.4	—	0.227	4.0
2.1% Pt/SiO_2 (W)	III	16.2	—	0.150	6.7

[a] Based on adsorption at 300 K.

[b] Based on H/Pt ratio (see Ref. (*9*)).

[c] From Ref. (*12*).

[d] After correction for irreversible adsorption on the support.

[e] Values obtained after treatment in 20% O_2/80% He at 673 K for 30 min followed by an LTR or HTR step.

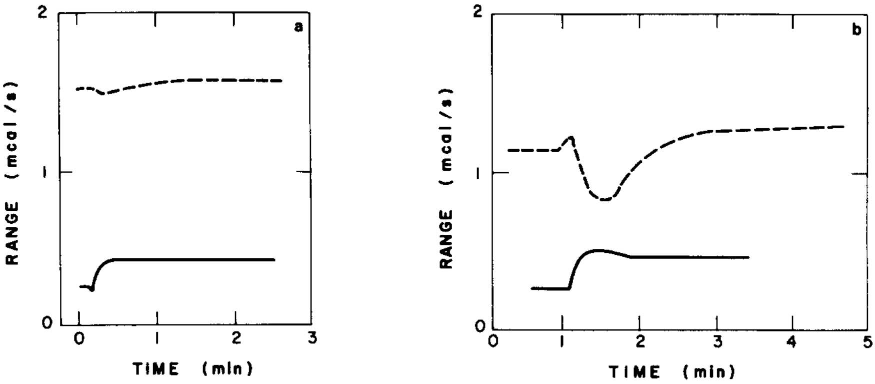

FIG. 1. (a) DSC baseline behavior at 300 K with pure SiO_2 after switching to 10% CO: Before all modifications, solid line; after modifications, dotted line. (b) DSC baseline behavior at 300 K with pure TiO_2 (HTR): Before modifications, solid line; after modifications, dotted line.

ports, an example of which is also shown in Fig. 1a. The baselines were determined in two ways: (1) by placing pure support samples in both the sample and reference cavities and (2) by purging the catalyst and the support in each cavity with pure Ar for 60 min at the adsorption temperature after the initial CO adsorption step, then reintroducing CO into the Ar flow and measuring the energy change. Both techniques usually gave similar results, with the exception of the Pt/TiO_2 (HTR) samples. The baseline behavior with pure TiO_2 in both cavities is shown in Fig. 1b. For the Pt/SiO_2, Pt/η-Al_2O_3, and Pt/S-A catalysts, the CO exotherms were easily measured on the 30- to 100-mg samples used and the baseline correction was minimal, as indicated in Fig. 2. The area under the curve represents the total energy change associated with the adsorption process. The baseline behavior for the Pt/TiO_2 catalysts was somewhat more complicated, as shown in Figs. 3 and 4. After the LTR pretreatment, when adsorption was still high and exotherm was still very strong, the correction for adsorption on the TiO_2 was not large compared to that on the Pt, and the baseline was either nearly flat or very similar to that in Fig. 1b. However, this correction was significant after an HTR step as shown in Fig. 4, primarily because of the small energy change during adsorption (note the change in scale). The difference in the baseline obtained after a 60-min purge and that in Fig. 1b can be seen.

The results of this study are listed in Table 3. In nearly all cases, calorimetric measurements were repeated a number of times on a given sample and the average energy changes are indicated. For the typical catalysts, CO uptake values were essentially insensitive to the number of pretreatment cycles so that the $\Delta H_{(ad)}$ values could be straightforwardly calculated. However, for the Pt/TiO_2 catalysts small changes in the

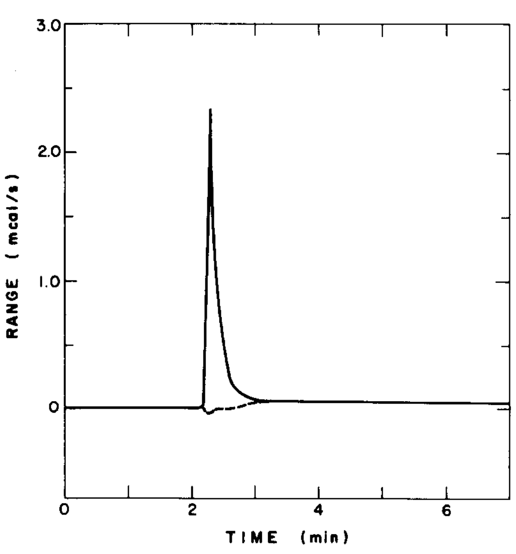

FIG. 2. DSC curve CO adsorption at 300 K on 2.1% Pt/SiO_2: Dotted line represents the baseline.

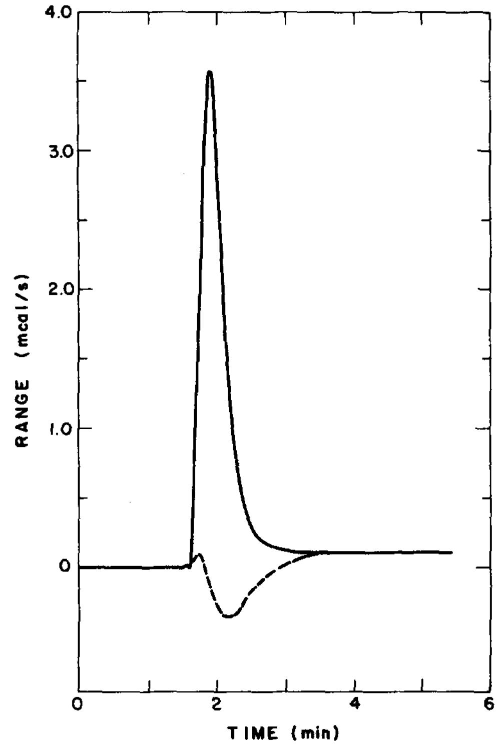

FIG. 3. DSC curve for CO adsorption at 300 K on 2.0% Pt/TiO$_2$ (LTR): Dotted line represents the baseline from either pure TiO$_2$ or from readsorpion after a 1-hr Ar purge at 300 K.

CO uptake occurred during the first two or three successive LTR pretreatments, and significant changes, on a relative basis, were observed after several repeated HTR cycles. For this reason, both adsorption and energy change measurements were required after *every* pretreatment step to obtain reproducible results on the Pt/TiO$_2$ (HTR) samples. Once stabilized by an intervening treatment in oxygen at 673 K, quite consistent data could be acquired as shown in Table 4.

DISCUSSION

Reported values for CO heats of adsorption on unsupported Pt have ranged from 20 to 44 kcal/mole (*1*, *13–26*). These values have been obtained on Pt films (*1*), field emission microscope tips (*14*), foils (*15*), ribbons (*16, 17*), and single crystals (*17–26*). The principal technique employed was TPD coupled with the usual assumptions of nonactivated adsorption and a first-order desorption process although isosteric heats of adsorption were determined in several studies (*20, 22–24*). If only the newer data are considered which were obtained in UHV systems, most $\Delta H_{(ad)}$ values fall between 23 and 36 kcal/mole. Similar detailed studies on supported Pt catalysts have not been reported, with the exception of the paper by Herz and McCready in which they applied TPD and estimated a value of 18 kcal/mole for the predominant, more weakly adsorbed CO species on Al$_2$O$_3$-supported Pt (*3*). Our study was initiated to help fill this void and provide information about CO bond strengths on Pt dispersed on different oxides. In particular, we wanted to determine if any significant support and/or crystallite size effects on $\Delta H_{(ad)}$ values existed in this family of Pt catalysts that had been thoroughly characterized by chemisorption and X-ray diffraction (XRD) methods. The direct measurement of isothermal, integral heats of adsorption using a calorimetric technique seemed most appro-

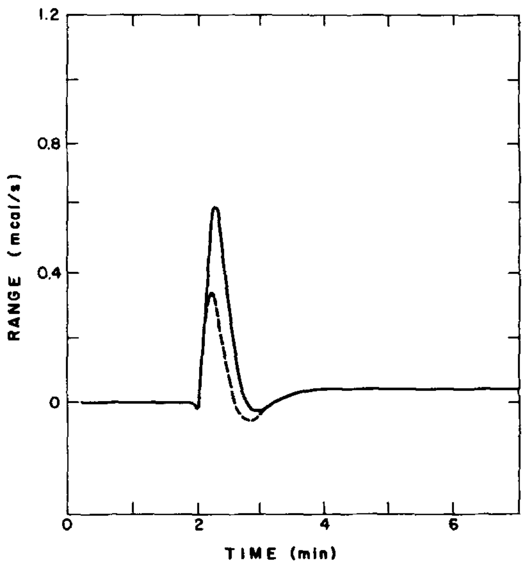

FIG. 4. DSC curve for CO adsorption at 300 K on 2.0% Pt/TiO$_2$ (HTR): Dotted line represents the readsorption baseline after a 1-hr Ar purge at 300 K.

TABLE 3

Heats of Adsorption of Carbon Monoxide on Supported Platinum

Catalyst	Sample	Weight (mg)	Pretreatment	Ads. temp (K)	No. of runs	Average energy change (mcal/g)	$\Delta H_{(ad)}$ (kcal/mole)
2.1% Pt/η-Al_2O_3	I	60.6	A	320	3	1162	23.7 ± 0.7
			A	215	4	1174	15.2 ± 0.4
	II	62.7	A	320	2	1178	24.0 ± 0.2
			A	215	2	1231	16.0 ± 0.1
1.5% Pt/SiO_2-Al_2O_3	I	32.2	A	320	3	613	23.1 ± 0.6
			A	215	3	583	19.4 ± 0.7
2.1% Pt/SiO_2	I	33.7	A	320	2	324	27.0 ± 2.5
			A	215	2	225	16.7 ± 1.7
	II	36.9	A	300	2	672	27.5 ± 2.5
2.1% Pt/SiO_2 (W)	III	37.3	A	320	4	514	31.7 ± 3.2
1.5% Pt/TiO_2 (LTR)	I	40.6	B[a]	320	1	1059	20.2
			B[b]	320	2	1049	20.0 ± 0.5
			B[a]	215	2	675	10.9 ± 0.5[c]
2.0% Pt/TiO_2 (LTR)	I[d]	108.6	B	300	2	691	21.6 ± 0.9
	II[d]	106.2	B	300	2	727	22.2 ± 0.9
	III[d]	98.4	B	300	3	721	22.0 ± 0.8
	IV	91.8	B	300	1	1597	21.4
1.5% Pt/TiO_2 (HTR)	I	64.5	C	320	5	105.4	23.4 ± 5.0
			C	215	5	46.0	9.2 ± 2.5[c]
2.0% Pt/TiO_2 (HTR)	I[d]	108.6	C	300	2	24.7	10.3 ± 3.6
	II[d]	106.2	C	300	2	58.7	23.5 ± 5.0
	III[d]	98.4	C	300	3	39.8	15.9 ± 3.9

[a] Pretreatment B except that T_{Red} = 175°C.

[b] Sixteen-hour reduction at 175°C.

[c] After correction for irreversible adsorption on the support.

[d] Values obtained after treatment in 20% O_2/80% He at 673 K for 30 min followed by an LTR or HTR step.

priate because difficulties which exist during TPD experiments with metal catalysts involving porous supports, such as pore diffusion and readsorption (*27, 28*), have no effect on the values obtained in our DSC system.

TABLE 4

Carbon Monoxide Adsorption on 2.0% Pt/TiO_2 at 300 K (Sample wt = 98.4 in DSC)

Sequence number[a]	Pretreatment	Energy change (mcal/g)	Uptake (μmol/g)	$\Delta H_{(ad)}$ (kcal/mole)
1	C	38.0	2.5	15.2
2	B	745	33.0	22.6
3	B	706	32.5	21.7
4	B	710	—	—
5	C	39.0	—	—
6	C	42.4	—	—

[a] Catalyst treated in 20% O_2 + 80% He (Ar) at 673 K for 30 min between each run.

For the Pt/SiO_2, Pt/Al_2O_3, and Pt/S-A catalysts, both chemisorption values and the exotherms obtained during adsorption were quite reproducible after the initial reduction and adsorption cycle. The $\Delta H_{(ad)}$ values in Table 3 are in excellent agreement with those determined for Pt in UHV systems, and they vary from 23 kcal/mole on 1.5% Pt/S-A to 32 kcal/mole on 2.1% Pt/SiO_2. This range is extremely similar to that which has been reported for a number of Pt crystallographic planes. That they are slightly low in comparison is anticipated because they are integral heats of adsorption associated with a saturated surface. Mc-

Cabe and Schmidt have shown that desorption activation energies drop continuously as surface coverage increases, with initial values on the (110), (111), (100), (211), and (210) planes varying from 26.0 to 36.2 kcal/mole and final values at saturation ranging from about 15 to 20 kcal/mole (*25*).

The Pt/TiO_2 (LTR) catalysts showed a distinguishable difference, and different samples repeatedly gave $\Delta H_{(ad)}$ values of 21 ± 1 kcal/mole. We attribute this primarily to the small crystallites in these samples, but some modification of the Pt adsorption sites by small amounts of TiO_x species in contact with the Pt surface, which can be produced even at low temperatures of 473 K by migrating hydrogen activated on the Pt, may have occurred. This behavior was more markedly enhanced by the HTR pretreatment, and after repeated cycling, heats of adsorption on the Pt/TiO_2 (HTR) catalysts were sometimes as low as 10–15 kcal/mole, as listed in Table 3. These results were not always obtained, however, and sometimes $\Delta H_{(ad)}$ values were similar to those for the Pt/TiO_2 (LTR) samples. We do not know the reason for this, but presume that it is a consequence of the degree of contact that exists between the Pt surface and the TiO_x species after each of the oxidation/HTR cycles. The greater the interfacial contact, the more pronounced should be the effect on CO bond strength. This decrease in bond strength may be due to (1) a promoter effect on the Pt sites by the TiO_x species, as suggested by Dumesic and coworkers (*29*), (2) the creation of a new Pt–support interface site which coordinates adsorbed CO differently (*30, 31*), or (*3*) the preferential blocking of the higher-energy sites on Pt by TiO_x. We cannot distinguish among these possibilities at the present time.

Although there appears to be a significant support effect when TiO_2 is used, our results also indicate a strong possibility that CO heats of adsorption on Pt are dependent upon crystallite size. If the results for the catalysts exhibiting "normal" CO uptakes are plotted versus the $CO_{(ad)}$/Pt ratio, which parallels crystallite size, and the type of support is ignored, a clear trend exists which is shown in Fig. 5. It indicates that CO bond strengths on Pt are greatest on large crystallites and decrease significantly as crystallite size decreases. This pattern is identical to that for H_2 adsorption on Pt (*9*), and is consistent with the recent study of Herz and McCready who found that the heat of adsorption of CO on Al_2O_3-supported Pt approached a limiting value of 18 kcal/mole as Pt dispersion approached unity (*3*). Additional forms of adsorbed CO, which gave a small, broad band extending to 750 K, would result in a somewhat higher integral $\Delta H_{(ad)}$ value; regardless, their result is included in Fig. 5 and it clearly is consistent with our observed trend. At this time we do not know if this is due to stabilization of certain Pt crystal planes by the support, such as SiO_2, for example, or if it is independent of the support and due only to statistical changes in the distribution of surface sites on Pt. It may also be a consequence of electronic modification of very

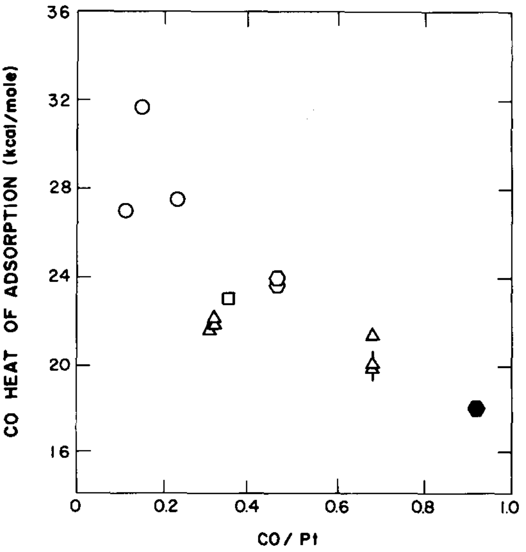

FIG. 5. Variation of CO $\Delta H_{(ad)}$ with CO/Pt (i.e., Pt crystallite size): 2.1% Pt/SiO_2, ○; 1.5% Pt/S-A, □; 2.1% Pt/η-Al_2O_3, ○; 2.0% Pt/TiO_2 (LTR), △; 1.5% Pt/TiO_2 (LTR), ⍋; 1% Pt/Al_2O_3, ●; (from Ref. (*3*)).

small crystallites by the support. Presently, we are studying the behavior of different Pt crystallite sizes on a given support to determine the explanation for this behavior.

At 215 K, heats of adsorption were significantly lower and varied between 15 to 19 kcal/mole for Pt on SiO_2, Al_2O_3, and S-A. This decrease is attributed to the increased population of lower-energy adsorption states at this temperature; however, we cannot completely discount the possibility that the filling of higher-energy states may have a small activation barrier. Again the Pt/TiO_2 catalysts have lower heats of adsorption, with the LTR sample having a value near 11 kcal/mole and the HTR sample giving a $\Delta H_{(ad)}$ value approaching 9 kcal/mole. These lower values, especially for the HTR sample, may be a consequence of a larger activation barrier for adsorption, or it may be that TiO_x species on the Pt surface preferentially block the high-energy sites. Future studies are required to resolve the possibility of activated adsorption.

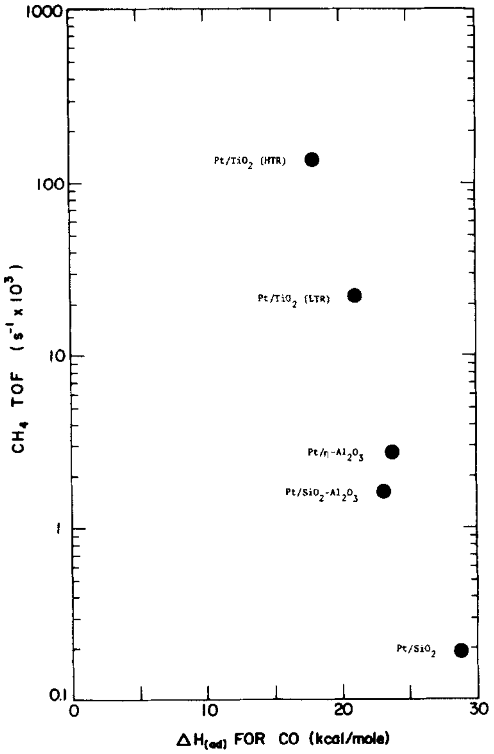

FIG. 6. Correlation of the methanation turnover frequency with CO heat of adsorption. These are average TOF values from Ref. (*7*) that were based on CO adsorbed on used samples. The $\Delta H_{(ad)}$ values are averaged from the results in Table 3.

In an earlier study, we found that the turnover frequency for methanation on Pt was very dependent upon the support, and three orders of magnitude existed between the least-active Pt/SiO_2 catalysts and the most-active Pt/TiO_2 (HTR) catalysts when chemisorbed CO was used to count surface sites (*7*). When the logarithm of the CH_4 TOF is plotted versus the CO heat of adsorption, an almost linear correlation exists, as shown in Fig. 6, which is nearly identical to the trend that occurs when these TOFs were plotted versus H_2 heats of adsorption (*9*). These results imply that the most active Pt methanation catalysts are those with the lowest heats of adsorption for both hydrogen and CO. We cannot distinguish between two possibilities: (1) the support creates a unique *active* site, at the Pt–support interface, for example, which enhances the rate-determining step and simultaneously and independently reduces the adsorption bond strengths (*30*); or (2) Pt surface atoms are modified, perhaps by the support acting as a promoter, such that heats of adsorption are decreased, and this decrease produces an increase in reaction rate because of the exponential dependence of the rate equation on $\Delta H_{(ad)}$ values; however, this dependence is small for Pt (*7*). The latter explanation, which implies that $\Delta H_{(ad)}$ is the only significant parameter, seems less likely because the heat of adsorption of CO on Cu is near that on the Pt/TiO_2 (HTR) catalyst yet there is a difference of 10^4 in the TOF for methanation (*6*). Consequently, we tend to prefer the former explanation at this time.

SUMMARY

A differential scanning calorimeter has been modified and integrated into a gas flow system to allow the rapid measurement of integral, isothermal heats of adsorption of

CO on Pt dispersed on SiO_2, η-Al_2O_3, SiO_2-Al_2O_3, and TiO_2. The catalysts which displayed "normal" adsorption behavior possessed a range of $\Delta H_{(ad)}$ values at 300 K between 21 and 32 kcal/mole, with the Pt/TiO_2 (LTR) samples having the lowest values. This variation in $\Delta H_{(ad)}$ under normal adsorption conditions appears to be a strong function of crystallite size, with weaker Pt–CO bonding occurring as Pt dispersion increases. Only the Pt/TiO_2 (HTR) samples, which possessed the decreased chemisorption capacity associated with the SMSI state, exhibited a significant support effect which decreased the heat of adsorption after repeated cycling. At 215 K the $\Delta H_{(ad)}$ values were lower, as expected, and the range of 15–20 kcal/mole on the typical catalysts indicated the filling of lower-energy states. Although a strong correlation existed between the turnover frequency for methanation and the CO heat of adsorption, the enhancement in activity cannot easily be explained by invoking only a decrease in the CO heat of adsorption.

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