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Direct Measurements of Heats of Adsorption on Platinum Catalysts

III. Potential Errors with Differential Scanning Calorimeters

In a recent paper, we reported integral heats of adsorption for H_2 adsorbed on Pt dispersed on a variety of oxide supports (*1*). These values were obtained using a modified commercial differential scanning calorimeter (DSC) operated in the isothermal mode (*1, 2*). Although the values obtained were very reproducible and fell within the wide spectrum of heats of adsorption reported in the literature, we observed that the integral Q_{ad} values were higher than anticipated compared to the initial heats of adsorption measured in UHV systems. In a subsequent study of H_2 adsorption on Pd, relatively high apparent Q_{ad} values were again observed; however, in this system we had an internal calibration standard that could be utilized—the heat of formation of β-phase Pd hydride (*2, 3*). When this apparent value was also found to be far too high when Ar was used as a carrier gas, it became apparent that an artifact existed which was producing erroneous energy change values. Further experiments showed that this problem was related to changes in the thermal conductivity of the gas in the sample cavity relative to the reference cavity, and it was especially severe with H_2 because of the large difference in thermal conductivity compared to Ar. This difficulty exists in calorimeters involving the measurement of a time-dependent electric power difference, which represents the energy change, when any process occurs to change the thermal conductivity of the gas surrounding the sample relative to that around the reference material; however, this problem is not explicitly stated in literature describing the use of these instruments (*4, 5*). Therefore, we undertook a study to clarify this problem so that others can avoid it in their studies and to develop a set of operating conditions which allow accurate heats of adsorption to be measured. In this paper we report corrected heats of adsorption for H_2 on the same family of Pt catalysts. The former aspect is discussed in greater detail elsewhere (*2*).

The supported Pt catalysts—2.1% Pt/SiO_2, 1.5% Pt/SiO_2–Al_2O_3, 2.1% Pt/η–Al_2O_3, and 2.0% Pt/TiO_2—were the same group utilized in the preceding study (*1*). The high purity Pt powder was Puratronic grade (99.999%) from Johnson Matthey Inc. The fresh catalysts were given one of three pretreatments, A, B, or C, involving reduction at 723, 473, or 773 K, respectively. Details are given in Table 1 of Ref. (*1*). As before, the series of pretreatments and adsorption cycles conducted in the DSC were paralleled on a corresponding sample in the adsorption system so that changes in uptake with cycling could be detected. Details of the adsorption systems have been given elsewhere (*6, 7*). The chemisorption procedure was described previously (*1*). The irreversible H_2 uptake was defined as that remaining after a 1 h evacuation at 300 K.

Thorough descriptions of the modifications made to the DSC, the gas handling system, the temperature and energy calibration procedures, and the influence of different DSC parameters have been provided elsewhere (*1, 2*). Pretreatments were again those listed in Table 1 of Ref. (*1*), using a 20% H_2/80% He (or Ar) mixture. The only difference was that purge times of 3 or 4 h after reduction were used to assure complete desorption of hydrogen. The sample

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was purged for 1 h at 300 K to remove weakly adsorbed hydrogen prior to the readsorption measurement. From a thorough study of hydrogen absorption in Pd and adsorption on Pt (*2*), a set of operating conditions was found which provides accurate energy change measurements during adsorption processes involving H_2—the use of pure He as a carrier gas with the DSC sink temperature near that of the adsorption temperature, i.e., $T_s = 290$ K in this case. Under these conditions heats of adsorption were remeasured for all the supported Pt catalysts and a Q_{ad} value was also determined for the Pt powder. The adsorption results for the Pt samples obtained under these optimum conditions are listed in Table 1 along with the dispersion, D, (fraction exposed) and the average Pt crystallite size, d_s, calculated using the relationship d_s (nm) = $1.13/D$ (*1*).

The severity of the problem that can exist in this differential power calorimeter when significant changes occur in the thermal conductivity of the gases surrounding the sample, but not the reference, does not seem to be recognized (*4, 5*). *An error due to this problem can exist during any adsorption/absorption process or reaction which causes a concentration change in the gas around the samples,* but it can be small if the thermal conductivities of all gases are similar. Therefore, the problems with Q_{ad} measurements for CO on Pt (*8*), and CO and O_2 on Pd (*9*) were minimal because of the similarity in thermal conductivities of CO, O_2, and Ar. Clearly, the greatest difficulty exists with H_2, which has the highest gas thermal conductivity, but the errors introduced can be markedly reduced by using He as a carrier gas, keeping the sink temperature near that of the sample, and by working at low H_2 pressures, thereby allowing accurate energy changes to be obtained

TABLE 1

H_2 Adsorption on Pt at 300 K

Catalyst (sample)	Pretreatment	DSC sample wt (mg)	H_2 Uptake (μmole/g)		D $\left(\frac{H_{ad}}{Pt_{total}}\right)$	Pt crystallite size (nm)	No. of DSC runs	Average energy change (mcal/g)		Q_{ad} (kcal/mole)	
			Total	Irreversible				Total H_2	Irreversible H_2	Total H_2	Irreversible H_2
1.5% $Pt/SiO_2–Al_2O_3$											
(I)	A	35.5	14.9	6.3	0.39	2.9	2	231.6	122.0	15.5 ± 0.2	19.4 ± 1.1
(II)	A	37.4	19.9	10.1	0.52	2.2	2	318.7	191.6	16.0 ± 0.1	19.0 ± 0.1
2.1% Pt/SiO_2											
(I)	A	33.0	13.5	6.0	0.25	4.5	2	182.8	104.5	13.5 ± 0.3	17.4 ± 0.4
(II)	A	34.8	6.0	3.1	0.11	10.3	2	82.3	48.9	13.7 ± 1.3	15.8 ± 2.8
2.1% Pt/η-Al_2O_3 (I)	A	61.0	22.7	14.4	0.42	2.7	2	353.7	230.5	15.6 ± 0.5	16.0 ± 0.8
2% Pt/TiO_2 (LTR)											
(I)	B	38.9	24.0	13.2	0.47	2.4	3	323.8	187.5	13.5 ± 0.3	14.2 ± 0.7
(II)	B	74.6	36.5	19.5	0.71	1.6	3	432.5	271.7	11.9 ± 0.2	13.9 ± 0.5
(III)	B	60.0	27.1	15.7	0.53	2.1	2	355.5	233.9	13.1 ± 1.1	14.9 ± 2.2
(IV)	B	69.0	25.6	14.7	0.50	2.3	3	304.8	190.1	11.9 ± 0.6	12.9 ± 0.7
Pt powder (I)	C	119.4	1.8	0.7	0.0007	1600	2	24.4	14.5	13.6 ± 1.1	20.7 ± 4.0
2% Pt/TiO_2 (HTR)											
(I)	C	38.9	1.5	0.4	[0.029]	—	4	16.3	5.8	10.9 ± 4.1	14.5 ± 8.2
(II)	C	74.6	1.2	0.4	[0.023]	—	2	18.7	7.4	15.6 ± 1.8	18.5 ± 4.5
(III)	C	60.0	1.2	0.3	[0.023]	—	4	18.2	5.2	15.2 ± 3.4	17.3 ± 5.8
(IV)	C	69.0	1.3	0.4	[0.025]	—	3	15.6	5.0	12.0 ± 3.5	12.5 ± 6.6

Note. Equilibrium $P_{H_2} = 10$ kPa.

(*2*). An awareness of this situation should help investigators avoid the problem in the future.

The results in Table 1 show a marked reduction in the integral heats of adsorption for hydrogen on Pt at 300 K compared to the apparent values reported earlier (*1*), and the values now fall between 13.5 and 16.0 kcal/mole H_2 for the typical catalysts, i.e., Pt powder and Pt dispersed on SiO_2, $SiO_2-Al_2O_3$, and Al_2O_3. Although the Q_{ad} values exhibited by Pt/TiO_2 after a low temperature reduction (LTR) are slightly lower, they are similar to those on the typical Pt catalysts. If all these values are plotted versus Pt crystallite size, there is no large variation in Q_{ad} on particles from 2 to 1600 nm, as shown in Fig. 1, although additional studies are required to ascertain any possible trend, independent of the support, on crystallites smaller than 3 nm. Consequently, the apparent trend of increasing Q_{ad} with decreasing dispersion reported in Ref. *1* was due to the artifact created by the change in thermal conductivity when Ar was used.

As the data represented in Fig. 1 were obtained under optimum conditions that gave accurate heat of formation values for Pd hydride formation (*2*), we consider them to be accurate representations of integral heats of adsorption of H_2 on Pt surfaces. Further verification of this conclusion comes from a comparison with UHV studies in which the change in Q_{ad} with hydrogen coverage was reported (*10–13*). From these results integral values were estimated by extrapolation to monolayer coverage, and the values for different crystal planes are listed in Table 2. The Q_{ad} values obtained here for the Pt powder, in which (111) planes are expected to dominate, are in very good agreement with those calculated from studies on single crystals, and the range of values obtained for all the catalysts easily falls within the range shown in Table 2. These integral Q_{ad} values are also very consistent with earlier H_2 heats of adsorption reported in the literature (*14, 15*). The average value obtained for the Pt/SiO_2 catalyst is similar to the value of approximately 16 kcal/mole H_2 estimated from the study of Lantz and Gonzalez, who measured the differential heat of adsorption for H_2 on SiO_2-supported Pt (*16*). A recent study by Mills *et al.* reported heats of adsorption near 30 kcal/mole H_2 on a 6.2% Pt/SiO_2 sample (*17*). However, they were also using a DSC with N_2 as the carrier gas; consequently, this value suffers from the same problem as our original data and it is erroneously high. Although Takasu *et al.* have reported a decrease in the desorption activation energy for H_2 from 12 to 8 kcal/mole as the Pt crystallite size decreased from 4.5 to 1.6 nm (*18*), these data were obtained from TPD studies using SiO_2-sup-

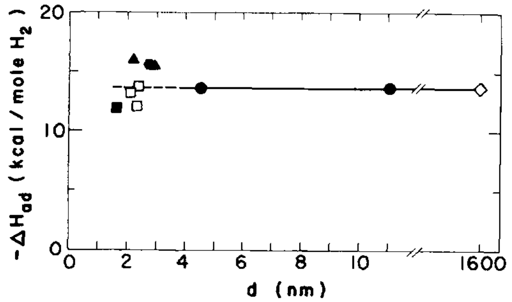

FIG. 1. Integral heats of adsorption at 300 K for H_2 on Pt versus crystallite size ($Q_{ad} = -\Delta H_{ad}$): ●, Pt/SiO_2; ●, $Pt/\eta-Al_2O_3$; ▲, $Pt/SiO_2-Al_2O_3$; □, Pt/TiO_2 (LTR); ■, Pt powder. Open symbols indicate O_2 exposure at 673 K prior to rereduction at 473 K.

TABLE 2

Integral Heats of Adsorption for Hydrogen at Monolayer Coverage

Plane	Q_{ad} (kcal/mole)	Authors (reference)
(111)	15.8	McCabe and Schmidt (*10*)
(111)	12.4	Norton *et al.* (*11*)[a]
(111)	8.5	Christmann *et al.* (*12*)
Film	20.2	Norton and Richards (*13*)
(110)	α-11.9 β-8.8	McCabe and Schmidt (*10*)
(210)	19.7	McCabe and Schmidt (*10*)
(211)	14.5	McCabe and Schmidt (*10*)

[a] D_2 used.

ported Pt, and the possible influence of pore diffusion and readsorption cannot be ruled out at this time. Finally, we must mention that the previously reported correlation of CH_4 turnover frequency with the H_2 heat of adsorption (*1*) clearly no longer exists and was also a result of the artifact created by changing thermal conductivity; however, the correlation of CH_4 TOF with CO Q_{ad} values still appears valid (*8*).

Although the lowest heats of adsorption were obtained with the Pt/TiO_2 (HTR) samples, these measurements contained the greatest uncertainty because of the very low uptakes. With this consideration in mind, the heat of adsorption of hydrogen on the remaining sites does not appear to be markedly decreased and, in fact, is quite similar to the other Pt catalysts within experimental error. This evidence supports the explanation that most of the decrease in hydrogen adsorption capacity is due to physical blockage of the Pt surface by the migration of the support. However, we do not know if all the remaining adsorption sites in the Pt/TiO_2 (HTR) sample are associated only with the Pt, because it has been reported that higher-energy adsorption sites on the titania surface can exist which can be filled by H atoms migrating from the Pt surface. Such sites were first proposed by White and co-workers in the Pt/TiO_2 system (*19, 20*), and they have also been observed recently by Raupp and Dumesic in the Ni/TiO_2 system (*21, 22*). We have found, as others have, that a treatment in O_2 after the HTR step followed by a LTR pretreatment typically restores "normal" adsorption behavior, presumably by reoxidizing the TiO_x species which had migrated onto the Pt surface back to TiO_2 and freeing the Pt surface. Such behavior greatly complicates any interpretations related to alterations in the adsorbed state of hydrogen on the Pt surface.

In summary, we have found that a significant artifact can occur in energy changes measured by differential scanning calorimeters, especially when H_2 is involved, and we want to bring this to the attention of the scientific community using this technique to study adsorption/absorption processes and reactions. However, appropriate conditions in the DSC can be selected to minimize this difficulty and to obtain accurate heat of adsorption measurements. By using such a method, we have obtained new integral Q_{ad} values for H_2 on Pt surfaces which are essentially free of this artifact and are consequently much lower than heats of adsorption reported by us recently, thus explaining the unusually high values for H_2 which we noted at the time (*1*). These more accurate Q_{ad} values are near 13.5 ± 2 kcal/mole H_2 for all the catalysts studied, they are in excellent agreement with integral values estimated from the UHV literature, and they exhibit no large change over a crystallite size range of 2–1600 nm. This behavior indicates the absence of large crystallite size or metal-support effects on H_2 heats of adsorption on Pt, and the decrease in H_2 adsorption on TiO_2-supported Pt is principally due to the physical blockage of Pt surface sites by migrating TiO_x species.

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