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Enthalpy Changes during O_2 Adsorption and H_2 Titration of Adsorbed Oxygen on Platinum

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Integral, isothermal heats of adsorption were measured for O_2 on UHP Pt powder and SiO_2-supported Pt, with the latter providing an average crystallite size range of 1.3–22.3 nm. The energy changes that occur during the titration of this chemisorbed oxygen by dihydrogen were also measured. The average Q_{ad} value of 67.9 ± 8.9 kcal/mol for well-dispersed Pt on Davison 57 silica compared to that of 52.6 ± 6.1 kcal/mol for the Pt powder indicates that a small increase may occur on very small Pt crystallites. The enthalpy of titration was relatively constant, with a value of $\Delta H_{titr} = -26.7 \pm 4.2$ kcal/mol H_2 obtained for all the Pt/SiO_2 samples compared to -24.5 ± 3.5 kcal/mol H_2 for the Pt powder. The use of a thermodynamic cycle not only gave an approximate value of 11 kcal/mol for the heat of adsorption of water on SiO_2, but also indicated that all the water desorbed from the Pt surface at 300 K thus allowing a complete monolayer of hydrogen to form.

INTRODUCTION

The heats of adsorption, Q_{ad}, for CO and H_2 on Pt dispersed on a variety of supports have been measured (*1–4*). Only three studies providing similar values for O_2 on supported Pt have been reported and they have produced widely diverging results, with Basset *et al.* finding a Q_{ad} value of 58 kcal/mol (*5*) and Briot *et al.* measuring values of 60–67 kcal/mol (*6*), whereas Mills *et al.* reported values of only 6–9 kcal/mol (*7*). Previous studies of O_2 adsorption on unsupported Pt have yielded heats of adsorption ranging from 28 to 72 kcal/mol. Having modified a differential scanning calorimeter to allow routine measurements of integral, isothermal heats of adsorption (*8*), it seemed worthwhile to measure Q_{ad} for O_2 adsorbed on Pt dispersed on a support that is noninteractive with oxygen, such as SiO_2, and to determine if this property is dependent upon crystallite size.

Another reason to examine not only O_2 chemisorption but also the H_2 titration of adsorbed oxygen relates to the use of the latter reaction to measure Pt dispersion. Benson and Boudart proposed 25 years ago that a threefold increase in sensitivity could be obtained by this method (*9*), and although this method has been widely used, some uncertainty has remained regarding the adsorption stoichiometries as Pt crystallite size varies (*10–12*). A recent study has verified that the saturation coverage of oxygen is less than that of hydrogen (*13*), and information about the Pt–O bond strength on Pt crystallites of different size could provide insight into this coverage limitation. In addition, exotherms during the titration (ΔH_{titr}) can give information related to the fate of the water that is formed. For these reasons, we have obtained integral Q_{ad} and ΔH_{titr} values for a family of Pt/SiO_2 catalysts with dispersions between 0.05 and 1 and compared them to those measured on unsupported ultrahigh-purity Pt powder.

Experimental

SiO_2 (Davison Grade 57, 220 m^2/g) and η-Al_2O_3 (Exxon Research and Eng. Co., 245 m^2/g) were used as support materials using

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incipient wetness and ion-exchange methods. Prior to the preparation of the catalysts the supports were calcined in air at 773 K for 1–4 hr to remove any carbonaceous impurities. The metal precursors, the method of preparation, and the metal loadings are given in a succeeding paper (*4*). A detailed description of the incipient wetness technique can be found in Ref. (*14*), while the method developed by Benesi *et al.* was used for the ion-exchanged catalysts (*15*). The 1.8%, 1.7%, and 2.2% Pt/SiO_2 catalysts were prepared in the laboratory of G. Ozin using Pt tris-ethylene and a low-temperature condensation process involving a silica which had been pretreated at 1073, 873, and 473 K, respectively (*16*). All the catalysts prepared from inorganic precursors were dried at 393 K overnight in air then stored in a desiccator. The final platinum weight loadings were determined by neutron activation analysis using a physical mixture of $Pt(NH_3)_4Cl_2$ and the appropriate support as the standard. The Pt powder used was Puratronic grade (99.999%) obtained from Johnson Matthey.

The systems for measuring gas uptakes have been described previously (*1, 3*), and pretreatment A in Ref. (*1*) was used for all samples; i.e., a 1-h reduction at 723 K in 20% H_2 followed by a 1-h evacuation at 698 K was used to obtain clean and reproducible Pt surfaces. Prior to the reduction step with some samples, the average Pt crystallite size was altered by various calcination procedures in oxygen, as noted in Tables 1 and 2. The method for determining the hydrogen and oxygen uptakes on these catalysts is standard and involves the extrapolation of isotherms measured between 50 and 200 Torr to zero pressure to correct for reversible adsorption on the support (*9, 12*). All measurements were done at room temperature (300 K). The samples prepared from Pt tris-ethylene were transferred in a N_2 dry box directly from sealed ampules into an adsorption cell, and they were then pretreated, chemisorption measurements were conducted, and a small portion was transferred to the DSC after passivation in oxygen. Isothermal energy changes were measured at 300 K using a modified Perkin–Elmer DSC-2C differential scanning calorimeter. A more detailed description of the calorimetric system and the method adopted for determining energy changes after making appropriate baseline corrections for H_2 is given in Refs. (*3, 8*). To obtain stable baselines upon the introduction of O_2, the procedure used with Pd catalysts was utilized (*17*).

RESULTS AND DISCUSSION

The exotherms during adsorption and titration were well behaved, as shown in Fig. 1. Integrating curves such as this produced the energy changes, ΔE, that are listed in Tables 1 and 2. The O_2 heats of adsorption, Q_{ad}, and the titration enthalpy changes, ΔH_{titr}, versus Pt crystallite size are shown in Fig. 2. The enthalpy changes for titration were very consistent for Pt particles ranging from 1 to 1600 nm, and most values lay between 20 and 30 kcal/mol whether a support was present or not. A wider variation was found among the Q_{ad} values for O_2 although most values fell between 50 and 75 kcal/mol. A number of studies have addressed oxygen adsorption on Pt surfaces, and those which provide heats of adsorption are cited in Table 3 along with the values reported and the method used to obtain them (*5–7, 18–27*). The wide range of Q_{ad} values is obvious, even if only the results for the Pt(100) surface are compared. On the unsupported Pt samples in the present study, the average Q_{ad} for O_2 and its standard deviation are 52.6 ± 6.1 kcal/mol, which is very consistent with most of these previous studies and indicates that the heat of adsorption does not drop too much as the surface becomes saturated with oxygen.

There is noticeable scatter among the Q_{ad} values for supported Pt and if the entire family of Pt/SiO_2 catalysts is taken, a value of 62.0 ± 11.3 kcal/mol for Q_{ad} is obtained. If the samples prepared from Pt tris-ethylene are excluded because of uncertainty of the

TABLE 1

Integral Heats of Adsorption of Oxygen on Pt (P_{O_2} = 10 kPa)

Sample	d^a (nm)	O_2 uptake (μmol/g cat)	O/Pt_T	ΔE^b (mcal/g cat)	Q_{ad} (kcal/mol O_2)
Pt powder					
I	1600	1.3		68.2	52.4 ± 5.9
II	1600	1.6		68.1	42.6 ± 1.5
III	1600	1.4		82.6	59.0 ± 6.1
IV	1600	1.7		93.7	55.1 ± 3.2
V^c	1600	0.9		48.4	53.8 ± 4.4
1.2% Pt/Al_2O_3	1.1	18.5	0.60	920.9	49.8 ± 2.5
0.7% Pt/SiO_2					
I	1.3	13.3	0.74	954.2	71.7 ± 10.3
II	1.4	9.5	0.54	630.9	66.4 ± 1.9
III^d	2.7	7.5	0.42	477.9	63.7 ± 3.6
0.6% Pt/SiO_2^e	4.0	5.0	0.32	369.3^i	73.3
2.7% Pt/SiO_2^f	6.5	11.4	0.17	557.4	48.9 ± 1.8
4.4% Pt/SiO_2	5.5	16.0	0.14	1120.4	70.0 ± 4.6
5.0% Pt/SiO_2					
I	3.9	29.5	0.23	2205.3	74.8 ± 1.3
II^g	22.3	7.5	0.05	551.6	73.5 ± 0.2
1.7% Pt/SiO_2					
I	1.9	19.0	0.44	1003^i	52.8
II^h	1.6	23.5	0.54	1273^i	54.2
1.8% Pt/SiO_2	2.0	21.5	0.46	1013^i	47.1
2.2% Pt/SiO_2	2.0	26.1	0.47	1212^i	46.4

[a] Average crystallite size determined from H chemisorption (Ref. (*4*)).
[b] Average of two runs.
[c] Physical mixture of Pt powder and SiO_2.
[d] Calcined in 20% O_2 at 623 K for 1 h.
[e] Sintered in 20% O_2 at 673 K for ½h.
[f] Sintered in 36% O_2 at 773 K for 12 h.
[g] Sintered in 20% O_2 at 673 K for 2 h.
[h] Calcined in 20% O_2 at 573 K for 1 h.
[i] One run only.

decomposition process and the different silica used, then Q_{ad} = 67.9 ± 8.6 kcal/mol for the remaining eight catalysts prepared by traditional means using only Davison 57 silica. Although this calorimetric technique cannot provide information about the distribution of adsorption sites, it indicates that for saturated O-covered surfaces there is a possibility that the integral heat of adsorption may be somewhat higher on small dispersed Pt particles. This same conclusion was reached in the recent paper of Briot *et al.* who measured a heat of adsorption of 60 kcal/mol for O_2 on a Pt/Al_2O_3 sample of 8.5% dispersion and of 67 kcal/mol for O_2 on a Pt–Al_2O_3 sample of 50% dispersion (*6*). Our average value for the well-dispersed Pt/SiO_2 catalysts prepared from the Davison 57 silica is in excellent agreement with the higher of these two values. Our results are also in reasonable agreement with the value of 58 kcal/mol reported by Basset *et al.* for a Pt/Al_2O_3 catalyst (*5*), but they are far higher than the values of 6–9 kcal/mol given by

TABLE 2

Enthalpy Changes for the Titration of Chemisorbed Oxygen by Dihydrogen at 300 K (P_{H_2} = 10 kPa)

Sample	d^a (nm)	H_2 uptake (μmol/g cat)	ΔE^b (mcal/g cat)	$-\Delta H_{\mathrm{Titr}}$ (kcal/mol O_2)	[H_{titr}/O_{ad}]
Pt powder					
I	1600	4.4	86.9	19.8 ± 1.7	3.4
II	1600	4.5	99.1	22.0 ± 0.7	2.8
III	1600	4.9	136.9	27.9 ± 0.9	3.5
IV	1600	4.4	116.6	26.5 ± 1.5	2.6
V[c]	1600	2.6	6.9	26.5 ± 0.6	2.9
1.2% Pt/Al_2O_3	1.1	79.0	1937.2	24.5 ± 0.5	4.3
0.7% Pt/SiO_2					
I	1.3	35.9	932.2	26.0 ± 1.4	2.7
II	1.4	32.1	803.2	25.0 ± 0.8	3.4
III[d]	2.7	18.3	471.6	25.8[i]	2.4
0.6% Pt/SiO_2 II[e]	4.0	11.3	270.4	23.9 ± 1.9	2.3
2.7% Pt/SiO_2[f]	6.5	26.1	798.0	30.6 ± 1.0	2.3
4.4% Pt/SiO_2	5.5	47.4	1794.4	37.9 ± 0.3	3.0
5.0% Pt/SiO_2					
I	3.9	98.5	2720.0	27.6 ± 1.8	3.5
II[g]	22.3	20.6	520.3	24.4 ± 1.0	3.0
1.7% Pt/SiO_2					
I	1.9	66.2	1810.3	27.3[i]	3.5
II	1.6	80.0	2104.8	26.3[i]	3.4
1.8% Pt/SiO_2	2.0	68.3	1455.1	21.3[i]	3.2
2.2% Pt/SiO_2	2.0	84.9	2106.1	24.8[i]	3.3

[a] Average crystallite size determined from H chemisorption (Ref. (*4*)).
[b] Average of two runs.
[c] Physical mixture of Pt powder and SiO_2.
[d] Calcined in 20% O_2 at 623K for 1 h.
[e] Sintered in 20% O_2 at 673 K for ½h.
[f] Sintered in 36% O_2 at 773 K for 12 h.
[g] Sintered in 20% O_2 at 673 K for 2 h.
[h] Calcined in 20% O_2 at 573 K for 1 h.
[i] One run only.

Mills *et al.* for SiO_2-supported Pt (*7*). Contamination is presumed to be the cause of the latter values which are far lower than any other reported Q_{ad} value. A value of 50 kcal/mol O_2 was obtained on a single highly dispersed Pt/η-Al_2O_3 sample, which is consistent with the value in Ref. (*5*) and is in especially good agreement with the Pt/SiO_2 samples prepared from Pt tris-ethylene. Our results indicate that if lower oxygen coverages do occur on very small Pt particles compared to bulk Pt surfaces, a weaker O–Pt bond is not the reason.

These catalysts behaved consistently during the H_2 titration reaction. The UHP Pt powder gave a titration ratio (H_{titr}/O_{ad}) of 3.0 ± 0.4, which is that originally proposed by Benson and Boudart (*9*) and very close to that measured on a Pt black which contained residual potassium (*12*, *13*), and for the twelve Pt/SiO_2 catalysts, the average ratio was also 3.0 (± 0.5). The entire family of

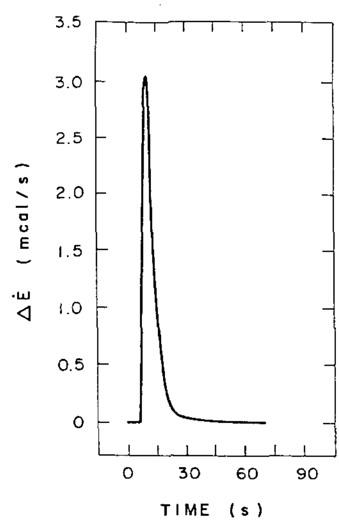

FIG. 1. Energy change, ΔE, measured at 300 K during the H_2 titration of chemisorbed oxygen on 0.7% Pt/SiO_2 (Sample II, 22.7 mg).

Pt/SiO_2 catalysts gave an average titration enthalpy change (with standard deviation) of $\Delta H_{\text{titr}} = -26.7 \pm 4.2$ kcal/mol H_2, while if only the samples prepared with the Davison 57 silica and typical Pt salts are considered, a similar value of $\Delta H_{\text{titr}} = -27.7 \pm 4.6$ kcal/mol H_2 is obtained for the exotherm. For the Pt powder, the average value is -24.5 ± 3.5 kcal/mol. For the titration reaction, a ΔH_{titr} value of -54 kcal/mol H_2 has been reported for a Pt/Al_2O_3 catalyst (*5*), whereas values between -17 and -22 kcal/mol H_2 have been reported for SiO_2-supported Pt (*7*).

The question of complete water desorption during the titration reaction has been discussed by O'Rear *et al.* (*13*), and all evidence indicates that it indeed desorbs from the Pt surface at 300 K. The heat of adsorption for H_2O on Pt (110) of 11 kcal/mol measured recently by Fusy and Ducros (*28*) would be in agreement with previous work demonstrating the desorption of water from Pt at temperatures near 300 K. Based upon the thermodynamic values reported here for O_2 adsorption and the titration reaction as well as the comparable values for H_2 adsorption (from Ref. (*4*)), a thermodynamic cycle can be proposed for both the SiO_2-supported Pt and the unsupported Pt. The following, with Pt_s representing a surface Pt atom, would apply for the supported Pt:

$$Pt_s{-}H \rightleftharpoons Pt_s + \tfrac{1}{2}H_{2(g)} \tag{1}$$

$$Pt_s + \tfrac{1}{2}O_{2(g)} \rightleftharpoons Pt_s{-}O \tag{2}$$

$$Pt_s{-}O + \tfrac{3}{2}H_{2(g)} \rightleftharpoons Pt_s{-}H + H_2O_{(ad)} \tag{3}$$

$$\underline{H_2O_{(g)} \rightleftharpoons H_{2(g)} + \tfrac{1}{2}O_{2(g)}} \tag{4}$$

$$H_2O_{(g)} \rightleftharpoons H_2O_{(ad)} \tag{5}$$

Thus an estimate for the heat of adsorption of water on SiO_2 can be obtained from the sum of the enthalpy changes in steps (1)

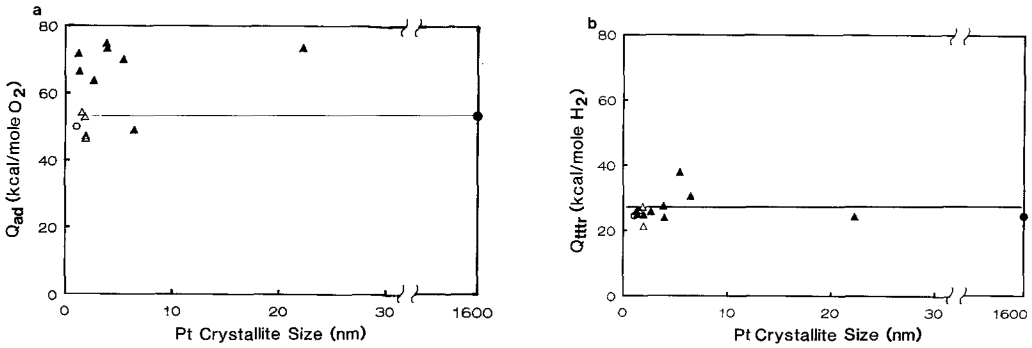

FIG. 2. (a) Integral heats of adsorption, Q_{ad}, for O_2 on Pt at 300 K; (b) enthalpy change for the titration of chemisorbed oxygen on Pt by dihydrogen at 300 K ($Q = -\Delta H$): Pt powder—● (average value), Pt/SiO_2 (inorganic precursor)—▲, Pt/SiO_2 (Pt trisethylene precursor)—△, Pt/η-Al_2O_3—○.

TABLE 3

Literature Values of Heats of Adsorption of O_2 on Pt

Pt	Adsorbed state	Q_{ad}	Method[a]	Ref.
Film		67–72	CAL	(*18*)
Filament		58	TPD	(*19*)
Filament	β_4	54	TPD	(*20*)
	β_2	39	TPD	(*20*)
100 (5 × 20)	β_1	46.0	TPD	(*21*)
	β_2	38.6	TPD	
Polycrystalline	β	40	TPD	(*22*)
	α	35	TPD	
(100)	β_1	44.7	TPD	(*23*)
	β_2	62.1	TPD	
	β_3	69.3	TPD	
(100)		28	TPD	(*24*)
(111)		45	TPD	(*25*)
(100)		38	TPD	(*26*)
Polycrystalline		44	TPD	(*27*)
film		38		
Pt/Al_2O_3		58[b]	CAL	(*5*)
Pt/Al_2O_3		60–67	CAL	(*6*)
Pt/SiO_2		6–9[c]	CAL	(*7*)

[a] Calorimetry—CAL; temperature-programmed desorption—TPD.

[b] Integral value at half-monolayer coverage.

[c] Integral value at monolayer coverage.

through (4), i.e., using the convention $Q = -\Delta H$, then $Q_{\mathrm{ad,H_2O}} = -\frac{1}{2}Q_{\mathrm{ad,H_2}} + \frac{1}{2}Q_{\mathrm{ad,O_2}} + \frac{3}{2}Q_{\mathrm{titr}} - Q_{\mathrm{form,H_2O}}$. Using the average values of 13.8, 67.9, and 27.7 kcal/mol for steps (1)–(3), respectively, and a value of $Q_{\mathrm{form,H_2O}} = 57.8$ kcal/mol, a value of $Q_{\mathrm{ad,H_2O}} = 11$ kcal/mol is obtained for water on the Davison 57 silica. This value is near that for the heat of liquefaction of H_2O (10.5 kcal/mol), as expected for silica (*29*), it is extremely close to the initial value of 10.5 kcal/mol reported by Pope for water on silicalite after heating to 820 K in air (*30*), and it is very consistent with the Q_{ad} values of 10 and 15 kcal/mol reported by Shen and Klier for P-doped silica after heating in air at 1073 and 923 K, respectively (*31*). Consequently, the performance of our calorimeter appears to be quite consistent. Basset *et al.* have reported a value of 18 kcal/mol for H_2O adsorbed on Al_2O_3 using a similar procedure (*5*); however, this value is less than that of 25 kcal/mol reported by Fubini *et al.* for the initial heat of adsorption of H_2O on η-Al_2O_3 at 298 K (*32*). For unsupported Pt no readsorption will occur in the catalyst bed and step (*3*) will change to $\mathrm{Pt_s - O + \frac{3}{2}H_{2(g)} \rightleftharpoons Pt_s - H + H_2O_{(g)}}$; thus the overall reaction should be thermoneutral. Placing the comparable average values of 13.6, 52.6, and 24.5 kcal/mol for steps (1)–(3) on the Pt powder gives a value of −1.5 kcal/mol, which may be considered zero within the uncertainty of these measurements. The consistency of these two calculations indicates that the estimate of Q_{ad} for H_2O on silica should be reasonable, and it adds further support to the assumption that water desorbs completely from Pt during the titration reaction and allows monolayer coverage of hydrogen equal to that on a clean Pt surface (*9*, *12*, *13*).

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