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THERMODYNAMICS OF REDUCTION AND OXIDATION REACTIONS ON OXIDIZED OR REDUCED Pt SUPPORTED ON γ-Al_2O_3

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The integral enthalpies of H_2 or O_2 reactions with oxidized or reduced Pt supported on γ-Al_2O_3 have been measured in a dual calorimeter at 60 ° C. These enthalpies were calculated assuming the formation of Pt_x^sO and Pt^sH surface groups and using accepted values of heat of H_2 and O_2 chemisorption on bare polycrystalline Pt. The calculated and measured reaction enthalpies agree under the following conditions: 1) Pt^sO and Pt_2^sO surface stoichiometries are acceptable ($1 \leqslant x \leqslant 2$) whereas Pt^sO_2 must be rejected ($x = 0.5$); 2) the water formed in the reduction or oxidation process must be dissociatively chemisorbed on the γ-Al_2O_3 surface; 3) the spiltover hydrogen is atomic and its enthalpy of combination with surface electron deficient site is about -10 kcal/g atom.

The significance of dispersion measurements is discussed in relation with hydrogen spillover. Neglecting spillover in reduction at 60 ° C leads to unrealistic values of dispersion.

1. Introduction

Although the hydrogen spillover processes occurring on insulator surfaces have been widely studied [1–3], the thermodynamics aspect has received much less attention. The heats of chemisorption of H_2 and O_2 on polycrystalline platinum have been reviewed by Toyoshima and Somorjai [4]. Let us define $\Delta\overline{H}_1$ and $\Delta\overline{H}_2$ as half the heats of chemisorption of O_2 and H_2 per mole, respectively,

$$\left.\begin{aligned}\Delta\overline{H}_1 &= \overline{H}(Pt_x^sO) - \overline{H}(Pt_x^s)\\ \Delta\overline{H}_2 &= \overline{H}(Pt^sH) - \overline{H}(Pt^s)\end{aligned}\right\} \tag{1}$$

The quoted values of heat of chemisorption per mole O_2 are between 39 and 67 kcal mol^{-1} which bring $\Delta\overline{H}_1$ in the order of -26 kcal. For H_2 the quoted values are between 8 and 21 kcal mol^{-1}, thus $\Delta\overline{H}_2$ in eq. (1) is in the order of -7 kcal. Vannice and coworkers [5] found integral heats of chemisorption on supported platinum in the range 13.5 ± 2.0 kcal mol^{-1}.

In this work we will report on the heats of reactions occurring on γ-alumina coated with 2% w/w Pt. First, we shall consider the oxidation of the prereduced and outgassed catalyst. Let n_s be the number of platinum atoms on the surface of the platinum particles. *By definition* n_s is the number of surface atoms forming $\mathrm{Pt^sH}$ surface groups at full coverage. As discussed later x in $(\mathrm{Pt}_x\mathrm{O})$ can be smaller or larger than 1. Let us call x_H the fraction of surface sites which remain $\mathrm{Pt^sH}$ after outgassing. The oxidation reaction is

$$n(\mathrm{O_2}) + n_s x_H(\mathrm{Pt^sH}) + n_s(1 - x_H)\mathrm{Pt^s} \rightarrow \frac{1}{x} n_s(\mathrm{Pt}_x^s\mathrm{O}) + \tfrac{1}{2} n_s x_H(\mathrm{H_2O}) \qquad (2)$$

with the stoichiometric requirement

$$n(\mathrm{O_2}) = \frac{1}{x} 0.5 n_s + 0.25 n_s x_H \qquad (3)$$

x_H being between 0 and 1.

The water produced in reaction (2) can escape as water vapor or it may be dissociatively chemisorbed on the alumina surface in reacting with a surface lattice oxygen $\mathrm{O_L^s}$ to form a surface OH group, or $\mathrm{OH_L^s}$

$$\mathrm{O_L^s} + \mathrm{H_2O} \rightarrow 2\mathrm{OH_L^s} + \Delta \bar{H}_d. \qquad (4)$$

Therefore, the measured heat of oxidation ΔH_o is

$$\Delta H_o = n_s x_H \Delta \bar{H}_2 + \frac{n_s}{x} \Delta \bar{H}_1 + \tfrac{1}{2} n_s x_H \Delta \bar{H}_d. \qquad (5)$$

If dissociative chemisorption of water does not occur, $\Delta \bar{H}_d$ must be replaced in eq. (5) by the enthalpy of gaseous water, $\bar{H}(\mathrm{H_2O_g}) = -57.8$ kcal. As shown later, $\Delta \bar{H}_d$ is about -15 kcal. The observed $\Delta \bar{H}_o = \Delta H_o / n\,(\mathrm{O_2})$ will be compared to the calculated $\Delta \bar{H}_o$ (eq. (5)) using either $\Delta \bar{H}_d$ or $\bar{H}(\mathrm{H_2O_g})$. In addition, from eq. (3) follow

$$n_s = 4n(\mathrm{O_2}) \Big/ \left(\frac{2}{x} + x_H\right) \qquad (6)$$

and the dispersion of the platinum $D_o = n_s/n_t$, with respect to oxygen; n_t is the total number of Pt atoms in the sample. D_o can be compared for arbitrary values of $0 \leqslant x_H \leqslant 1$ with the dispersion measured according to the standard procedure recalled later [6]. Note that we neglect oxygen spillover because of the high energy content of the $\mathrm{Pt}_x^s\mathrm{O}$ bond, which makes the dissociation of $\mathrm{Pt}_x^s\mathrm{O}$ into $\mathrm{Pt^s}$ and atomic oxygen unlikely.

Under outgassing the catalyst after oxidation, an unknown $(1 - x_o)$ fraction of the $\mathrm{Pt}_x^s\mathrm{O}$ groups is lost. Thereafter, upon exposure to $\mathrm{H_2}$, the following reaction can be postulated

$$n(\mathrm{H_2}) + \frac{1}{x} n_s x_o(\mathrm{Pt}_x^s\mathrm{O}) + n_s(1 - x_o)(\mathrm{Pt^s}) \rightarrow n_s(\mathrm{Pt^sH}) + \frac{1}{x} n_s x_o(\mathrm{H_2O}) + n(\mathrm{H^s}) \qquad (7)$$

where $\mathrm{H^s}$ represents the spiltover hydrogen. By contrast with the oxidation, we do not neglect hydrogen spillover because breaking a Pt^sH bond is much easier than breaking a Pt^sO bond. The stoichiometry requires that

$$n(H_2) = 0.5n_s + \frac{1}{x} n_s x_o + 0.5n \tag{8}$$

where x_o is between 0 and 1. Again, H_2O produced in reaction (7) may either escape in the gas phase or be chemisorbed, as shown in reaction (4). The spiltover hydrogen may react with an electron deficient site L on the alumina surface according to reaction (9)

$$L + H^s \rightarrow LH^s + \Delta \overline{H}_3. \tag{9}$$

The measured $\Delta \overline{H}_R = \Delta H_R / n(H_2)$ is obtained by calculating

$$\Delta H_R = \frac{1}{x} n_s x_o \Delta \overline{H}_d - \frac{1}{x} n_s x_o \Delta \overline{H}_1 + n_s \Delta \overline{H}_2 + n \Delta \overline{H}_3 \tag{10}$$

if spiltover hydrogen is atomic hydrogen H·. In that case the dissociation is called homolytic: $H_2 \rightarrow 2H\cdot$. By contrast heterolytic dissociation, $H_2 \rightarrow H^+ + H^-$, would yield protonic hydrogen which could combine with an alumina lattice oxygen O_L^{2-} in forming an OH_L group. This reaction which must not be confused with water chemisorption will be discussed later. If the comparison between experimental and calculated ΔH_o indicates that reaction (4) is likely, $\Delta \overline{H}_d$ will also be used in eq. (10). Otherwise $\Delta \overline{H}_d$ is replaced by $\overline{H}(H_2O_g)$. The observed $\Delta \overline{H}_R = \Delta H_R / n(H_2)$ will be compared to the calculated $\Delta \overline{H}_R$, using the same values of $\Delta \overline{H}_1$ and $\Delta \overline{H}_2$ as in eq. (5) and from this comparison $\Delta \overline{H}_3$ will be calculated for acceptable values of x_H and x_o. Some information on the nature of electron deficient site L may, hopefully, be obtained from $\Delta \overline{H}_3$.

Note that n, the number of spiltover H^s, is a function of both x_H (through n_s, eq. (3)) and x_o. It is implicitly assumed that O_2 does not react with LH, otherwise ΔH_o in the second and further oxidation step should be larger than ΔH_o measured in the first cycle. This is not observed as shown later. All reactions and outgassing steps were carried out at 60 °C in the calorimetric system used for this study. At this low outgassing temperature x_o should be one or slightly smaller than 1 while x_H should be smaller than x_o because of the large difference in the (Pt_x^sO) and (Pt^sH) bond energy.

For reasons explained hereafter, the dissociation of H_2 onto Pt^s is probably homolytic ($H_2 \rightarrow 2H\cdot$). Hence, the possibility that two atomic hydrogens recombine onto the surface of γ-Al_2O_3, exists. In that event, according to eq. (8), $n(H_2)$ would be $(0.5n_s + (1/x)n_s x_o)$. As shown by the analysis of the experimental data, recombination is unlikely, the surface concentration in spiltover hydrogen being probably too low.

2. Nature of the spiltover hydrogen

The following experiment will show that the molecular hydrogen dissociation is most probably homolytic. Suppose that $P\%$ of Pt coated alumina is intimately mixed with (1 − P%) (w/w) of a transition metal oxide (OX), able to intercalate atomic hydrogen. The heat of intercalation of H^s into OX provides an additional driving force, scavenging to some extent the spiltover hydrogen. Moreover, the enthalpy of the reaction of the formation of the hydrogen bronze $H_yVMoO_{5.5}$ is −30.5 kcal/mol H_2, when $OX \equiv VMoO_{5.5}$ is coated with 1% Pt [7]. Through this direct spillover process y is ≈ 3. It may be anticipated that in the mixture y will not reach the maximum loading obtained when OX is coated with Pt. Indeed, the specific surface area of the γ-Al_2O_3 being 200 m^2/g, and that of the transition metal oxide being 12 m^2/g, the fraction of Pt, on the Pt loaded Al_2O_3, in direct contact with OX is small ($\leqslant 2\%$) and most of the intercalated hydrogen (per g OX) comes from the hydrogen spilling over on the large γ-Al_2O_3 surface area. A fraction of H^s will be trapped as LH^s and the efficiency of the overall system $(1 - P)OX + P(Pt, Al_2O_3)$ may be expected to be low when compared to the system where the platinum particles are directly supported on OX. Although this aspect is not central to the aim of this paper, the evidence of what can be called the indirect spillover process is evidenced in fig. 1, where the bottom solid line shows the hydrogen uptake (as H atom) by a 2% Pt/γ-Al_2O_3, oxidized in air and outgassed overnight at 60 °C. For the specified γ-Al_2O_3 used in this work the

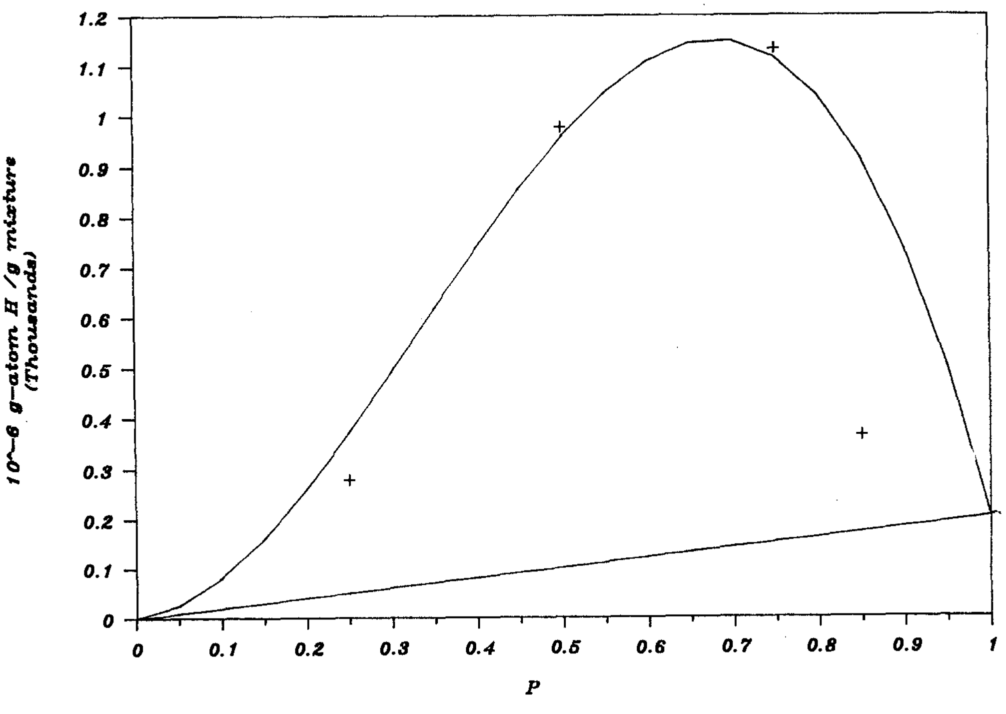

Fig. 1. Dots: H uptake (10^{-6} g atom/g) by a mixture of P (w/w) 2% Pt/γ-Al_2O_3 and $(1 - P)$ (w/w) $VMoO_{5.5}$. a) Bottom solid line: uptake by the 2% Pt/γ-Al_2O_3 alone. b) Top solid line: empirical equation (11).

maximum uptake for $P = 1$ is $0.204 * 10^{-3}$ g atom H/g Al_2O_3. The dots show the measured uptake by the mixture of P (w/w) (Pt, Al_2O_3) and $(1 - P)$ (w/w) OX.

Since a reduction of the transition metal(s) occurs in the bronze formation as has been evidenced by XPS studies [8,9], the spiltover hydrogen must be atomic and the H_2 dissociation should be homolytic on platinum supported on alumina. The top solid line in fig. 1 represents the empirical equation

$$2n(H_2) * 10^3 \text{ g atom H/g mixture} = 0.685\, P^2(1 - P) + 0.204P. \tag{11}$$

The reason why P is at the power of 2 is not understood so far. The sole purpose of fig. 1 is to show that, if a strong atomic hydrogen acceptor is present, a fraction of n, in eq. (8), escapes the fate shown in eq. (9).

3. Experimental

Material

γ-Al_2O_3 (characterized by its XRD pattern) was impregnated with H_2PtCl_6 and calcined for 2 hr in air at 400 °C. The Pt content was 2% w/w. The catalyst was reduced in a flow of H_2 at 450 °C for 4 hr and then re-exposed to ambient atmosphere for more than one week.

Procedure and Results

The dual calorimeter has been described previously [7]. One of the Seebeck envelopes was filled with γ-Al_2O_3 and the other one with 2% Pt/γ-Al_2O_3. Each envelope contained approximately 1 g of material. After transfer inside the calorimeter the oxidized Pt catalyst was maintained into contact with ~ 200 Torr H_2 at 60 °C, the gas circulating within the system for about 12 hr. The system

Table 1
Experimental results: H_2 and O_2 uptakes per mol Al_2O_3 ($M = 102$ g) and integral heats of oxidation ($\Delta \overline{H}_o$) and reduction ($\Delta \overline{H}_R$)

$n(O_2)$ (10^{-3} mol)	$-\Delta \overline{H}_o$ (kcal/mol O_2)	$n(H_2)$ (10^{-3} mol)	$-\Delta \overline{H}_R$ (kcal/mol H_2)
Exp.1: prereduction at 60 °C			
2.9	na	10.8	9.5
2.2	na	12.1	5.3
Exp.2: prereduction at 60 °C			
3.2	38.4	11.0	6.8
2.7	40.0	9.2	6.4
3.1	29.5	9.4	5.9
3.4	30.8	9.2	9.1
2.7	31.0	6.8	6.4
1.9	35.3	6.5	7.6

was then outgassed overnight and ~ 50 Torr O_2 were circulated for about 12 hr. Thereafter, the system was outgassed again for 12 hr and H_2 was circulated for 12 h. The temperature was always maintained at 60 ° C. This set of oxidation and reduction was repeated over and over again while ΔH_o and ΔH_R were recorded (table 1).

The average hydrogen uptake, $n(H_2)$, was $(102 \pm 20) * 10^{-6}$ mol/g, while the average O_2 uptake was $n(O_2) = (28 \pm 7) * 10^{-6}$ mol/g. The average ΔH_R and ΔH_o were -0.72 ± 0.12 cal/g and -0.96 ± 0.1 cal/g, respectively. The relatively large experimental errors are due to the small amount of Pt atoms in the system, the total number, n_t, being $102 * 10^{-6}$ g atom Pt/g γ-Al_2O_3.

The determination of the Pt dispersion using the standard procedure [6] was carried out in a BET type all-glass instrument. Two chemisorption isotherms at 27 ° C are shown in fig. 2. From the intercept of the straight part of the isotherm, D_{st} was $40 \pm 2\%$. The standard procedure for measuring dispersion consists of three steps. First, the catalyst is reduced by hydrogen at a temperature $\geqslant 450$ ° C, and x_o is assumed to be zero. Then, the sample is outgassed at $\geqslant 450$ ° C, which should bring the residual fraction of Pt^sH, namely x_H, to zero. Finally, the chemisorption isotherm of H_2 is measured at room temperature and the molecular hydrogen uptake at the intercept, is made equal to $2n_s$. In this procedure, the spiltover hydrogen is neglected.

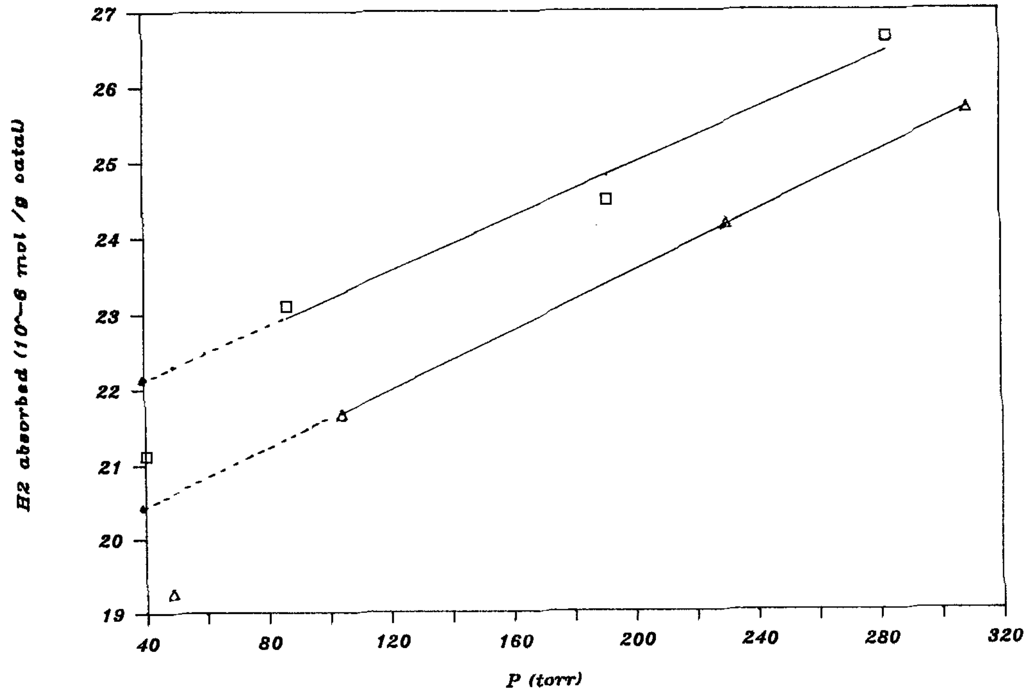

Fig. 2. Duplicated H_2 adsorption isotherms (25 ° C) on 2% Pt/γ-Al_2O_3, pretreated according to the standard procedure [6]. The Pt dispersion D_{st} is $40 \pm 2\%$.

4. Discussion

$\Delta\overline{H}_d$ defined by eq. (4) plays an important role in the calculation of ΔH_o (eq. (5)) and $\Delta\overline{H}_R$ (eq. (10)). It has been measured [10] for the (endothermic) enthalpy variation associated with the dehydroxylation of crystalline aluminum hydroxides

$$2\ OH_L \rightarrow H_2O_g + O_L - \Delta\overline{H}_d \tag{13}$$

occurring in the temperature range between 300 and 400 °C and found to be about 15 ± 1 kcal for various aluminum hydroxides. With respect to the experimental uncertainty, the correction which should be applied in order to obtain the corresponding value at standard temperature is negligible.

The first step in the interpretation of the experimental results is in calculating n_s from $n(O_2)$ and various values of x_H and x equal to 2, 1 or 0.5 corresponding to Pt^s_2O, Pt^s, or Pt^sO_2, respectively. The second step is in calculating ΔH_o from eq. (5) and in comparing the calculated and experimental $\Delta\overline{H}_o$, as x_H decreases from 1 to 0. In using $\Delta\overline{H}_1$ and $\Delta\overline{H}_2$ in the range of possible values recalled in the introduction, the first striking evidence is that we have to consider the dissociative adsorption of water shown by eq. (4). Substituting $\Delta\overline{H}_d$ by $\overline{H}(H_2O_g)$ leads

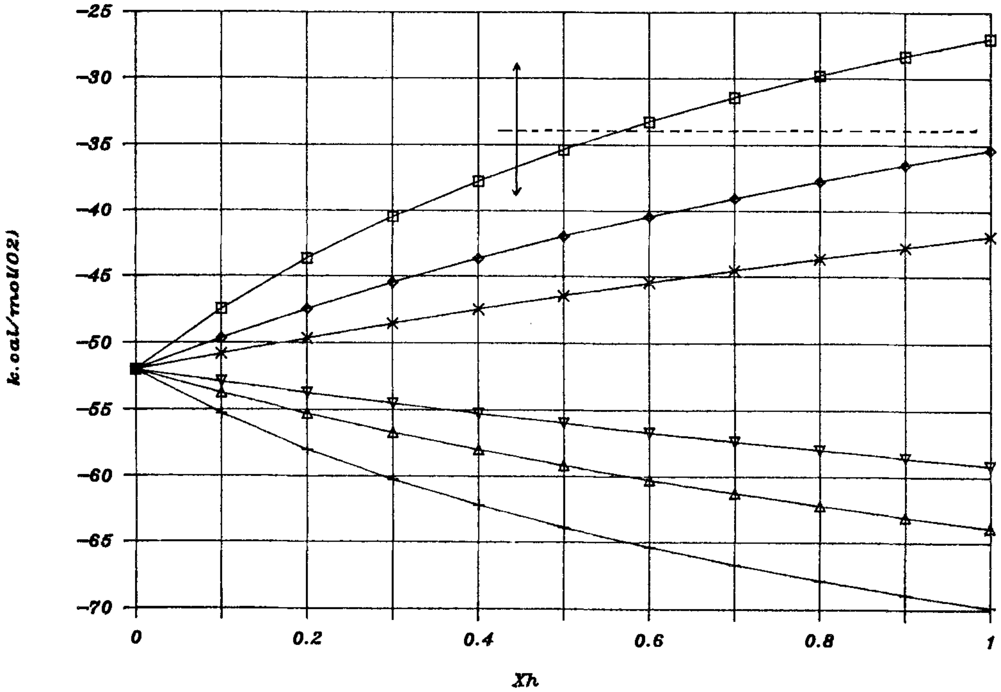

Fig. 3. Dashed line: observed $\Delta\overline{H}_o$; arrow: error bar. Symbols: calculated $\Delta\overline{H}_o$ for three Pt^s_xO stoichiometries. $x = 2$: □, with surface hydroxylation; +, with formation of H_2O_g. $x = 1$: ◇, with surface hydroxylation; △, with formation of H_2O_g. $x = 0.5$: ×, with surface hydroxylation; ▽, with formation of H_2O_g.

consistently to too low $\Delta \overline{H}_o = \Delta H_o / n(O_2)$ as shown in fig. 3. The calculated $\Delta \overline{H}_o$ is obtained in using $\Delta \overline{H}_1 = -26$ kcal and $\Delta \overline{H}_2 = -7$ kcal, the corresponding heats of O_2 and H_2 chemisorption being 52 kcal mol^{-1} and 14 kcal mol^{-1}, respectively. $\Delta \overline{H}_1$ and $\Delta \overline{H}_2$ could be within ±10% of the chosen values and still $\Delta \overline{H}_o$ would be within the margin of error, but dissociative chemisorption of water on $Pt/\gamma\text{-}Al_2O_3$ is mandatory to fit the experimental results.

In addition, fig. 3 shows: (i) that $x = 0.5$ leads consistently to too low $\Delta \overline{H}_o$ and (ii) that $x_H \geqslant 0.4$. Thus, on the basis of the oxidation enthalpy the subsurface structure Pt^sO_2 must be rejected under the experimental conditions used in this work.

The heat of physisorption of water by alumina has been neglected for three reasons, namely (i) at the working temperature (60 ° C) the gas circulation within the calorimeters should remove the water from the surface into the gaseous phase; (ii) the heat effects in both calorimeters (one containing the Pt coated alumina and the other, the uncoated alumina) cancel; and (iii) the circulation device contains a liquid nitrogen trap.

The next step is in calculating $\Delta \overline{H}_R = \Delta H_R / n(H_2)$ through eq. (10) using the above $\Delta \overline{H}_1$, $\Delta \overline{H}_2$ and $\Delta \overline{H}_d$ and the values of n_s (eq. (6)) and n (eq. (8)) while $x_H < x_o$ and $x_H \geqslant 0.4$. These calculations are carried out for $x = 2$ and $x = 1$

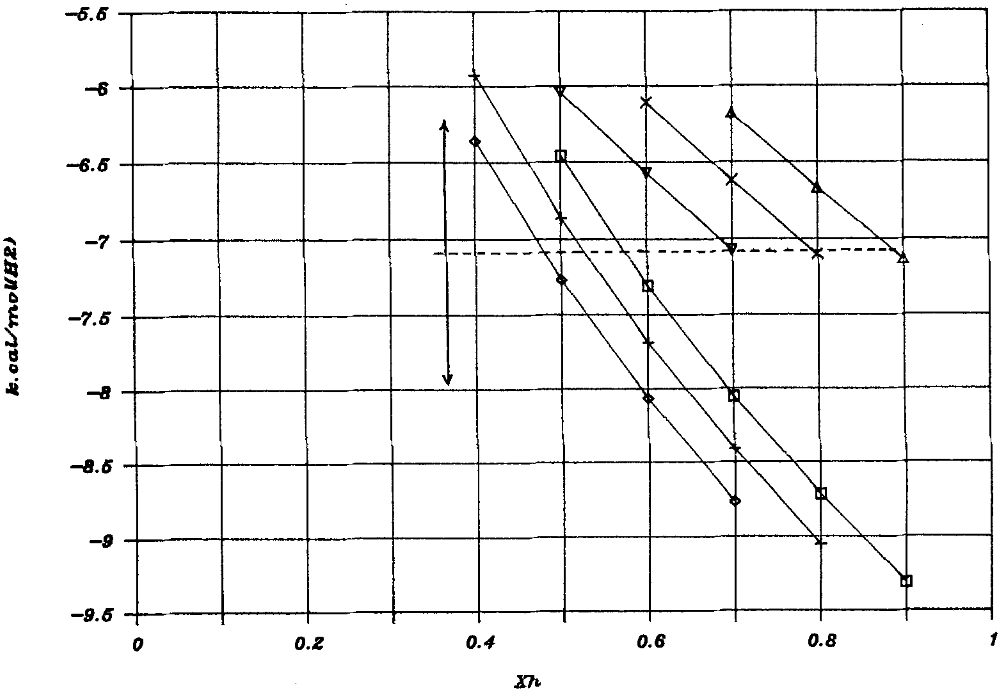

Fig. 4. Dashed line: observed $\Delta \overline{H}_o$; arrow: error bar. Symbols: calculated $\Delta \overline{H}_o$ for three Pt_x^sO stoichiometries. $x = 2$: □, $x_o = 1$; +, $x_o = 0.9$; ◇, $x_o = 0.8$ $x = 1$: △, $x_o = 1$; ×, $x_o = 0.9$; ▽, $x_o = 0.8$.

only, since $x = 0.5$ has been rejected. $\Delta \overline{H}_3$ has been varied between -5 kcal and -15 kcal. If $\Delta \overline{H}_3$ is -5 kcal or -15 kcal, the calculated $\Delta \overline{H}_R$ are significantly either too high or too low when compared to the observed $\Delta \overline{H}_R$. $\Delta \overline{H}_3 \approx -10 \pm 2.5$ kcal is an acceptable approximation as shown in fig. 4 where x_o has been maintained between the limits $0.8 \leqslant x_o \leqslant 1$. The values of $\Delta \overline{H}_R$ larger than -5.9 kcal mole^{-1} or smaller than -9.5 kcal mole^{-1} have been rejected as being outside the margin of experimental errors.

Figs. 3 and 4 seem to indicate that $x = 2$ is a better choice than $x = 1$, since for the latter the calculated values are consistently above (fig. 4) or below (fig. 3) the averaged observed $\Delta \overline{H}_R$. However, and in view of the uncertainties on $\Delta \overline{H}_1$ and $\Delta \overline{H}_2$, the measurement of $\Delta \overline{H}_R$ and $\Delta \overline{H}_o$ cannot unambigously indicate the Pt_xO stoichiometry, but for the fact that x must be between 1 and 2.

The Pt dispersions are calculated from the oxygen uptake, as shown in fig. 5. For matter of comparison, the Pt dispersion calculated from the hydrogen uptake by assuming either that $n > 0$ or that the amount of spiltover hydrogen is negligible are shown in fig. 5, also. In that case, the dispersion depends on x_o (eq. (8)). Neglecting n yields dispersions much higher than D_{st} while by taking n into account, the dispersions calculated from oxygen uptake (D_o) are very close to D_{st}, when $x = 1$ and higher than D_{st} for $x = 2$.

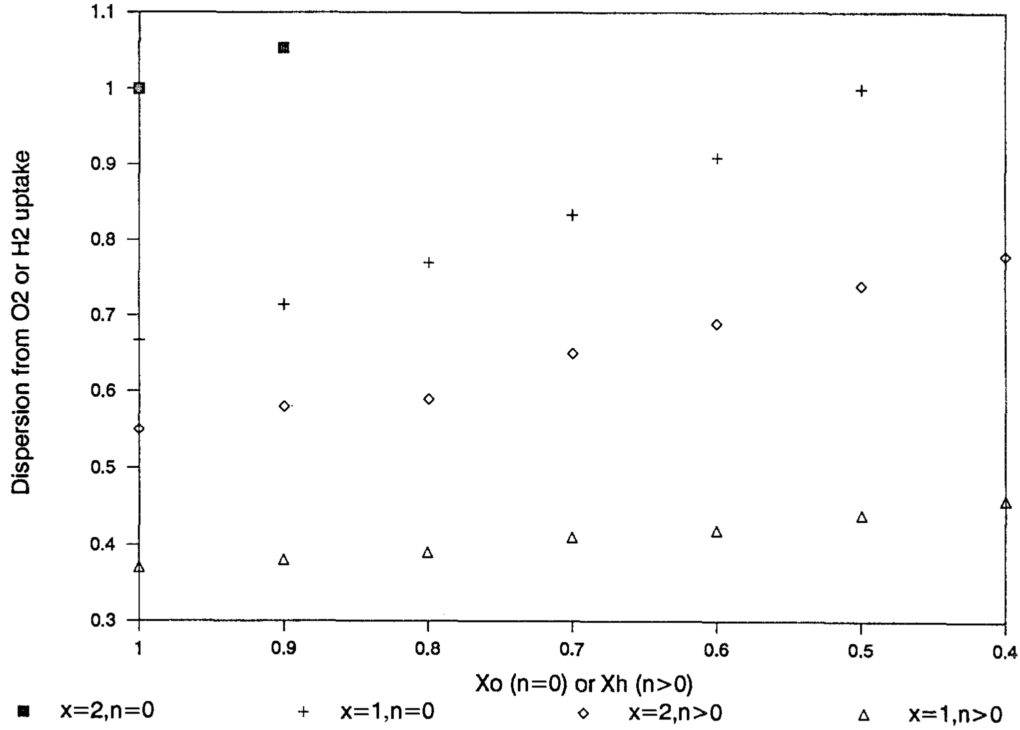

Fig. 5. Comparison between the Pt dispersion obtained by assuming either that there is no hydrogen spillover ($n = 0$) for $x = 2$: □; $x = 1$: +, or that spillover cannot be neglected ($n > 0$) for $x = 2$: ◇ or $x = 1$: △. For $n > 0$, the dispersion is obtained from oxygen uptake D_o, eq. (6). D_{st} is 0.4 ± 0.02.

Table 2
Amount of spiltover hydrogen: $n(H^s)(10^6$ g atom)/g γ-Al_2O_3 and corresponding $n(H^s)/n_s$ between parentheses. Top: $x = 2$; Bottom: $x = 1$.

x_o	x_H						
	1	0.9	0.8	0.7	0.6	0.5	0.4
1	–	86 (1.5)	79 (1.3)	72 (1.1)	64 (0.9)	54 (0.7)	44 (0.5)
0.9	–	–	85 (1.4)	78 (1.2)	71 (1.0)	62 (0.8)	52 (0.6)
0.8	–	–	–	85 (1.3)	78 (1.1)	69 (0.9)	60 (0.7)

x_o	x_H						
	1	0.9	0.8	0.7	0.6	0.5	0.4
1	–	88 (2.3)	84 (2.1)	79 (1.9)	74 (1.7)	69 (1.6)	64 (1.4)
0.9	–	–	92 (2.3)	87 (2.1)	83 (1.9)	78 (1.8)	73 (1.6)
0.8	–	–	–	96 (2.3)	92 (2.1)	87 (2.0)	82 (1.8)

The amount of spiltover hydrogen calculated in using eq. (8) as shown is in table 2. Assuming $x = 2$ yields $0.7 < n/n_s < 1.5$, while $1.8 < n/n_s < 2.3$ for $x = 1$, in the accepted ranges of x_o and x_H. Whatever the case, n is not negligible and the number of LH sites on the γ-Al_2O_3 surface is between 1.3 and $3 * 10^{13}/cm^2$.

On the basis of titration experiments carried out under conditions similar to those used in our calorimetric technique, Benson and Boudart [11] suggested Pt^sO and Pt^sH stoichiometries $(x = 1)$ for Pt black and supported platinum on η-Al_2O_3. Their results on Pt/η-Al_2O_3 are, in fact, very similar to ours, but they neglected the spiltover hydrogen. In the enthalpy balance expressed by eq. (10), neglecting n is the same as considering $\Delta H_3 = 0$. In this case $\Delta \overline{H}_R$ is positive for $x = 1$ and is about 5 kcal $mole^{-1}$ higher than the calculated ΔH_R in fig. 4 for $x = 2$. Variations of $\Delta \overline{H}_1$ and $\Delta \overline{H}_2$ within ±20% do not reconcile observed and measured $\Delta \overline{H}_R$ in neglecting spiltover hydrogen.

The pretreatment and adsorption temperatures, as well as the order in which the hydrogen and oxygen adsorption have been carried out, effect chemisorption, as already emphasized by Gruber [12] who showed that O_2 adsorption at 350 °C followed by outgassing at 500 °C and H_2 adsorption at 250 °C yielded a value $R = n(H_2)/n(O_2) = 2$ for highly dispersed Pt ($\sim$ 90%) and 0.7 for low dispersion ($\sim$ 30%). Using pulses of H_2 and O_2 at room temperature on a Pt/Al_2O_3 catalyst, Freel [13] consistently obtained Pt^sH and Pt^sO stoichiometries in agreement with quoted results by Wilson and Hall, who were using a static method. However, the spiltover hydrogen was neglected, also.

While the Pt^sH stoichiometry (at saturation) seems widely accepted, the surface oxygen stoichiometry appears to be more controversial. From works by Smith et al. [14], Gland et al. [15], Gland [16], and Niehus et al. [17] on Pt(111), the consensus seems to be that molecular adsorption predominates below 100 K, atomic adsorption predominates between 150 K and 500 K, whereas above 500 K subsurface oxide is formed. At low O_2 pressure (~ 6000 L) Niehus et al. [17] observed a Auger peak to peak ratio of about 0.5 for O_{510}/Pt_{230} and a 2X2 LEED structure, which was also observed by Gland et al. [15]. It is difficult, however, to decide from the experiments performed on unsupported Pt(111) at low pressure the surface stoichiometry of the Pt^s-oxygen environment for supported Pt at higher O_2 pressure.

The effect of decomposing the Pt salt onto the support by calcination and reduction at high temperature should not be neglected as well, as outlined by Lietz et al. [18] and Lieske et al. [19], especially when H_2PtCl_6 is the precursor. These authors suggested that chloride influences the sintering, the dispersion, and the metal redispersion in O_2 at temperatures between 300 and 600 ° C, because of the formation of $[Pt^{IV}O_xCl_y]$ complexes. On the basis of a band at 325 nm in the UV-VIS spectra, they suggested PtO_2 as being the surface species, but were unable to distinguish it from Pt_2O. Figueras et al. [20] have suggested that the band at 325 nm could be due to the formation of a molecular charge transfer complex between electron deficient Pt and acidic aluminum sites. Anyway, reduction at 500 ° C in H_2 destroys the $[Pt^{IV}O_xCl_y]$ surface complex.

At this point an important question has to be put forward. Thanks to the analysis of the thermodynamic data, we know that we cannot neglect the hydrogen spillover phenomenon in the system described here. On the other hand, the hydrogen uptake observed in the standard procedure for measuring D_{st} is $40.8*10^{-6}$ g atom/g γ-Al_2O_3, that is a number smaller than the amount of hydrogen spiltover estimated in table 2. Even if the high temperature prereduction and outgassing used in the standard procedure is likely to lower x_o to zero, canceling $(1/x)n_s x_o$ in eq. (8), still the $n(H_2)$ uptake observed at 60 ° C is larger than n_s obtained from D_{st}, whereas the same surface stoichiometry, namely Pt^sH is postulated. Hence, the following question arises. Do the high temperature pretreatment and outgassing kill the $\underline{L}$ sites able to trap $\underline{H}^s$ and to drive the hydrogen spillover? Indeed, since ΔH_3 is smaller than ΔH_2, suppressing the L sites suppresses this driving force. Perhaps, the water dissociative adsorption is a prerequisite for the formation of electron deficient sites, since the formation of the L electron deficient sites would be suppressed, if $x_o = 0$ after outgassing at high temperature. The nature of these sites is still unknown, but it should be noted that the hydroxylation of the surface is likely to change the coordination number of surface aluminum and to affect the electron transfer between the Al_2O_3 surface and the Pt particles evidenced by ESR measurements carried out by Hulzinga and Prins [21]. It is obvious that this question deserves further studies and, in particular, the system Pt/SiO_2 should be analyzed in the same way as the Pt/Al_2O_3 system.

In summary, the advantages of the thermodynamic study of the oxidation-reduction cycle carried out on supported platinum is in providing two additional equations (eq. (5) and (10)) which, combined with the measurement of the H_2 and O_2 uptakes, shed a new light on the reaction mechanisms. In addition, this study shows that the dissociation of H_2 on Pt coated γ-Al_2O_3 does not produce protonic hydrogen. Indeed, the enthalpy of formation of a hydroxyl group from H^+ and O_L^{2-} being about -113 kcal mol^{-1} on alumina [22], this reaction is ruled out by the thermodynamic data presented here, since the enthalpy associated with the trapping of the protonic species by this reaction would be 10 times larger than the calculated ($\Delta \bar{H}_3$) enthalpy of formation of the LH site. That the dissociation of H_2 is homolytic and, consequently, that spiltover hydrogen is atomic is well in line with the formation of hydrogen bronzes in an admixture of Pt/Al_2O_3 and of a transition metal oxide.

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