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Journal of Molecular Catalysis A: Chemical 188 (2002) 201–208

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Enthalpies of reduction–oxidation of alumina-supported platinum

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Received 1 February 2002; received in revised form 30 April 2002; accepted 15 May 2002

Abstract

A calorimetric technique is described for measuring the reaction enthalpies of reduction of PtO_x/Al_2O_3 with hydrogen and oxidation of Pt/Al_2O_3 with oxygen. The enthalpies of reduction–oxidation were determined at $T_{red} = 670$ and $T_{ox} = 770$ K for PtO_x/Al_2O_3 and Pt/Al_2O_3, respectively. The measurements revealed that the heat of reduction (ΔH_{red}) is relatively constant and has a value of -103 kJ $\pm$ 3 kJ (mol H_2)$^{-1}$ for various platinum oxides. The particle size of platinum metals, however, had a profound effect on the bulk oxide formed and heat of oxide formation (ΔH_f). The platinum oxide formed at 770 K was PtO_2 for $d < 2.0$ nm, but this became Pt_2O for $d > 4.0$ nm. The ΔH_f also varied with platinum oxide species from -190 kJ (mol O_2)$^{-1}$ for PtO_2 to -168 kJ (mol O_2)$^{-1}$ for Pt_2O. Based on a thermodynamic cycle, it was demonstrated that the consistency in ΔH_{red} for various platinum oxides was attributed to the variations of heat of adsorption of water ($\Delta H_{ad,H_2O}$) on alumina-supported platinum.

Keywords: Platinum; Heat of reduction; Heat of oxide formation; Calorimetry

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1. Introduction

Supported platinum catalysts have been currently used for oxidation, not only as a major component in the automotive exhaust catalyst, but also as a combustion catalyst in the total oxidation of hydrocarbons [1–4]. The following formation and breakage of Pt^s–O_x bonds on the surface of platinum are essential steps in these heterogeneous oxidation processes:

$$Pt^s + \tfrac{1}{2}xO_2 \rightarrow Pt^s - O_x \qquad (1)$$

$$Pt^s - O_x + RH \rightarrow Pt^s + CO_2 + H_2O \qquad (2)$$

where the superscript s and the subscript x denote the atoms exposed to the surface of platinum particles and the chemical stoichiometry of the adsorption, respectively.

The oxidation/reduction behavior of supported platinum crystallites has been widely studied in literature [5–17]. Variations in oxidations not only induced a change in their size distribution and morphology [5–8] but also generated platinum oxides of different stoichiometry [9–17]. However, the reaction enthalpies of reduction–oxidation for supported platinum catalysts have been scarcely studied. The heat of reduction (ΔH_{red}), reported in literature, varies from -85 to -130 kJ (mol H_2)$^{-1}$ [18]. The heat of oxide formation (ΔH_f) of powdered platinum oxide, reported

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PII: S1381-1169(02)00332-1

in literature, also varies from −134 to −222 kJ (mol $O_2)^{-1}$ [18–22].

In this paper, we employ a simultaneous thermogravimetry (TG)–differential scanning calorimetry (DSC) technique to measure the ΔH_{red} and ΔH_f of the nanometer ranged (<60 Å) platinum particles supported on alumina. Particular emphasis is placed on the variation in the extent of oxidation with the size effect of platinum particles on the ΔH_f values.

2. Experimental

2.1. Sample preparation

Platinum catalysts of various platinum loadings were prepared by impregnating γ-Al_2O_3 (Merck, surface area = 108 m^2/g) with different amounts of an aqueous H_2PtCl_4 solution. The obtained slurries were dried at 380 K overnight and then calcined at 770 K for 4 h before storing as testing samples. The platinum loading on these samples was determined by the atomic-emission technique with a Perkin-Elmer Sciex Elan 5000 ICP-MS instrument.

The dispersion (D, fraction of the exposed atoms) of platinum on these samples was volumetrically determined by chemisorption of hydrogen at 300 K. The average diameter, d (nm) of platinum was calculated by using the formula 1.1 (D) [23,24]. The second and third columns of Table 1 list the dispersions and particle sizes for the prepared samples, respectively.

2.2. Calorimetric measurement

The measurement of reaction enthalpies of reduction of PtO_x/Al_2O_3 with hydrogen and oxidation of Pt/Al_2O_3 with oxygen were pursued in a dual port Setaram TG–DSC calorimeter. This instrument permitted evacuation treatments to a vacuum pressure of 2×10^{-1} Torr as well as a simultaneous TG and DSC measurement in the temperature range between the ambient temperature, 280, and 970 K. A pure support was mounted in the reference port as a blank to cancel the potential changes in Δm (weight) and q (heat) caused by the support.

Each testing sample was purged with an Ar flow of 30 ml/min on raising the system temperature from the room temperature to 670 K at a rate of 10 K/min. After the temperature reached 670 K, 190 Torr hydrogen was introduced from auxiliary inlet into the Ar flow for 1 h to reduce the sample. A loss in sample weight and an evolution of heat during this reduction were simultaneously observed by the calorimeter. After the hydrogen reduction, the sample temperature was subsequently raised further to 720 K to desorb the adsorbed hydrogen. The reduced sample was raised to 770 K and then 190 Torr oxygen was introduced from the auxiliary inlet into the Ar flow for 1 h. The oxidation phenomena were examined by the calorimeter through a gain in weight as well as a simultaneous evolution of heat.

Table 1
Heat of reduction on PtO_x/Al_2O_3 at 670 K

Sample	Hydrogen chemisorption		Reduction of PtO_x	
	D	d (nm)	Oxide species[a]	$-\Delta H_{red}$ (kJ(mol $H_2)^{-1}$)
0.82% Pt	1.00	1.0	PtO_2	106
2.12% Pt	1.02	1.0	PtO_2	100
4.13% Pt	0.80	1.3	PtO_2	104
5.75% Pt	0.50	2.0	Pt_3O_4 (or mixture of PtO/PtO_2)[b]	102
			PtO	102
7.86% Pt	0.38	2.6	Pt_3O_4 (or mixture of PtO/PtO_2)[b]	108
			PtO	104
9.94% Pt	0.21	4.8	Pt_2O	100

[a] The reduced sample were further converted into platinum oxides by re-oxidized at 770 K with 1 h pulse of 190 Torr oxygen.

[b] Under 2 h pulse of 380 Torr oxygen.

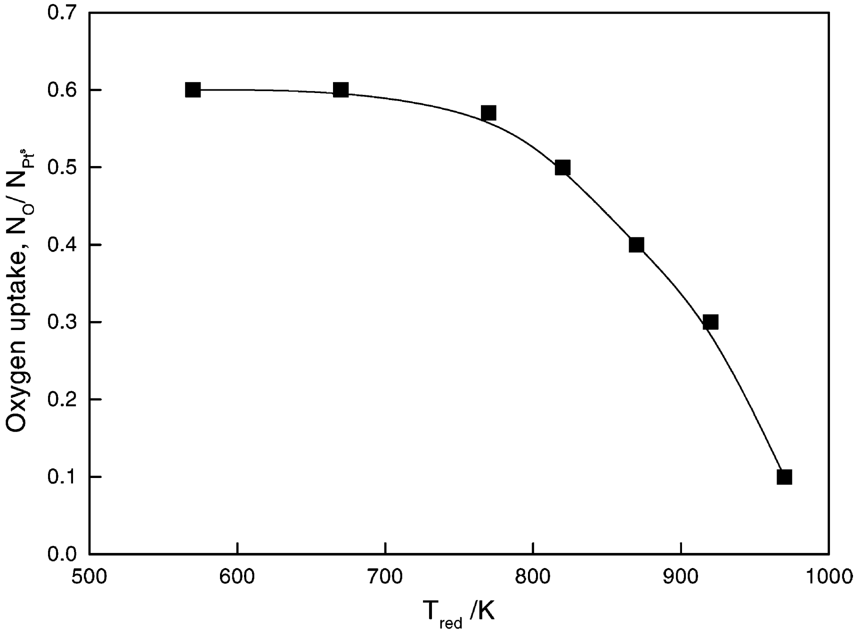

Fig. 1. The oxygen uptake of 4.13% Pt/Al_2O_3 sample at 300 K under various reduction temperatures.

3. Results and discussion

3.1. Reduction of PtO_x/Al_2O_3

Fig. 1 indicates the oxygen uptake (in terms N_O/N_{Pt^s}, where N_{Pt^s} denotes the number of platinum atoms exposed to surface) of 4.13% Pt/Al_2O_3 at 300 K under various reduction temperatures, T_{red}. When the samples were severely reduced with hydrogen at higher temperature, the oxygen uptake decreased gradually. The decrease in N_O/N_{Pt^s} ratio indicates the degree of sintering of platinum metal. In reduction temperature range between 570 and 670 K, the platinum atoms remain completely dispersed. As the temperature exceeds 820 K, the platinum particles can diffuse across the support to aggregate to form larger particles, which causes the N_O/N_{Pt^s} ratio decrease. Since the melting point of platinum is higher than that of palladium, according by the Taman temperature, the migration of platinum metal was not pronounced; the stability of platinum is higher than that of palladium for well-dispersed supported catalyst. However, the rate of sintering of metals on a support also depends on the volatility of metal oxide in oxidative atmosphere. The platinum oxide is more volatile [25–27] than palladium oxide, resulting in the higher rate of sintering. In order to avoid the sintering of platinum metals, we reduced samples at 670 K.

Each fresh sample includes both PtO_xCl_y and PtO_x species when calcined at 770 K. Fig. 2 represents the time profile of the fraction of reduction ($f = \Delta m_t/\Delta m$, where Δm_t and Δm denote the weight loss at a reduction time t and at the 3×10^3 s reduction time, respectively) of fresh (including both PtO_xCl_y and PtO_x species) and re-oxidized (only PtO_x species) samples during reduction at 670 K. The chemical reactions for the reduction of PtO_xCl_y and PtO_x with hydrogen can be represented by Eqs. (3) and (4), respectively.

$$PtO_xCl_y + (x + \tfrac{1}{2}y)H_2 \rightarrow Pt + xH_2O + yHCl \quad (3)$$

$$PtO_x + xH_2 \rightarrow Pt + xH_2O \quad (4)$$

It can be seen that the reduction of the re-oxidized sample is faster than that of the fresh sample. The chloride complex existing in the fresh sample may be removed slowly after a long time and therefore, the reduction is hindered. The decrease in the reduction rate

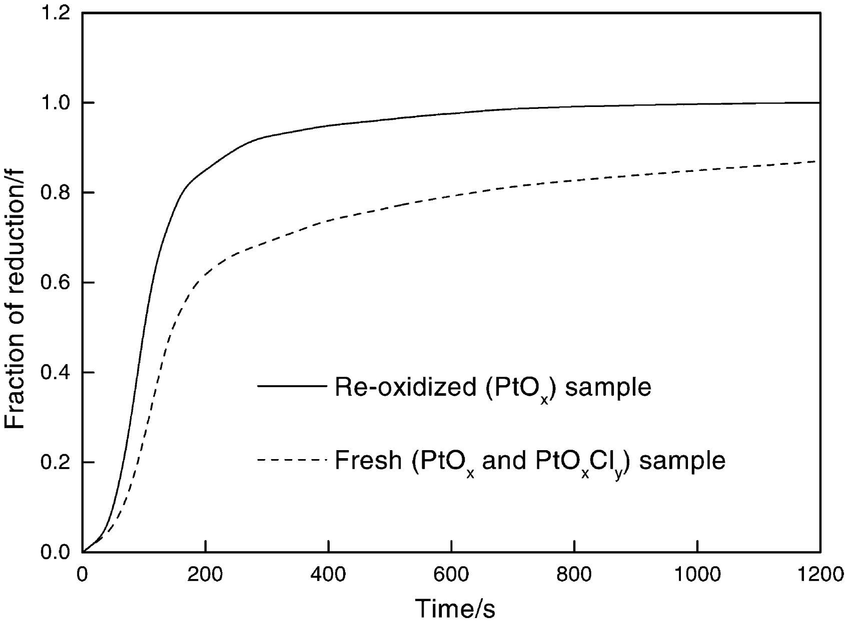

Fig. 2. Time profile for the fraction of reduction of fresh and re-oxidized samples during reduction at 670 K.

of the two samples beyond $f = 0.6$ could be attributed primarily to the increase in the inter-diffusion distance of the H_2O away from the surface through the voids, thereby increasing the significance of the role of mass transfer in the rate-controlling process. The diffusion rate of H_2O in the pores has a definite influence on the reduction rate. In the re-oxidized sample, the diffusion of H_2O can be considered to be relatively easier. This means that the chemical reaction would proceed inside the grains at the latter stages of the reduction.

In order to measure the heat of reduction (ΔH_{red}) of PtO_x/Al_2O_3 catalysts, the reduced fresh sample was converted into platinum oxide by re-oxidation with oxygen at 770 K in the calorimeter to remove the chloride species. Fig. 3 represents a time profile of TG–DSC measurement in the reduction of 34.8 mg 4.13% PtO_x/Al_2O_3 with hydrogen at 670 K. The measurement indicated that the reduction was an exothermic reaction accompanied with a loss in weight. The rate of reduction was fast at the initial stage, but decreased gradually with the reaction time. Table 1 lists the ΔH_{red} of PtO_x/Al_2O_3 at 670 K for the re-oxidized samples. The observed ΔH_{red} was relatively constant. The ΔH_{red} gave an average reduction enthalpy (with standard deviation) of $-103\,\text{kJ} \pm 3\,\text{kJ}$ $(\text{mol } H_2)^{-1}$ for various platinum oxide species and did not vary significantly with the particle size. The ΔH_{red} is closed to the results reported by Sen and Vannice [18] for titration of adsorbed oxygen on platinum powder ($-102\,\text{kJ} \pm 15\,\text{kJ}$ $(\text{mol } H_2)^{-1}$) and Pt/SiO_2 catalyst ($-112\,\text{kJ} \pm 18\,\text{kJ}$ $(\text{mol } H_2)^{-1}$).

3.2. Oxidation of Pt/Al_2O_3

In previous studies [14,28], it was suggested that the effect of the platinum oxidation was related with the temperature and the particle size of platinum. Oxidation of Pt/Al_2O_3 above 720 K achieves the maximum N_O/N_{Pt} ratio. The ratio in PtO_x approaches 2.0 (indicating a stoichiometry of PtO_2) for the highly dispersed samples ($D > 80\%$). Interestingly, the maximum ratio varied with the particle size of platinum, oxygen pressure and time of oxidation. Table 2 lists the oxidation of Pt/Al_2O_3 under 770 K under various conditions. The N_O/N_{Pt} ratio varied from 2.04 (PtO_2 with $d < 1.5$ nm) to 0.51 (Pt_2O with $d > 4.5$ nm). Interestingly, a similar size-dependent result has been suggested in literature [29] for platinum oxide when supported platinum is oxidized with oxygen. For Pd/Al_2O_3, a dioxide (PdO_2) was formed

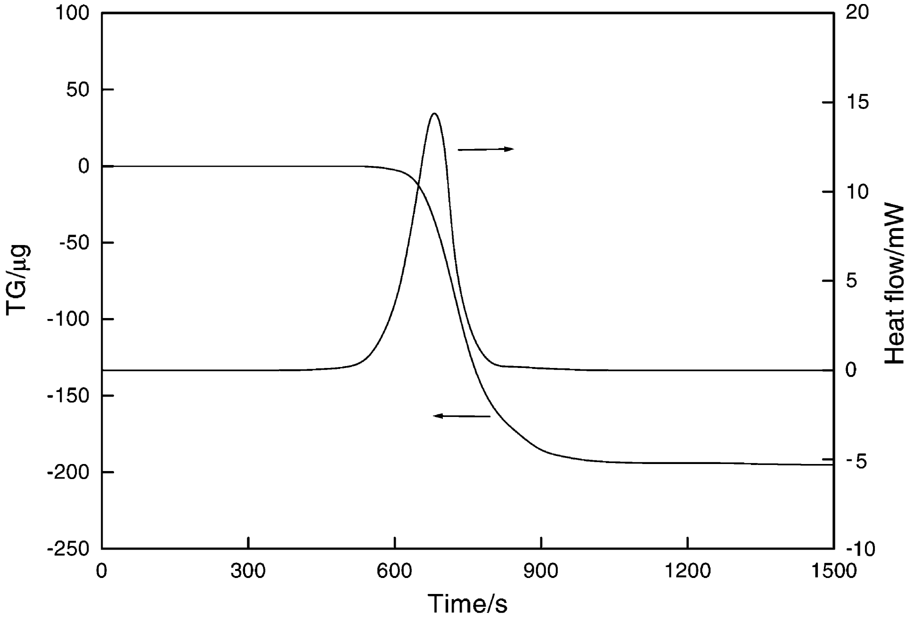

Fig. 3. The TG–DSC results of reduction of 34.8 mg 4.13% PtO_x/Al_2O_3 sample with 190 Torr hydrogen at 670 K.

Table 2
Oxidation of Pt/Al_2O_3 catalyst at 770 K with various conditions

Sample	d (nm)	t_{ox} (h)	P_{O_2} (Torr)	N_O/N_{Pt}	$-\Delta H_f$ (kJ(mol O_2)$^{-1}$)
0.82% Pt	1.0	2	380	2.05	190
		1	190	2.04	193
2.12% Pt	1.0	2	380	2.00	190
		1	190	1.98	189
4.13% Pt	1.3	2	380	2.02	192
		1	190	1.89	186
5.75% Pt	2.0	2	570	1.36	184
		2	380	1.34	184
		1	190	1.02	180
7.86% Pt	2.6	2	570	1.33	182
		2	380	1.34	184
		1	190	0.99	180
9.94% Pt	4.8	2	570	1.35	182
		2	380	1.10	178
		2	190	0.51	166
		1	190	0.52	168

Note: t_{ox}, time of oxidation; P_{O_2}, partial pressure of oxygen.

for $d < 1.8$ nm, and PdO for $d > 2.0$ nm [30]. For Rh/Al_2O_3, a dioxide (RhO_2) or a sesquixode (Rh_2O_3) was formed depending on whether the diameter was larger or smaller than 1.5 nm [31]. These reveal that the particle sizes of supported platinum metals (Pt, Pd and Rh) have a profound effect on the degree of oxidation. The oxidation of bulk Pt/Al_2O_3 catalysts at 770 K will lead to various stable platinum oxide species: PtO_2, Pt_3O_4, PtO, Pt_2O or mixtures of different oxidation states. These species have been suggested in literature [9–12]. Moore and Pauling [9] prepared PtO by fusing $PtCl_2$ with KNO_3. Muller and Roy [10] investigated the platinum–oxygen system at elevated temperature (670–1170 K) and pressure (25–3500 atm) and found Pt_3O_4 and PtO_2. Otter and Dautzenberg [11] showed that the chemisorption of oxygen on platinum crystallite at 270 K led to formation of a layer of $Pt^s{}_2O$ on the surface (where Pt^s denotes the platinum atoms exposed to surface). Based on EXAFS results, Joyner [12] reported that oxidation of Pt/Al_2O_3 at 770 K led to a formation of bulk PtO_2.

From quantitative standpoint and possible species lists, the plausible mechanisms of oxidation reaction are shown in Eqs. (5)–(7):

$$\mathrm{Pt} \xrightarrow{P_{O_2}=190\,\mathrm{Torr},\ t_{ox}=1\,\mathrm{h}} \mathrm{PtO_2} \qquad (d < 2.0\,\mathrm{nm}) \tag{5}$$

$$\mathrm{Pt} \xrightarrow{P_{O_2}=190\,\mathrm{Torr},\ t_{ox}=1\,\mathrm{h}} \mathrm{PtO} \xrightarrow{P_{O_2}=380\,\mathrm{Torr},\ t_{ox}=2\,\mathrm{h}} \mathrm{Pt_3O_4}$$
$$(\text{or a mixture of PtO/PtO}_2,\ 2.0\,\mathrm{nm} < d < 4.0\,\mathrm{nm}) \tag{6}$$

$$\mathrm{Pt} \xrightarrow{P_{O_2}=190\,\mathrm{Torr},\ t_{ox}=1\,\mathrm{h}} \mathrm{Pt_2O} \xrightarrow{P_{O_2}=380\,\mathrm{Torr},\ t_{ox}=2\,\mathrm{h}}$$
$$\mathrm{PtO} \xrightarrow{P_{O_2}=570\,\mathrm{Torr},\ t_{ox}=2\,\mathrm{h}} \mathrm{PtO_4}$$
$$(\text{or a mixture of PtO/PtO},\ d > 4.0\,\mathrm{nm}) \tag{7}$$

The extent of the bulk oxidation depended strongly on the particle size of supported platinum. Interestingly, different oxide species can be distinguished from the gravimetric results. The N_O/N_{Pt} stoichiometry of stable oxides definitely increased with the particle size. As the particles become smaller (for $d < 1.5$ nm), the x in PtO_x approaches to 2. This is because the bulk is rapidly oxidized due to short distance from the surface for small particles. The larger particles, however, are difficult to oxidize since the surface adsorbed oxygen atoms migrate hardly into the subsurface layer to further oxidize. The oxide species depended on the pressure of oxygen (P_{O_2}) within various particle sizes: the formation of PtO or Pt_3O_4 (or a mixture of PtO/PtO_2) was preferred for P_{O_2} ~190 Torr or P_{O_2} ~380 Torr, respectively in the $2.0\,\mathrm{nm} < d < 4.0\,\mathrm{nm}$ range; and the formation of Pt_2O or Pt_3O_4 (or a mixture of PtO/PtO_2) was preferred for P_{O_2} ~190 Torr or P_{O_2} ~570 Torr, respectively for $d > 4.0$ nm.

The last column of Table 2 lists the heat of oxide formation (ΔH_f) of the stable stoichiometric platinum oxides in the oxidation of various Pt/Al_2O_3 samples at 770 K. The particle size of platinum metals has a profound effect on the formation of stable platinum oxides and ΔH_f value. The obtained various species possess different ΔH_f value. The $-\Delta H_f$ changed from 190 (for PtO_2) to 168 kJ $(\mathrm{mol\ O_2})^{-1}$ (for Pt_2O). The Fig. 4 correlates the $-\Delta H_f$ with the stoichiometry. An obvious species-dependent relation is found for our samples.

$$-\Delta H_f(\mathrm{kJ(mol^{-1}\ O_2)}) = 163 + 14x \tag{8}$$

Table 3
Heat of oxide formation reported in previous literature for various platinum oxides

Method	Platinum oxides	$-\Delta H_f$ (kJ (mol $O_2)^{-1}$)	References
C–C equation[a]	PtO_2	222	[22]
Electrochemical	PtO_x	188	[32]
Electrochemical	PtO_x	175	[33]
Electrochemical	PtO_2	167 ± 42	[19]
CRC data	Pt_3O_4	163	[21]
Calorimetric	PtO	142	[34]

[a] Calculated by Clausius–Clapeyron equation.

The evolved heat of oxide formation increased by about 20 kJ $(\mathrm{mol\ O_2})^{-1}$ as the stoichiometry, x in PtO_x, increased from 0.5 to 2.0. The formation enthalpy of platinum oxide, reported in literature [19,21,22,32–34], also varies from 222 to 142 kJ $(\mathrm{mol\ O_2})^{-1}$ for various samples of platinum oxides (Table 3). We believe that the difference between these comes from the variations of the size of platinum particle and the stoichiometry of PtO_x.

3.3. *Heat of adsorption of water on Pt/Al_2O_3*

The enthalpy of reduction is independent of the reactant while the enthalpy of oxidation depends on the product formed. Comparison of oxidation and reduction, the heat of adsorption of water on Pt/Al_2O_3 can be critical. Based upon the thermodynamic values reported here for the heat of oxide formation and the heat of reduction, a thermodynamic cycle can be proposed for the Al_2O_3-supported platinum. The following equations would apply to the supported platinum:

$$\mathrm{Pt} + \tfrac{1}{2}x\mathrm{O_{2(g)}} \rightarrow \mathrm{PtO}_x \tag{9}$$

$$\mathrm{PtO}_x + x\mathrm{H_{2(g)}} \rightarrow \mathrm{Pt} + x\mathrm{H_2O_{(ad)}} \tag{10}$$

$$x\mathrm{H_2O_{(g)}} \rightarrow x\mathrm{H_{2(g)}} + \tfrac{1}{2}x\mathrm{O_{2(g)}} \tag{11}$$

$$x\mathrm{H_2O_{(g)}} \rightarrow x\mathrm{H_2O_{(ad)}} \tag{12}$$

Thus, an estimate for the heat of adsorption of water on Al_2O_3-supported platinum can be obtained from the sum of the enthalpy changes in steps (5) through (7), i.e.:

$$-\Delta H_{ad,H_2O}(\mathrm{kJ\,mol^{-1}}) = \tfrac{1}{2}x\Delta H_{f,PtO_x} + x\Delta H_{red} - x\Delta H_{f,H_2O} \tag{13}$$

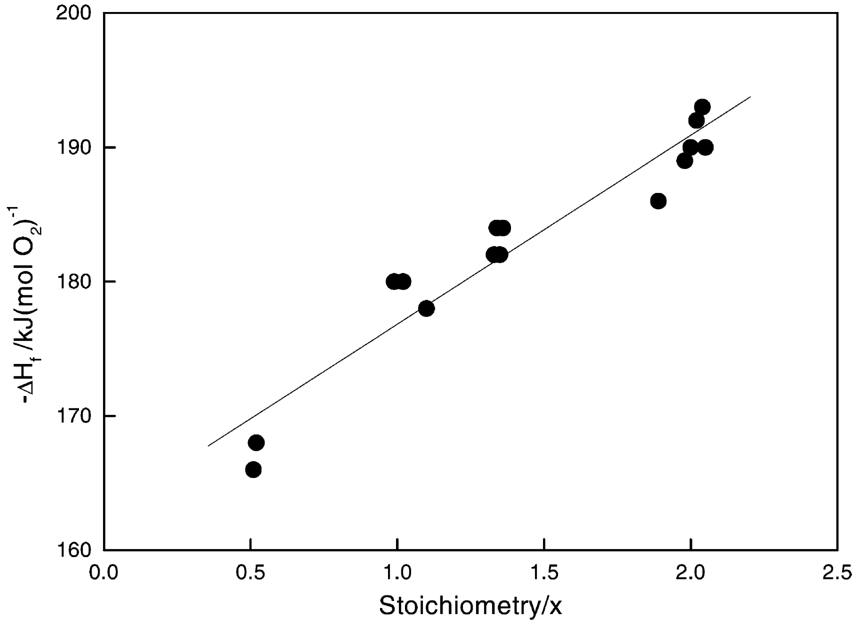

Fig. 4. Dependence of $-\Delta H_{\mathrm{f}}$ of platinum oxides on the stoichiometric x.

Table 4
Summary of the enthalpies for platinum oxides

Oxide species	$-\Delta H_{\mathrm{red}}$ (kJ (mol H_2)$^{-1}$)[a]	$-\Delta H_{\mathrm{af,PtO}_x}$ (kJ (mol O_2)$^{-1}$)	$-\Delta H_{\mathrm{ad,H_2O}}$ (kJ mol^{-1})[b]
PtO_2	103	190	88
Pt_3O_4	105	184	60
PtO	103	180	49
Pt_2O	100	168	29

[a] Both enthalpies are average value.

[b] Calculated from the following equation: $-\Delta H_{\mathrm{ad,H_2O}}(\mathrm{kJ\,mol^{-1}}) = \frac{1}{2}x\Delta H_{\mathrm{f,PtO}_x} + x\Delta H_{\mathrm{red}} - x\Delta H_{\mathrm{f,H_2O}}$.

Using the average values of previous measurements (listed in Table 4) for steps (5) and (6), respectively, and a value of $-\Delta H_{\mathrm{f,H_2O}} = 242\,\mathrm{kJ\,mol^{-1}}$, values of $-\Delta H_{\mathrm{ad,H_2O}}$ are obtained. The $-\Delta H_{\mathrm{ad,H_2O}}$ is formed to be 88, 60, 49 and 29 kJ mol^{-1}, respectively, for 0.82% Pt/Al_2O_3 ($d = 1.0\,\mathrm{nm}$), 5.75% Pt/Al_2O_3 ($d = 2.0\,\mathrm{nm}$), 7.86% Pt/Al_2O_3 ($d = 2.6\,\mathrm{nm}$) and 9.94% Pt/Al_2O_3 ($d = 4.8\,\mathrm{nm}$). Fusy and Ducros [35] measured the heat of adsorption for H_2O on Pt (1 1 0) of 46 kJ mol^{-1} during the titration reaction. Basset et al. [36] measured a value of 78 kJ mol^{-1} for H_2O adsorbed on Pt/Al_2O_3. However, Fubini et al. [37] reported a value of 105 kJ mol^{-1} for the initial heat of adsorption of H_2O on η-Al_2O_3. Apparently, it was demonstrated that the consistency in ΔH_{red} for various platinum oxides was attributed to the variations of heat of adsorption of water on alumina-supported platinum. The smaller particle size has more strongly adsorbed H_2O on Pt/Al_2O_3 that obstructs the escape of water from the surface.

4. Conclusions

The simultaneous measurements of TG and DSC provided meaningful information on reduction–oxidation processes of alumina-supported platinum catalysts. The results revealed that the heat of reduction,

ΔH_{red}, was relatively constant and had a value of $-103\,\mathrm{kJ} \pm 3\,\mathrm{kJ}$ (mol^{-1} H_2) for various platinum oxides. However, the particle size of platinum metals had a profound effect on the oxidation and heat of oxide formation, ΔH_{f}.

Acknowledgements

The author acknowledges the financial support of this study by the National Science Council of the Republic of China.

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