

Platinum–oxide species formed by oxidation of platinum crystallites supported on alumina

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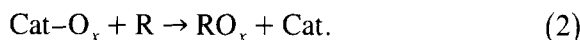
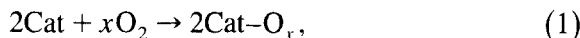
Abstract

Pt/Al₂O₃ samples of different platinum loadings are prepared by impregnating γ -Al₂O₃ with PtCl₄ solution. Reduced Pt/Al₂O₃ samples are oxidized by dioxygen to examine the variation of Pt–O_x (platinum–oxide) species with the oxidation temperature. Four different Pt–O_x species are characterized according to their reduction temperature (T_r) found in the temperature-programmed reduction (TPR) experiments. They are assigned as surface platinum oxide ($T_r = -25^\circ\text{C}$), PtO ($T_r = 50^\circ\text{C}$), PtO₂ ($T_r = 100^\circ\text{C}$) and PtAl₂O₄ ($T_r = 220^\circ\text{C}$), respectively, mainly according to their $N_{\text{O}}/N_{\text{Pt}}$ stoichiometry found in the TPR and their desorption kinetics found in the technique of temperature-programmed desorption (TPD). These four species alternate as the dominant Pt–O_x products on Pt/Al₂O₃ samples when the oxidation temperature is raised to 25°C, 300°C, 500°C and 600°C, respectively.

Keywords: TPR; TPD; Platinum oxide; Graphic plot

1. Introduction

Catalytic oxidation of hydrocarbon (R) with dioxygen is an important process for manufacturing a variety of chemicals and a useful method for eliminating organic pollutants. The mechanism of the catalytic oxidation includes an oscillation of the active ingredient of a catalyst between a reduced form (Cat) and an oxidized form (Cat–O_x) according to



The activity of the oxidation catalysts therefore depends heavily on the nature of Cat–O_x. Since

alumina-supported Pt has been widely used as an oxidation catalyst [1,2], an examination of the detailed interaction between dioxygen and supported platinum crystallites (Eq. (1)) is a pertinent topic to study.

Platinum oxides of various chemical stoichiometries, i.e., Pt₃O₈ [3], α -, β -PtO₂ [4–8], Pt₃O₄ [3,9], PtO [7,8,10], and Pt₂O [11,12], have been suggested in literature as the Pt–O_x species in Pt/Al₂O₃ catalysts (Table 1). The specific Pt–O_x species on Pt/Al₂O₃ varied with the dispersion of platinum and the treatment condition. Both Dautzenberg et al. [11] and Lietz et al. [12] demonstrated that interaction between oxygen and platinum crystallites at 0°C led to formation of a layer of Pt_{(s)2}O on their surface (where Pt_(s) denotes platinum atoms ex-

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Table 1
Platinum oxide species suggested in literatures

Authors	Sample	Oxidation condition		Method	O/Pt	Oxide species (PtO _x)	Ref.
		T (K)	P (P _{O₂} /Torr)				
Dautzenberg et al.	0.8% Pt/ γ -Al ₂ O ₃	273	0.1	O ₂ -chemisorption (continue flow)	0.5	Pt ₂ O	[11]
Lietz et al.	0.5% Pt/ α -Al ₂ O ₃	273	air	O ₂ -chemisorption (pulse titration)	0.5	Pt ₂ O	[12]
		573		TPR	2	α -PtO ₂	[4]
		873		TPR	2	β -PtO ₂	[4]
Mills et al.	90 ~ 100% dispersed Pt/Al ₂ O ₃	r.t. for 19 h	air	TPR	2	PtO ₂	[5]
Wagstaff et al.	Pt-Ir/Al ₂ O ₃	623	air	TPR	1	PtO	[10]
Yao et al.	3.3 ~ 23.1% Pt/Al ₂ O ₃	773	air	TPR	1.82 ~ 0.5	Pt, PtO, PtO ₂ mixed	[7]
	0.78 ~ 1.64% Pt/Al ₂ O ₃				2	PtO ₂	[7]
McNicol et al.	Pt/Al ₂ O ₃	773	air	volumetric adsorption	2	PtO ₂	[6]
Weller et al.	Pt. black	773		XRD	3.7	Pt ₃ O ₄	[12]
David et al.	Pt black			XRD	1.33	Pt ₃ O ₄	[9]
Muller et al.	Pt black			XRD	1.33	Pt ₃ O ₄	[3]
	Pt black			XRD	2.67	Pt ₃ O ₈	[3]

posed to the surface). Mills et al. [5] reported that highly dispersed platinum on Pt/Al₂O₃ was rapidly oxidized by air to form bulk PtO₂ at room temperature. Based on EXAFS (extended X-ray absorption fine structure) study, Fukushima et al. [13] suggested that the extent of platinum oxidation at room temperature decreased with an increase in the diameter (*d*) of platinum crystallites (100% for *d* < 1.0 nm to 50% for *d* ~ 2.6 nm). Yao et al. [7] used TPR (temperature-programmed reduction) traces to distinguished two platinum oxide phases on Pt/Al₂O₃ calcined at 400°C: a three-dimensional particulate phase and a two-dimensional dispersed phase. Based on EXAFS results, Joyner [14] reported that oxidation of Pt/Al₂O₃ at 500°C led to a formation of bulk PtO₂.

In this work, a variation on the chemical nature of Pt–O_{*x*} species formed on oxidation of reduced Pt/γ-Al₂O₃ with the oxidation temperature is studied by TPR technique. Four supported Pt–O_{*x*} species are identified according to their reduction temperature in the TPR results.

2. Experimental

Two Pt/Al₂O₃ samples of different platinum loadings (1.0 and 5.0 weight percentage, respectively) were prepared by impregnating γ-Al₂O₃ (Merck Co., surface area 108 m²/g) with PtCl₄ solution according to the technique of incipient wetness. Obtained slurries were dried in ambient air and calcined for 4 h at 500°C before stored in capped bottles as chloride samples (PtO_{*x*}Cl_{*y*}). The chloride samples were further reduced by flowing hydrogen at 400°C for 2 h to convert the supported PtO_{*x*}Cl_{*y*} to Pt crystallites [4]. The reduced sample was then oxidized in a flow of 5 vol.% O₂ in He for 2 h at a predetermined calcination temperature (*T*_o = 25°C, 100°C, 300°C, 400°C, 500°C and 600°C) to convert the platinum crystallites into platinum oxides. These oxidized samples were then cooled in pure He for subsequent TPR or tem-

perature-programmed desorption (TPD) characterization.

Both the TPR and the TPD studies were performed in the same apparatus described in a previous work [15]. A 30 ml min⁻¹ flow of 10 vol.% H₂ in Ar was used to reduce both the chloride and the oxidized samples in TPR experiments. The rate of hydrogen consumption was monitored by a thermal conductivity detector (TCD) when the sample temperature was raised from –60°C to 400°C at a constant rate of 7 K min⁻¹. A flow of He (purity of 99.9999%) was used in the TPD experiments to purge away the oxygen desorbed from the oxidized samples upon heating from 25°C to 900°C at a rate of 10 K min⁻¹. The rate of oxygen desorption was monitored by the TCD in the downstream of the He flow.

The dispersion (*D*) of platinum on chloride samples was measured by hydrogen chemisorption at room temperature under the assumption that H/Pt_s = 1.1 [16] at the monolayer chemisorption. Prior to the chemisorption measurement, each sample was pretreated with a reduction by flowing hydrogen and an evacuation at 400°C. The chemisorption was performed volumetrically in a vacuum system described in a previous study [15]. Obtained dispersion (*D*) of platinum on the samples is listed in Table 2. Measured dispersion of the samples should not change significantly upon the calcination and TPR treatments performed in this study at temperature less than 500°C [17]. However, the calcination at 600°C will probably cause a loss of Pt due to desorption of PtO₂.

3. Results and discussion

3.1. Temperature-programmed reduction

The TPR traces for chloride samples of varied Pt loadings are shown in Fig. 1. The Pt species on these chloride samples should be in the form of PtO_{*x*}Cl_{*y*} complex because they were prepared from PtCl₄ precursor [4]. This figure

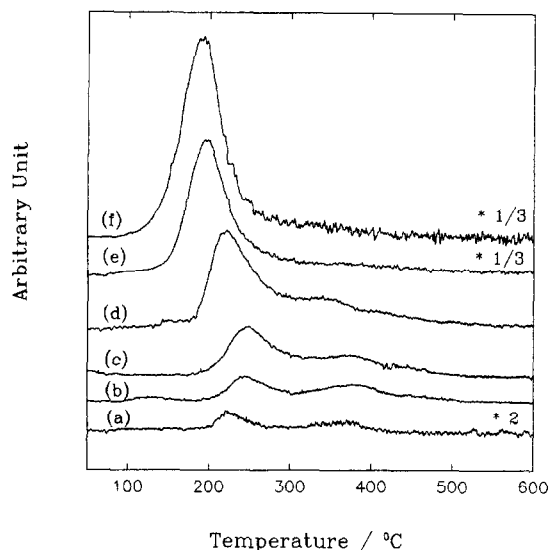
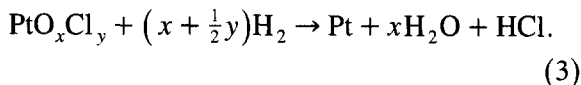


Fig. 1. TPR spectra for reduction of PtO_xCl_y species on samples of $\text{Pt}/\text{Al}_2\text{O}_3$. (a) 0.1% $\text{Pt}/\text{Al}_2\text{O}_3$, (b) 0.25% $\text{Pt}/\text{Al}_2\text{O}_3$, (c) 0.5% $\text{Pt}/\text{Al}_2\text{O}_3$, (d) 1% $\text{Pt}/\text{Al}_2\text{O}_3$, (e) 3% $\text{Pt}/\text{Al}_2\text{O}_3$, (f) 5% $\text{Pt}/\text{Al}_2\text{O}_3$.

indicates that two kinds of PtO_xCl_y complex, a three-dimensional bulk phase and a two-dimensional dispersive phase of the PtO_xCl_y according to the temperature of reduction (T_r). The 5% $\text{Pt}/\text{Al}_2\text{O}_3$ sample was mounted mainly with the bulk PtO_xCl_y , which displayed a TPR peak at $T_r \sim 200^\circ\text{C}$. A substantial part of PtO_xCl_y on the 1% $\text{Pt}/\text{Al}_2\text{O}_3$ sample was in the dispersive

phase. An interaction with the Al_2O_3 support raised the T_r of this phase to around 350°C .

The coordinated chloride ions in PtO_xCl_y should be removed from platinum by a 400°C reduction in hydrogen [4], i.e.,



The platinum crystallites reduced may be further converted into platinum oxide ($\text{Pt}-\text{O}_x$) by oxidation with oxygen:



Eq. (4) is a nonstoichiometric chemical equation because the actual chemical composition of the $\text{Pt}-\text{O}_x$ varied with the oxidation temperature.

Fig. 2 shows TPR characterizations of the 5% $\text{Pt}/\text{Al}_2\text{O}_3$ sample oxidized at different temperatures. A comparison of these TPR traces with those in Fig. 1 revealed that the oxidized $\text{Pt}-\text{O}_x$ species were reduced at lower temperatures (mainly $T_r < 150^\circ\text{C}$) than the PtO_xCl_y (T_r in the range between 150 and 400°C). Obviously, the coordinated chloride ions in PtO_xCl_y complex inhibited the reduction of platinum ions and these chloride ions can be removed from platinum upon the 400°C reduction.

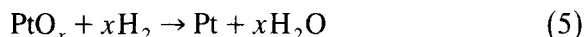
The TPR traces in Fig. 2 indicated that the

Table 2

Effects of reoxidation temperature (T_0) on the TPR and TPD characterization of $\text{Pt}/\text{Al}_2\text{O}_3$ samples

Sample	Dispersion (%)	T_0 ($^\circ\text{C}$)	TPR N_0/N_{Pt}	TPD			
				N_0/N_{Pt}	n	$E_d/\text{kJ mol}^{-1}$	ν/s^{-1}
1.0% $\text{Pt}/\text{Al}_2\text{O}_3$	100	25	0.76	0.81	2	198	1.76×10^9
		100	0.95				
		300	1.01	0.97	2	216	8.03×10^9
		400	1.62				
		500	1.80	1.66	1	222	8.91×10^9
		600	1.49				
5.0% $\text{Pt}/\text{Al}_2\text{O}_3$	65	25	0.46	0.73	2	186	9.76×10^9
		100	0.86				
		300	1.29	1.03	2	195	5.54×10^{10}
		400	1.90				
		500	1.80	1.76	1	248	3.23×10^{11}
		600	0.16				

reduction of Pt–O_x species on the oxidized 5% Pt/Al₂O₃ samples, i.e.,



varied with the temperature of oxidation (T_o). These traces are composed mainly by four peaks at different reduction temperatures (T_r). They are tentatively designated as species A ($T_r = -25^\circ\text{C}$), M ($T_r = 50^\circ\text{C}$), D ($T_r = 100^\circ\text{C}$) and S ($T_r = 220^\circ\text{C}$), respectively. All these four peaks also appeared in the TPR spectra of Fig. 3 from the oxidized samples of 1% Pt/Al₂O₃. These four peaks indicate that Pt atoms on the reoxidation Pt/Al₂O₃ samples have at least four different chemical environments.

Relative area of these four peaks varied in Fig. 2 with the oxidizing temperature. Trace (a) of Fig. 2 indicated that species A was the only Pt–O_x species when the 5% Pt/Al₂O₃ was oxidized at $T_o = 25^\circ\text{C}$. As the T_o was increased, the abundance of the species A gradually decreased and other species alternated as the dominant species. Species M, D, and S became the major species when the reduced Pt/Al₂O₃ sample was oxidized at 300°C (trace c), 500°C (trace d) and 600°C (trace f), respectively. A

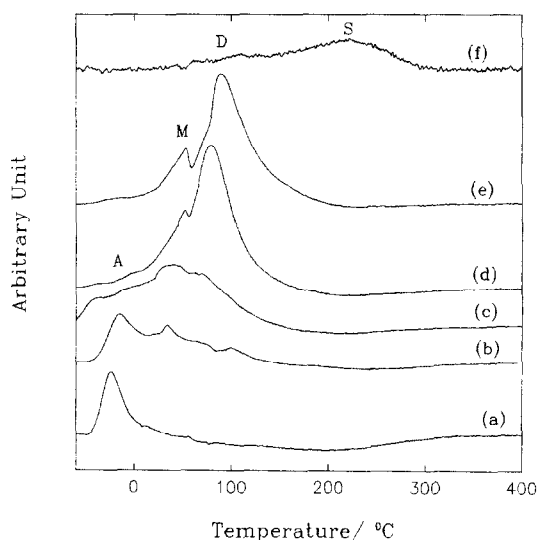


Fig. 2. TPR spectra of 5% Pt/Al₂O₃ after reoxidation at varied temperatures (T_o). (a) 25°C , (b) 100°C , (c) 300°C , (d) 400°C , (e) 500°C , (f) 600°C .

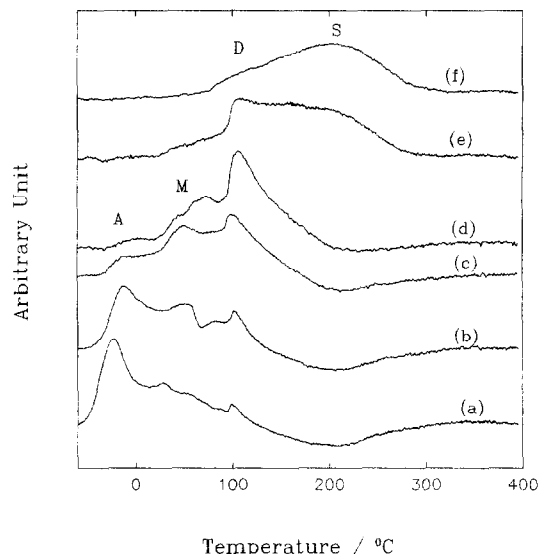


Fig. 3. TPR spectra of 1% Pt/Al₂O₃ after reoxidation at varied temperatures (T_o). (a) 25°C , (b) 100°C , (c) 300°C , (d) 400°C , (e) 500°C , (f) 600°C .

similar variation of the TPR peaks with T_o is also found in Fig. 3 for the 1% Pt/Al₂O₃ sample.

The amount of oxygen atom (N_o) reduced in TPR experiments has been calibrated with the hydrogen consumption and converted to N_o/N_{Pt} ratios (where N_{Pt} denotes the number of platinum atom in each sample). The variation of the N_o/N_{Pt} ratios provides valuable insight into the chemical composition of the four Pt–O_x species on the oxidized Pt/Al₂O₃. The N_o/N_{Pt} ratio of species A, the dominant species upon a oxidation treatment at $T_o = 25^\circ\text{C}$, had a value less than 1.0 and increased with the dispersion of platinum. This peak is therefore assigned to a reduction of surface platinum oxide (Pt_s–O). From a comparison between the N_o/N_{Pt} ratio found in TPR and the dispersion of platinum crystallites found in the hydrogen chemisorption, the Pt_s–O species probably has a chemical stoichiometry of Pt_sO_{0.7} in our samples.

The dominant peak in the TPR traces of Figs. 2 and 3 varied with the oxidation temperature. Peak M ($T_r = 50^\circ\text{C}$) and peak D ($T_r = 100^\circ\text{C}$) became the major peak when T_o was raised to

300°C (trace c) and 500°C (trace e), respectively. These two peaks are assigned to the reduction of PtO and PtO₂ since the total peak area of the trace (c) and the trace (e) displayed a $N_{\text{O}}/N_{\text{Pt}}$ ratio of 1.15 ± 0.15 and 1.80, respectively. The deviation from the stoichiometric value of $N_{\text{O}}/N_{\text{Pt}} = 1.0$ and 2.0 of these two ratio reflected that PtO or PtO₂ was merely the dominant species on these samples.

An oxidation of Pt/Al₂O₃ sample at 600°C caused a drastic change in the supported Pt–O species. Peak S ($T_r = 200^\circ\text{C}$) became the only signal noticed in the TPR (trace f). This high T_r peak indicated that the thermal stability of this Pt–O_x species is rather high. Since MAI₂O₄ spinel species have been found in many alumina-supported metallic (including Co [18], Ni [19], Cu [20], and Pd [21]) samples upon high temperature calcination, and all these MAI₂O₄ species had a higher T_r temperature than their corresponding M–O species, peak S is therefore assigned to the reduction of PtAl₂O₄ species, i.e.,



The $N_{\text{O}}/N_{\text{Pt}}$ ratio in the trace (f) of both Figs. 2 and 3 was smaller than 1.0 and decreased with an increase in the platinum loading on Pt/Al₂O₃ samples. Obviously, not all of the platinum atoms would fall into the surface holes of Al₂O₃ and be converted into the PtAl₂O₄ species upon the 600°C calcination. Some of the bulk PtO_x

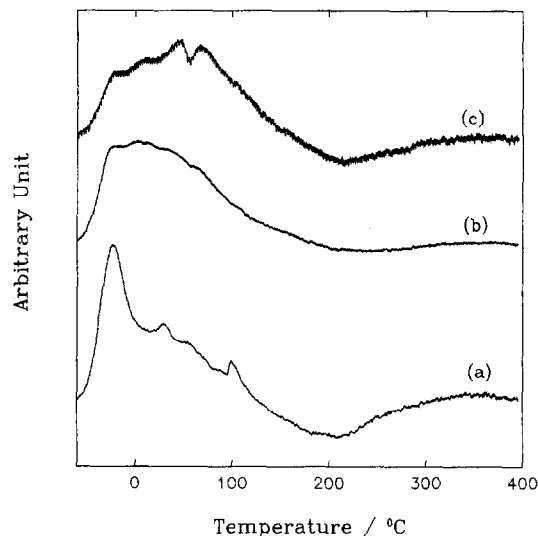
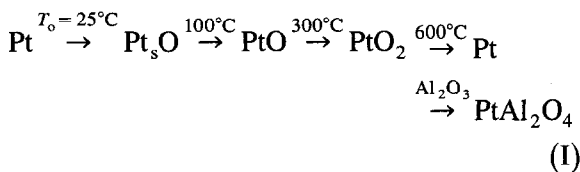


Fig. 4. TPR spectra of 1% Pt/Al₂O₃ after reoxidation at 25°C for (a) 2 h, (b) 10 h, (c) 19 h.

would directly convert to platinum crystallite by desorbing oxygen, i.e.,



Accordingly, we found that four platinum oxide species, i.e., Pt_sO_{0.7}, PtO, PtO₂ and PtAl₂O₄, may be formed after 2 h oxidization of Pt/Al₂O₃ samples with dioxygen. These species can be characterized with the T_r value in the TPR experiments (Table 3). Their relative abundance varied mainly with the oxidation temperature, according to a reaction sequence of:



Nevertheless, the optimized T_0 for the formation of each PtO_x species varied with the dispersion of platinum and the duration of oxidation. As mentioned in the Introduction section, a lower oxidation temperature (than the temperature indicated in the sequence in Eq. (I)) is generally found from a Pt/Al₂O₃ sample with a

Table 3
Reduction temperature of various platinum species supported on γ -Al₂O₃

Oxide species	Reduction temperature in TPR/°C
bulk PtO _x Cl _y	150 ~ 300
inter surfacial PtO _x Cl _y	300 ~ 400
Pt _(s) O (A)	–25
PtO (M)	50
PtO ₂ (D)	100
PtAl ₂ O ₄ (S)	220

higher platinum dispersion. Fig. 4 also revealed that the fraction of PtO and PtO₂ on the 1% Pt/Al₂O₃ sample oxidized at 25°C would increase with the duration of oxidation.

3.2. Temperature-programmed desorption

The suggested chemical nature of the four Pt–O_x species has also been examined via the technique of TPD. Fig. 5 displays variation of TPD traces obtained from 5% Pt/Al₂O₃ samples oxidized at different temperatures. The desorption of oxygen (Eq. (7)) from Pt_sO ($T_0 = 25^\circ\text{C}$), PtO ($T_0 = 300^\circ\text{C}$) or PtO₂ ($T_0 = 500^\circ\text{C}$) occurred at a temperature around 600°C. Wigner–Polanyi [22] proposed that the rate of decomposition (F) at a temperature T in a TPD experiment should follow a rule of

$$F = \frac{d[\text{O}_2]}{dt} = \nu N \theta^n \exp(-E_d/RT). \quad (\text{II})$$

In this equation, ν , N , θ , n and E_d represent the pre-exponential factor, the total number of adsorbed species, the fraction of volatile constituent remaining in the sample at the temperature T , the reaction order, and the activation energy of desorption, respectively. Taking the

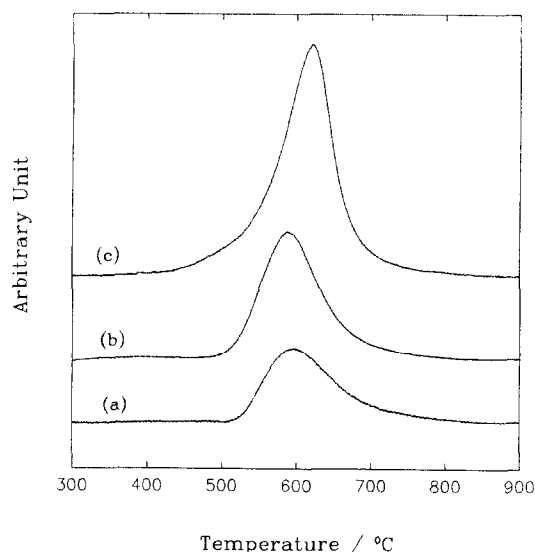


Fig. 5. TPD spectra of 5% Pt/Al₂O₃ after reoxidation at varied temperatures (T_0). (a) 25°C, (b) 300°C, (c) 500°C.

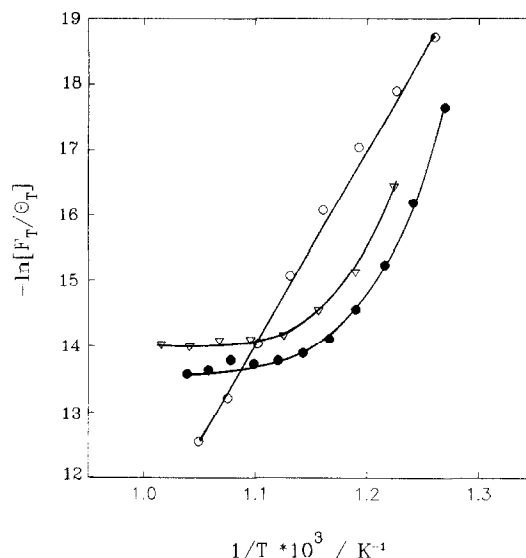


Fig. 6. Graphic plot of $\ln[F_T/\theta_T]$ versus $1/T$ from TPD traces of 5% Pt/Al₂O₃ at varied reoxidation temperatures (T_0). ∇ , 25°C; \bullet , 300°C; \circ , 500°C.

logarithm on both sides, Eq. (II) can be rearranged into

$$\ln(F/\theta^n) = \ln \nu N - E_d/RT. \quad (\text{III})$$

Since the variation of both F and θ with the temperature T can be found from a TPD trace, a graphic plot of $\ln(F/\theta^n)$ with T^{-1} should yield a straight line if a proper desorption order (n) is accepted.

The graphic plot of Eq. (III) is used in this study for the TPD traces in Fig. 5. Fig. 6 displayed the plot when $n = 1$ was accepted. A straight line is obtained from the trace (c) of the 500°C oxidized sample. The linear plot indicates that the desorption of oxygen from the Pt–O_x species formed during the 500°C oxidation proceeded with a first order kinetics. Unambiguously, the Pt–O_x species is PtO₂ which was desorbed according to a reaction of



Both the graphic plots for the TPD traces (a) and (b) exhibited concave curves in Fig. 6. Obviously the oxygen desorption from Pt_sO and PtO followed a reaction order higher than one. Another graphic plot of Eq. (III) on the TPD

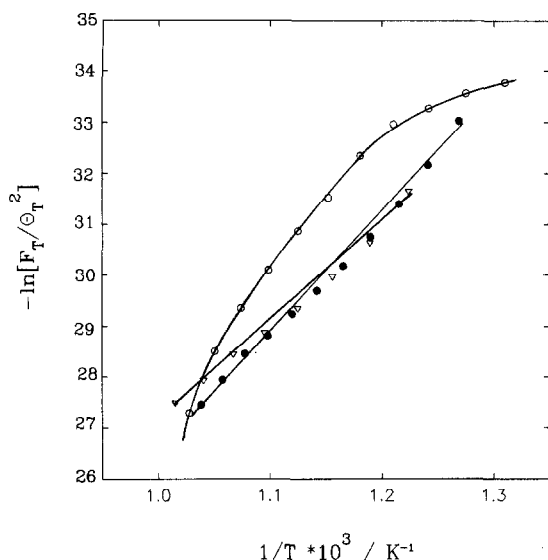


Fig. 7. Graphic plot of $\ln[F_T / \theta_T^2]$ versus $1/T$ from TPD traces of 5% Pt/Al₂O₃ at varied reoxidation temperatures (T_0). ∇ , 25°C; \bullet , 300°C; \circ , 500°C.

traces of Fig. 5 was then tried on accepting $n = 2$. Fig. 7 indicated that linear plots were definitely obtained, at this time, from the TPD traces (a) and (b). Therefore, the desorption of oxygen from Pt₅O and PtO was proceeded with a second order elementary reaction of



4. Conclusions

According to the reduction temperatures (T_r) and the $N_{\text{O}}/N_{\text{Pt}}$ stoichiometry in the TPR results, four different platinum oxide species, Pt₅O, PtO, PtO₂ and PtAl₂O₄, were verified on Pt/Al₂O₃ samples. The formation of these platinum oxide species depended on the oxidation temperature.

The graphic plot of TPD traces displayed that the desorption of oxygen from Pt₅O and PtO species were proceeded with the second order reaction kinetics. On the other hand, the oxygen

desorption from the PtO₂ species followed the first order reaction kinetics.

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