Journal of Thermal Analysis, Vol. 46 (1996) 305-315

GRAPHIC DETERMINATION OF KINETIC PARAMETERS IN TEMPERATURE-PROGRAMMED DESORPTION OF OXYGEN FROM ALUMINA-SUPPORTED PdO

T. Y. Chou, C. P. Hwang and C. T. Yeh

Department of Chemistry, National Tsing-Hua University, Hsinchu, 30043, Taiwan,
Republic of China

(Received January 5, 1995; in revised form April 4, 1995)

Abstract

A graphic method is proposed to determine all of the kinetic parameters in Wigner-Polanyi equation of desorption. A desorption rate curve from a single temperature-programmed desorption experiment is required by this method to determine the order of reaction (n), the activation energy (E_d) and the pre-exponential factor (ν) of the equation. The proposed method has been applied to the oxygen desorption from PdO/Al_2O_3 samples prepared by impregnating γ-Al_2O_3 with H_2PdCl_4 solution used as examples. From the graphic method, the values of $n=2$, and $\nu=1.37\pm0.80\times10^9$ s^{-1} were successfully determined for the desorption. The value of E_d depended on the dispersion of palladium (D) on PdO/Al_2O_3 samples, and was expressed by the equation: $E_d=175+174D$ kJ·mol^{-1}. This graphic method is a direct and time-saving technique, on comparing with other methods suggested in the literature, for analysis of data from temperature-programmed desorption of simple desorption processes.

Keywords: graphic method, kinetic parameters, PdO/Al_2O_3, TPD

Introduction

Temperature-Programmed Desorption (TPD) is a useful technique employed to study the kinetics of desorbing volatile constituents from solid samples [1]. A TPD experiment includes heating a sample according to a programmed temperature, typically linear in time, and monitoring the desorption rate of volatile constituent as a function of temperature.

The basic equation generally accepted for the rate of desorption was proposed by Wigner and Polanyi [2]

$$\text{Rate} = \nu N\theta^n \exp(-E_d/RT) \qquad (1)$$

0368-4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

where N, ν, θ, n and E_d represent the total number of desorbable species, pre-exponential factor, fraction of the specimens remaining in the sample, order of reaction and activation energy, respectively. Among them, ν, n and E_d are parameters of interest to investigators.

Redhead [3] was the pioneer who tried to evaluate these basic parameters. From rate measured in a single TPD curve, he was able to determine ν from preassumed E_d, or vice versa. Since then, many theoretical studies have been performed towards making a direct determination of these parameters from TPD curves without preassumption of either E_d or ν. Different modified methods have been established: variation of heating rate (β) [4, 5], variation in initial coverage (a series of experiments with different initial coverage) [6–8], analysis of peak width (to measure E_d only) [9], curve fitting [10], mutistep temperature program [11], etc. Among them, the method of β variation developed by Cvetanovic and Amenomiya [4] has been widely used to evaluate E_d. Notably, a series of TPD experiments with different β is required for this method to obtain a relation between peak temperature of maximum desorption rate (T_p) and β. On plotting $\ln(\beta/T_p^2)$ *vs.* T_p^{-1} a straight line is obtained with its slope$=-E_d/R$. In this approach, E_d can be determined without any preassumption of reaction order or pre-exponential factor.

In this study, desorption of oxygen from palladium oxide supported on alumina is investigated. We want to report that E_d as well as other important kinetic parameters of the desorption process can be simultaneously obtained from a single TPD curve through a graphic plot of desorption data.

Experimental

The Pd/Al_2O_3 samples of different palladium loadings (0.5, 1.0, 2.0 and 5.0 weight percent) were prepared with the incipient wetness technique by impregnating γ-Al_2O_3 (Merck, with a surface area of 108 m^2/g) with H_2PdCl_4 solution. Obtained slurries were dried in ambient air and calcined for 4 h at 773 K for converting supported $PdCl_2$ into PdO.

The dispersion (D, fraction of metal atoms exposed to the surface of the metal crystallites in each sample) of palladium on PdO/Al_2O_3 samples was measured by hydrogen chemisorption [12]. Prior to chemisorption measurement, each sample was pretreated under a reducing condition by flowing hydrogen and evacuation at 573 K. The chemisorption was performed volumetrically in a vacuum system at 298 K equipped with a digital pressure gauge from Texas Instrumentation. Obtained dispersion (D) of palladium is shown in Table 1 to generally decrease with the loading of palladium on the samples ($D=100\%$ for 0.5% PdO/Al_2O_3, $D=15\%$ for 5.0% PdO/Al_2O_3).

The TPD apparatus was comprised of a U-shaped sample cell bent from a 4 mm I.D. quartz tubing. After 0.15 g sample of PdO/Al_2O_3 was loosely packed in the bottom part of the cell, a flow of He (purity 99.999% with a rate of 30 ml·min^{-1}) was passed through the sample cell. The temperature of the sample was subsequently raised by a temperature-programmed controller at a constant rate of $\beta=10$ deg·min^{-1} (except β variation experiments), and the rate of oxygen desorption was monitored by a thermal conductivity detector (TCD) in the downstream of the He flow.

The graphic method

PdO is unstable at elevated temperatures and tends to desorb oxygen upon heating. A typical TPD spectrum for desorption of oxygen from PdO/Al_2O_3 is shown in Fig. 1. The rate of desorption at temperature T is represented in this figure as F_T which is converted from Eq. (1) by

$$F_T = \text{Rate}/N = \nu\theta^n \exp(-E_d/RT) \qquad (2)$$

where N is the number of total oxygen atoms desorbable in the TPD. Since T, the temperature of our TPD experiments, is raised at a linear rate of

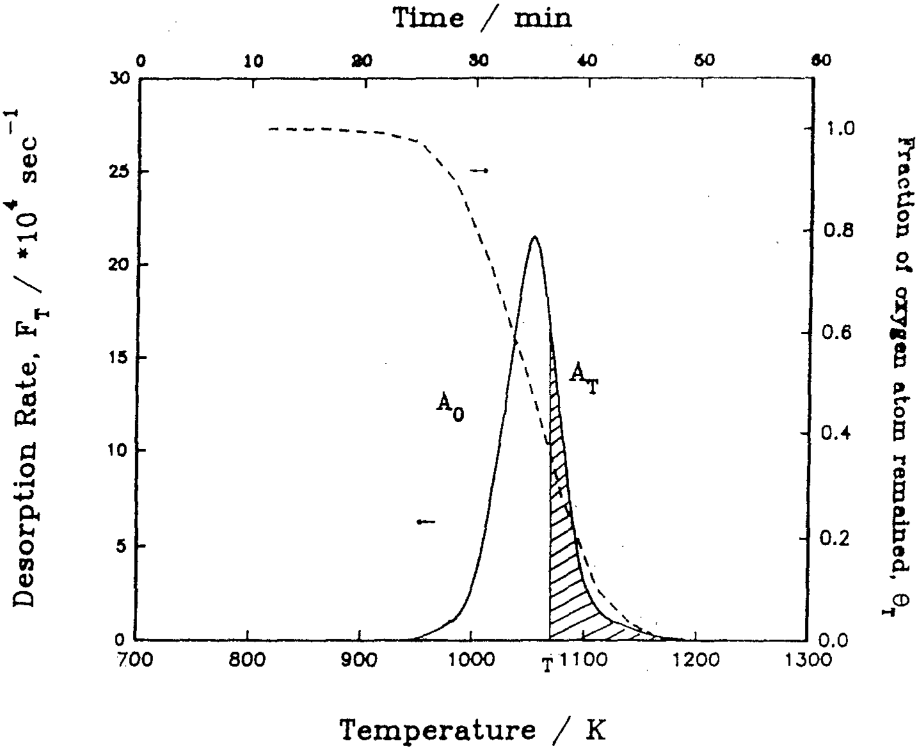

Fig. 1 A typical TPD spectrum of desorption dioxygen from 2% PdO/Al_2O_3 (D=26%). Data of dotted line was calculated from Eq. (3)

β deg·min^{-1}, the temperature in the abscissa may be replaced with time (t) using a relation $T=T_0+\beta t$, where T_0 is the initial temperature at $t=0$. Accordingly, the full peak area (represented by A_0) is one (a unitless number). Figure 1 also shows a shadowed part of the TPD peak. The area of the shadowed part (represented as A_T) indicates the amount of adsorbed species remaining undesorbed on the sample at the temperature T. Consequently, the fraction of the desorbable species remaining at temperature T is

$$\theta_T = A_T/A_o \qquad (3)$$

The temperature dependent θ_T of the typical TPD spectrum is shown as dotted line in Fig. 1. From Eq. (2), we obtain

$$\ln[F_T/\theta_T^n] = \ln\nu - E_d/RT \qquad (4)$$

If n, ν and E_d do not change during the entire TPD experiment, a graphic plot of $\ln[F_T/\theta_T^n]$ *vs.* T^{-1} should give a straight line when a proper n value is ac-

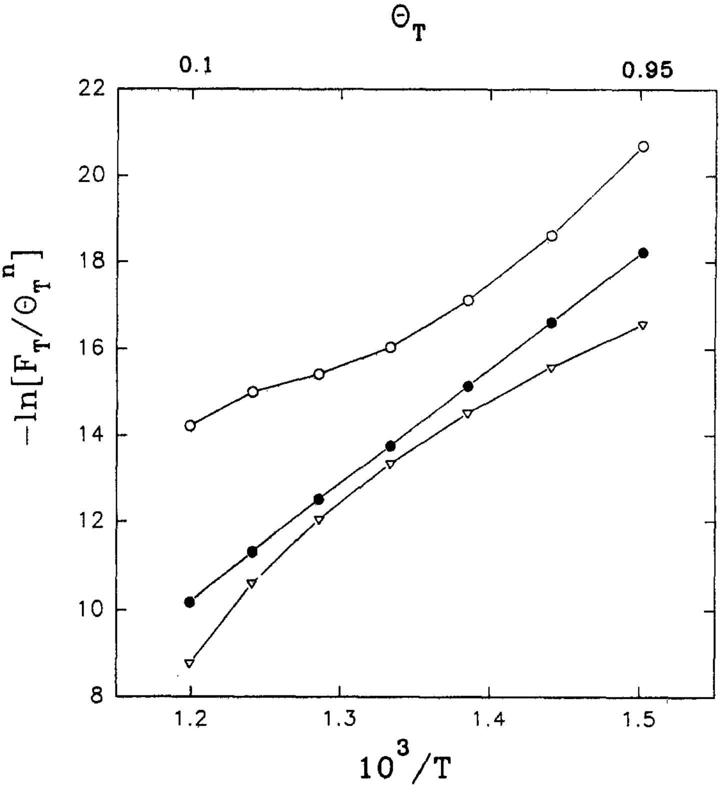

Fig. 2 Plot of ln(F_T/θ_T^n) *vs.* $1/T$ for 2% PdO/Al_2O_3. o: first order; •: second order; ∇: third order

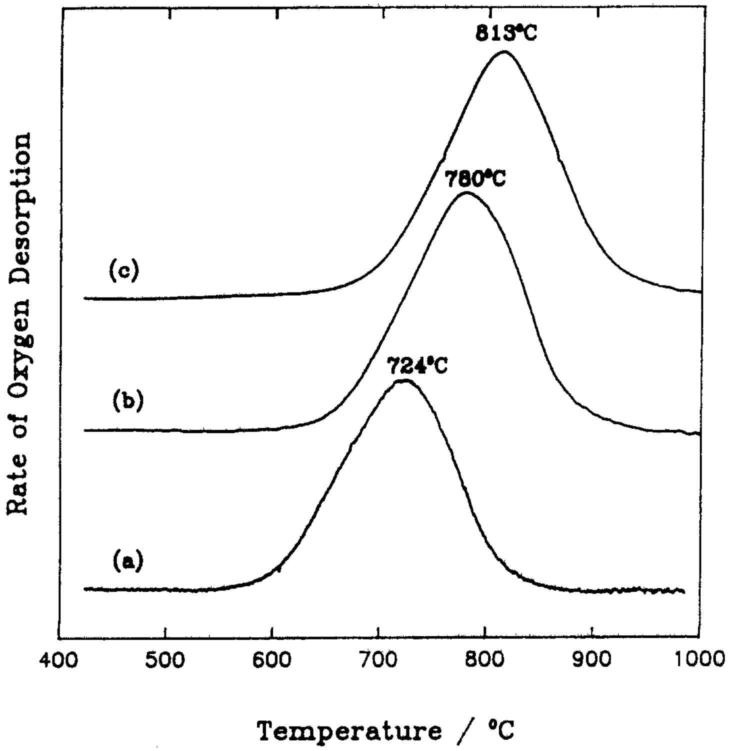

Fig. 3 Dependence of TPD curve for 2% PdO/Al_2O_3 ($D=26\%$) with heating rate (β). (a) $\beta=5$ deg·min^{-1}, (b) $\beta=10$ deg·min^{-1}, (c) $\beta=20$ deg·min^{-1}

cepted. The slope and the intercept of the obtained straight line should be $-E_d/R$ and lnv, respectively.

Results and discussion

A plot of Eq. (4) for the TPD experiment shown in Fig. 1 has been made. Figure 2 indicate that a concave or convex curve was obtained for the 2% PdO/Al_2O_3 sample when $n=1$ or $n=3$ was respectively selected for the plot. However, an expected straight line came out in the θ range between 0.10 and 0.95 when $n=2$ was selected. Obviously, the desorption process proceeds with in the second other of θ, and may be described by an elementary reaction of

$$2PdO \rightarrow 2Pd+O_2$$

The slope of the straight line in Fig. 2 suggests an E_d of 221 kJ·mol^{-1}.

The method of β variation proposed by Cvetanovic and Amenomiya [4] was subsequently performed to check the E_d of this 2% PdO/Al_2O_3 sample. Figure 3 indicates that TPD peaks varied with accepted β. The temperature of peak maximum (T_p) increased with increasing β. A plot of $\ln(\beta/T_p^2$ *vs.* $T_p^{-1})$ for the spectra shown in Fig. 3 gave a straight line. The slope ($-E_d/R$) of the straight line suggests an E_d value of 218 kJ·mol^{-1}. This value closely correlates with the value (221 kJ·mol^{-1}) determined by our graphic method.

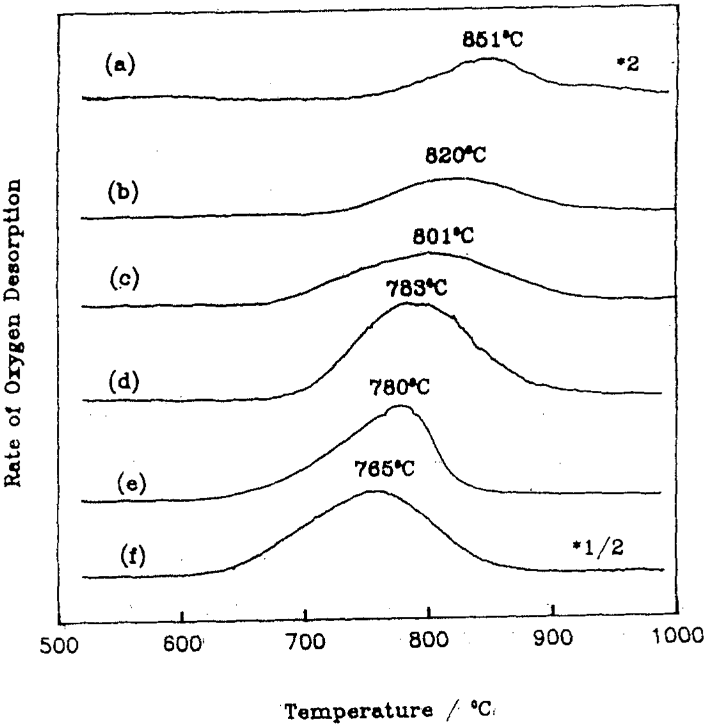

Fig. 4 TPD spectrum for PdO/Al_2O_3 samples of varied palladium loadings. (a) 0.5% PdO/Al_2O_3, (D=100%); (b) 1% PdO/Al_2O_3, (D=80%); (c) 1% PdO/Al_2O_3, (D=58%); (d) 2% PdO/Al_2O_3, (D=31%); (e) 2% PdO/Al_2O_3, (D=26%); (f) 5% PdO/Al_2O_3, (D=15%)

Figure 4 shows a series of TPD spectra obtained from PdO/Al_2O_3 samples of various palladium dispersions. The desorption of oxygen is shown in the TPD spectra to have shifted towards a higher temperature when the dispersion of palladium was increased. Calculated θ_T values from Eq. (3) for these TPD spectra are presented in Fig. 5. Graphic plot of Eq. (4) is made in Fig. 6 for each sample using F_T and θ_T data shown in Figs 4 and 5. On accepting n=2 as the desorption order, a good straight line is always obtained (Fig. 6) for each sample in the θ range between 0.10 and 0.90. All of these straight lines, as calculated by the least square method, approach a common intercept, suggesting a preexponential factor of $\nu=1.37\pm0.80\times10^9$ s^{-1}. The value of E_d can be calcu-

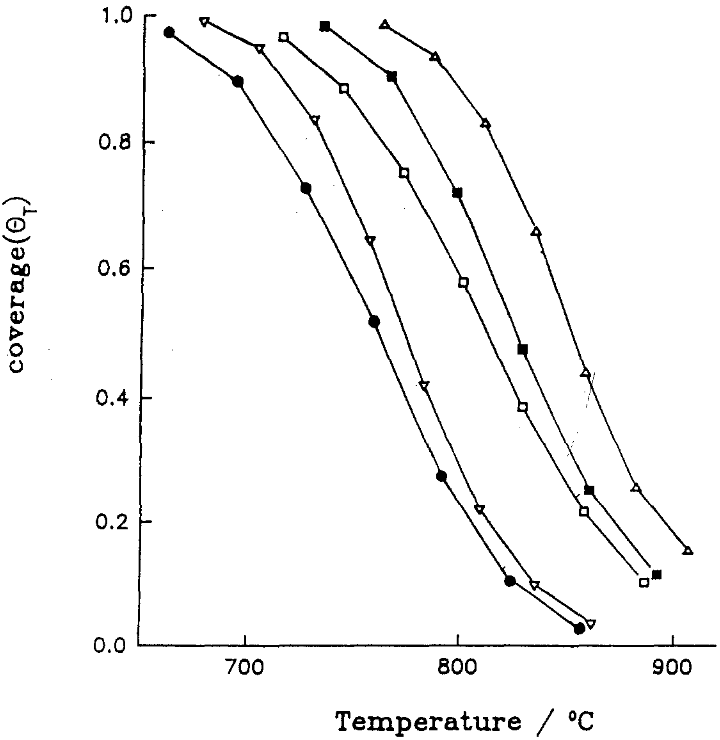

Fig. 5 Dependence of θ_T for PdO/Al$_2$O$_3$ samples with varied palladium loadings on temperature. ●: 5% PdO/Al$_2$O$_3$, (D=15%); ∇: 2% PdO/Al$_2$O$_3$, (D=26%); □: 1% PdO/Al$_2$O$_3$, (D=58%); ■: 1% PdO/Al$_2$O$_3$, (D=80%); Δ: 0.5% PdO/Al$_2$O$_3$, (D=100%)

Table 1 Variation of desorption energy (E_d) and preexponential factor (ν) of desorption oxygen from PdO/Al$_2$O$_3$ with the dispersion of palladium crystallites

Sample	Dispersion/	E_d /kJ·mol^{-1}		$10^{-9}\nu$/
	%	Graphic method[a]	β variation method[b]	s^{-1}
0.5% Pd/Al$_2$O$_3$	100	349	361	1.29
1.0% Pd/Al$_2$O$_3$	80	310	302	1.83
1.0% Pd/Al$_2$O$_3$	58	270	281	0.16
2.0% Pd/Al$_2$O$_3$	31	239	227	1.78
2.0% Pd/Al$_2$O$_3$	26	221	218	2.52
5.0% Pd/Al$_2$O$_3$	15	202	210	0.66

Average 1.37 ±0.8

a) The method developed in this study

b) Ref. [4]

lated from the slope of each straight line in Fig. 6 as shown in Table 1, E_d increases with increasing dispersion of the palladium, and is empirically correlated with dispersion (Fig. 7) by a linear equation of

$$E_d = 175 + 174D \text{ kJ}\cdot\text{mol}^{-1} \tag{5}$$

This empirical equation suggests that the activation energy required for desorption of oxygen from supported palladium crystallites increases with increasing palladium dispersion (or decreasing particle size). The smaller the size of palladium crystallites, the higher becomes the strength of PdO bond on them.

Table 1 also compares E_d values obtained from our graphic method with those from the β variation method [4]. The discrepancy between the two methods is less than 5% for each sample. Therefore we have proven that the graphic method suggested in this study can provide all the parameters in the basic Wigner-Polanyi desorption equation for this desorption process.

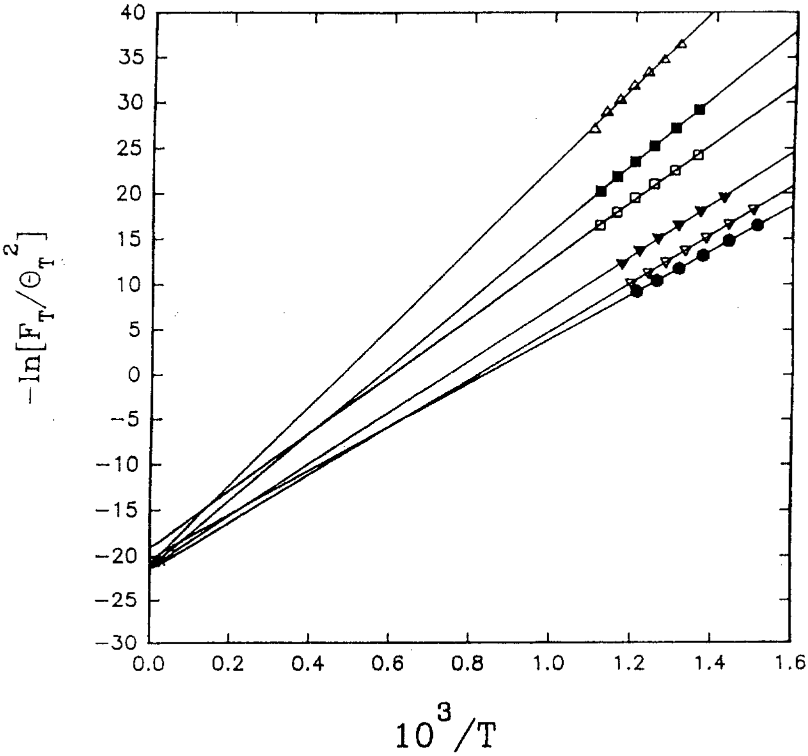

Fig. 6 Plot of Eq. (4) for TPD curves from various PdO/Al_2O_3 samples. ●: 5% PdO/Al_2O_3, (D=15%); ∇: 2% PdO/Al_2O_3, (D=26%); ▼: 2% PdO/Al_2O_3, (D=31%); □: 1% PdO/Al_2O_3, (D=58%); ■: 1% PdO/Al_2O_3, (D=80%); △: 0.5% PdO/Al_2O_3, (D=100%)

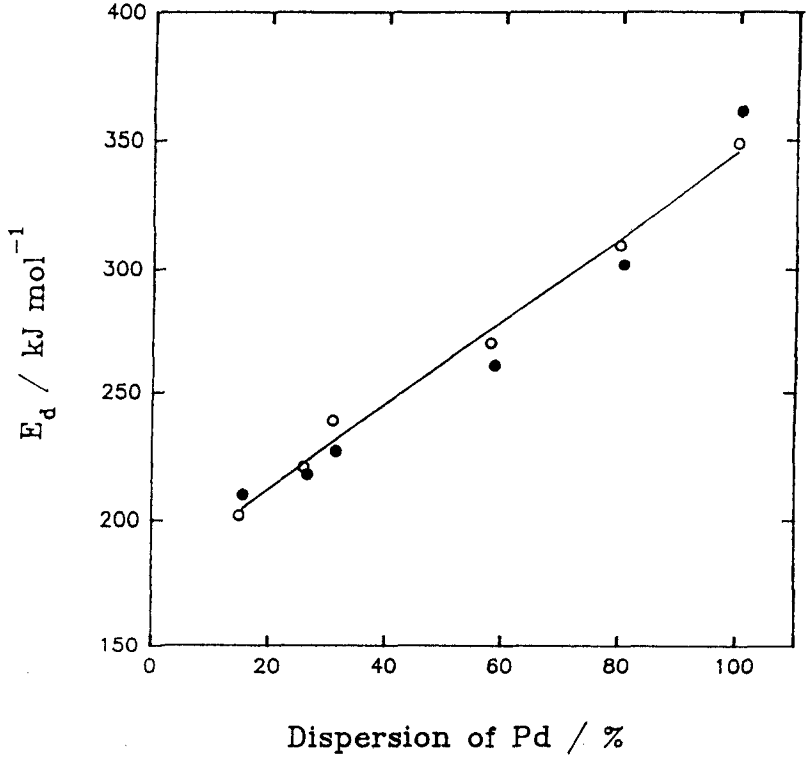

Fig. 7 Variation in the activation energy of oxygen atom desorption from palladium with the dispersion of palladium on PdO/Al_2O_3. •, β variation method; o, the graphic method

The environment of oxygen atoms on PdO crystallites are not homogeneous. A small fraction of oxygen atoms may be weakly adsorbed in the form of PdO_2 at corners of the crystallites. Oxygen atoms of crystallites at the $PdO–Al_2O_3$ interface may be strongly bonded due to interaction of Al_2O_3. Behavior of oxygen desorption of these minor species may differ from that of bulk PdO. Therefore a good linear relationship was found in Fig. 2 only for θ range between 0.10 and 0.95. On expanding the range to 0 and 1.0, a minor deviation from the linear relationship was observed at both ends. A high desorption energy (for strong adsorption sites) at the low coverage end and a low desorption energy (for weak adsorption sites) at the high coverage end were found from the slope in Fig. 8.

In conclusion, the graphic method proposed in this study has been applied to analyze the kinetics of oxygen desorption from PdO/Al_2O_3. All the meaningful parameters, i.e., E_d, ν and n were successfully obtained. Nevertheless, this graphic method relies heavily on a good range of coverage with homogeneous (similar) activation energy. We are sort of lucky on accepting the system of desorption oxygen from PdO/Al_2O_3 samples freshly prepared by impregnation

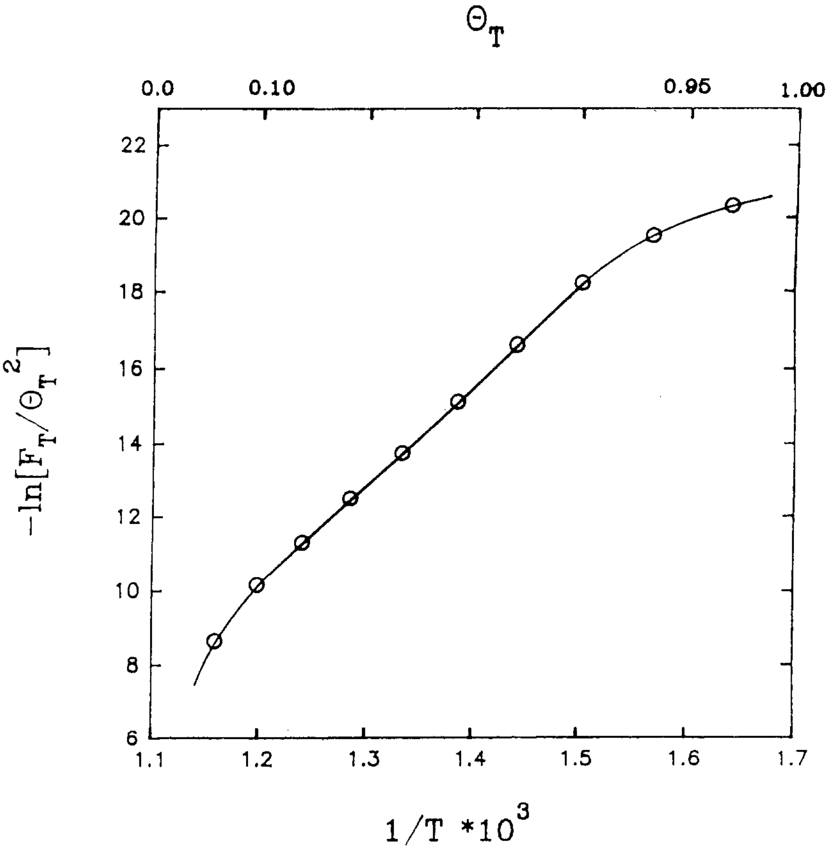

Fig. 8 Plot of $\ln(F_T/\theta_T^2)$ *vs.* $1/T$ for 2% PdO/Al_2O_3 (D=26%) on expanding θ_T range to 0 and 1.0

of H_2PdCl_4 on Merck Al_2O_3. This method would not be suitable for studying desorption processes in which the activation energy changes with the coverage. Desorption of oxygen from unsupported PdO powders is a failed example because the diffusion effect may seriously affect the rate of desorption.

* * *

The authors would like to thank the National Science Council of R.O.C. for financial support of this manuscript under Contract No.: NSC 83-0208-M-007-094.

References

1 J. L. Falconer and J. A. Schwarz, Catal. Rev. Sci. Eng., 25 (1983) 141.
2 R. S. Hansen and V. J. Mimeault, Experimental Techniques in Catalytic Research, New York 1968, p. 220.
3 P. A. Redhead, Vacuum, 12 (1962) 203.

4 R. J. Cvetanovic and Y. Amenomiya, Adv. Catal., 17 (1967) 103.
5 J. L. Falconer and R. Madix, Surf. Sci., 48 (1975) 393.
6 K. Christman, G. Ertl and T. Pignet, Surf. Sci., 54 (1976) 365.
7 J. L. Falconer and R. J. Madix, J. Catal., 48 (1977) 262.
8 J. A. Schwarz, Surf. Sci., 87 (1979) 525.
9 C. M. Chan, R. Aris and W. H. Weinberg, Appl. Surf. Sci., 4 (1980) 234.
10 C. Pisaani, G. Rabino and F. Ricca, Surf. Sci., 41 (1974) 277.
11 S. O. Vasquez, J. Chem. Soc. Faraday Trans., 88 (1992) 2051.
12 C. T. Yeh, G. Chen and W. T. Chou, Appl. Catal., 8 (1983) 389.