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Computer simulation of derivative TPD

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Abstract

In this paper, the advantages of employing a Derivative Temperature-Programmed Desorption (DTPD) curve in TPD analysis are demonstrated. Based on a series of theoretical DTPD curves obtained by computer simulation with double assumption of zero signal noise and no temperature gradients across the sample, a comparison is made between the TPD and DTPD curves, and it is found that the approach can (a) estimate desorption order, (b) raise resolving power, and (c) eliminate baseline drift. The equations for calculating kinetic parameters from DTPD curves are also presented. The results show that these equations are valid.

Keywords: Computer simulation; Derivative TPD curve; TPD

1. Introduction

Elucidation of the interaction of reactants with catalyst surfaces is of primary importance in heterogeneous reaction systems. In the past twenty years, although techniques such as AES, XPS, HREELS, etc., have become popular, some traditional methods such as TPD and TPR have been found to be indispensable [1]. Generally speaking, an ultra-high vacuum is required in studies of the bonding between adsorbates and surfaces when modern techniques are used and in situ studies under reaction conditions are very difficult. Temperature-programmed desorption (TPD), however, can be conducted under reaction conditions and has wide application in catalytic research [1–5].

Although the TPD technique is simple, it is rather difficult to extract all the information present in the TPD curve. In order to exploit TPD fully, many researchers

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have undertaken a theoretical approach [6–14]. Generally speaking, TPD diagrams can be used qualitatively to obtain information about the number of adsorption forms on the surface and their relative stability. When catalyst surfaces are being analyzed, one finds that in most cases there are more than one kind of binding site and the desorption of adsorbants might produce overlapping peaks. It is generally accepted that better resolution between overlapping peaks can be achieved by using lower heating rates; however, the method is found to be ineffective in a number of cases [15].

Quantitative analysis of TPD curves allow calculation of the Arrhenius kinetic parameters for desorption [1,2,8,10,15]. Although there are better methods for calculating these parameters from TPD curves with a single-peak profile [1,2,8,10,15], it is difficult to analyze overlapping peaks quantitatively. There is a "simplex method" for resolving overlapping peaks [13]. However, before using such a method, it is necessary to estimate the number of peaks present in the profile from the peak shape. Therefore, whether in a qualitative or quantitative way, it is very important to improve the resolving power of the TPD curve.

Derivative spectra have been widely applied in UV, IR, AES and ESR to enhance resolving power [16–18]. In the present work, in order to improve resolving power of the TPD curves, we propose the adoption of a derivative temperature-programmed desorption (DTPD) curve. In the following sections, we describe simulation of the DTPD curves by computer, discuss the characteristics of the DTPD curves, and present the equations for calculation of kinetic parameters from the DTPD curves.

2. Computer simulation of theoretical DTPD curves

2.1. *The definition of DTPD*

The curve of $-\mathrm{d}\theta/\mathrm{d}T \sim T$ is generally called a TPD curve. Hence the curve of $-\mathrm{d}^2\theta/\mathrm{d}T^2 \sim T$ is the first DTPD curve, and the curve of $-\mathrm{d}\theta^3/\mathrm{d}T^3 \sim T$ the second. Higher-order DTPD curves can similarly be defined.

2.2. *Mathematical equations*

On the surface of a catalyst, although there might be many kinds of active sites, one can assume that each kind is homogeneous, i.e. the desorption of each adsorbent conforms to the model

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)\theta^n \qquad (1)$$

and with a constant heating rate, $\mathrm{d}T/\mathrm{d}t = \beta$, Eq. (1) becomes

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T} = \left(\frac{A}{\beta}\right)\exp\left(-\frac{E}{RT}\right)\theta^n \qquad (2)$$

with A the pre-exponential factor, T temperature, E activation energy, β heating rate, n order, θ surface coverage, t time, and R the gas constant. Eq. (2) can be rearranged and integrated

$$-\int_{\theta_0}^{\theta} \frac{1}{\theta^n}\mathrm{d}\theta = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{3}$$

where θ_0 is the initial surface coverage. Writing

$$F(T) = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{4}$$

and if $X = E/RT$, one can get

$$F(T) = \frac{EA}{R\beta}\int_0^{(E/RX)} \exp(-X)\mathrm{d}\left(\frac{1}{X}\right) \tag{5}$$

Because in most chemical desorption, $X \gg 1$, Eq. (5) can be expressed as [19]

$$F(T) = \frac{EA}{R\beta}\left[\frac{\exp(-X)}{X^2}\left(1 - \frac{2!}{X} + \frac{3!}{X^2} - \frac{4!}{X^3} + \cdots + (-1)^{m-1}\frac{m!}{X^{m-1}}\right)\right] \tag{6}$$

where m is a positive integer.

From Eqs. (3) and (4)

$$\theta = \theta_0 \exp[-F(T)] \qquad (n = 1) \tag{7a}$$

$$\theta = [(n-1)F(T) + \theta_0^{1-n}]^{(1/1-n)} \qquad (\mathrm{n} \neq 1) \tag{7b}$$

From Eqs. (7) and (2)

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\exp[-F(T)]\theta_0 \qquad (n = 1) \tag{8a}$$

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)[(n-1)F(T) + \theta_0^{(1-n)}]^{(n/1-n)} \qquad (n \neq 1) \tag{8b}$$

Eq. (2) can be differentiated to give

$$-\frac{\mathrm{d}^2\theta}{\mathrm{d}T^2} = -\left(\frac{\mathrm{d}\theta}{\mathrm{d}T}\right)\left[\left(\frac{n}{\theta}\right)\left(\frac{\mathrm{d}\theta}{\mathrm{d}T}\right) + \frac{E}{RT^2}\right] \tag{9}$$

Eq. (9) can be differentiated to give

$$-\frac{\mathrm{d}^3\theta}{\mathrm{d}T^3} = \left(-\frac{\mathrm{d}^2\theta}{\mathrm{d}T^2}\right)\left[\frac{E}{RT^2} - \frac{2n}{\theta}\right]\left(-\frac{\mathrm{d}\theta}{\mathrm{d}T}\right) - \left(-\frac{\mathrm{d}\theta}{\mathrm{d}T}\right)\left[\frac{n}{\theta^2}\left(-\frac{\mathrm{d}\theta}{\mathrm{d}T}\right)^2 + \frac{2E}{RT^3}\right] \tag{10}$$

If the parameters A, E, n, β and θ_0 are known, theoretical TPD, first DTPD and second DTPD curves can be simulated by using Eqs. (6)–(10). According to this principle, computer programs were written. A series of theoretic curves have been simulated.

3. Characteristics of DTPD

3.1. Characterization of DTPD

Figs. 1 and 2 are respectively the TPD, first DTPD and second DTPD curves of first- and second-order desorption. One can see that after differentiation, the single peak of the TPD curve, is converted into one positive peak and one negative peak in the first DTPD curve; while there are two positive peaks and one negative peak in the second DTPD curve. Moreover, the peaks of the DTPD curves are sharper than those of the original TPD curves. For first-order desorption (Fig. 1), the maximum height of the positive peak is smaller than the maximum height of the negative peak (absolute value)

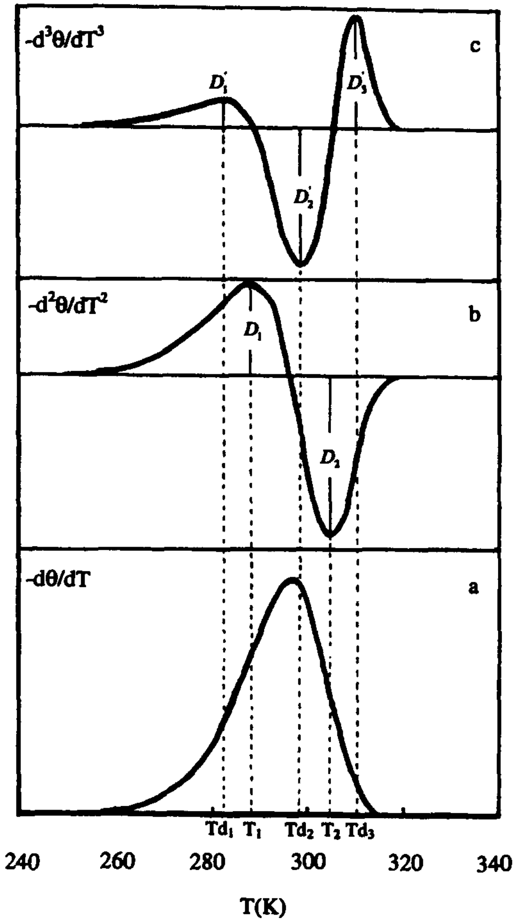

Fig. 1. Theoretical DTPD curves: $n = 1$, $A = 10^{13}\,s^{-1}$, $E = 83.684\,kJ\,mol^{-1}$, $\theta_0 = 1$, $\beta = 10\,K\,min^{-1}$. a, TPD curve; b, first DTPD curve; c, second DTPD curve.

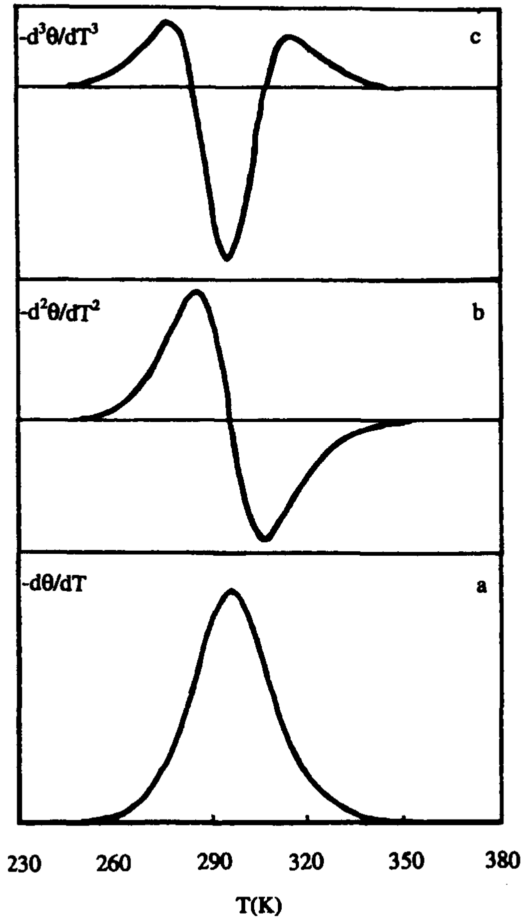

Fig. 2. Theoretical DTPD curves: $n = 2$, $A = 10^{13}\ \mathrm{s}^{-1}$, $E = 83.684\ \mathrm{kJ\ mol}^{-1}$, $\theta_0 = 1$, $\beta = 10\ \mathrm{K\ min}^{-1}$. a, TPD curve; b, first DTPD curve; c, second DTPD curve.

in the first DTPD curve; and the maximum height of the positive peak at the lower temperature is smaller than the one of the positive peak at the higher temperature in the second DTPD curve. For second-order desorption (Fig. 2), the shapes are markedly different: the absolute values of the maximum heights of the positive and negative peaks are approximately the same in the first DTPD curve; and in the second DTPD curve, one sees a group of symmetrical peaks. Therefore, from the characteristics of the DTPD curves, one can determine the order of desorption fairly easily.

3.2. *Separation of overlapping peaks*

As shown in Fig. 3, overlapping peaks corresponding to two kinds of state are difficult to distinguish in the TPD curve. However, it is obvious in the first DTPD curve

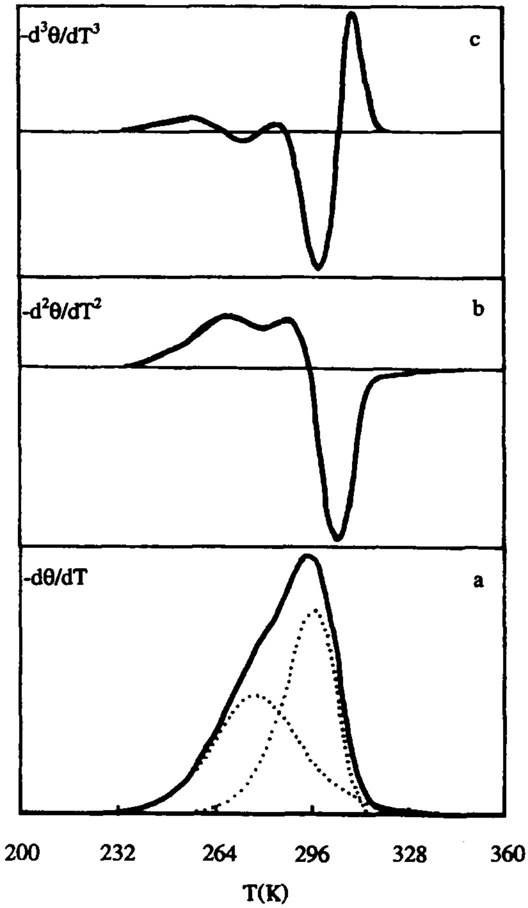

Fig. 3. Theoretical DTPD curves of overlapped peaks. State 1: $n = 1$, $A = 10^{13}\,\mathrm{s}^{-1}$, $E = 83.684\,\mathrm{kJ\,mol}^{-1}$, $\theta_0 = 1$, $\beta = 10\,\mathrm{K\,min}^{-1}$. State 2: $n = 2$, $A = 10^{10}\,\mathrm{s}^{-1}$, $E = 63.353\,\mathrm{kJ\,mol}^{-1}$, $\theta_0 = 1$, $\beta = 10\,\mathrm{K\,min}^{-1}$. a, TPD curve; b, first DTPD curve; c, second DTPD curve.

that there are two positive peaks (at 267 and 288 K) and two negative peaks (at 280 and 304 K). Because each state would have one positive and one negative peak in the first DTPD curve, the first DTPD curve with two positive peaks and two negative peaks indicates the existence of two states. The second DTPD curve shows three positive peaks (at 257, 284, and 309 K) and two negative peaks (at 275 and 299 K). Because each state would have two positive peaks and one negative peak in the second DTPD curve, from the second DTPD curve with three positive peaks and two negative peaks, one can conclude that there are two states present. Therefore, both the first and second DTPD curves reveal that there are two states of desorption present in the peak profile in Fig. 3. Hence the DTPD curves can reveal the number of states present.

3.3. Elimination of baseline drift

As shown in Fig. 4, when there is a linear baseline drift, the TPD curve is obviously affected. However, in the first DTPD curve, the baseline is raised slightly and in the second DTPD curve there is no change at all. When there is a second-order-function baseline drift, there are changes in the TPD and the first DTPD curves. However, in the second DTPD curve, the baseline is only raised, indicating that as far as the elimination

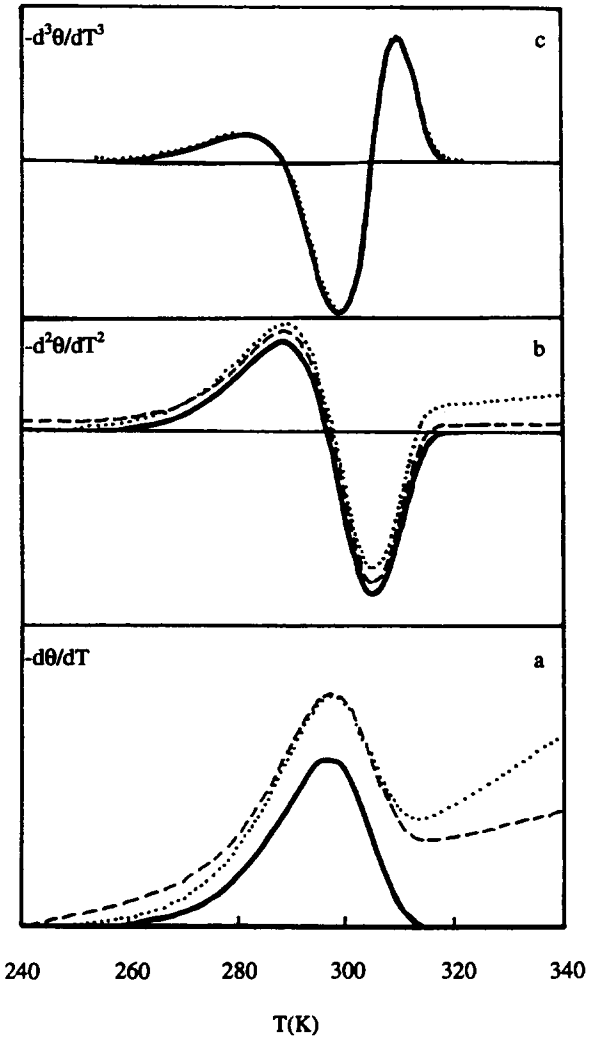

Fig. 4. Theoretical DTPD containing baseline drift: $n = 1$, $A = 10^{13}\,s^{-1}$, $E = 83.684\,kJ\,mol^{-1}$, $\theta_0 = 1$, $\beta = 10\,K\,min^{-1}$. a, TPD curve; b, first DTPD curve; c, second DTPD curve; —, no baseline, – – –, containing linear baseline drift; ····, containing second-order-function baseline drift.

of baseline drift is concerned, DTPD curves have advantage over TPD curves, while the second DTPD curves have advantage over the first DTPD curves. This is because any function can be expressed as

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T}=C_0+C_1T+C_2T^2+C_3T^3+\cdots+C_mT^m \tag{11}$$

On differentiation

$$-\frac{\mathrm{d}^2\theta}{\mathrm{d}T^2}=C_1+2C_2T+3C_3T^2+\cdots+mC_mT^{m-1} \tag{12}$$

one can see that the constant term is eliminated and the linear term has become a constant term, resulting in the elimination of the linear baseline drift. Eq. (12) can be differentiated to give

$$-\frac{\mathrm{d}^3\theta}{\mathrm{d}T^3}=2C_2+6C_3T+\cdots+(m-1)mC_mT^{m-2} \tag{13}$$

One can see that the $(C_0 + C_1 T)$ term of Eq. (11) is eliminated, i.e. the second-order term has become the constant term, indicating that the second-order-function baseline drift is eliminated. It can be seen that higher-order DTPD curves can eliminate lower-order-function baseline drift.

4. Equations for calculating desorption kinetic parameters from DTPD curves

According to Murray and White's expression [20], Eq. (2) can be written as

$$\ln\left(\frac{\theta_0}{\theta}\right)=\frac{A}{\beta}\left(\frac{RT^2}{E}\right)\left(1-\frac{2RT}{E}\right)\exp\left(-\frac{E}{RT}\right)\quad (n=1) \tag{14a}$$

$$\frac{1}{\theta}\left(1-\frac{\theta}{\theta_0}\right)=\frac{A}{\beta}\left(\frac{RT^2}{E}\right)\left(1-\frac{2RT}{E}\right)\exp\left(-\frac{E}{RT}\right)\quad (n=2) \tag{14b}$$

In general, $2RT/E \ll 1$, and Eq. (14) can be simplified as

$$\ln\left(\frac{\theta}{\theta_0}\right)=\frac{A}{\beta}\left(\frac{RT^2}{E}\right)\exp\left(-\frac{E}{RT}\right)\quad (n=1) \tag{15a}$$

$$\frac{1}{\theta}\left(1-\frac{\theta}{\theta_0}\right)=\frac{A}{\beta}\left(\frac{RT^2}{E}\right)\exp\left(-\frac{E}{RT}\right)\quad (n=2) \tag{15b}$$

From Eqs. (2) and (15), one can get

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T}=-\frac{E\theta}{RT^2}\ln\left(\frac{\theta}{\theta_0}\right)\quad (n=1) \tag{16a}$$

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T}=-\frac{E\theta}{RT^2}\left(\frac{\theta}{\theta_0}-1\right)\quad (n=2) \tag{16b}$$

From Eqs. (16) and (9), one can get

$$-\frac{d^2\theta}{dT^2} = -\theta\ln\left(\frac{\theta}{\theta_0}\right)\left[\ln\left(\frac{\theta}{\theta_0}\right)+1\right]\left(\frac{E}{RT^2}\right)^2 \quad (n=1) \tag{17a}$$

$$-\frac{d^2\theta}{dT^2} = -\theta\left(\frac{\theta}{\theta_0}-1\right)\left[2\left(\frac{\theta}{\theta_0}\right)-1\right]\left(\frac{E}{RT^2}\right)^2 \quad (n=2) \tag{17b}$$

Eq. (17) can be differentiated to give

$$-\frac{d^3\theta}{dT^3} = -\theta\ln\left(\frac{\theta}{\theta_0}\right)\left[\left(\ln\left(\frac{\theta}{\theta_0}\right)\right)^2+3\ln\left(\frac{\theta}{\theta_0}\right)+1\right]\left(\frac{E}{RT^2}\right)^3 \quad (n=1) \tag{18a}$$

$$-\frac{d^3\theta}{dT^3} = -\theta\left(\frac{\theta}{\theta_0}-1\right)\left[6\left(\frac{\theta}{\theta_0}\right)^2-6\left(\frac{\theta}{\theta_0}\right)+1\right]\left(\frac{E}{RT^2}\right)^3 \quad (n=2) \tag{18b}$$

From similar procedures, one can get

$$-\frac{d^4\theta}{dT^4} = -\theta\ln\left(\frac{\theta}{\theta_0}\right)\left[\left(\ln\left(\frac{\theta}{\theta_0}\right)\right)^3+6\left(\ln\left(\frac{\theta}{\theta_0}\right)\right)^2 + 7\ln\left(\frac{\theta}{\theta_0}\right)+1\right]\left(\frac{E}{RT^2}\right)^4 \quad (n=1) \tag{19a}$$

$$-\frac{d^4\theta}{dT^4} = -\theta\left(\frac{\theta}{\theta_0}-1\right)\left[24\left(\frac{\theta}{\theta_0}\right)^3-36\left(\frac{\theta}{\theta_0}\right)^2 + 14\left(\frac{\theta}{\theta_0}\right)-1\right]\left(\frac{E}{RT^2}\right)^4 \quad (n=2) \tag{19b}$$

4.1. First DTPD

Because at the extreme value points of the first DTPD curve, i.e. at $T=T_1$ and T_2, $(d/dt)(-d^2\theta/dT^2)=0$ (Fig. 1), according to Eq. (18), one can obtain

$$\left[\ln\left(\frac{\theta}{\theta_0}\right)\right]^2+3\left[\ln\left(\frac{\theta}{\theta_0}\right)\right]+1=0 \quad (n=1) \tag{20a}$$

$$6\left(\frac{\theta}{\theta_0}\right)^2-6\left(\frac{\theta}{\theta_0}\right)+1=0 \quad (n=2) \tag{20b}$$

From Eqs. (20a) and (20b) respectively, one can obtain

$$\frac{\theta}{\theta_0}=0.68, 0.073 \quad (n=1; T=T_1, T_2) \tag{21a}$$

$$\frac{\theta}{\theta_0}=0.79, 0.21 \quad (n=2; T=T_1, T_2) \tag{21b}$$

At the extreme values of $(-\mathrm{d}^2\theta/\mathrm{d}T^2)_{T=T_1} = D_1$ and $(-\mathrm{d}^2\theta/\mathrm{d}T^2)_{T=T_2} = D_2$ (Fig. 1), from Eqs. (15), (17) and (21), one can obtain
When $n = 1$

$$E = \frac{RT_1^2}{0.4}\left(\frac{D_1}{\theta_0}\right)^{1/2} \quad \text{or} \quad \frac{RT_2^2}{0.56}\left(-\frac{D_2}{\theta_0}\right)^{1/2} \tag{22}$$

$$A = 0.38\left(\frac{\beta E}{RT_1^2}\right)\exp\left(\frac{E}{RT_1}\right) \quad \text{or} \quad 2.62\left(\frac{\beta E}{RT_2^2}\right)\exp\left(\frac{E}{RT_2}\right) \tag{23}$$

When $n = 2$

$$E = \frac{RT_1^2}{0.31}\left(\frac{D_1}{\theta_0}\right)^{1/2} \quad \text{or} \quad \frac{RT_2^2}{0.31}\left(-\frac{D_2}{\theta_0}\right)^{1/2} \tag{24}$$

$$A = 0.27\left(\frac{\beta E}{\theta_0 RT_1^2}\right)\exp\left(\frac{E}{RT_1}\right) \quad \text{or} \quad 3.76\left(\frac{\beta E}{\theta_0 RT_2^2}\right)\exp\left(\frac{E}{RT_2}\right) \tag{25}$$

According to Eqs. (22)–(25), activation energies and pre-exponential factors can be calculated from first DTPD curves.

4.2. Second DTPD

Because at the extreme value points of the second DTPD curve, i.e. at $T = T_{d_1}, T_{d_2}$ and T_{d_3}, $(\mathrm{d}/\mathrm{d}T(-\mathrm{d}^3\theta/\mathrm{d}T^3) = 0$ (Fig. 1), according to Eq. (19), one can obtain

$$\left[\ln\left(\frac{\theta}{\theta_0}\right)\right]^3 + 6\left[\ln\left(\frac{\theta}{\theta_0}\right)\right]^2 + 7\ln\left(\frac{\theta}{\theta_0}\right) + 1 = 0 \quad (n = 1) \tag{26a}$$

$$24\left(\frac{\theta}{\theta_0}\right)^3 - 36\left(\frac{\theta}{\theta_0}\right)^2 + 14\left(\frac{\theta}{\theta_0}\right) - 1 = 0 \quad (n = 2) \tag{26b}$$

The two equations can be resolved to give

$$\frac{\theta}{\theta_0} = 0.85, 0.26, 0.011 \quad (n = 1; T = T_{d_1}, T_{d_2}, T_{d_3}) \tag{27a}$$

$$\frac{\theta}{\theta_0} = 0.91, 0.50, 0.092 \quad (n = 2; T = T_{d_1}, T_{d_2}, T_{d_3}) \tag{27b}$$

At the extreme values of $(-\mathrm{d}^3\theta/\mathrm{d}T^3)_{T=T_{d_1}} = D'_1$, $(-\mathrm{d}^3\theta/\mathrm{d}T^3)_{T=T_{d_2}} = D'_2$, $(-\mathrm{d}^3\theta/\mathrm{d}T^3)_{T=T_{d_3}} = D'_3$ (Fig. 1), Eqs. (15), (18), and (27) can be simplified
When $n = 1$

$$E = \left(\frac{RT_{d_1}^2}{0.42}\right)\left(\frac{D'_1}{\theta_0}\right)^{1/3} \quad \text{or} \quad \left(\frac{RT_{d_2}^2}{0.75}\right)\left(-\frac{D'_2}{\theta_0}\right)^{1/3} \quad \text{or} \quad \left(\frac{RT_{d_3}^2}{0.73}\right)(D'_3)^{1/3} \tag{28}$$

$$A = \frac{0.16\beta E}{RT_{d_1}^2}\exp\left(\frac{E}{RT_{d_1}}\right) \quad \text{or} \quad \frac{1.34\beta E}{RT_{d_2}^2}\exp\left(\frac{E}{RT_{d_2}}\right) \quad \text{or} \quad \frac{4.51\beta E}{RT_{d_3}^2}\exp\left(\frac{E}{RT_{d_3}}\right) \tag{29}$$

When $n = 2$

$$E = \left(\frac{RT_{d_1}^2}{0.35}\right)\left(\frac{D'_1}{\theta_0}\right)^{1/3} \quad \text{or} \quad \left(\frac{RT_{d_2}^2}{0.50}\right)\left(-\frac{D'_2}{\theta_0}\right)^{1/3} \quad \text{or} \quad \left(\frac{RT_{d_3}^2}{0.35}\right)\left(\frac{D'_3}{\theta_0}\right)^{1/3} \tag{30}$$

$$A = \frac{0.10\beta E}{\theta_0 R T_{d_1}^2}\exp\left(\frac{E}{RT_{d_1}}\right) \quad \text{or} \quad \frac{\beta E}{\theta_0 R T_{d_2}^2}\exp\left(\frac{E}{RT_{d_2}}\right), \quad \text{or} \quad \frac{9.87\beta E}{\theta_0 R T_{d_3}^2}\exp\left(\frac{\mathrm{E}}{RT_{d_3}}\right) \tag{31}$$

By using Eqs. (28)–(31), desorption activation energies and pre-exponential factors can be calculated from second DTPD curves.

4.3. The test of the equations by simulated DTPD curves

According to Eqs. (22)–(25), activation energies and pre-exponential factors were calculated by using the positive peak and the negative peak of the simulated first DTPD curve. The results are shown in Table 1. From Table 1, it can be seen that the

Table 1
Quantitative results of the first derivative TPD curves simulated by computer

Theoretical			Calcd.[a]			
n	lg A	E/J mol^{-1}	lg A_1	E_1/J mol^{-1}	lg A_2	E_2/J mol^{-1}
1	13	41842	13.19	42269	13.69	44583
1	13	62763	13.19	63353	14.00	67156
1	13	83684	13.20	84538	13.98	89232
1	13	104605	13.20	105697	14.00	111647
1	13	125526	13.21	127070	14.00	133961
1	13	146447	13.20	148041	13.99	156146
1	13	167368	13.20	169155	14.00	178544
1	5	83684	5.17	84776	6.04	95734
1	8	83684	8.18	84688	9.03	92337
1	10	83684	10.19	84700	11.02	90981
1	15	83684	15.21	84772	15.98	88617
2	13	41842	13.13	42043	14.64	46541
2	13	62763	13.13	63135	14.63	69633
2	13	83684	13.12	84023	14.63	92797
2	13	104605	13.13	105170	14.62	115680
2	13	125526	13.13	126233	14.62	138798
2	13	146447	13.13	147196	14.64	162146
2	13	167368	13.13	168284	14.62	184992
2	5	83684	5.12	83969	6.62	101287
2	8	83684	8.11	83951	9.62	96671
2	10	83684	10.13	84128	11.62	94676
2	15	83684	15.11	83960	16.64	91814

[a] A_1 and A_2 are respectively the calculated pre-exponential factors from the positive and negative peaks of the first derivative TPD curves. E_1 and E_2 are respectively the calculated desorption activation energies from the positive and negative peaks of the first derivative TPD curves.

calculated activation energies and pre-exponential factors from the positive peaks are consistent with the actual values. However, the calculated results from the negative peaks have some deviation. This is because certain approximate treatments introduced in the calculation are more appropriate at low temperature than at high temperature. Therefore, in the analysis of first DTPD curves, positive peaks should be used.

Any of the three peaks in the second DTPD curve is suitable for the calculation of the desorption kinetic parameters. According to Eqs. (28)–(31), the activation energies and pre-exponential factors were calculated using the positive and negative peaks of the simulated second DTPD curve. The results are shown in Table 2. From Table 2, it can be seen that the calculated activation energies and the pre-exponential factors from positive peaks at low temperature are consistent with the actual values. However, calculated results from negative and positive peaks at higher temperature have some deviation. This is also because certain approximating treatments introduced in the calculation are more appropriate at low temperature than at high temperature.

Table 2
Quantitative results of the second derivative TPD curves simulated by computer

Theoretical			Calcd.[a]					
n	$\lg A$	$E/\mathrm{J\,mol^{-1}}$	$\lg A_1$	$E_1/\mathrm{J\,mol^{-1}}$	$\lg A_2$	$E_2/\mathrm{J\,mol^{-1}}$	$\lg A_3$	$E_3/\mathrm{J\,mol^{-1}}$
1	13	41842	12.51	40424	13.70	43779	14.17	45248
1	13	62763	12.52	60692	13.68	65525	14.23	68152
1	13	83684	12.50	80776	13.69	87433	14.23	90780
1	13	104605	12.51	101099	13.70	109325	14.23	113413
1	13	125526	12.51	121342	13.70	131130	14.22	135974
1	13	146447	12.51	141468	13.71	153163	14.23	158765
1	13	167368	12.51	161740	13.71	175033	14.23	181410
1	5	83684	4.49	77529	5.65	90496	6.23	98216
1	8	83684	7.49	79232	8.68	89065	9.23	94266
1	10	83684	9.49	79922	10.69	88316	11.22	92442
1	15	83684	14.51	81186	15.72	87261	16.23	90023
2	13	41842	12.32	39859	13.87	44181	15.13	47976
2	13	62763	12.31	59822	13.87	66219	15.12	71793
2	13	83684	12.29	79567	13.86	88161	15.13	95743
2	13	104605	12.30	99567	13.87	110325	15.14	119693
2	13	125526	12.29	119451	13.85	132070	15.12	143234
2	13	146447	12.30	139535	13.86	154117	15.12	167079
2	13	167368	12.30	159468	13.87	176289	15.13	191063
2	5	83684	4.38	76261	5.87	92040	7.2	108572
2	8	83684	7.36	78186	8.87	90149	10.18	101776
2	10	83684	9.33	78889	10.86	89132	12.16	98760
2	15	83684	14.30	80132	15.87	87759	17.12	94408

[a] A_1, A_2 and A_3 are respectively the calculated pre-exponential factors from the positive peak at low temperature, and the negative and positive peaks at high temperature of the second derivative TPD curves. E_1, E_2 and E_3 are respectively the calculated desorption activation energies from the positive peak at low temperature, and the negative and positive peaks at high temperature of the second derivative TPD curves.

Therefore, in the analysis of second DTPD curves, positive peaks at low temperature should be used.

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References

[1] S. Bahtia, J. Beltramini and D.D. Do, Catalysis Today, 7 (1990) 1.
[2] R.J. Cvetanovic and V. Amenomiya, Catal. Rev.-Sci. Eng., 6 (1972) 21.
[3] Y.P. Arnaud, Appl. Sci., 62 (1992) 21.
[4] B. Fastrup, M. Muhler, H. Nygard Nielsen and L. Pleth Nielsen, J. Catal., 142 (1993) 135.
[5] A. Rochefort, F.L. Peltier and J.P. Boitiaux, J. Catal., 145 (1994) 409.
[6] J.A. Konvalinka, J.J.F. Scholten and J.C. Rasser, J. Catal., 48 (1977) 365.
[7] P.I. Lee and J.A. Schwarz, J. Catal., 73 (1982) 272.
[8] J.L. Falconer and J.A. Schwarz, Catal. Rev.-Sci. Eng., 25 (1983) 14.
[9] J.S. Riech and A.T. Bell, J. Catal., 85 (1984) 143.
[10] Y.H. Hu, Petrochemical Technology of China, 15 (1986) 167.
[11] J.M. Criado, P. Malet and G. Munuera, Langmuir, 3 (1987) 973.
[12] T. Ioannides and X.E. Verykios, J.Catal., 120 (1989) 157.
[13] Y.H. Hu, A.M. Huang, J.X. Cai and H.L. Wan, Chem. J. Chin. Univ., 13 (1992) 952.
[14] Y.H. Hu, H.L. Wan and K.R. Tsai, Chem. J. Chin. Univ., 14 (1993) 238.
[15] P. Malet, in J.L.G. Fierro (Ed.), Studies in Surface Science and Catalysis, Vol. 57B, Elsevier Science, Amsterdam, 1990, p. B333, and references cited therein.
[16] R.N. Hager, Jr., Anal. Chem., 45 (1973) 1131A.
[17] J. Alvarer and M.C. Asensio, in J.L.G. Fierro (Ed.), Studies in Surface Science and Catalysis, Vol. 57A, Elsevier Science, Amsterdam, 1990, p. A79, and references cited therein.
[18] M. Che, B. Canosa and A.R. Gonzalez-Elipe, J. Phys. Chem., 90 (1986) 618.
[19] A.W. Smith and S. Aranoff, J. Phys. Chem., 62 (1958) 684.
[20] M.P. White, J. Trans. Br. Ceram. Soc., 54 (1955) 15.