Thermochimica Acta, 208 (1992) 275–281
Elsevier Science Publishers B.V., Amsterdam

Temperature programmed desorption (TPD) from catalyst surfaces: the symmetry of the TPD curve as a function of the kinetic model

Jiří Málek

Joint Laboratory of Solid State Chemistry of the Czechoslovak Academy of Sciences and Institute of Chemical Technology, 532 10 Pardubice (Czech and Slovak Federal Rep.)

José M. Criado

Instituto de Ciencias de Materiales, C.S.I.C., Universidad de Sevilla, 41071 Seville (Spain)

(Received 3 December 1991)

Abstract

It is known that the shape of the temperature programmed desorption (TPD) curve is closely related to the desorption mechanism. This paper presents an analysis of the problem. The mathematical expression for the shape index of the TPD curve is derived and discussed. A simple method has been described which allows determination of the most suitable kinetic model. The method was used to analyze the experimental data of Ying and Madix for the decomposition of formic acid on a copper surface.

The study of thermal decomposition and/or desorption of chemisorbed species from catalyst surfaces, known as temperature programmed desorption (TPD), provides considerable information about the kinetic behaviour of the particular system. The TPD data have been analyzed in the literature for both first and second order desorption with and without the influence of readsorption.

There are various methods for determining the kinetic model of the desorption process from experimental TPD data. One of these methods is the shape index analysis, which was first used by Kissinger [1] to analyze the decomposition of solids followed by methods of thermal analysis. Several authors [2–7] have considered the applicability of this concept to TPD. A general expression has been derived for the shape index (S) covering the above mentioned mechanisms of the desorption process [5].

Correspondence to: J. Málek, Joint Laboratory of Solid State Chemistry, Czechoslovak Academy of Sciences and Institute of Chemical Technology, 532 10 Pardubice, Czech and Slovak Federal Rep.

This equation was later corrected [6] and some further aspects of the shape index analysis were discussed.

We have found, however, that the theoretical values of S published in these papers are probably miscalculated. This fact implies some doubts about the conclusions drawn previously. Therefore it seems necessary to revise the analysis of the problem.

The desorption rate of gases adsorbed on the surface of a catalyst obeys the general kinetic law

$$-\mathrm{d}\theta/\mathrm{d}t = A\exp(-E/RT)f(\theta) \tag{1}$$

where θ represents the surface coverage, A is the preexponential factor of Arrhenius, E is the activation energy of the desorption process in the case of no readsorption or the adsorption enthalpy in the free readsorption limit, and the symbols R and T have their usual meaning. The function $f(\theta)$ depends on the desorption kinetics, and its algebraic expression, integral form and both first and second derivatives are summarized in Table 1 for these important cases: first order desorption without the influence of readsorption (1W), first order desorption with equilibrated readsorption (1R1), second order desorption without the influence of readsorption (2W) and, finally, second order desorption with equilibrated readsorption (2R2).

The shape index is usually defined according to Kissinger [1] as the absolute ratio of the slope of the tangents to the TPD peak at the inflection points, which can be formulated analytically as

$$S = \frac{(\mathrm{d}^2\theta/\mathrm{d}t^2)_{i=1}}{(\mathrm{d}^2\theta/\mathrm{d}t^2)_{i=2}} \tag{2}$$

where the subscripts $i = 1$ and $i = 2$ refer to the first and second inflection points, respectively.

Equation (1) can be integrated between the initial coverage θ_0 and θ

TABLE 1

Algebraic expressions of the kinetic model functions for different desorption kinetics

Model	$f(\theta)$	$f'(\theta)$	$f''(\theta)$	$g(\theta)$
1W	θ	1	0	$-\ln(\theta/\theta_0)$
1R1	$\dfrac{\theta}{1-\theta}$	$\dfrac{1}{(1-\theta)^2}$	$\dfrac{2}{(1-\theta)^3}$	$\theta-\theta_0-\ln(\theta/\theta_0)$
2W	θ^2	2θ	2	$\dfrac{1}{\theta}-\dfrac{1}{\theta_0}$
2R2	$\dfrac{\theta^2}{(1-\theta)^2}$	$\dfrac{2\theta}{(1-\theta)^3}$	$\dfrac{2+4\theta}{(1-\theta)^4}$	$\dfrac{1}{\theta}-\dfrac{1}{\theta_0}-\theta+\theta_0+2\ln(\theta/\theta_0)$

yielding the expression

$$g(\alpha)=\int_{\theta_0}^{\theta}\frac{\mathrm{d}\theta}{f(\theta)}=-\frac{AE}{\beta R}\mathrm{e}^{-x}\left[\frac{\pi(x)}{x}\right] \tag{3}$$

where $x = E/RT$ is the reduced activation energy and β is the heating rate applied in a TPD experiment. The term $\pi(x)$ is an approximation of the temperature integral. There are many approximate expressions of $\pi(x)$ in the literature. According to our experience, the rational expression of Senum and Yang [9] is sufficient

$$\pi(x)=\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \tag{4}$$

Differentiating eqn. (1) with respect to time and combining with eqn. (3), we obtain the equation for the derivative of the TPD peak in the form

$$(\mathrm{d}^2\theta/\mathrm{d}t^2)=\left[\frac{\beta Rx}{E\pi(x)}\right]^2 g(\theta)f(\theta)[f'(\theta)g(\theta)+x\pi(x)] \tag{5}$$

From eqns. (1) and (5) a mathematical expression for the shape index of a TPD peak is obtained

$$S=\left|\frac{f(\theta_1)g(\theta_1)[f'(\theta_1)g(\theta_1)+x_1\pi(x_1)]}{f(\theta_2)g(\theta_2)[f'(\theta_2)g(\theta_2)+x_2\pi(x_2)]}\right|\left[\frac{x_1\pi(x_2)}{x_2\pi(x_1)}\right]^2 \tag{6}$$

where θ_1 and θ_2 are values of the surface coverage at the first and second inflection points of a TPD peak corresponding to the roots of the equation

$$\begin{aligned}&f'(\theta_i)g(\theta_i)[f'(\theta_i)g(\theta_i)+3x_i\pi(x_i)]\\&\quad+f''(\theta_i)f(\theta)g^2(\theta_i)x_i\pi(x_i)[x_i\pi(x_i)-2\pi(x_i)]=0\end{aligned} \tag{7}$$

Thus, if the value of x_i is known the shape index can be calculated using eqns. (6) and (7). It can be shown that, for a given initial coverage, x_i depends only on the reduced activation energy at the maximum of a TPD peak (x_p) and is invariant with respect to the heating rate. This provides a formulation of the $\Delta x_i(x_p)=|x_p-x_i|$ function characteristic for each kinetic model, as shown in Fig. 1 for $\theta_0=1$. It is seen that $\Delta x_2<\Delta x_1$ for all kinetic models analyzed. This asymmetry becomes greater for low values of x_p, especially when readsorption takes place.

In the context of the foregoing, the shape index can be expressed as a function of x_p. These $S(x_p)$ dependences calculated using eqns (3), (6) and (7) are presented in Fig. 2 for $\theta_0=1$. It can be seen that the value of the shape index decreases steadily with increasing x_p for all the kinetic models analyzed. Contrary to these results, increasing $S(x_p)$ dependences have been published in some earlier works [4, 6]. This discrepancy seems to arise from the incorrect assumption that $\Delta x_i \rightarrow 0$. There is also missing a multiplicative factor $[x_1\pi(x_2)/x_2\pi(x_1)]$ in the equation for S published in

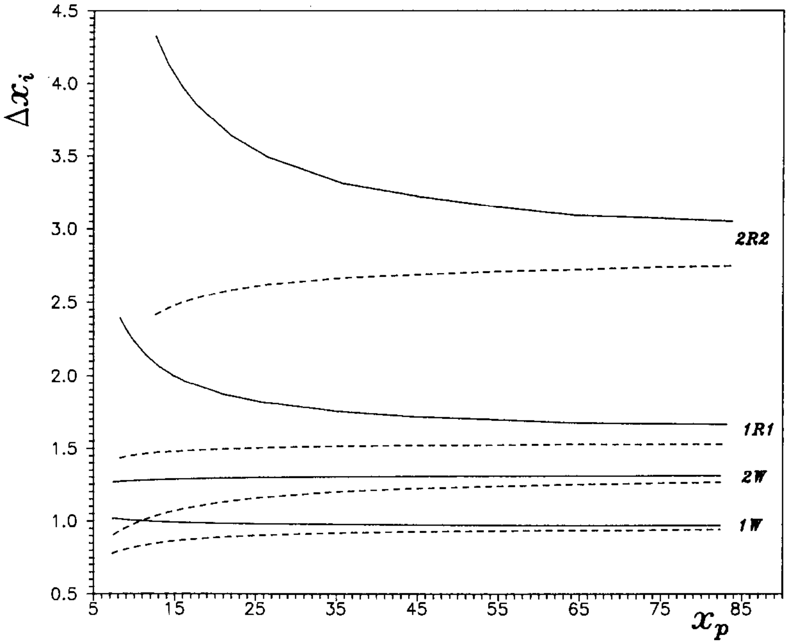

Fig. 1. The $\Delta x_i(x_p)$ dependence for the 1W, 1R1, 2W and 2R2 models calculated for $\theta_0 = 1$. The solid and broken lines correspond to $i = 1$ and $i = 2$, respectively.

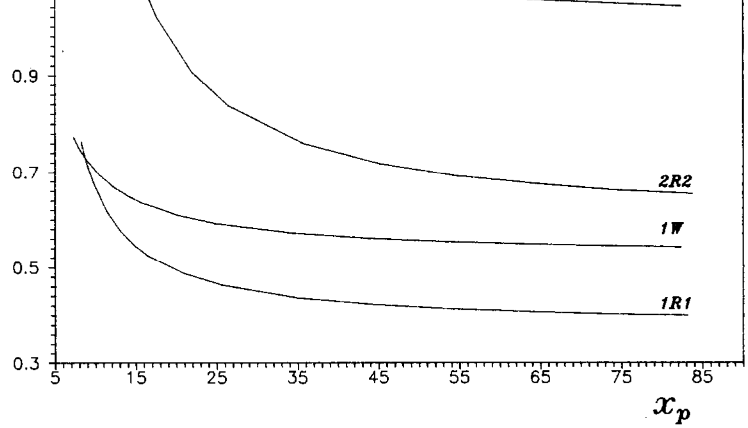

Fig. 2. The dependence of the shape index versus x_p for the 1W, 1R1, 2W and 2R2 models ($\theta_0 = 1$).

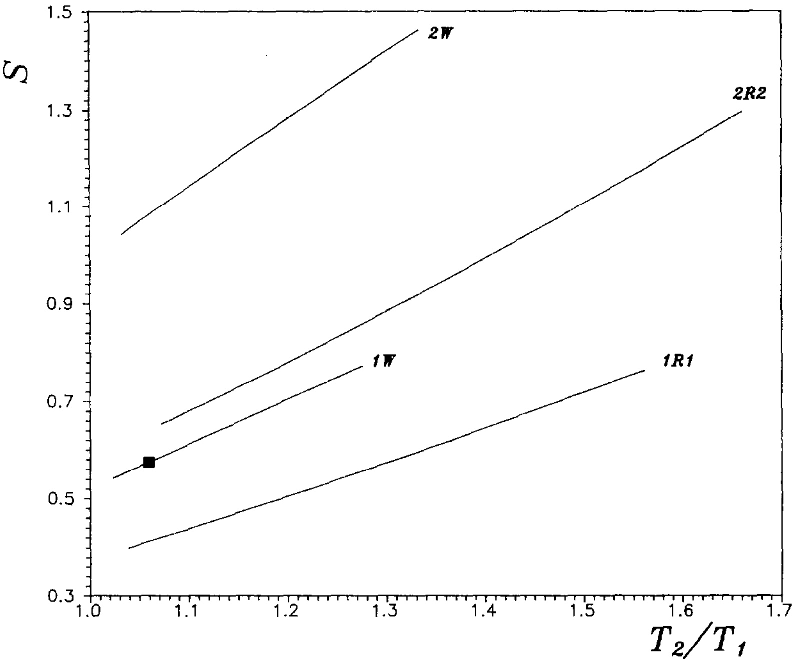

Fig. 3. The dependence of the shape index versus T_2/T_1 ratio for the 1W, 1R1, 2W and 2RS models ($\theta_0 = 1$). The filled square corresponds to the data shown in Fig. 4.

earlier papers [4, 6]. Therefore all these previously published results are probably erroneous.

It might be concluded that the changes of the shape index with x_p within a relatively broad range may complicate an unambiguous determination of the actual desorption kinetics [6]. We have found, however, that there is a practically linear relationship between the shape index and the T_2/T_1 ratio characteristic of each kinetic model, as shown in Fig. 3 for $\theta_0 = 1$. The parameters k and q corresponding to the equation

$$S = k(T_2/T_1) + q \tag{8}$$

are summarized in Table 2. The shape index as well as the T_2/T_1 ratio can

TABLE 2

The constants of eqn. (8) for different desorption kinetics

Model	k	q
1W	0.195 ± 0.001	−0.395 ± 0.002
2W	1.399 ± 0.004	−0.398 ± 0.005
1R1	0.692 ± 0.005	−0.323 ± 0.006
2R2	1.008 ± 0.011	−0.514 ± 0.014

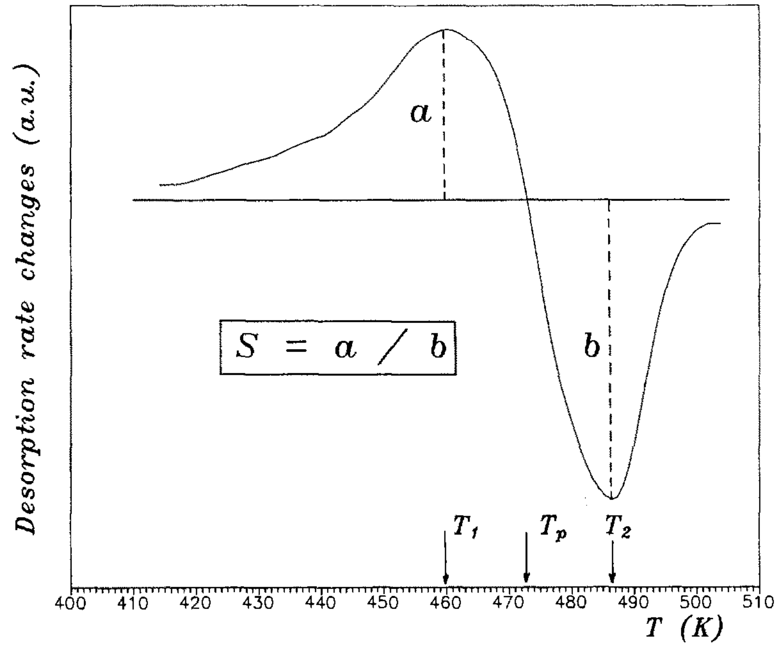

Fig. 4. The derivative of the TPD curve of CO_2 desorption from a Cu(110) surface [8].

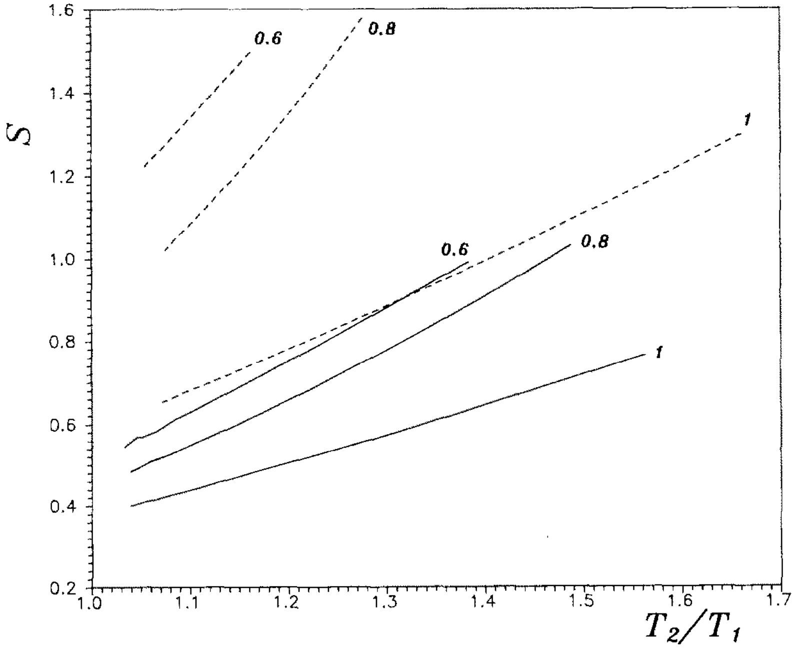

Fig. 5. The influence of the initial coverage on the S versus (T_2/T_1) dependence for first and second order desorption with equilibrated readsorption. The solid and broken lines correspond to the 1R1 and 2R2 models, respectively. The numbers represent the values of θ_0.

be easily obtained from a derivative of the TPD curve (see Fig. 4), which allows determination of the most probable kinetic model. It is noteworthy that the linear relationship of the shape index and the T_2/T_1 ratio found in this paper is in contradiction with the power dependence $S \approx (T_2/T_1)^4$ expected in some earlier work [4, 6].

The suitability of this shape index analysis can be demonstrated using the TPD data of CO_2 desorption reported by Ying and Madix [8] for the catalytic decomposition of formic acid on an oriented copper single crystal. The analysis of the first derivative of these TPD data shown in Fig. 4 leads to a T_2/T_1 value of 1.057 and an S value of 0.57. These values, shown by the filled square in Fig. 3, are in very good agreement with the 1W model proposed by the above authors [8].

It should be pointed out, however, that the method based on the S versus T_2/T_1 linear relationship can be used without any restriction only for the desorption processes without readsorption (i.e. the 1W and 2W models) because in these cases S does not depend on the initial coverage [5, 6]. On the other hand, for both 1R1 and the 2R2 model, the value of the shape index strongly depends on the initial coverage, as shown in Fig. 5. Therefore, if the desorption process is influenced by readsorption, the shape index analysis cannot be applied unless the initial coverage is known a priori.

REFERENCES

1 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
2 J.A. Konvalinka and J.J.F. Scholten, J. Catal., 48 (1977) 374.
3 I. Carrizosa, J.M. Criado and V. Rives, J. Catal., 52 (1978) 547.
4 J.M. Criado, P. Malet, G. Munuera and V. Rives, Thermochim. Acta, 38 (1980) 37.
5 E.E. Ibok and D.F. Ollis, J. Catal., 66 (1980) 391.
6 J.M. Criado, P. Malet, G. Munuera and V. Rives, J. Catal., 75 (1982) 428.
7 D.F. Ollis and E.E. Ibok, J. Catal., 75 (1982) 433.
8 D.H.S. Ying and R.J. Madix, J. Catal., 61 (1980) 48.
9 G.I. Senum and R.T. Yang, J. Therm. Anal., 11 (1977) 445.