

THE STUDY OF DIFFUSION PROCESSES IN THE THERMODESORPTION RESULTS

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A consecutive model of surface reaction, consisting of two steps (desorption and diffusion) was applied. It was concluded that diffusion modifies the temperature programmed desorption spectra, although the single peak curves appear. The differential method for calculation of kinetic parameters based on the T_M shift give values close to predicted ones only in the cases when particular steps are rate limiting. Generally, the desorption process have to be considered as a complex reaction, with the overall kinetic parameters. As a consequence of diffusion influence, the overall kinetic parameters are smaller than those for desorption step was obtained.

Keywords: diffusion, kinetic parameters, temperature programmed desorption (TPD)

Introduction

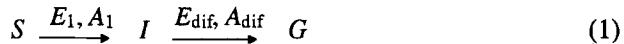
Temperature programmed desorption (TPD) is often used in the evaluation of kinetic parameters of desorption. However, the accuracy of obtained data could be (in some cases) unreliable, because of complex reaction mechanism [1, 2]. The mechanism of surface reaction is usually composed of elementary reactions: desorption, diffusion, jumps between active centres and, very often, readsorption [2]. Therefore, this complexity of the mechanism of desorption should be taken into account in the evaluation of kinetic parameters from TPD results.

In the cases of porous materials, the desorption step is obviously followed by diffusion into the micropore of solid phase. The experimental resolution of these two steps is not possible during the TPD procedure. From the chemical kinetics point of view, each of these processes can be rate limiting particularly, in the cases where rate constants varies many orders of magnitudes ($k_{des} \gg k_{dif}$, or $k_{des} \ll k_{dif}$) but, generally, the overall reaction rate is dependent on both steps. Therefore, in the cases where rate constants of both steps are of the same order

($k_{des} = k_{dif}$) the shape and position of temperature programmed desorption spectra (TDS) can be affected by diffusional limitations. The phenomenon of diffusion is very important for overall surface reaction. However, as a result of reaction mechanism consisting of two steps, desorption and diffusion, TDS having only one peak appears. Consequently, the evaluation of kinetic parameters of particular steps is not possible. So, only the kinetic parameters of overall reaction mechanism could be obtained using TPD methods. The calculations of theoretical TDS, obtained with postulated mechanism, could be a method for investigation of diffusion influence on the reliability of obtained kinetic parameters and the profile of TDS.

Model and computational method

In this paper, previously developed of two consecutive steps was applied [3]:



Here, S demonstrates molecule of adsorbate bonded with active site on the surface. The model of intermediate or precursor state existing during the surface reaction (a loosely bonded intermediate able to migrate on the surface), already postulated by King *et al.* [1, 2], was accepted here. In the scheme (1) I denotes this precursor and G denotes free gas molecule. E_1 and E_{dif} are activation energies of two steps, while A_1 and A_{dif} are their pre-exponential factors.

Recently developed model (1) gave the complex function for overall reaction rate, θ , in non-isothermal conditions (only the linear relationship between temperature and time was assumed) [3]:

$$\theta = \frac{dN_G}{dT} = A_{dif} \exp\left(-\frac{E_{dif}}{RT}\right) \exp(-A_{dif} I_2(u)) (i)_o + a_1 (s)_o L(u) \quad (2)$$

Here, N_G is a number of desorption molecules; $(i)_o$ and $(s)_o$ are initial partial surface coverages (at $T = T_o$) of species I and S , respectively. In Eq. (2), following notation was introduced:

$$I_1(u) = \int_{T_o}^u \frac{1}{f(t)} \exp\left(-\frac{E_1}{RT}\right) dT, \text{ and } I_2(u) = \int_{T_o}^u \frac{1}{f(t)} \exp\left(-\frac{E_{dif}}{RT}\right) dT \quad (3)$$

Also,

$$L(u) = \int_{T_o}^u \frac{1}{f(t)} \exp\left(-\frac{E_1}{RT} - A_1 I_1(T) + A_2 I_2(T)\right) dT \quad (4)$$

In Eqs (3) and (4), u is a final temperature of integration. Here, $T = f(t)$ and thus, $dT = f'(t)dt$, so it follows that: $dT/dt = f'(t)$, which has the meaning of desorption rate.

Evidently, the overall reaction rate depends on four kinetic parameters (activation energies and pre-exponential factors for both steps) and desorption rate. The differentiation of Eq. (2) with respect to temperature gives the relation between temperature of peak maximum T_M and kinetic parameters. This function have to be dependent on all kinetic parameters and quite different of well known equation obtained in the case of first rate reaction [4, 5].

The explicit calculations of reaction rate needs calculation of complex integrals. Here, we calculated the values of integrals (3), and (4) by using the Gauss-Kronrod method of numerical integration [6]. This method gives high accuracy of calculations; in addition, it gives estimate of the accuracy of the calculated results.

All of calculations are performed on a PC AT computer, with a MS Fortran 4.10 compiler. A program for computations of theoretical TDS is written in Fortran 77 language, and is available on request.

Results and discussions

In this paper, we studied the influence of diffusion step on the overall thermodesorption process, and so, on the TDS. Kinetic parameters of diffusion step were varies for many order of magnitudes. Diffusion coefficient D_0 was varied from $10^{-10} \text{ m}^2/\text{s}$ to $10^{-7} \text{ m}^2/\text{s}$; these values correspond to the diffusion of different gases in the most of microporous materials [7]. Pre-exponential factor for diffusion was assumed to be:

$$A_{\text{diff}} = \frac{D_0 \pi^2}{r_0^2} \ln \frac{6}{\pi^2} \quad (6)$$

This equation was obtained after the reorganization of the solution of second Fick's law for spherical particle [8], where r_0 is the radius, and was set to be $10 \text{ } \mu\text{m}$.

As it was shown [3], the influence of pre-exponential factor of diffusion step can not be neglected in the interpretation of single peak thermodesorption spectra originated from desorption of weakly bonded molecules. Activation energy for diffusion is close in value to the heat of condensation; so it is usually an order of magnitude smaller than the activation energy of desorption of chemisorbed species [9, 10]. But, in the cases of strongly bonded large organic molecules, (such as pyridine) the ratio E_1/E_{dif} becomes lower, and the influence of

activation energy of diffusion on the function (2), and thus, on the profile of TDS is expected. Here, we studied both possible cases of diffusion influence.

Figure 1 presents a set of computed TDS simulating the surface reaction taking place at weak active sites. This series was obtained by the variation of pre-exponential factor A_{dif} between 200 s^{-1} and 1 s^{-1} (corresponding to change of diffusion coefficient from $10^{-9} \text{ m}^2/\text{s}$ to $10^{-7} \text{ m}^2/\text{s}$), while all other kinetic parameters and heating rate are kept constant.

The calculated spectra shown in Fig. 2 simulate surface reaction taking place at strong active centers ($E_1 = 180 \text{ kJ/mol}$). Activation energy for diffusion step (E_{dif}) was varied, and the set of curves with similar values of T_M was obtained. However, broadening of spectra is observed with increasing of parameter E_{dif} .

Obviously, the whole family of curves presented in Fig. 1 is placed between

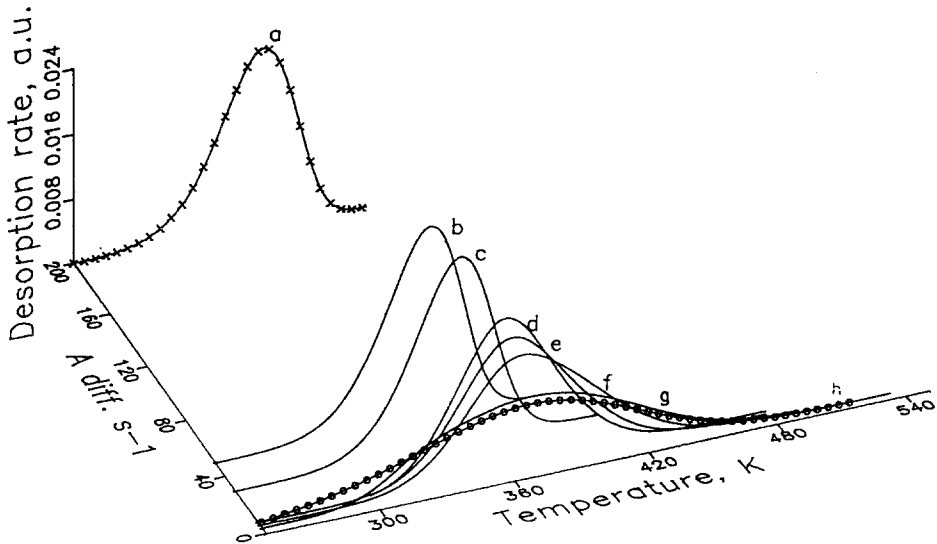


Fig. 1 The set of TDS calculated using common parameters: $E_1 = 50 \text{ kJ/mol}$, $A_1 = 10^6 \text{ s}^{-1}$, $E_{\text{dif}} = 20 \text{ kJ/mol}$; and varying parameter A_{dif} : a) $A_{\text{dif}} = 200 \text{ s}^{-1}$, b) $A_{\text{dif}} = 100 \text{ s}^{-1}$, c) $A_{\text{dif}} = 50 \text{ s}^{-1}$, d) $A_{\text{dif}} = 30 \text{ s}^{-1}$, e) $A_{\text{dif}} = 10 \text{ s}^{-1}$, f) $A_{\text{dif}} = 8 \text{ s}^{-1}$, g) $A_{\text{dif}} = 6 \text{ s}^{-1}$, h) $A_{\text{dif}} = 4 \text{ s}^{-1}$. Spectra marked with * is computed with desorption parameters: $E_1 = 50 \text{ kJ/mol}$, $A_1 = 10^6 \text{ s}^{-1}$. Spectra marked with \circ is computed with diffusion parameters: $E_{\text{dif}} = 20 \text{ kJ/mol}$, $A_{\text{dif}} = 4 \text{ s}^{-1}$

two limiting boundary curves – characteristic for consecutive mechanism: first one with desorption (curve *) and second one with diffusion (o) as rate limiting step. Evidently, increasing influence of diffusion (decreasing of pre-exponential factor A_{dif}) leads to the changes in TDS profile: curves becomes broader and their temperatures of peak maximum, T_M , shift toward higher values. Curves a

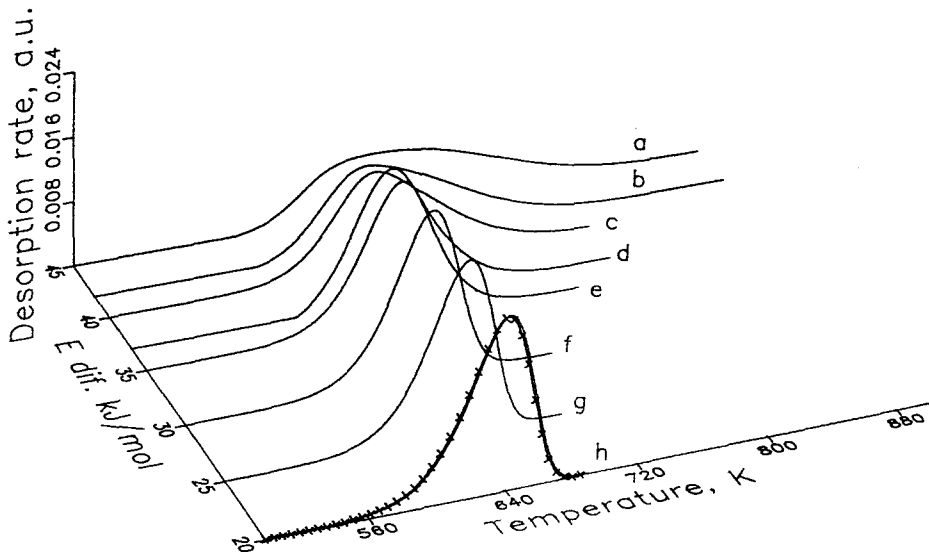


Fig. 2 The series of calculated TDS obtained varying parameter E_{dif} , and using common parameters: $E_1 = 180$ kJ/mol, $A_1 = 10^{13}$ s $^{-1}$, $A_{dif} = 10$ s $^{-1}$; and varying parameter E_{dif} : a) $E_{dif} = 20$ kJ/mol, b) $E_{dif} = 25$ kJ/mol, c) $E_{dif} = 30$ kJ/mol, d) $E_{dif} = 35$ kJ/mol, e) $E_{dif} = 37$ kJ/mol, f) $E_{dif} = 40$ kJ/mol, g) $E_{dif} = 42$ kJ/mol, h) $E_{dif} = 45$ kJ/mol

and h are almost identical with limiting ones. Also, the curve h at Fig. 2 is overlapped with spectra marked (*), presenting simple desorption reaction. However, a number of spectra on both figures simulate surface reaction dependent on all kinetic parameters.

The result of variation of heating rate while all kinetic parameters kept constant and equal as in the case of curve c in Fig. 1, is presented in Fig. 3. Usual shift towards higher temperatures with increasing heating rate is observed.

Obviously, the complex surface consecutive reaction including desorption and diffusion steps always leads to a single peak TPD spectra. In the cases where a single peak TDS appear, it is suitable to apply the differential method for calculation of kinetic parameters, based on T_M shift obtained for different heating rate [4, 5] (denoted here as Redhead's).

In Table 1, kinetic parameters assumed in consecutive model, and those evaluated using Redhead's equation (overall kinetic parameters), are compared. These results indicate that parameters calculated using Redhead's equation are close in values to kinetic parameters of particular steps, only when diffusion or desorption is rate limiting step (rows 1 and 9 in the Table 1). In the cases where both consecutive processes have influence on reaction rate, overall kinetic parameters between those for desorption and diffusion step are obtained. Gener-

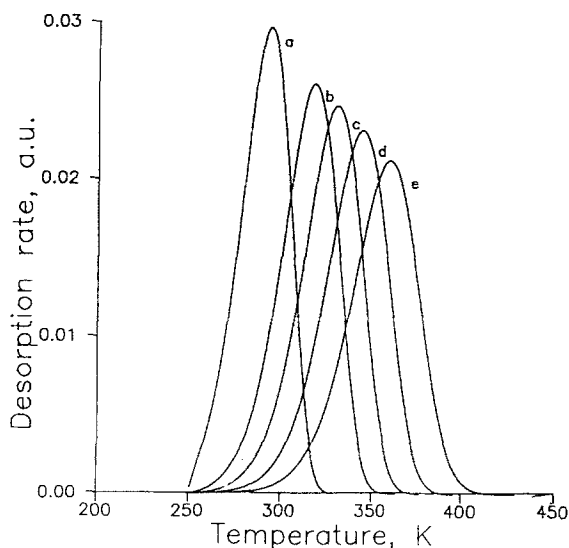


Fig. 3 The series obtained using common parameters: $E_1 = 50 \text{ kJ}\cdot\text{mol}^{-1}$, $A_1 = 10^6 \text{ s}^{-1}$, $E_{\text{dif}} = 20 \text{ kJ}\cdot\text{mol}^{-1}$, $A_{\text{dif}} = 50 \text{ s}^{-1}$; and varying heating rate β : a) $\beta = 1 \text{ deg}\cdot\text{min}^{-1}$, b) $\beta = 5 \text{ deg}\cdot\text{min}^{-1}$, c) $\beta = 10 \text{ deg}\cdot\text{min}^{-1}$, d) $\beta = 20 \text{ deg}\cdot\text{min}^{-1}$, e) $\beta = 40 \text{ deg}\cdot\text{min}^{-1}$

Table 1 The comparison of kinetic parameters predicted in calculation of theoretical TDS and those obtained using Redhead's equation (overall kinetic parameters)

Parameters used in consecutive model				Overall kinetic parameters	
$E_1 /$ kJ/mol	$A_1 /$ s^{-1}	$E_{\text{dif}} /$ kJ/mol	$A_{\text{dif}} /$ s^{-1}	$E_{\text{overall}} /$ kJ/mol	$A_{\text{overall}} /$ s^{-1}
50	10^6	20	200	47.1	$3 \cdot 10^5$
50	10^6	20	100	43.8	$8 \cdot 10^4$
50	10^6	20	50	41.3	$2.5 \cdot 10^4$
50	10^6	20	40	40.3	$1.7 \cdot 10^4$
50	10^6	20	20	38.7	$7 \cdot 10^3$
50	10^6	20	10	36.1	$2 \cdot 10^3$
50	10^6	20	8	35.6	$1.5 \cdot 10^3$
50	10^6	20	6	32.4	$4 \cdot 10^2$
50	10^6	20	4	20	4
180	10^{13}	20	10	154.6	$7 \cdot 10^{10}$
180	10^{13}	25	10	151.8	$3 \cdot 10^{10}$
180	10^{13}	30	10	136.7	$1 \cdot 10^9$
180	10^{13}	35	10	130.4	$4 \cdot 10^8$
180	10^{13}	40	10	120	10^8
180	10^{13}	45	10	77	$5 \cdot 10^3$

ally, the overall kinetic parameters cannot be assigned to any of both consecutive steps.

It is evident from the results presented in Table 1 that in the most of cases, the overall kinetic parameters are smaller than desorption parameters predicted in the calculation of theoretical TDS.

Evidently, even one single peak TPD spectra appear, it should not be treated as simple desorption results.

The diffusion process has to be taken into account in the evaluation of kinetic parameters from the TPD results. The parameters D_0 (A_{dif}) and E_{dif} , applied here correspond to diffusion of most gases (from small inorganic molecules such as ammonia or carbon dioxide, to large organic molecules) in microporous systems. Obviously, in the most of systems gas-microporous solid materials, the desorption reaction has to be considered as complex reaction, with the overall kinetic parameters. Generally, as a consequence of diffusional influence, the overall activation energy and overall pre-exponential factor of surface reaction are lower than those for simple desorption reaction.

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Zusammenfassung — Ein konsekutives Modell für Oberflächenreaktionen, bestehend aus zwei Schritten (Desorption und Diffusion) wird angewendet. Dabei zog man die Schlußfolgerung, daß das temperaturabhängige Desorptionsspektrum durch Diffusion modifiziert wird, wenn sich auch Single-Peak-Kurven ergeben. Die auf der Verschiebung von T_M basierende Differentialmethode zur Berechnung der kinetischen Parameter liefert nur in denjenigen Fällen Werte, die mit den prognostizierten übereinstimmen, in denen Einzelschritte geschwindigkeitsbestimmend sind. Ganz allgemein ist der Desorptionsvorgang als komplexe Reaktion mit kinetischen Bruttoperametern zu berücksichtigen. Als Folge des Einflusses der Diffusion sind die kinetischen Bruttoperameter kleiner als die für den Desorptionsschritt.