Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 483-492

EVALUATION OF DESORPTION ENERGY DISTRIBUTIONS FROM TPD SPECTRA ON A HETEROGENEOUS SOLID SURFACE

*V. I. Bogillo** *and V. P. Shkilev*

Institute of Surface Chemistry, National Academy of Sciences, 31 Prospect Nauki
252022 Kiev, Ukraine

Abstract

The condensation approximation (CA) and numerical regularization procedure (RP) methods used to solve a Fredholm integral equation of the first kind describing the adsorption equilibria on a heterogeneous solid surface under isothermal conditions have been adopted in the present study to evaluate desorption energy distributions from temperature-programmed desorption (TPD) spectra. From comparisons of the computational results obtained by means of these methods on the basis of simulated TPD spectra, it follows that the CA gives stable solutions for wide desorption energy distributions and it can be used successfully for calculations from wide and clear resolved peaks in the TPD spectra. The use of the RP is more advantageous for acquisition of the distributions from closely related narrow peaks in the TPD spectra.

Keywords: desorption energy distribution, heterogeneous solid surface, non-isothermal kinetics, TPD spectra

Introduction

Intrinsic and induced heterogeneity in surface sites are often present on most solids. The non-isothermal desorption of preadsorbed probes is one of the best methods known for accurate measurement of the desorption activation energies as equal to the adsorption heats and hence to characterize the catalysts or adsorbents from the dependence of the desorption energy on the surface coverage. The strength of the surface sites from which the probe molecules desorb is frequently simply characterized by the temperature of the peak maximum in the desorption spectra. More information is obtained by evaluating the energies of desorption and, if possible, their distribution. Since the desorption spectra are often poorly resolved, curve decomposition techniques have been used. A common procedure used in practice consists in performing the desorption at various initial surface coverages, with following calculation of the plot of the desorption energy *vs.* the

---

* Author for correspondence: e-mail: val@ucs.freenet.kiev.ua

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

coverage. However, only a limited region of this dependence, and related to it the desorption energy distribution curve, is accessible from the different TPD spectra.

The simplest approach to a resolution of this problem is based on the approximate solution of the integral equation for the desorption kinetics on the heterogeneous surface by using the condensation approximation (CA), which does not produce an unstable solution in the case of a wide desorption energy distribution function. The application of the CA approach to describe the isothermal desorption kinetics was developed in [1]. This approach has been modified in the present study to describe the desorption kinetics under non-isothermal conditions. The desorption energy distributions evaluated in this manner are compared with those computed by using the more exact numerical modified regularization procedure (RP).

Results and discussion

The overall rate of desorption from the heterogeneous solid surface is given by

$$\frac{\mathrm{d}N}{\mathrm{d}t}=\int_{E_{d(min)}}^{E_{d(max)}}\frac{\mathrm{d}N_i(E_{d(i)})}{\mathrm{d}t}\rho(E_d)\mathrm{d}E_d \tag{1}$$

where the local first-order desorption rate from the *i*-th patches possessing desorption activation energy $E_{d(i)}$ is determined as

$$\frac{\mathrm{d}N_i(E_{d(i)})}{\mathrm{d}t}=-A_dN_i(E_{d(i)})\exp\left(-\frac{E_{d(i)}}{RT}\right) \tag{2}$$

where $N_i(E_{d(i)})$ is the number of adsorbed molecules possessing desorption activation energy $E_{d(i)}$, A_d is the desorption pre-exponential factor and $\rho(E_d)$ is the desorption activation energy distribution function, and $E_{d(min)}$ and $E_{d(max)}$ are the lower and upper limits of this function.

The local surface coverage $\Theta_i(E_{d(i)})$ is due to the coverage of sites of type *i* and this is defined as

$$\Theta_i(E_{d(i)})=\frac{N_i(E_{d(i)})}{N_{max}}$$

where N_{max} is the maximum overall concentration of the *n* types of surface sites under the following condition:

$$\sum_{i=1}^{n}\Theta_i(E_{d(i)})=1$$

In order to simplify the evaluation of the experimental desorption spectra, two assumptions are commonly used: (i) the pre-exponential factor A_d is constant, and (ii) the desorption from the different kinds of sites with E_d occurs through a non-associative mechanism. All ensuing relations correspond to the desorption of localized adsorbed molecules, i.e. the activation energy of surface diffusion of these molecules is higher than their desorption activation energy.

Condensation approximation

The CA consists in replacing the kernel of Eq. (1) ($\mathrm{d}N_i(E_{d(i)})/\mathrm{d}t$) by the stepped function. Let us assume that in the desorption process the occupied sites are released sequentially, i.e. at each moment of time the sites with desorption activation energy lower than E_{dc} are emptied and those with desorption activation energy higher than E_{dc} are filled:

$$\Theta_i(E_{d(i)}) = \begin{cases} 1 & \text{for } E_{d(i)} \geq E_{dc(i)} \\ 0 & \text{for } E_{d(i)} < E_{dc(i)} \end{cases} \tag{3}$$

It can be inferred that the patches with desorption activation energy $E_{d(i)}$ are released at temperature T such that the local desorption rate ($\mathrm{d}N_i(E_{d(i)}/\mathrm{d}t$) has a maximum. If the desorption temperature varies linearly with time:

$$T = T_o + \beta t \tag{4}$$

where T_o is the initial desorption temperature and β is the heating rate, the desorption energy $E_{d(i)}$ does not depend on the surface coverage $\theta_{(i)}$ of the i-th patch, and the relation between the desorption activation energy and this temperature maximum can be derived by equating the first derivative of the desorption rate (Eq. (2)) with respect to temperature to zero, and solving this differential equation. This solution can be written:

$$A_d \exp\left(-\frac{E_{dc}}{RT}\right) = \frac{\beta E_{dc}}{RT^2} \tag{5a}$$

or, after rearrangement and taking logarithms of both sides of Eq. (5a), one can obtain

$$\frac{E_{dc}}{RT} = \ln\left(\frac{A_d T}{\beta}\right) - \ln\left(\frac{E_{dc}}{RT}\right) \tag{5b}$$

The distribution function $\rho(E_{dc})$ can be derived from Eq. (6):

$$\Theta(T) = \int_{E_{dc(min)}}^{E_{dc(max)}} \rho(E_{dc})\mathrm{d}E_{dc} \tag{6}$$

where $\Theta(T)=N/N_0$ is the surface coverage and N_0 is the total number of surface sites.

From Eq. (6), it immediately follows that

$$\frac{\mathrm{d}\Theta}{\mathrm{d}T}=-\rho(E_{\mathrm{dc}})\frac{\mathrm{d}E_{\mathrm{dc}}}{\mathrm{d}T} \tag{7}$$

and

$$\rho(E_{\mathrm{dc}})=-\frac{\mathrm{d}\Theta}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}E_{\mathrm{dc}}} \tag{8}$$

Let us introduce a function $F(T,E_{\mathrm{dc}})$ such that

$$F=\frac{E_{\mathrm{dc}}}{RT}-\ln\left(\frac{A_{\mathrm{d}}T}{\beta}\right)+\ln\left(\frac{E_{\mathrm{dc}}}{RT}\right) \tag{9}$$

The partial derivatives of this function with respect to T and E_{dc} can be written as

$$\frac{\partial F}{\partial T}=-\frac{E_{\mathrm{dc}}}{RT^2}-\frac{2}{T} \tag{10}$$

and

$$\frac{\partial F}{\partial E_{\mathrm{dc}}}=\frac{1}{RT}+\frac{1}{E_{\mathrm{dc}}} \tag{11}$$

Derivative $\mathrm{d}T/\mathrm{d}E_{\mathrm{dc}}$, which is needed to calculate the desorption energy distribution function from experimental TPD spectra (Eq. (8)), is then given by the following equation:

$$\frac{\mathrm{d}T}{\mathrm{d}E_{\mathrm{dc}}}=-\frac{\dfrac{\partial F}{\partial E_{\mathrm{dc}}}}{\dfrac{\partial F}{\partial T}}=\frac{\dfrac{1}{RT}+\dfrac{1}{E_{\mathrm{dc}}}}{\dfrac{E_{\mathrm{dc}}}{RT^2}+\dfrac{2}{T}}=\frac{E_{\mathrm{dc}}+RT}{E_{\mathrm{dc}}-RT}\,\frac{RT^2}{E_{\mathrm{dc}}+2RT} \tag{12}$$

Let us denote the variable E_{dc}/RT by x. The derivative of T with respect to E_{dc} can be written as

$$\frac{\mathrm{d}T}{\mathrm{d}E_{\mathrm{dc}}}=\frac{1+x}{R(2x+x^2)} \tag{11}$$

We can then calculate the function $\rho(E_{\mathrm{dc}})$ from the single TPD spectrum (i.e. from the dependence of $\mathrm{d}\Theta/\mathrm{d}t$ on T) in accordance with following procedure:

i) Solution of the non-linear Eq. (12):

$$x = \ln\left(\frac{A_d T}{\beta}\right) - \ln(x) \tag{12}$$

for each temperature point T ranging from the minimum (T_o) to the maximum (T_{max}) measured temperatures and determination of the desorption activation energy $E_{dc}=RTx$ for each T value.

ii) Calculation of the function $\rho(E_{dc})$ at given T from the following equation:

$$\rho(E_{dc}) = -\frac{d\Theta}{dt}\frac{1}{\beta}\frac{1+x}{R(2x+x^2)} \tag{13}$$

This approach was used to determine the silica surface distribution function with respect to the water desorption energy, and the dependence of the apparent desorption energy on the silica surface coverage [2].

However, use of the CA to calculate the desorption energy distribution function leads to smoothing of the complex distribution curve having narrow closely spaced peaks in the TPD spectra. Therefore, we have developed a more exact method for calculation of such complex desorption energy distribution curves. This is based on use of the RP.

Regularization procedure

The total desorption rate from the heterogeneous solid surface is equal to the weighted sum of the discrete local rates from the different surface sites (i):

$$\frac{d\Theta}{dt} = \sum_{i=1}^{n}\alpha_i\frac{d\theta_i}{dt} \tag{14}$$

where α_i is the fraction of the sites of the i-th kind and $\sum_{i=1}^{n}\alpha_i = 1$. Since

$$\frac{d\theta_i}{dt} = -A_d\theta_i \exp\left(-\frac{E_{d(i)}}{RT}\right) \tag{15}$$

and the value of θ_i is related to the initial surface coverage at $t=0$ ($\theta_{i(o)}$) in accordance with the equation

$$\theta_i = \theta_{i(o)}\exp\left[-A_d \exp\left(-\frac{E_{d(i)}}{RT}\right)t\right] \tag{16}$$

the expression for the local rate can be written in the more detailed form as

$$\frac{\mathrm{d}\theta_{(i)}}{\mathrm{d}t}=-\theta_{i(o)}A_{d}\exp\left(-\frac{E_{d(i)}}{RT}\right)\exp\left[-A_{d}\exp\left(-\frac{E_{d(i)}}{RT}\right)t\right] \tag{17}$$

As $n\rightarrow\infty$, the sum in Eq. (14) can be rewritten in the integral form

$$\frac{\mathrm{d}\Theta}{\mathrm{d}t}=\int_{0}^{\infty}\frac{\mathrm{d}\theta}{\mathrm{d}t}\rho(E_{d})\mathrm{d}E_{d} \tag{18}$$

In the case of first-order desorption kinetics, the differential equations for the different sites can be solved independently (Eq. (2)) without knowledge of the distribution function $\rho(E_d)$. Therefore, the first step for solving Eq. (18) consists in the solution of Eq. (2) for each kind of surface site and determination of the kernel of Eq. (18). The next step involves the solution of the integral Eq. (18) by means of the RP.

Taking into consideration Eq. (4) this solution for Eq. (2) can be written as

$$\theta=\theta_{(o)}\exp\left\{\frac{A_{d}E_{d}}{\beta R}\left[E_{1}(u)-\frac{\exp(-u)}{u}-E_{1}(u_{o})+\frac{\exp(-u_{o})}{u_{o}}\right]\right\} \tag{19}$$

where $\theta_{(o)}$ is the initial fraction of the site with E_d at $t=0$, $u=E_d/RT$ and $u_o=E_d/RT_o$. The real integral function $E_1(u)$ is determined as

$$E_{1}(u)=\int_{u}^{\infty}\frac{\exp(-t)}{t}\mathrm{d}t \tag{20}$$

This function can be approximated by a known power standard series. It should be mentioned that the distribution function $\rho(E_d)$ which is calculated after substituting θ from Eq. (19) into Eq. (18) corresponds to the distribution with respect to desorption energy only for the filled surface sites. Then, in reality, the calculated desorption energy distribution function $\theta(E_d)$ is an apparent function ($\rho(E_d)_{app}$) and is equal to the product of the real distribution function ($\rho(E_d)_{real}$) and the initial local surface coverage ($\theta_{(o)}$).

From a mathematical point of view, Eq. (1) is a Fredholm integral equation of the first kind. Solving this equation with respect to the desorption energy distribution (DED) function is a numerically ill-posed problem, i.e. small changes in the measured desorption rate, caused by experimental errors, can significantly distort the sought-for function. One method to solve ill-posed problems is the RP [3, 4]. The fundamental idea of the numerical regularization is to replace the ill-posed problem of minimizing the select function by a well-posed problem which smoothes the calculated distribution function and distorts the original problem insignificantly. Hence, solving the integral equation is replaced by minimization of the functional $\Phi[\rho(E_d)]$:

$$\Phi[\rho(E_{\mathrm{d}})] = \left\{ \int_{E_{\mathrm{d(min)}}}^{E_{\mathrm{d(max)}}} \frac{\mathrm{d}\theta_{(\mathrm{Ed})}}{\mathrm{d}t}\rho(E_{\mathrm{d}})\mathrm{d}E_{\mathrm{d}} - \frac{\mathrm{d}\Theta}{\mathrm{d}t} \right\}^2 + \alpha\int_{E_{\mathrm{d(min)}}}^{E_{\mathrm{d(max)}}} \rho^2(E_{\mathrm{d}})\mathrm{d}E_{\mathrm{d}} \qquad (21)$$

where α ($1 \geq \alpha > 0$) is the regularization parameter that is dependent on the relative experimental error.

The choice of the optimal of the regularization parameter α is crucial for the sought-for DED function. A very low value of the regularization parameter gives rise to spurious peaks, while too high a value oversmoothes the DED function.

In the present study, the following method, consisting of two steps, has been used to find the optimal regularization parameter. First, function (21) was minimized at $\alpha=0$. The value of this minimum may then serve as a measure of the accuracy of the experimental data for m points in the TPD spectrum:

$$\xi = \min\left[\frac{1}{m}\sum_{j=1}^{m} \left(\frac{\mathrm{d}\Theta}{\mathrm{d}t} - \frac{\mathrm{d}\theta_{\mathrm{Ed}}}{\mathrm{d}t}\rho^{\mathrm{o}}(E_{\mathrm{d}}) \right)^2 \right]^{1/2} \qquad (22)$$

In the second step, the value of α is calculated at which the DED function $\rho^1(E_{\mathrm{d}})$ minimizing function (21) satisfies the following condition:

$$\eta\xi = \left[\frac{1}{m}\sum_{j=1}^{m} \left(\frac{\theta_{\mathrm{Ed}}}{\mathrm{d}t}\rho^{\mathrm{o}}(E_{\mathrm{d}}) - \frac{\mathrm{d}\theta_{\mathrm{Ed}}}{\mathrm{d}t}\rho^{1}(E_{\mathrm{d}}) \right)^2 \right]^{1/2} \qquad (23)$$

In the present study, parameter η was taken as equal to 1.

The special convenience of this method is that the solution may be improved by varying the free parameter η. The necessity of the free parameter stems from the fact that there is no method of finding the stable solution for ill-posed problems without taking into account errors in input data [5]. This means that, if the accuracy of a measured TPD spectrum is unknown, the choice of a regularization parameter will always be subjective. None of the existing methods for choosing parameter α can be strictly proved and all of them give, in one case or another, unsatisfactory results. Without a free parameter η, one has to be satisfied with the solution even if it is either oversmoothed or contains spurious peaks.

A computer program was used here to calculate the DED function with respect to positive values of $\rho(E_{\mathrm{d}})$. In this program, the integrals were computed by the trapezoid method. Minimization of function (18) was performed by the conjugate gradient method. The regularization parameter was determined by using a generalized deviation principle. The half-interval procedure was used to solve the equations of the deviation. The advantage of the RP is the possibility to calculate more points on a desired DED function than the number of experimental points available, as in the case of the CA.

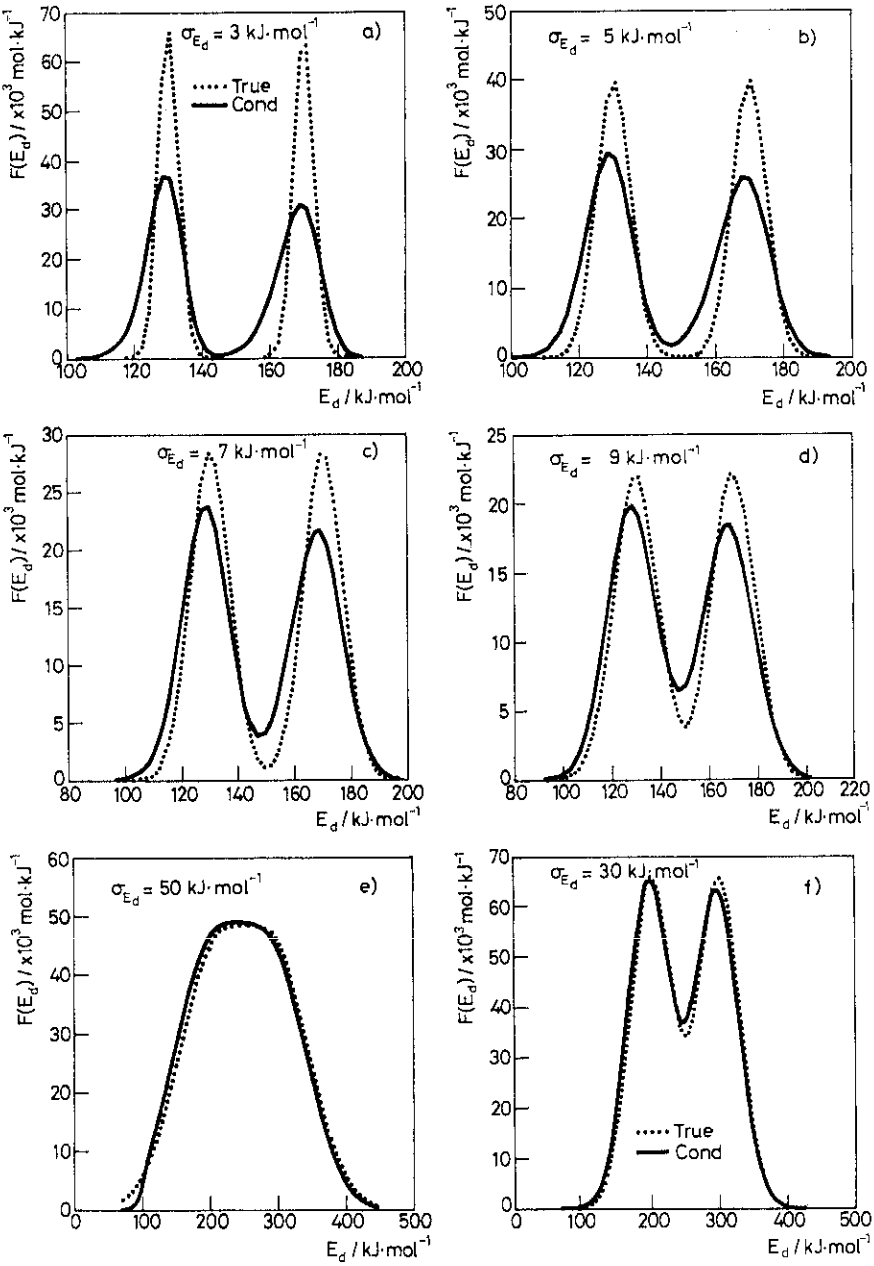

Fig. 1a–f Desorption energy distributions, simulated by bi-gaussian distribution (dotted lines) or calculated from the simulated TPD spectra by using the condensation approximation (solid lines). The initial parameters of the simulated distributions are given in Table 1

The TPD spectra for testing both methods were simulated by using the bi-gaussian distributions

$$\rho(E_\mathrm{d}) = f_1 \frac{1}{\sqrt{2\pi}\sigma_{\mathrm{n}(1)}} \exp\left(-\frac{(E_\mathrm{d}-\overline{E_{\mathrm{d}(1)}})^2}{2\sigma^2_{\mathrm{n}(1)}}\right) + \\ + (1-f_1)\frac{1}{\sqrt{2\pi}\sigma_{\mathrm{n}(2)}} \exp\left(-\frac{(E_\mathrm{d}-\overline{E_{\mathrm{d}(2)}})^2}{2\sigma^2_{\mathrm{n}(2)}}\right) \tag{24}$$

where $\overline{E_{\mathrm{d(i)}}}$ stands for the most probable desorption energy (average value) for the i-th gaussian peak (i=1, 2) and $\sigma_{\mathrm{n(i)}}$ for the mean square deviation of the $E_{\mathrm{d(i)}}$ value, and f_1 is the relative concentration of the sites with $\overline{E_{\mathrm{d(i)}}}$ ($1 \geq f_1 \geq 0$).

The desorption energy distributions calculated by using the CA and the modified RP at various $\sigma_{\mathrm{n(i)}}$ values and the difference between the average desorption energies from these two types of surface site at f_1=0.5 are presented in Fig. 1a–f. The heating rate is equal to 0.02 K s^{-1}, A_d is $1 \cdot 10^{11} \mathrm{s}^{-1}$ and the average desorption energies of the first and second peaks are 130 and 170 kJ mol^{-1} in Fig. 1a–d, whereas in Fig. 1e, f the heating rate is equal to 0.097 K s^{-1}, $A_\mathrm{d}=1 \cdot 10^{3} \mathrm{s}^{-1}$ and the average desorption energies of these peaks are 200 and 300 kJ mol^{-1}, respectively. The desorption energy distribution functions calculated by using the CA and modified RP are denoted by solid and dotted lines, respectively. The initial $\overline{E_{\mathrm{d(i)}}}$ and $\sigma_{\mathrm{n(i)}}$ values used in the simulation of the TPD spectra are given in Table 1. Further, the mean square deviations of the desorption energy for the two peaks in the simulated distribution curves are equal and are given in Fig. 1a–f. It turns out that the distribution curves calculated by using the RP coincide completely with the simulated curves.

Table 1 Parameters of the simulated and calculated desorption energy distributions by using the condensation approximation and modified regularization method

No.	$\overline{E_{\mathrm{d}(1)}}$/	$\overline{E_{\mathrm{d}(2)}}$/	$\sigma_{\mathrm{n}(1)}$/	$\sigma_{\mathrm{n}(2)}$/	A_d/	β/	σ_1/	σ_2/	*Cheb*/
	kJ mol^{-1}				s^{-1}	K s^{-1}	kJ mol−1	kJ mol−1	s^{-1}
a	130	170	3	3	10^{11}	0.02	0.0181	0.0623	0.174
b	130	170	5	5	10^{11}	0.02	0.0158	0.0700	0.196
c	130	170	7	7	10^{11}	0.02	0.0108	0.0350	0.103
d	130	170	9	9	10^{11}	0.02	0.0089	0.0100	0.030
e	200	300	50	50	10^{13}	0.097	0.0088	0.00046	0.012
f	200	300	30	30	10^{13}	0.097	$3.6 \cdot 10^{-6}$	0.00044	$2.8 \cdot 10^{-5}$

Notes: The f_1 value (Eq. (24)) was taken as 0.5;
The number of points in the simulated TPD spectra was 41;
The initial surface coverage was taken as 1 in all simulations;
σ_1 and σ_2 are mean square deviations for smoothed (1) and unsmoothed (2) solutions performed by the RP;
Cheb is the maximum deviation of the calculated TPD spectra by the RP from the simulated spectra.

It is evident from Fig. 1a–f and Table 1 that the CA gives stable solutions for wide desorption energy distribution functions and it can be used successfully for calculations from wide clear resolved peaks in TPD spectra. The application of the RP is more advantageous for acquisition of the desorption energy distributions from closely related narrow peaks.

Conclusions

The CA and RP methods used to solve a Fredholm integral equation of the first kind describing the adsorption equilibria on a heterogeneous solid surface under isothermal conditions were adopted in the present study of evaluate the desorption energy distributions from TPD spectra on a heterogeneous solid surface.

From comparisons of the computational results obtained by means of these methods on the basis of simulated TPD spectra, it follows that the CA gives stable solutions for wide desorption energy distribution functions and it can be used successfully for calculations from wide clear resolved peaks in the TPD spectra. The used of the RP is more advantageous for acquisition of the distributions from closely related narrow peaks in these spectra.

These methods can be usefully applied to evaluate the desorption energy distributions for various molecular acid/base probes from the heterogeneous surface of adsorbents and catalysts and the dependences of the apparent desorption energy on the surface coverage on the basis of experimental TPD MS spectra and DTG curves. Examples of the use of these methods to determine the desorption energy distributions from TPD MS spectra of physically adsorbed and structural water on various silica surfaces and from DTG curves of adsorbed liquid-molecular probes on mesoporous silica gels were presented in recent papers [2, 6, 7].

References

1 G. F. Cerafolini and N. Re, J. Collolid Interface Sci., 174 (1995) 428.
2 V. I. Bogillo, L. S. Pirnach and A. Dabrowski, Langmuir, 13 (1997) 928.
3 A. N. Tikhonov, Dokl. Akad. Nauk USSR, 39 (1943) 195.
4 B. Hunger, M. V. Szombathely, J. Hoffmann and P. Brauer, J. Thermal Anal., 44 (1995) 293.
5 A. S. Leonov and A. G. Jagola, Vestn. Moscow Univ., Ser. 3: Fiz., Astron., 36 (1995) 28.
6 V. I. Bogillo and P. Staszczuk, J. Therm. Anal. Cal., 55 (1999) 493
7 V. I. Bogillo, D. Glazewski and P. Staszczuk, in Proc. of III. Intern. Symp. Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids, Torun, Poland, Aug. 9–16, 1998, 22.