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A method for simulating temperature programmed desorption peaks

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Abstract

A procedure for simulating temperature programmed desorption (TPD) peaks is discussed with the aim of determining the shape of a TPD peak and the temperature range, where it is placed, when starting from the knowledge of the peak area (corresponding to the volume of gas adsorbed), of the values of the kinetic parameters (related to the energetic interactions adsorbate–adsorbent), and of some important experimental parameters.

Finally the goodness of the method is checked by simulating a peak at different heating rate and comparing the value of the activation energy, taken as a starting point, with the one that is calculated from the variation of the peak maximum in the temperature scale with the heating rate. © 1997 Elsevier Science B.V.

Keywords: Temperature programmed desorption; Peak simulation; Kinetic analysis

1. Introduction

When performing kinetic evaluation in temperature programmed desorption experiments, the starting point is always the exploitation of the general equation:

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = k \cdot f(\theta)$$

which relates the rate of desorption $-(\mathrm{d}\theta/\mathrm{d}t)$ to some function of the fractional surface coverage, θ, through the rate constant k, which is governed by the Arrhenius equation:

$$k = A \cdot e^{-E/RT}$$

where, E is the activation energy associated with the process and A is the pre-exponential factor. The function $f(\theta)$ is usually not known and can provide useful information about the mechanism of the desorption and therefore about the mechanism of adsorption itself.

As reported elsewhere [1], there is the possibility of deducing the function $f(\theta)$ and the kinetic parameters by analysing a single peak: the above equation of the rate of desorption can be rewritten in the form:

$$h_t = k \cdot f\left(\frac{A - A_t}{A}\right),$$

by taking into account that at every instant of the desorption process, the peak height h_t is proportional to the rate of desorption and the fractional surface coverage θ to be uncovered is proportional to the ratio between the residual area $(A-A_t)$ and the total peak area A (Fig. 1).

It is therefore possible to determine, from a single peak, the kinetic mechanism which governs the pro-

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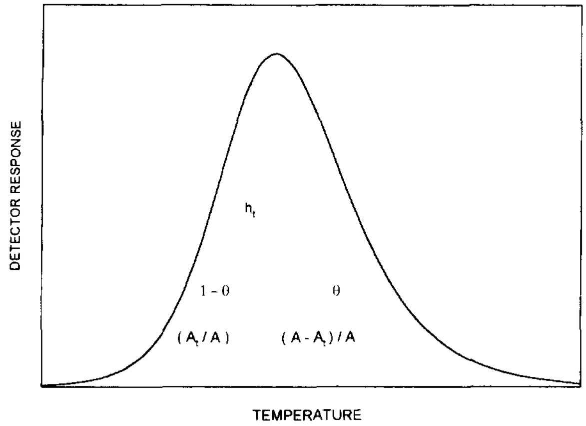

Fig. 1. A simplified TPD peak showing the main peak parameters.

cess, by checking which function can give the best Arrhenius plot. But in some cases, this procedure can give unsatisfactory results, because the straight line does not cover the full range of the fractional surface coverage and it is not possible to distinguish if this discrepancy is due to some experimental problem (for example a not perfect linear heating) or to the occurrence of multiple peaks (for example a central peak with a shoulder).

Therefore, it is useful to reconstruct a TPD peak by a computer calculation starting from the knowledge of the kinetic parameters and of the function $f(\theta)$: a theoretical curve of this type can therefore be compared with the experimental peak, improving its kinetic analysis.

The kinetic mechanisms for desorption, which can be investigated, can involve surface heterogeneities and diffusional limitations, but in this analysis only first and second order kinetics, with or without readsorption, will be analysed in order to outline a general method, taking into account that diffusional limitations can be avoided during the experimentation, and that surface heterogeneity is important above all at the beginning of desorption, for large surface coverages.

2. Method

As reported in [1], the kinetic equation for a first order desorption (without readsorption):

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = k \cdot \theta$$

can be rearranged and written in the form:

$$h_t = \frac{ZA}{\beta C_s} e^{-E/RT} \left(\frac{A - A_t}{A}\right)$$

where h_t is the peak height at the time t, and temperature T, Z is the pre-exponential factor, E is the activation energy, A is the total peak area, β is the linear heating rate, C_s is the chart speed of the strip chart recorder, A_t is the area developed by the detector signal at the time t and temperature T.

The simulation procedure involves the necessity of calculating h_t only as a function of T, taking Z and E as the starting point. This means to divide the partial area A_t in two parts, that is the area A_{t-1} and the trapezoid area $(h_t + h_{t-1}) \cdot \delta/2$, where δ is the interval between two points. By approximating the initial heights and therefore the initial areas, it is possible to calculate every height, because A_{t-1} and h_{t-1} are always known (Fig. 2). Therefore, since $A_t = A_{t-1} + [(h_t + h_{t-1}) \cdot \delta]/2$, we can write, for first order kinetics, after simple algebraic manipulations:

$$h_t = \frac{(Z/2\beta C_s) \cdot e^{-E/RT} \cdot (2A - 2A_{t-1} - \delta \cdot h_{t-1})}{(1 + (Z\delta/2\beta C_s) \cdot e^{-E/RT})}$$

The kinetic equation for a second order desorption (without readsorption):

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = k \cdot \theta^2$$

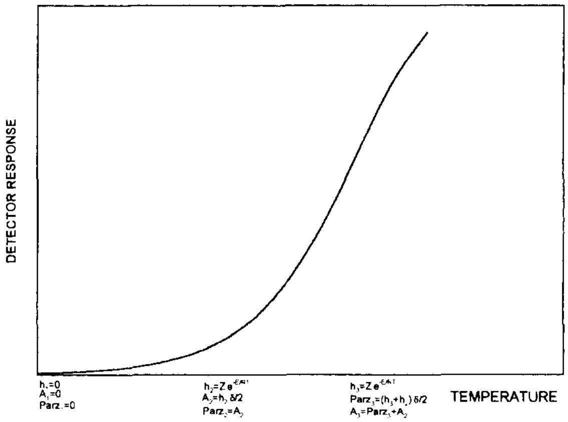

Fig. 2. Analysis of the approximate evaluation of heights and areas at the beginning of the peak.

can be rewritten as:

$$h_t = \frac{ZA}{\beta C_s} e^{-E/RT} \left(\frac{A - A_t}{A} \right)^2$$

and with a similar procedure it is possible to obtain an equation, which relates h_t and T:

$$\begin{aligned} &\left(\frac{Z \cdot \delta^2}{4 \cdot A \cdot \beta \cdot C_s} e^{-E/RT} \right) h_t^2 \\ &\quad - \left(1 + 2\delta \frac{(2A - 2A_{t-1} - \delta h_{t-1}) \cdot Z}{4 \cdot A \cdot \beta \cdot C_s} e^{-E/RT} \right) h_t \\ &\quad + \left(\frac{(2A - 2A_{t-1} - \delta h_{t-1})^2 \cdot Z}{4 \cdot A \cdot \beta \cdot C_s} e^{-E/RT} \right) = 0 \end{aligned}$$

This is an equation of second rank and therefore has two solutions, but only one has physical meaning, and it is therefore possible to find the value of h_t at every predetermined temperature.

The kinetic equation for a first order desorption with readsorption:

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = k \cdot \frac{\theta}{1 - \theta}$$

can be rewritten as:

$$h_t = Z' \cdot e^{\Delta H^0/RT} \left(\frac{A - A_t}{A_t} \right)$$

where $Z' = [(FC_wA)/(S\beta C_s)]e^{\Delta s^0/R}$ is the "pre-exponential factor" (It must be taken into account that F is the carrier gas flow rate, C_w is the recorder chart width, and the S is the recorder sensitivity.) The elaboration of this equation according to the same criteria allows to obtain a second rank equation in h_t:

$$\begin{aligned} &\delta \cdot h_t^2 + (\delta Z' e^{-\Delta H^0/RT} + (2A_{t-1} + \delta h_{t-1})) \cdot h_t \\ &\quad - Z' e^{-\Delta H^0/RT} (2A - (2A_{t-1} + \delta h_{t-1})) = 0 \end{aligned}$$

which can be solved by giving, at every temperature, a solution with a physical meaning.

Finally, the fourth case remains to be considered, that is the second order desorption with readsorption. In this case the kinetic equation:

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = k \cdot \left(\frac{\theta}{1 - \theta} \right)^2$$

can be rewritten in the form:

$$h_t = Z' \cdot e^{\Delta H^0/RT} \left(\frac{A - A_t}{A_t} \right)^2$$

The elaboration of this equation leads to an equation of third rank, whose solution is somewhat complex, because the values of h_t at the beginning of the peak are very small and quite different from those at the centre: the computer procedure must therefore use different numerical methods, according to the range of the value of h_t.

The equation to be solved (which obviously shows only one solution with physical meaning) is:

$$\begin{aligned} &\delta^2 \cdot h_t^3 + (2\delta I_{t-1} - Z' e^{-\Delta H^0/RT} \delta^2) \cdot h_t^2 \\ &\quad + (I_{t-1}^2 - 2I_{t-1} Z' e^{-\Delta H^0/RT} \delta \\ &\quad + 4AZ' e^{-\Delta H^0/RT} \delta) \cdot h_t \\ &\quad - Z' e^{-\Delta H^0/RT} (I_{t-1}^2 + W_{t-1}) = 0 \end{aligned}$$

where: $I_{t-1} = 2A_{t-1} + \delta h_{t-1}$ and $W_{t-1} = 4A^2 - 8AA_{t-1} - 4A\delta h_{t-1}$.

The computer program therefore, accepts as input data, the total peak area, the recorder chart speed, the interval between two examined points, the heating rate of the catalyst, the starting temperature of the peak and finally the pre-exponential factor (which contains some experimental parameters also) and the activation energy. It allows to choose among the different kinetic mechanism and give as output data heights, lengths (along x-axis), temperature and areas at every temperature, either on video or in a text file, in order to perform any type of analysis.

Herewith four simulated TPD peaks are shown, each referring to one of these four cases.

1. First order desorption without readsorption (Fig. 3).
2. Second order desorption without readsorption (Fig. 4).
3. First order desorption with readsorption (Fig. 5).
4. Second order desorption with readsorption (Fig. 6).

It is possible to verify the validity of the simulations by means of two procedures. The first lies in determining for each peak the four Arrhenius plots and checking the linearity of the plot corresponding to the proposed kinetic model. As an example it is reported in Fig. 7 the Arrhenius plots for the first order peak of Fig. 3.

It is therefore possible to check that the first order Arrhenius plot shows a good linearity nearly in the

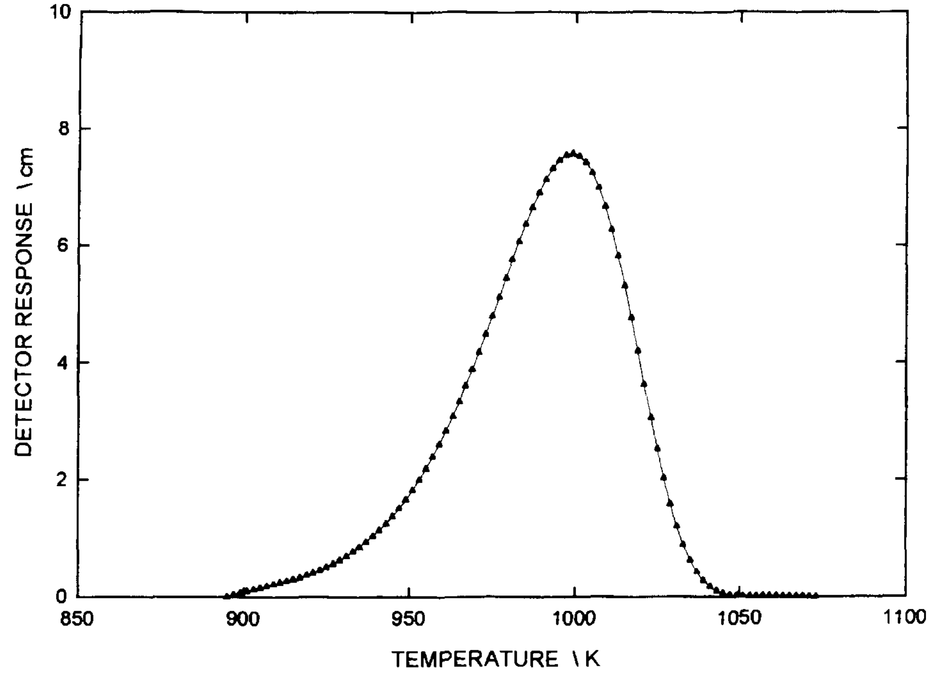

Fig. 3. Simulation of a first order desorption peak. A_{tot}=27 cm^2; C_s=0.5 cm min^{-1}; δ=0.25 cm; β=8°C min^{-1}; T_i=895 K; E_{att}= 377770 J mol^{-1}; Z=1.66×10^{20}.

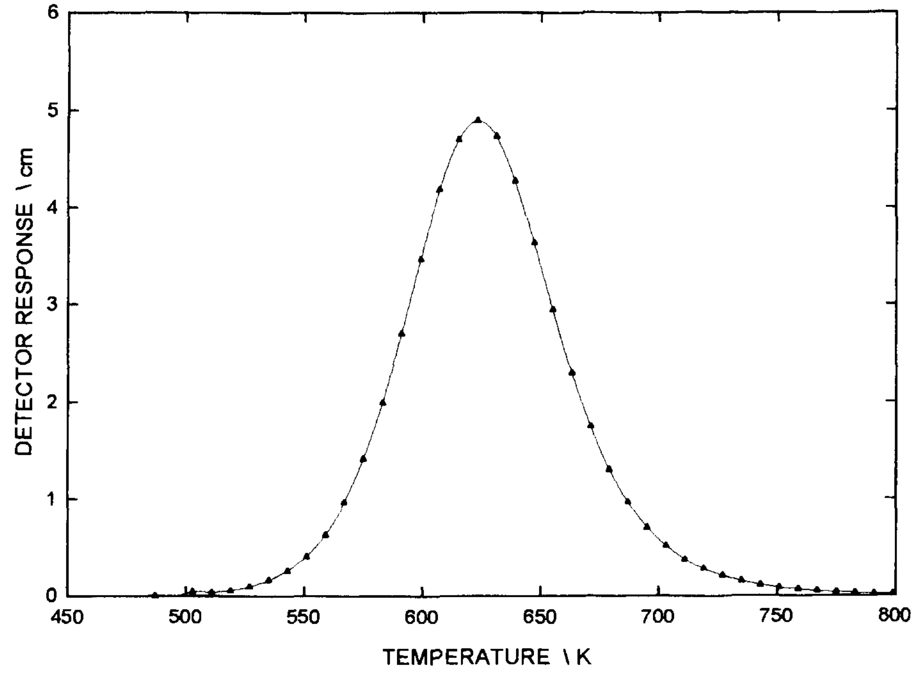

Fig. 4. Simulation of a second order desorption peak. A_{tot}=25.3 cm^2; C_s=0.5 cm min^{-1}; δ=0.5 cm; β=8°C min^{-1}; T_i=487 K; E_{att}= 146300 J mol^{-1}; Z=2.5×10^{12}.

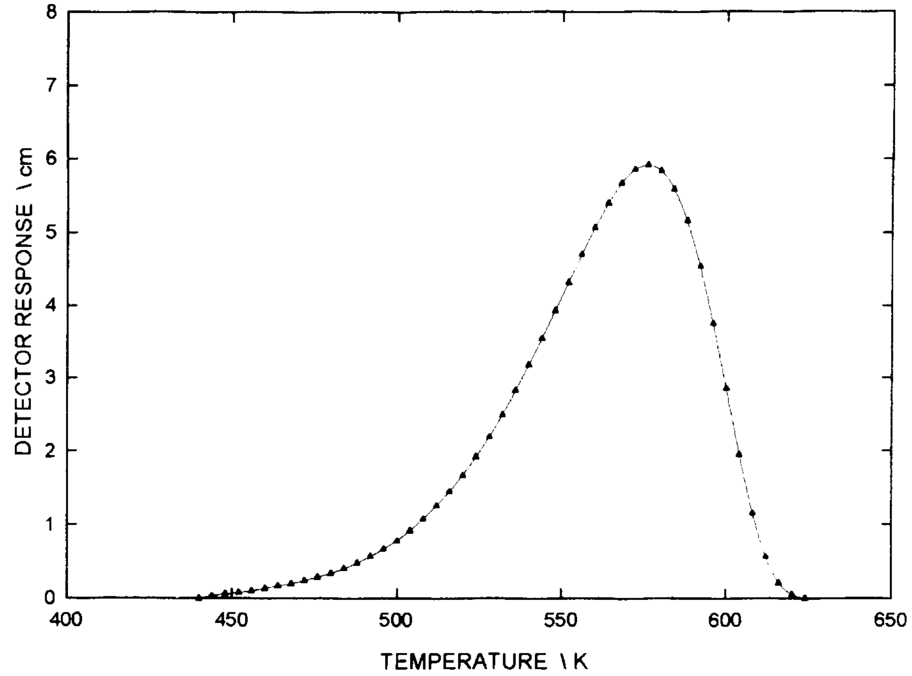

Fig. 5. Simulation of a first order desorption peak with readsorption. $A_{tot}=25$ cm^2; $C_s=0.5$ cm min^{-1}; $\delta=0.25$ cm; $\beta=8$°C min^{-1}; $T_i=440$ K; $H^0=180000$ J mol^{-1}; ln $Z=40$.

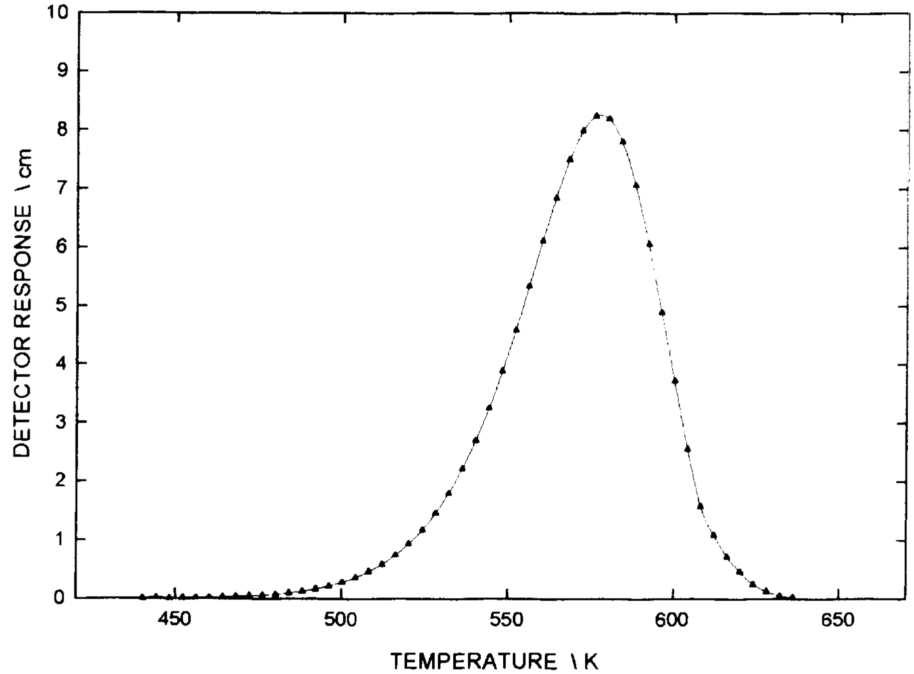

Fig. 6. Simulation of a second order desorption peak with readsorption. $A_{tot}=28.2$ cm^2; $C_s=0.5$ cm min^{-1}; $\delta=0.25$ cm; $\beta=8$°C min^{-1}; $T_i=440.2$ K; $\Delta H^0=125000$ J mol^{-1}; ln $Z=89.9$.

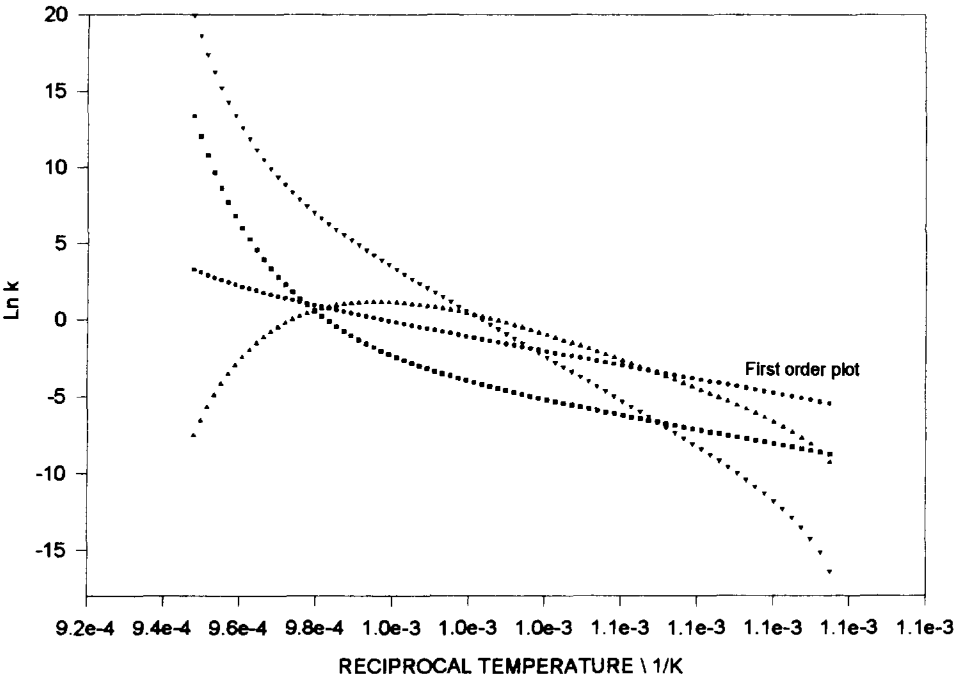

Fig. 7. Arrhenius plots for the first order desorption illustrated in Fig. 3. The slope gives the value of $-E/R$ and the intercept on the ordinate gives the logarithm of pre-exponential factor.

complete range of the temperatures, that is of the surface coverage.

By means of closer examinations it is possible to see that the linearity of the first order plot ranges from θ=1 to θ=0.015, and therefore it is possible to conclude that the desorption fits the model of the first order kinetics in the *entire* range of fractional surface coverage.

The other Arrhenius plots are evidently not linear in all range of the fractional surface coverage or in a large part of that.

The calculations of the activation energy and of the pre-exponential factor give values in complete agreement with the starting values of the simulation, that is E_{att}=375 000 J mol^{-1} and Z=1.5×10^{19}.

The second procedure is based on simulating the same peak at three different heating rates, as shown in Figs. 8 and 9 for the simulated first order peak of Fig. 3.

Keeping in mind that it is possible to exploit the method based on the heating rate variation [2] and therefore by plotting the value of $(2\ln T_M - \ln\beta)$ versus $1/T_M$, an activation energy of 380 200 J mol^{-1} and a pre-exponential factor of 2.8×10^{19} have been found, in good agreement with the starting values used for the simulation.

3. Conclusions

The kinetic analysis of a temperature programmed desorption peak is a procedure which can give in many cases, unreliable results. The widely used analysis of the peak maximum temperature shift with increasing heating rate is sensitive to minor experimental errors, such as slight differences in surface coverage [3]. But, above all, different heating rates can affect up to different extent some physical and chemical factors, such as for example thermal lag and eventual readsorption.

Keeping in mind that it is very important optimising the instrumental apparatus, the analysis of a single peak appears therefore more reliable; in this perspective the reconstruction of a theoretical peak can be important from a practical point of view because it allows to distinguish the different effect of the kinetic

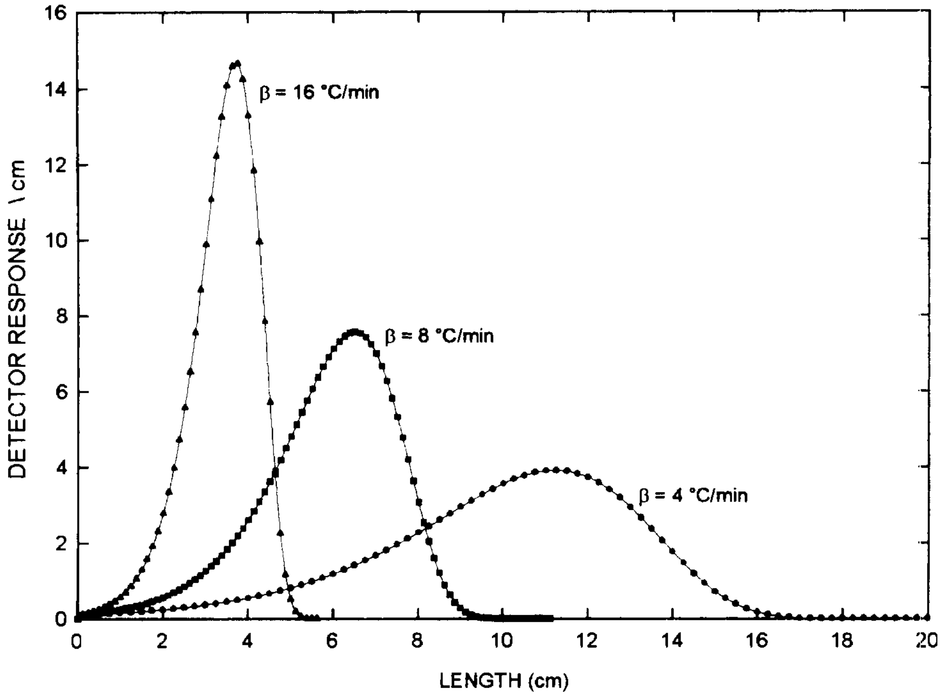

Fig. 8. Simulation at three different heating rates of a first order peak: the peaks are reported as function of the axis length (expressed in cm.), in order to see the invariance of the total area.

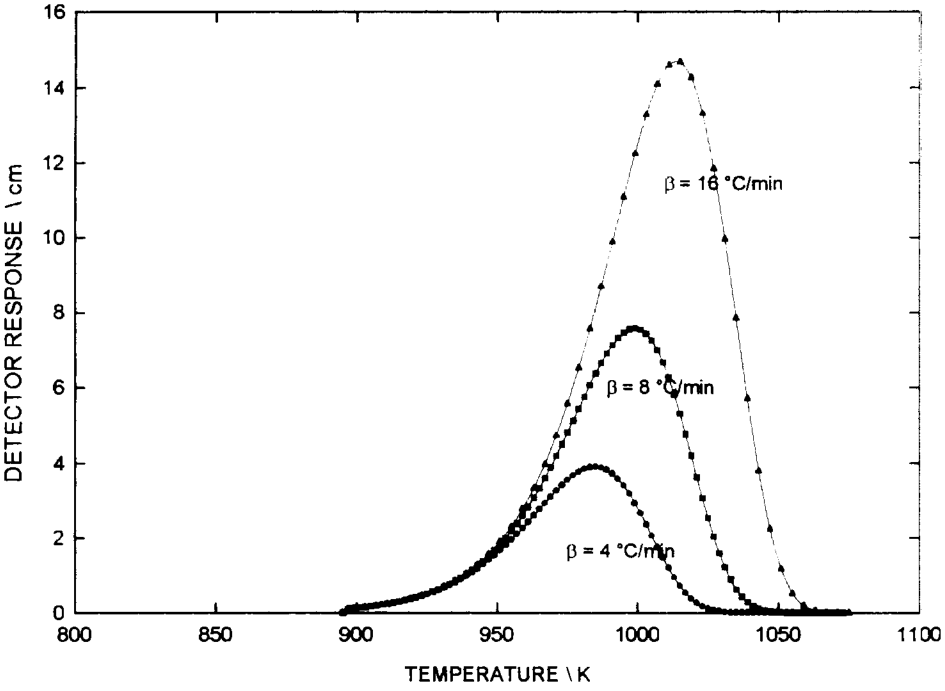

Fig. 9. Simulation at three different heating rates of a first order peak: the peaks are reported as function of the temperature. in order to see the shift towards higher temperature of T_M.

order of the pre-exponential factor and of the activation energy on the shape of the peak.

It is possible to compare an experimental peak with a theoretical one and to infer the existence of diffusional effects or to define the presence of multiple peaks, due to desorption of different adsorbed species.

Appendix

LIST OF THE PROGRAM TPD.BAS

```
10    COLOR 7,1
20    CLS
30    PRINT. PRINT. PRINT'PRINT: PRINT: PRINT
40    PRINT "SIMULATION OF A TPD PEAK DESCRIBED BY 1st OR 2nd ORDER KINETICS"
50    PRINT:PRINT
60    PRINT "by"
70    PRINT:PRINT
80    PRINT "Roberto Spinicci"
90    PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: INPUT "Press a key to continue"; Q$
100   IF Q$="s" THEN GOTO 140
110   DEFDBL A-H
120   DEFINT I
130   DEFDBL J-Z
140   DIM ALT(280)
150   DIM AREA(280)
160   DIM TEMP(280)
170   DIM X(280)
180   DIM Y(280)
190   DIM PARZ(280)
200   DIM W(280)
210   DIM ALFA(280)
220   DIM OTA(280)
230   DIM ETA(280)
240   DIM J(280)
250   DIM HA(280)
260   DIM HB(280)
270   DIM HC(280)
280   DIM HQ(280)
290   DIM HD(280)
300   DIM HR(280)
310   DIM HT(280)
320   DIM HZ(280)
330   DIM HU(280)
340   DIM HV(280)
350   OPEN "O",#1, "TPD.DAT"
360   REM
370   REM DATA INPUT
380   REM
390   CLS
400   INPUT "The peak total area is (cmq) : ":A
410   PRINT
420   INPUT "The recorder chart speed is (cm/min) :": CS
430   PRINT:
440   INPUT "The interval between two examined point is (cm): ";DELTA
450   PRINT
460   INPUT "The heating rate of the catalyst sample is (K/min) :"; BETA
470   PRINT
480   INPUT "The starting temperature of the peak is (K) : "; TT
490   PRINT
500   PRINT " You must input now the preexponential factor. Remember that for desorption with readsorption this term expresses: ln (F*Cw/S)*exp(DSϕ/R)"
510   PRINT
520   INPUT "The preexponential factor is :"; Z
530   PRINT
540   INPUT "The activation energy or (in case of desorption with readsorption, the heat of adsorption is (J/mol): ";ATT
550   PRINT
560   REM
570   REM CHOICE OF THE DESORPTION KINETIC ORDER
580   REM
590   INPUT "The kinetic order is: "; N
600   PRINT
610   CLS
620   PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: "You can choose the type of kinetic mechanism"; PRINT "with or without readsorption)"; PRINT "and start the simulation.";
630   PRINT: PRINT: PRINT: PRINT: PRINT: PRINT
640   IF N=2 GOTO 1420
```

```
650  REM
660  REM CHOICE BETWEEN A KINETICS OF 1ST ORDER WITHOUT OR WITH READSORPTION
670  REM
680  INPUT "The kinetics is affected by readsorption?"; C$
690  IF C$="y" GOTO 950
700  CLS
710  PRINT: PRINT'PRINT: PRINT': PRINT: 'PRINT
720  PRINT "Now the program is performing the calculations of heights, partial areas and of temperatures of the peak, for a kinetics of 1st ORDER WITHOUT READSORPTION, then it is writing the related values in the file TPD.DAT and show them on video"
730  PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: INPUT " Press a key to continue"; Q$
740  IF Q$="y" THEN GOTO 750
750  REM
760  REM CALCULATION OF A PEAK OF 1ST ORDER WITHOUT READSORPTION
770  REM
780  TEMP(1)=TT
790  ALT(1)=0
800  AREA(1)=0
810  X(1)=0
820  PARZ (1)=AREA(1)
830  FOR I=2 TO 280
840  CONTATOR=1
850  TEMP (I)=TEMP (I-1)+ (DELTA*BETA/CS)
860  Y(I)=(Z/2*BETA*CS))*(EXP(-ATT/(8.314*TEMP(I)))))
870  W(I)=(2*A)-(2*AREA(I-1))-(ALT (I-1)*DELTA)
880  ALT(I)=W(I)*Y(I)/(1+(Y(I)*DELTA))
890  PARZ(I)=(ALT(I)+ALT(I-1))*DELTA/2
900  AREA(I)=AREA(I-1)+PARZ(I)
910  X(I)=X(I-1)+DELTA
920  IF AREA(I)=>A THEN GOTO 940
930  NEXT I
940  GOTO 1210
950  CLS
960  PRINT: PRINT: PRINT: PRINT: PRINT: PRINT
970  PRINT "Now the program is performing the calculations of heights, partial areas and of temperatures of the peak, for a kinetics of 1st ORDER WITH READSORPTION; then it is writing the related values in the file TPD.DAT and show them on video"
980   PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: PRINT: INPUT" Press a key to continue"; Q$
990  IF Q$="y" THEN GOTO 1000
1000 REM
1010 REM CALCULATION OF A PEAK OF 1ST ORDER WITH READSORPTION
1020 REM
1030 TEMP (1)=TT
1040 ALT(1)=0
1050 X(1)=0
1060 AREA(1)=0
1070 PARZ(1)=AREA(1)
1080 FOR I=2 TO 280
1090 CONTATOR=I
1100 TEMP (I)=TEMP (I-1)+ (DELTA*BETA/CS)
1110 ALF(I)=EXP(Z-(ATT/(8.314*TEMP(I))))
1120 Y(I)=DELTA*ALT(I-1)+2*AREA(I-1)
1130 W(I)=Y(I)+ALF(I)*DELTA
1140 J(I)=ALF(I)*(2*A-Y(I))
1150 ALT(I)=(-W(I)+SQR((W(I)^2)+4*DELTA*J(I)))/(2*DELTA)
1160 PARZ(I)=(ALT(I)+ALT(I-1))*DELTA/2
1170 AREA(I)=AREA(I-1)+PARZ (I)
1170 X(I)=X(I-1)+DELTA
1190 IF AREA(I)=>A THEN GOTO 1210
1200 NEXT I
1210 CLS
1220 REM
1230 REM PRINTING ON VIDEO AND WRITING IN THE FILE OF THE CALCULATED PARAMETERS
1240 REM
1250 PRINT
```

```
1260   PRINT TAB(5);"HEIGHTS"; TAB(22);
       "LENGTHS"; TAB(36); "AREAS";
       TAB(54); "TEMPERATURES"
1270   PRINT
1280   FOR I=1 TO CONTATOR
1290   PRINT TAB (1); ALT(I); TAB(25); X(I);
       TAB(32); AREA(I); TAB(55); TEMP(I)
1300   WRITE#1, X(I); ALT(I); AREA(I); TEM-
       P(I)
1310   NEXT I
1320   WRITE # 1, CONTATOR
1330   CLOSE # 1
1340   INPUT "Do you want to see the TPD
       peak?"; B$
1350   IF B$="N" GOTO 2480
1360   GOSUB 2760
1370   INPUT "Do you want to print the obtained
       results? (y/n)"; Z$
1380   IF Z$="N"GOTO 1400
1390   GOSUB 2520
1400   END
1410   PRINT
1420   INPUT "The kinetics is affected by read-
       sorption? (y/n)"; C$
1430   REM
1440   REM CHOICE BETWEEN THE KI-
       NETICS OF 2ND ORDER WITH OR
       WITHOUT READSORPTION
1450   REM
1460   CLS
1470   IF C$="Y" GOTO 1750
1480   PRINT: PRINT: PRINT: PRINT: PRINT:
       PRINT
1490   PRINT "Now the program is performing the
       calculations of heights, partial a readsorp-
       tion and of temperatures of the peak, for a
       kinetics of 2nd order without readsorption
       then it is writing the related values in the
       file TPD.DAT and show them on video"
1500   PRINT: PRINT: PRINT: PRINT: PRINT:
       PRINT: PRINT: PRINT: PRINT : PRINT:
       PRINT: PRINT: PRINT: INPUT" Press a
       key to continue"; Q$
1510   IF Q$="y" THEN GOTO 1520
1520   REM
1530   REM CALCULATION OF A PEAK OF
       SECOND ORDER WITHOUT READ-
       SORPTION
1540   REM
1550   COST=Z/(4*BETA*CS*A)
1560   TEMP(1)=TT
1570   ALT(1)=0
1580   AREA(1)=0
1590   X(1)=0
1600   PARZ(1)=AREA(1)
1610   FOR I=2 TO 280
1620   CONTATOR=I
1630   TEMP(I)=TEMP(I-1)+(DELTA*BETA/
       CS)
1640   ALF(I)=EXP(-ATT/(8.314*TEMP(I)))
1650   W(I)=(2*A)-(2*AREA(I-1))-(ALT
       (I-1)*DELTA)
1660   Y(I)=2*DELTA*W(I)*COST*ALFA
       (I)+1
1670   J(I)=COST*ALFA(I)* W((I)^2)
1680   ALT(I)=(Y(I)-(SQR(Y(I)^2-4*J(I)*
       (DELTA^2)COST*ALFA(I))))/(2*COS-
       T*ALFA(I)*DELTA^2))
1690   PARZ(I)=(ALT(I)+ALT(I-1))*DELTA/2
1700   AREA(I)=AREA(I-1)+PARZ (I)
1710   X(I)=X(I-1)+DELTA
1720   IF A-AREA(I)<.01 THEN GOTO 1740
1730   NEXT I
1740   GOTO 2320
1750   PRINT: PRINT: PRINT: PRINT: PRINT:
       PRINT:
1760   PRINT "Now the program is performing
       the calculations of heights, partial areas
       and of temperature of the peak, for a
       kinetics of 2nd ORDER WITH READ-
       SORPTION; then it is writing the related
       values in the file TPD.DAT and show them
       on video"
1770   PRINT: PRINT: PRINT: PRINT: PRINT:
       PRINT: PRINT: PRINT: PRINT : PRINT:
       PRINT: PRINT: PRINT: INPUT" Press a
       key to continue"; Q$
1780   IF Q$="s" THEN GOTO 1790
1790   REM
1800   REM CALCULATION OF A PEAK OF
       SECOND ORDER WITH READSORP-
       TION
1810   REM
1820   TEMP (1)=TT
1830   ALT(1)=0
1840   AREA(1)=0
```

```
1850 X(1)=0
1860 PARZ(1)=AREA(1)
1870 FOR I=2 TO 280
1880 CONTATOR=I
1890 TEMP(I)=TEMP(I-1)+(DELTA*BETA/CS)
1900 ALFA(I)=EXP(Z-(ATT/(8.314*TEMP))))
1910 Y(I-1)=2*AREA(I-1)+DELTA*ALT(I-1)
1920 W(I-1)=4*(A^2-2*A*AREA(I-1)-A*DELTA*ALT(I-1))
1930 REM Solving the 3rd rank equation: x^3+HA*x^2+HB*x+HC=0
1940 HA(I)=(1/DELTA)*(2*Y(I-1)-DELTA*ALFA(I))
1950 HB(I)=(1/(DELTA^2))*((Y(I-1)^2)-2*DELTA*ALFA(I)*Y(I-1)+4*ALFA(I)*A*DELTA)
1960 HC(I)=-(ALFA(I)/(DELTA^2))*((Y(I-1)^2)+W(I-1))
1970 HQ(I)=(3*HB(I)-HA(I)^2)/9
1980 HR(I)=(9*HA(I)*HB(I)-27*HC(I)-2*(HA(I)^3))/54
1990 REM Calculation of the equation discriminant,HD
2000 HD(I)=HQ(I)^3+HR(I)^2
2010 IF HD(I)<0 THEN GOTO 2090
2020 REM Calculation of the real root, when HD is equal to zero or positive
2030 HZ(I)=HR(I)-SQR(HD(I)): HU(1)=HR(I)+SQR(HD(I))
2040 HT(I)=EXP(LOG(ABS(HZ(I)))/3)
2050 IF HZ(I)<0 THEN HT(I)=-HT(I)
2060 HV(I)=EXP(LOG(ABS(HU(I)))/3)
2070 IF HU(I)<0 THEN HV(I)=-HV(I)
2080 ALT(I)=HV(I)+HT(I)-HA(I)/3: GOTO 2250
2090 REM Calculation of the real root, when HD is negative
2100 COEFF=HR(I)/(SQR(-HQ(I)^3))
2110 IF COEFF>.9 GOTO 2160
2120 ALT1=2*SQR(-HQ(1))*COS(3.141592654#/6-COEFF^7*5/336-COEFF^5/40-COEFF^3/18-COEFF/3)-HA(I)/3
2130 ALT2=2*SQR(-HQ(I))*COS((3.141592654#/6-COEFF^7*5/336-COEFF^5/40-COEFF^3/18-COEFF/3)+120*3.141592654#/180)-HA(I)/3
2140 ALT3=2*SQR(-HQ(1))*COS((3.141592654#/6-COEFF^7*5/336-COEFF^5/40-COEFF^3/18-COEFF/3)+240*3.141592654#/180)-HA(I)/3
2150 GOTO 2200
2160 IF COEFF>.9999999 THEN COEFF=.9999999
2170 ALT1=2*SQR(-HQ(I))*COS ((SQR(1-COEFF^2))/3)-HA(I)/3
2180 ALT2=2*SQR(-HQ(I))*COS ((SQR(1-COEFF^2))/3)+120*3.141592654#/180)-HA(I)/3
2190 ALT3=2*SQR(-HQ(I))*COS ((SQR(1-COEFF^2))/3)+240*3.141592654#/180)-HA(I)/3
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