DESORPTION KINETIC PARAMETERS AS DEDUCED FROM TEMPERATURE PROGRAMMED DESORPTION CURVES

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Temperature programmed desorption is a typical non-isothermal method and therefore it needs a careful experimentation and a careful evaluation of the experimental data, in order to obtain meaningful kinetic parameters.

A simple treatment of the data and some criteria, concerning the experimental methodology are therefore indicated, having in mind not only the advantages but also the difficulties and the limitations of a non-isothermal approach to kinetic studies.

Temperature programmed desorption (T. P. D.) is a widespread technique because of the possibility to obtain many informations about the desorption process, and therefore about the interactions between the catalyst and the adsorbed gas. The kinetic parameters obtained from T. P. D. curves are often deduced by means of the methods developed by Amenomyia and Cvetanovic and subsequently by other researchers [1—3]. But little attention has been paid to the disadvantages which are contained in this non-isothermal method, probably because of its derivation from flash-desorption, whose aims and whose philosophy have been retained.

The use of complex mathematical methods, based on the analysis of one or of many curves, can be therefore useless if a careful experimentation is not performed. To obtain meaningful kinetic parameters a simpler mathematical method is here developed which is based on the analysis of only one peak, with the assumption that no surface reaction accompanies the desorption and that an equilibrium distribution of the states of the adsorbed molecules exists and therefore the Arrhenius equation and the transition state theory can be applied.

In fact the methods which have been developed to analyze the T. P. D. peaks are based on the assumption that the entire desorption process, corresponding to a peak, can be described by only one kinetic law, whose parameter, or whose validity can be ascertained by a complicated mathematical modelling. This way of processing the experimental data excludes the possibility that a desorption process can be divided in

different ranges, and therefore, since an effective discrimination among kinetic models is often very difficult, the desorption process can be described by a model, which is not correct or which is applied in a not appropriate range. Thus even the concept of variable activation energy, intended to describe a rather complicate phenomenon, like surface heterogeneity, can be sometimes inadequate.

Development of a mathematical method of analysis

The kinetic analysis of non-isothermal rate measurements is based on a linear temperature increase from an initial value T_0:

$$T = T_0 + \beta t$$

where β is the linear heating rate; moreover it is based on the validity of the Arrhenius equation for the rate constant:

$$k = Ze^{-\frac{E}{RT}}$$

and it is based on the possibility of describing this rate by means of a function of the reaction advancement degree: in a desorption process, if we indicate the fractional surface coverage by means of θ, and the fraction of not covered surface by means of $(1 - \theta)$, this expression becomes:

$$\frac{d(1 - \theta)}{dt} = kf(\theta)$$

and therefore

$$\frac{d(1 - \theta)}{dT} = \frac{1}{\beta}\frac{d(1 - \theta)}{dt}$$

and finally

$$\frac{d(1 - \theta)}{dT} = \frac{k}{\beta} f(\theta).$$

If we use the differential method of analysis, we can write:

$$\frac{d(1 - \theta)}{dT} = \frac{Z}{\beta} e^{-\frac{E}{RT}}$$

and subsequently

$$\frac{\frac{d(1 - \theta)}{dT}}{f(\theta)} = \frac{Z}{\beta} e^{-\frac{E}{RT}}.$$

By taking the logarithms, we obtain:

$$\ln\left[\frac{\dfrac{d(1-\theta)}{dT}}{f(\theta)}\right] = \ln\frac{Z}{\beta} - \frac{E}{RT}.$$

If the function $f(\theta)$ has been properly chosen, we should obtain a straight line by plotting

$$\ln\frac{\dfrac{d(1-\theta)}{dT}}{f(\theta)}$$

versus $1/T$: its slope gives therefore the value of the activation energy, E, and its intercept on the y-axis gives the value of the preexponential factor, Z.

This method is somewhat less accurate than the integral one [4], but is far simpler and sufficiently accurate, since we must take into account the possible sources of experimental errors, mainly attributable to the variation of the thermocouple sensitivity in the large investigated temperature field, to the possible temperature inhomogeneities inside the catalyst (whose amount must be kept therefore to a minimum), to the problems of heat dissipation from the furnace.

As in the greatest part of the cases, we refer to a catharometric detector, settled in an apparatus similar to the one described in Fig. 1, by which it is possible to perform either continuous flow adsorption or pulse adsorption runs, therefore allowing the possibility of ensuring many different initial fractional surface coverages.
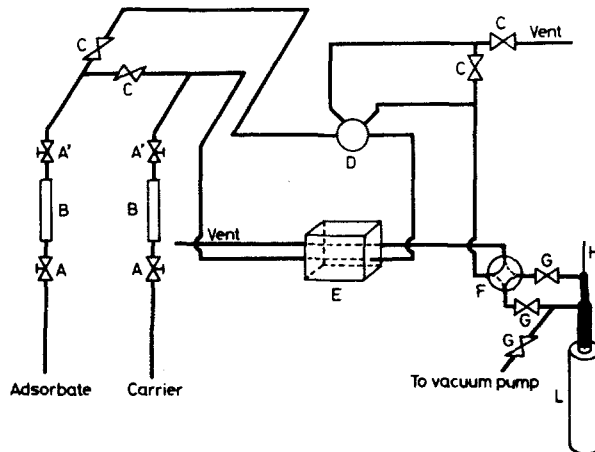
Fig. 1 A typical T. P. D. apparatus: A = upstream gas flow controller; A′ = downstream gas flow controller; B = rotameter; C = on-off valve; D = gas sampling valve; E = hot wire detector; F = four way valve; G = vacuum on off valve; H = thermocouple; I = reactor; L = furnace

By means of an apparatus of this type it is possible to perform adsorption runs either by pulse or by continuous flow technique.

The catharometer reveals the amount of desorbed gas within the stream of carrier gas in the sensing side, as compared to the stream of carrier gas, only, in the reference side. If dv is the infinitesimal volume of desorbed gas which is detected by the catharometer, if Δv is the total volume of the previously adsorbed gas, and if $d(1 - \theta)$ is the infinitesimal fraction of not covered surface, which corresponds to the detected amount dv, we can write:

$$dv = d\theta \, \Delta v$$

and therefore

$$\frac{dv}{dt} = \frac{d\theta}{dt} \, \Delta v. \tag{1}$$

In a typical T. P. D. peak, as reported in Fig. 2, it is possible to deduce that dv/dt, that is the amount of desorbed gas detected in the unit time, is reported on the y-axis.
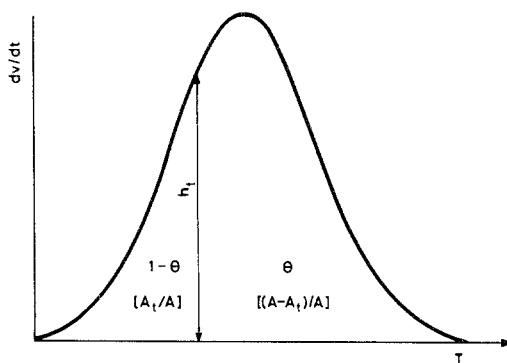

Fig. 2 A typical T. P. D. peak, showing the most meaningful experimental parameters

In fact the signal coming from the catharometer is a measurement of the molar fraction of the solute, x_s, and therefore it is possible to write:

$$\text{rec. pen deflection} = Kx_s = K \frac{f_s}{f_s + f_c} = \frac{K}{f} f_s$$

where f_s, f_c, and f are respectively the flow rates of the solute, of the carrier, and the total flow rate. Keeping in mind that f can be considered constant, we obtain:

$$\text{rec. pen deflection} = \frac{K}{f} v_s = K' \frac{dv}{dt}$$

and therefore the recorder pen deflection is directly proportional to dv/dt, that is the amount of the solute (the desorbed gas) detected in the unit time.

Following a procedure derived from differential scanning calorimetry, where similar concepts hold [5], the peak height at the time t, that is at the temperature T, is related to the value of dv/dt by means of the detector sensitivity, expressed as the molar fraction of solute (that is of the adsorbed gas) detected in the unit time, which is necessary for a full scale deflection of the pen recorder:

$$\text{full scale pen deflection} = K' \frac{dv}{dt}_{\text{full def.}} = K'S.$$

If we indicate by C_w the chart width of the recorder, a relation is therefore valid:

$$\frac{\frac{dv}{dt}}{S} = \frac{h_t}{C_w} \tag{1'}$$

where h_t is the peak height at the time t; we can therefore write:

$$\frac{dv}{dt} = \frac{h_t}{C_w} S$$

and remembering the relation (1) we can write

$$\frac{d(1-\theta)}{dt} = \frac{1}{\Delta v} \frac{h_t}{C_w} S \tag{2}$$

$$d(1-\theta) = \frac{1}{\Delta v} \frac{h_t}{C_w} S \, dt.$$

We can now substitute the variable "temperature" (that is "time") with the variable "length", on the x-axis, by introducing the recorder chart speed, C_s, which can be expressed by the relation:

$$C_s = \frac{ds}{dt}.$$

Thus, we can write:

$$d(1-\theta) = \frac{S}{\Delta v C_w C_s} h_t \, ds.$$

But we have also: $h_t \, ds = dA_t$, where dA_t is the infinitesimal area subtended by the peak at the time t. If we indicate the total area by A, we obtain by integrating $d(1-\theta)$ between 0 and 1 and dA_t between 0 and A:

$$1 = \frac{S}{\Delta v C_w C_s} A.$$

Therefore:

$$\Delta v = \frac{AS}{C_w C_s}.$$

We can now write the equation (2) in the form:

$$\frac{d(1-\theta)}{dt} \frac{C_w C_s}{AS} \frac{h_t S}{C_w} = \frac{h_t C_s}{A}.$$

Assuming the validity of the classical equation for desorption:

$$\frac{d(1-\theta)}{dT} = \frac{k}{\beta} \theta^n,$$

and keeping in mind that $\theta = \dfrac{A - A_t}{A}$ and $1 - \theta = \dfrac{A_t}{A}$ it is possible to write:

$$\frac{h_t C_s}{A} = \frac{k}{\beta} \left(\frac{A - A_t}{A}\right)^n,$$

that is:

$$\frac{h_t C_s}{A} = \frac{Z}{\beta} e^{-\frac{E_d}{RT}} \left(\frac{A - A_t}{A}\right)^n$$

and taking the logarithms:

$$\ln \frac{h_t}{(A - A_t)^n} = \ln \frac{Z}{\beta C_s A^{n-1}} - \frac{E_d}{RT}. \tag{3}$$

If the value of n has been correctly determined, the plot of $\ln (h_t/(A - A_t)^n)$ versus $1/T$ gives a straight line with slope $-E_d/R$ and intercept $\ln (Z/\beta C_s A^{n-1})$, where Z is the preexponential factor and E_d is the activation energy.

The most important advantage of the above described method is represented by the possibility of finding different ranges of θ, where an appropriate kinetic law gives a straight Arrhenius plot: this means that a desorption process could be described by a certain law up to a certain value of the fractional surface coverage, and by another law above that value, depending on the dominance of one or the other between the competing mechanisms with different kinetic parameters; moreover this could mean that the desorption process can be described by one law in the whole range of the fractional surface coverage, even if this law is characterized by a sudden variation of the kinetic parameters.

On the other hand we must underline that the shape of a T. P. D. peak indicates that the corresponding integral curve has a sigmoidal shape and evidences three intervals. In the first one we have an acceleratory progression of the reaction according to a power-like equation:

$$\frac{d(1-\theta)}{dt} = k(1-\theta)^{1-\frac{1}{n}}$$

in the second one the advancement of the reaction is linear versus time and in the third one we have a decay period, which is described by a decay-like equation:

$$\frac{d(1-\theta)}{dt} = k\theta^n.$$

If the continuous curve can be divided into some intervals, which are described by different equations, it means that its kinetics is very complex and cannot be easily described by equations, which are phenomenological and must give a meaningful value of parameters, which in their turn are related to properties at atomic scale. However in most cases the shape of a T. P. D. peak is similar to the one reported in Fig. 3a, rather than to the one in Fig. 3b, and therefore the greatest part of the corresponding sigmoidal curve can be described by a decay-like equation (with or without diffusion or readsorption), as it is possible to see in Fig. 3c. (This is compared with a sigmoidal curve in Fig. 3d where only the final part of the process is described by a decay-like equation.)

In practice this reduces the "complexity degree" of a T. P. D. peak, and it appears meaningful to apply one of the classical desorption equations, in order to obtain the desired kinetic parameters, even if the possibility remains that a variation of the
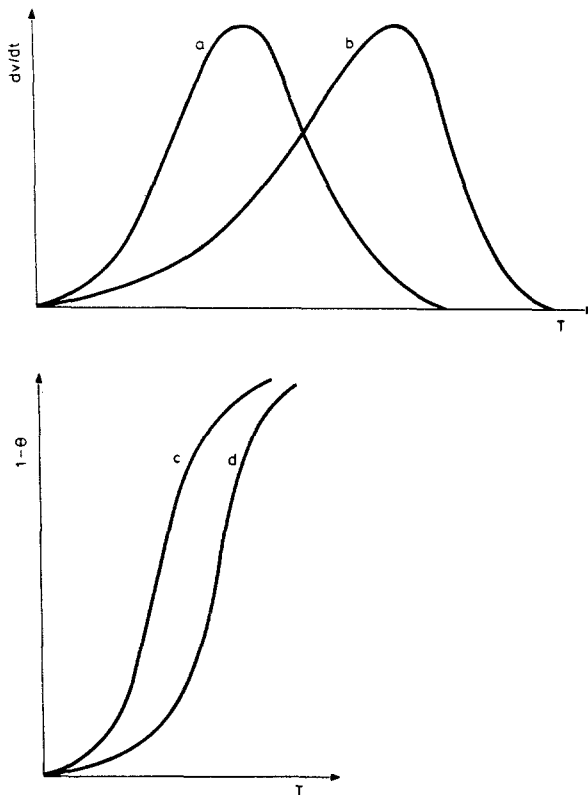

Fig. 3 Possible kinds of desorption peaks: a) symmetrical and b) unsymmetrical; integrated curves of these kinds of desorption peaks: c) symmetrical and d) unsymmetrical

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kinetic model can be necessary in order to describe the desorption mechanism in the entire range of the process.

In this possibility the fact must be also included that diffusion can affect the desorption rate at the beginning (molecules become mobile before desorbing and the diffusion activation energy is lower than the desorption one) and that the readsorption can affect the desorption rate in the central and in the final part of the process, when the surface is more and more uncovered.

But the diffusion and, above all, the readsorption rather require a careful reexamination of the problem of the complexity of a T. P. D. peak: indeed these two phenomena are often undesirable and must be considered limitations for the true desorption process.

The literature evidences [6–8] the experimental conditions, which are necessary to avoid these limitations, or evidences the methods for obtaining meaningful kinetic parameters when these processes are the rate limiting step.

However, before examining in detail how diffusion and readsorption can influence a T. P. D. peak, it is useful to compare this analytical procedure for describing the complexity of a T. P. D. peak with the one which is based on the concepts of surface heterogeneity and of variable activation energy [9]. Indeed it must be underlined immediately that a description of the surface heterogeneity only by means of the variable activation energy is not completely adequate because it is strictly related to the activation entropy and therefore to the preexponential factor, as it is tested by the existence of the compensation effect [10].

Moreover, it is well known [11] that an asymmetry of the T. P. D. peak is claimed as a proof of surface heterogeneity and of variable activation energy versus the surface coverage.

But it has been already evidenced that such a type of complexity of the T. P. D. peak can be explained as well by a variation of the kinetic model; and such a variation must be supported by a variation of the desorption mechanism, indicating, therefore, the presence of surface heterogeneity. On the basis that a variation of the kinetic model is accompanied by a variation of the activation energy and of the preexponential factor, it appears evident that the contrast between these two analytical procedures is only apparent: indeed the way of analyzing a T. P. D. peak, here developed, leads to investigate every kinetic parameter during the desorption process: therefore the variation of the activation energy alone must be considered as a particular case.

A further development of the above shown analytical procedure can be interesting by introducing the concept of the variable activation energy versus the surface coverage: this variability can be expressed by a linear relationship [12]:

$$E_d = E_d^0 + \alpha R T \theta$$

or by a logarithmic relationship [13]:

$$E_d = E_d^0 + \alpha R T \ln \theta.$$

Therefore the classical equation for desorption becomes:

$$\frac{d(1-\theta)}{dT} = \frac{Z}{\beta} e^{-\frac{E_d^0}{RT}} e^{-\alpha\theta}\theta^n.$$

and in the second instance:

$$\frac{d(1-\theta)}{dT} = \frac{Z}{\beta} e^{-\frac{E_d^0}{RT}} e^{-\alpha \ln\theta}\theta^n.$$

The possibility of obtaining meaningful kinetic parameters in the presence of surface heterogeneity is then reached by performing isothermal desorption runs; indeed in the analysis of an isothermal desorptogram we can write simplified relations:

$$\frac{d(1-\theta)}{dt} = K e^{-\alpha\theta}\theta^n$$

or in the second instance:

$$\frac{d(1-\theta)}{dt} = K' e^{-\alpha \ln\theta}\theta^n$$

and, by taking the logarithms:

$$\ln\frac{\frac{d(1-\theta)}{dT}}{\theta^n} = \ln K - \alpha\theta$$

or in the second instance:

$$\ln\frac{\frac{d(1-\theta)}{dT}}{\theta^n} = \ln K' - \alpha \ln\theta.$$

We can therefore write:

$$\ln\frac{h_t}{(A-A_t)^n} = \ln k - \alpha\frac{A-A_t}{A}$$

or in the second instance:

$$\ln\frac{h_t}{(A-A_t)^n} = \ln k' - \alpha \ln\frac{A-A_t}{A}.$$

It is therefore possible to plot $\ln(h_t/(A-A_t)^n)$ versus $(A-A_t)$ or versus $\ln(A-A_t)$: if the value of n has been chosen correctly, we obtain in one or in the other instance a rectilinear diagram, whose slope gives the value of α, indicating also how the activation energy varies in function of the fractional surface coverage.

After having determined α from an isothermal desorption run, we can perform the examination of the T. P. D. peak, reconsidering the equation (3), which becomes:

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$$\ln \frac{h_t}{(A - A_t)^n} + \alpha \frac{A - A_t}{A} = \ln \frac{Z}{\beta C_s A^{n-1}} - \frac{E_d^0}{RT}$$

or

$$\ln \frac{h_t}{(A - A_t)^n} + \alpha \ln \frac{A - A_t}{A} = \ln \frac{Z}{\beta C_s A^{n-1}} - \frac{E_d^0}{RT}$$

according to the relationship between E_d and θ.

In the first or in the second instance we obtain a rectilinear diagram, by plotting the first member versus $1/T$, and we can determine the values of Z and E_d^0.

Some experimental instances have been analysed by means of the above described procedure and the results have been compared with the ones obtained by means of the classical procedures.

Therefore, a reinvestigation has been performed about the temperature programmed desorption of propylene previously adsorbed on zinc oxide, whose kinetic features have been already described elsewhere [14].

A desorptogram shows a low temperature desorption peak, due to a weakly bound reversibly chemisorbed form of propylene and a high temperature desorption peak due to a strongly bound form, which desorbs with reaction, and appears to be due to benzene.

As far as the low temperature peak is concerned, a kinetic analysis has been performed by plotting $\ln h_t/(A - A_t)^n$ versus $1/T$: the best alignment has been obtained for a first order kinetic model (see Fig. 4) and an activation energy of 71.8 kJ/mol and a preexponential factor of $3 \cdot 10^8$ have been found, therefore confirming the previously obtained results.

However we must take into account that this analytical procedure is based on experimental conditions which justify the applicability of the Arrhenius equation and of the transition state theory for the reaction rate: it is therefore assumed that during desorption quasi-equilibrium conditions must be realized, but this implies that low heating rates must be used, in such a way that the deviations from the equilibrium distributions, deriving from the desorption process, are adjusted according to the transition state theory, even if there are strong adsorbate-adsorbent interactions, which can affect the equilibrium distribution.

These experimental conditions favour unavoidably the occurrence of readsorption: indeed it is very difficult, and in some instances impossible, to avoid this phenomenon, which causes a progressive decrease of the reaction rate, while decreasing the fractional surface coverage [15, 16], even if the effects of this phenomenon are sometimes attenuated by the effect of the increasing temperature, which does not play a favourable role for readsorption.

In this context some developments of this analytical procedure must be carefully considered: for example the applicability of a Freundlich isotherm (and therefore of logarithmic variation of E_d versus θ) for explaining the surface heterogeneity, has a
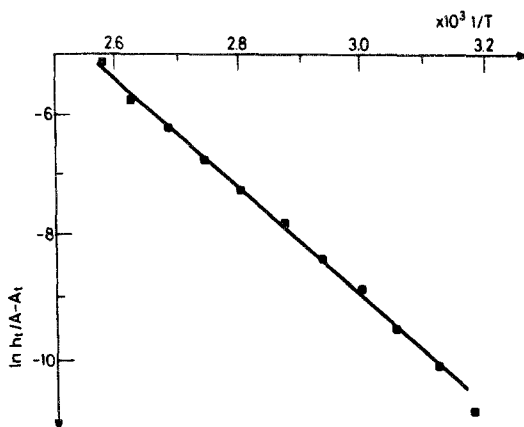
Fig. 4 Arrhenius plot for a first order kinetic model obtained from a T. P. D. low temperature peak of the propylene desorption from the zinc oxide surface

sure validity only at low surface coverages, and therefore in the range where the influence of readsorption is more pronounced.

On the basis of these considerations it is easy to obtain, therefore, meaningless kinetic parameters, especially as far as the activation energy is concerned.

The application of the classical equation for desorption with readsorption leads therefore to obtain meaningful results, indeed we can write:

$$\frac{d(1 - \theta)}{dt} = k_d \theta^n - k_a (1 - \theta)^n C$$

where k_d and k_a are respectively the desorption and adsorption rate constants, and C is the concentration of solute (desorbed gas) in the gas phase.

According to the classical treatment [6], if the validity of the relation:

$$F \ll \Delta v K (1 - \theta)^n$$

is ensured, K being the adsorption equilibrium constant, we can write:

$$\frac{d(1 - \theta)}{dT} = \frac{KF}{\beta \Delta v} \frac{\theta^n}{(1 - \theta)^n}$$

that is:

$$\frac{h_t C_s}{A} = \frac{KF}{\beta \Delta v} \frac{\left(\frac{A - A_t}{A}\right)^n}{\left(\frac{A_t}{A}\right)^n}$$

and therefore:

$$\frac{h_t A_t^n}{(A - A_t)^n} = \frac{FC_w}{\beta S} e^{\frac{\Delta S^0}{R}} e^{-\frac{\Delta H^0}{RT}}$$

and taking the logarithms:

$$\ln \frac{h_t A_t^n}{(A - A_t)^n} = \ln \frac{FC_w}{\beta S} + \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}.$$

Therefore, if we have fixed the correct value of n, a plot of $\ln h_t A_t^n/(A - A_t)^n$ versus $1/T$ gives a straight line with slope $- \Delta H^0/R$ and an intercept corresponding to the logarithmic term in the right member of this equation.

However, unfortunately, the catharometer sensitivity is not expressed usually by means of S, which must be determined therefore by means of the equation $(1')$.

We can therefore evaluate the two thermodynamic parameters ΔH^0 and ΔS^0, for the adsorption process.

As a typical case of desorption with readsorption we can report the example of the temperature programmed desorption of H_2 from the surface of silica supported nickel [17]. Literature evidences that this desorption process follows a second order kinetics, and the corresponding kinetic parameters are given [18, 19].

Figure 5 shows that two types of adsorbed hydrogen exist on this catalyst: the attempts of fitting a second order kinetic model to the peak at higher temperature leads to the Arrhenius plot reported in Fig. 6a. It is evident that, because of readsorption, the process maintains at a fixed temperature a greater value of θ (indeed the process ends at higher temperatures): therefore the corresponding value of $(A - A_t)^2$ is greater. But the value of the rate and therefore of h_t is first lower and becomes progressively greater than in absence of readsorption: in the final part of the desorption its increase is certainly greater than the one of $(A - A_t)$, and therefore the slope of $\ln h_t/(A - A_t)^2$ is first decreasing and subsequently increasing.

If the second order equation with readsorption is applied, we obtain a better alignment of the Arrhenius plot, but the final correct result is obtained when we introduce the correction for the presence of surface heterogeneity.

After having determined the value of α ($\alpha = 8.8$ kJ/mol) we can determine the Arrhenius plot reported in Fig. 6b obtaining an activation energy of 86.1 kJ/mol in the range $0.93 > \theta > 0.15$.

Conclusions

The increasing number of papers on T. P. D. testifies the growing interest this technique is arousing. However, even if the necessary apparatus can be relatively simple and can induce many researchers to use T. P. D. as a catalyst characterization tool, it is to underline that temperature programmed desorption is a non-isothermal technique and involves a great number of problems.

Therefore, a careful experimentation is needed to ensure experimental conditions, which allow us to obtain meaningful kinetic parameters and therefore to characterize not only catalyst active centers, but also the desorption process.
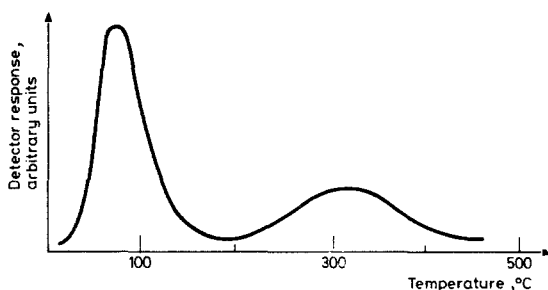
Fig. 5 A typical desorptogram for temperature programmed desorption of H_2 adsorbed on 15% Ni/SiO$_2$
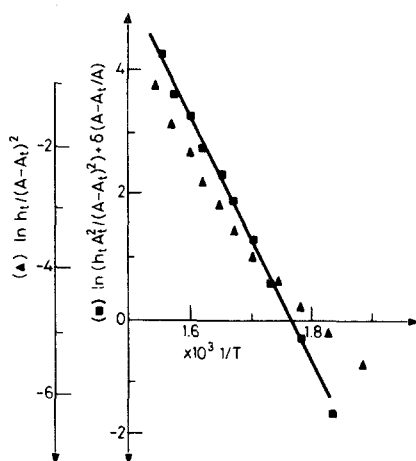

Fig. 6 Arrhenius plot related to the higher temperature peak of Fig. 5, for a second order kinetic law a), and for a second order kinetic law in presence of surface heterogeneity

And, if this type of characterization becomes the goal of the research, it follows that attention must be paid to the complexity of the mechanism, to its development and to its correct interpretation from a mathematical point of view.

An analytical treatment of a T. P. D. peak is here indicated, which allow us to ascertain the kinetic parameters at every value of the fractional surface coverage: this type of treatment should help, therefore, to offer a deeper insight in the mechanism of desorption.

All these considerations exclude that two or more simultaneous desorption processes or that desorption with reaction could occur: however it is worth noting that in many cases a desorptogram presents complications of this kind: even more it is therefore necessary to perform a careful experimentation, which includes the investigation of a large range of carrier gas flow rates and of heating rates, and includes also the exploitation of many adsorption temperatures and of isothermal desorption

runs, in order to separate simultaneous desorption processes or to avoid the effects of contemporaneous reactions, and therefore in order to be able to apply this analytical treatment.

References

1 R. J. Cvetanovic and Y. Amenomyia, Catal. Rev., 6 (1972) 21.

2 J. A. Konvalinka, J. J. F. Scholten and J. C. Rasser, J. Catal., 48 (1977) 365.

3 J. M. Criado, P. Malet and G. Munuera, Thermochim. Acta, 33 (1979) 345.

4 J. Simon, J. Thermal Anal., 5 (1973) 271.

5 G. Beech, J. Cehm. Soc., (A) (1969) 1903.

6 R. J. Gorte, J. Catal., 75 (1982) 164.

7 R. K. Herz, J. B. Kiela and S. P. Marin, J. Catal., 56 (1982) 66.

8 D. M. Jones and G. L. Griffin, J. Catal., 75 (1982) 164.

9 R. J. Cvetanovic and Y. Amenomyia, Advan. Catal., 17 (1967) 103.

10 J. L. Taylor and W. H. Weinberg, Surf. Sci., 78 (1978) 259.

11 Y. Tokoro, M. Misono, T. Uchijima, Y. Yoneda, Bull. Chem. Soc. Jpn., 51 (1978) 85.

12 S. Ceckiewicz and M. Kozik, Surf. Sci., 110 (1981) 491.

13 P. Malet and G. Munuera, Ads. at the gas-solid and liquid-solid interface, Elsevier Scientific Publishing Company, Amsterdam, 1982, p. 383.

14 R. Spinicci and A. Tofanari, J. Thermal Anal., 23 (1982) 45.

15 C. Bendorf and F. Z. Thieme, Z. Phys. Chem. N. F., 87 (1975) 40.

16 F. Sweet and E. Rideal, Actes du XII. Congrès International du Catalyse, Paris Edition Technip, Paris, 1960, p. 175.

17 R. Spinicci and A. Tofanari, sent for publication to React. Kinet. Catal. Letters.

18 P. I. Lee and J. A. Schwarz, J. Catal., 73 (1982) 272.

19 J. Lapujoulade and K. S. Neil, Surf. Sci., 35 (1973) 288.

Zusammenfassung — Die temperaturprogrammierte Desorption ist eine typische nicht-isotherme Methode, und deshalb ist eine sorgfältige Versuchsausführung und Auswertung der experimentellen Daten notwendig, um sinnvolle kinetische Parameter zu erhalten. Es werden deshalb eine einfache Behandlung der Daten und einige die experimentelle Methodologie betreffende Kriterien vorgestellt und anhand von experimentellen Beispielen erläutert, wobei nicht nur die Vorteile, sondern auch die Schwierigkeiten und Grenzen eines nicht-isothermen Verfahrens bei kinetischen Untersuchungen Erwähnung finden.

Резюме — Температурно-программированная десорбция является типичным неизотермическим методом и поэтому требует тщательного проведения эксперимента и тщательной оценки экспериментальных данных с целью получения разумных кинетических параметров. В связи с этим, указана простая обработка данных и некоторые критерии относительно методики проведения эксперимента, имея в виду не только преимущества, но также трудности и ограничения неизотермического приближения к кинетическим исследованиям.