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A procedure for the kinetic processing of multiple peaks in temperature programmed desorption

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Abstract

On the basis of the analysis of the features of temperature programmed desorption curves and of the advantage of extracting kinetic parameters and deducing desorption mechanism from the analysis of a single peak, a procedure which allows when necessary, the existence of multiple peaks and their deconvolution, is described. It also confirms the goodness of the results by means of a non-linear regression method of analysis and by means of the comparison with reconstructed rising temperature desorption curves. © 1997 Elsevier Science B.V.

Keywords: Temperature programmed desorption; Multiple peaks; Deconvolution method

1. Introduction

Temperature programmed desorption is a well established technique for characterising adsorptive properties of catalysts towards reactants and products of a certain reaction, and therefore for characterising the catalysts active sites

A desorption peak can allow the evaluation at the different temperatures, of the rate of desorption of a certain gaseous adsorbate from a catalyst surface; this rate is usually expressed by an equation, which relates the decrease of the fractional surface coverage in unit time to function of the fractional surface covered.

$$\mathrm{d}\theta/\mathrm{d}T = kf(\theta)$$

where θ is the fractional surface covered $f(\theta)$ is a function, which usually describes a first or second order desorption without or with readsorption. The value of k at the different temperatures is generally assumed to be governed by the Arrhenius equation:

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

where A is the pre-exponential factor, E is the activation energy and R is the gas constant. Different procedures have been suggested to calculate the kinetic parameters and evaluate the desorption mechanism [1–3]: they are fundamentally based on the analysis of a single peak or on the analysis of the same peak at different heating rates.

The simplicity of the apparatus has allowed an extension of their technique and therefore its peculiarities have been cleared out in many papers and reviews [4,5]: but, despite this apparent simplicity and availability of a number of procedures for the elaboration of the experimental data, much attention

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must be paid to experimental factors, which can affect the meaning of the results.

There are factors which can be derived from the intrinsic features of the catalytic system. Above all, the occurrence of a surface reaction during the desorption process must be recognised, in order to relate the peak to the true chemical event: this can affect the kinetic mechanism of the entire process up to a different extent, according to the heating rate. Moreover the re-adsorption, the surface mobility of the adsorbed species during desorption, the surface heterogeneity can affect the shape of the peak in a different way according to the heating rate. Diffusion phenomena can also be present during desorption and care must be taken in avoiding or minimising them with a proper choice of the carrier gas flow rate. In addition there is also the possibility that the catalyst is characterised by active sites of similar energy, giving shoulders accompanying the main peak [6].

These are however factors which can also be derived from the experimental parameters, which can be varied from run to run. Temperature of adsorption and dynamic conditions of adsorption (pulse or continuous adsorption), sample weight and carrier gas flow rate during desorption are surely the most important parameters. But other factors are equally important : for example the dead volume between catalyst and detector can introduce backmixing phenomena in the flow of the carrier gas and modify the shape of the peak, and therefore must be kept to a minimum. The type of reactor and also the consequent presence of possible heat or mass transfer limitations can be important and care must be taken in designing the reactor [7].

Particular attention must be obviously paid to the extraction of meaningful kinetic parameters from a desorption peak accompanied by one or more shoulders (multiple peak). In such a case the heating rate can play an important role in enhancing, for example, readsorption, or surface mobility phenomena influencing therefore the relative position of the maxima and the relative area of the peaks:it appears therefore not convenient to develop a kinetic analysis of the peak by means of different experiments at different heating rates, and it appears more convenient to carry out a kinetic analysis on a single peak, with the aim of clearing out, in the peak examined and for the experimental conditions employed, the validity of a proposed mechanism, eventually for a well determined range of the fractional surface coverage.

2. Discussion

The procedure is based, above all, on the possibility of simulating by means of a computer program a temperature programmed desorption peak of first or second order, with or without readsorption. A computer program has been therefore developed [8] to reconstruct a TPD peak of the above mentioned types, starting from a knowledge of the activation energy, pre-exponential factor, starting temperature heating rate and peak area.

The method of kinetic analysis, which has been followed [9] in analysis of the peaks observed experimentally, is based on the observation that a certain peak height, h_t is proportional to the actual rate of gas evolution (volume of gas evolved in the unit time), in its turn proportional to the actual desorption rate. On the other hand the fractional surface covered can be expressed by the ratio of the residual peak area (determined by the corresponding height and corresponding to $(A-A_t)$ over the total peak area, that is A.

Therefore the expression:

$$-\mathrm{d}\theta/\mathrm{d}T = k \cdot f(\theta)$$

assumes a form of this type:

$$h_t \propto kf((A-At)/A)$$

In particular one can obtain for desorption without readsorption:

$$h_t = \mathrm{const} \cdot e^{-E/RT} \cdot ((A-A_t)/A)^{\mathrm{n}} \quad (\mathrm{n} = 1;2)$$

(where E is the activation energy) and for desorption with readsorption:

$$h_t = \mathrm{const} \cdot e^{-\Delta H/RT} \cdot ((A-A_t)/A)^{\mathrm{n}} \quad (\mathrm{n} = 1;2)$$

where ΔH is the heat of adsorption.

Since in these equations there are two dependent variables (h_t and A_t) and one independent variable (T), the possibility of performing a deconvolution of two or more experimental peaks, by using these equations directly in a procedure of non linear least square analysis is quite complicated. Therefore the four peaks have been expressed by means of an empirical equation with adjustable coefficients which can describe symmetrical and asymmetrical peaks:

$$y = \left(\frac{a_0}{1+\exp\left(-\left(\frac{x-a_1+\frac{a_2}{2}}{a_3}\right)\right)}\right) * \left(1-\frac{a_0}{1+\exp\left(-\left(\frac{x-a_1-\frac{a_2}{2}}{a_4}\right)\right)}\right)$$

where y is the height h_t and x is the temperature T.

This equation can combine a sigmoidal curve with a reverse sigmoidal one of different width to produce an asymmetric peak: a_0 controls the height of the peak a_1 controls the centre of the peak, a_2, a_3, a_4 control respectively the separation of the two sigmoidal, that is the width of the left sigmoidal and the width of the right (reverse) sigmoidal.

It has been possible to adjust the five coefficients in such a way as to reconstruct every one of the four types of peaks by means of a procedure of non-linear least squares analysis, and therefore it has been possible to find an easier way to perform a deconvolution of a multiple TPD peak.

The deconvoluted peaks can be subsequently analysed in two steps. By means of the above mentioned procedure the classical Arrhenius plots can be obtained and therefore the values of the activation energy and of the pre-exponential factor for the kinetic mechanisms can be obtained. Then these values can be used as first approximation values in a procedure of non linear least squares analysis, according to the Marquardt–Levenberg algorithm [10], in order to fit the reconstructed peak heights on the basis of the proposed kinetic models to the experimental peak, and therefore to ascertain the goodness of the procedure.

As an example, this procedure can be applied to analyse a TPD peak, obtained in temperature programmed desorption of oxygen from 2% K_2O/ ZnO, a catalyst for methane coupling.

In Fig. 1 it is proposed that this peak, which shows a well formed shoulder in its descending part and therefore evidences two processes, probably related to two different types of active sites, which occur almost contemporarily.

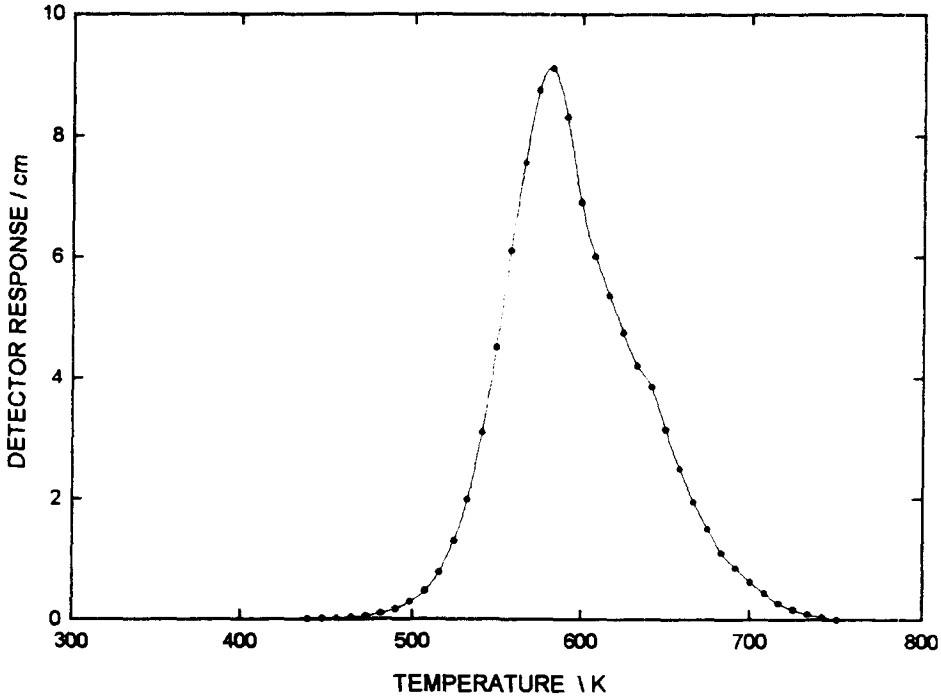

Fig. 1. TPD peak of O_2 from K_2O/ZnO. Adsorption of O_2 at room temperature. Desorption at 8°C min^{-1} with carrier gas (He) flow rate of 100 cm^3 min^{-1}.

By means of the suggested procedure it has been possible to find that the peak can be deconvoluted in two peaks, which can be described by means of the above reported equation with the following values of the five parameters:

1. a_0=15.2; a_1=579.4; a_2=25.5; a_3 16.7; a_4=8.9 for the first peak;
2. a_0=15.9; a_1=625.4; a_2=60.3; a_3 25.9; a_4=48.9 for the second peak.

In the Fig. 2 it is possible to see the two peaks and in Fig. 3 the complete experimental peak and the complete calculated peak.

The values of the parameters obtained for the first peak are in a ratio, which is typical of a second order desorption with readsorption, while the values for the second peak indicate that it is described by a second order desorption (without readsorption).

On these basis both peaks have been elaborated , in order to obtain the reciprocal temperatures, the areas at the different temperatures, the corresponding values of θ and of $(1-\theta)$ and therefore to obtain the natural logarithm of the rate constant for every kinetic model at the different temperatures: this allows to draw the various Arrhenius plots, which are reported in Fig. 4 for the first peak and in Fig. 5 for the second peak.

The rectilinear plots for second order with readsorption model related to the first peak, and for second order model related to the second peak, confirm that the peaks are described by these kinetic laws in a very large range of θ. It is possible therefore to define the values of the pre-exponential factor (intercept on the ordinate axis), and the value of the adsorption enthalpy for the first peak and of the activation energy for the second peak(slope of the plot). The results are:

1. $Z=8\cdot10^{38}$; ΔH=411.6 kJ mol^{-1} (for the first peak described by the 2nd order with readsorption);
2. $Z=8.6\cdot10^{13}$; E_{att}=182.1 kJ mol^{-1} (for the second peak described by the 2nd order

It must be reminded however at this point that the values of the pre-exponential factors contains constant terms derived from the starting assumptions of the type of the kinetic analysis: the values of the frequency factors can be obtained only by taking into account these constant terms.

A further confirmation to these results can be obtained, by exploiting these values as first approx-

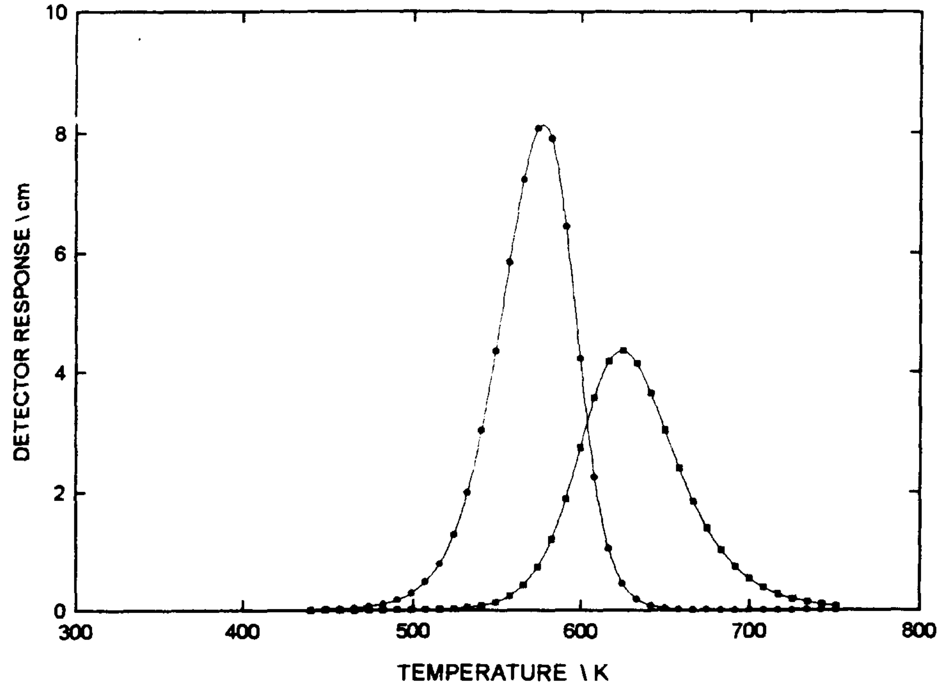

Fig. 2. Plot showing the deconvolution of the composite TPD peak of O_2 from K_2O/ZnO in the two peaks.

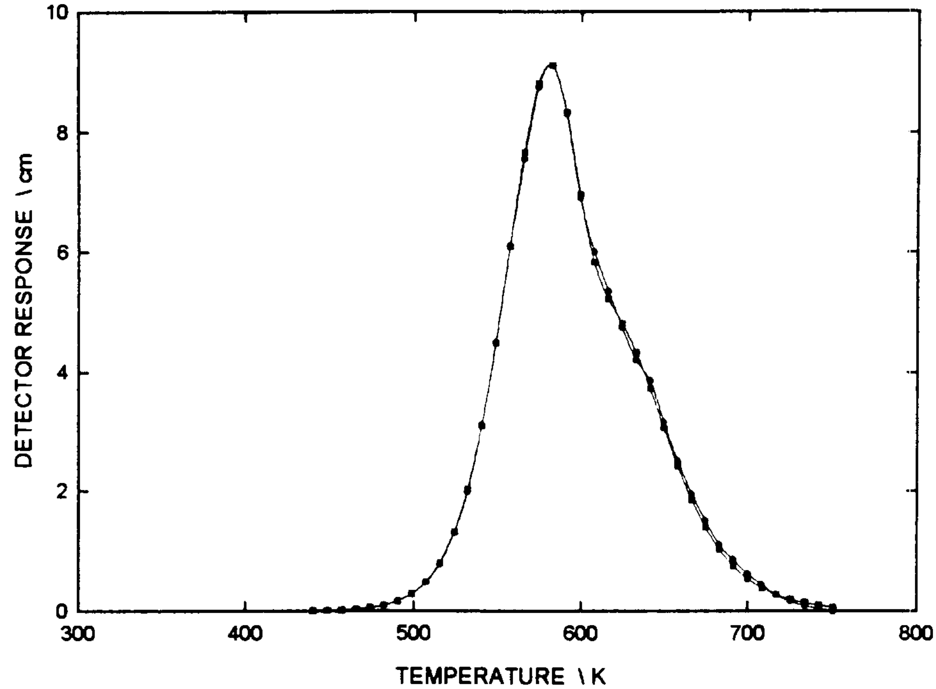

Fig. 3. The peak obtained by the deconvolution procedure surperimposed on the composite TPD peak of O_2 from K_2O/ZnO.

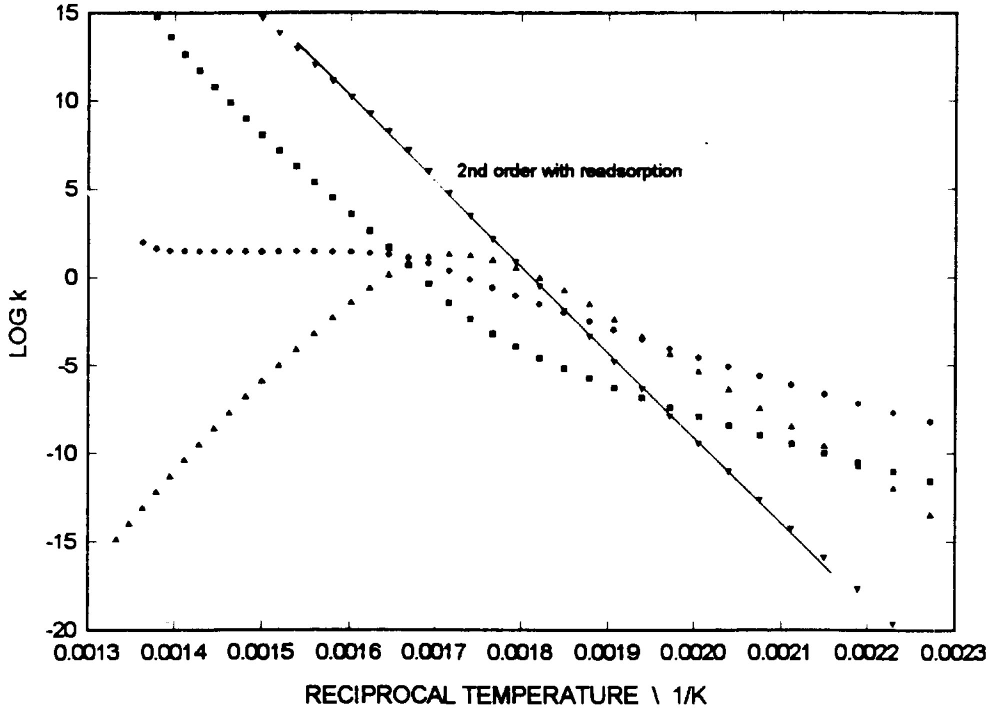

Fig. 4. Arrhenius plot derived from the first of the two peaks obtained by the deconvolution procedure superimposed on the composite peak of O_2 from K_2O/ZnO.

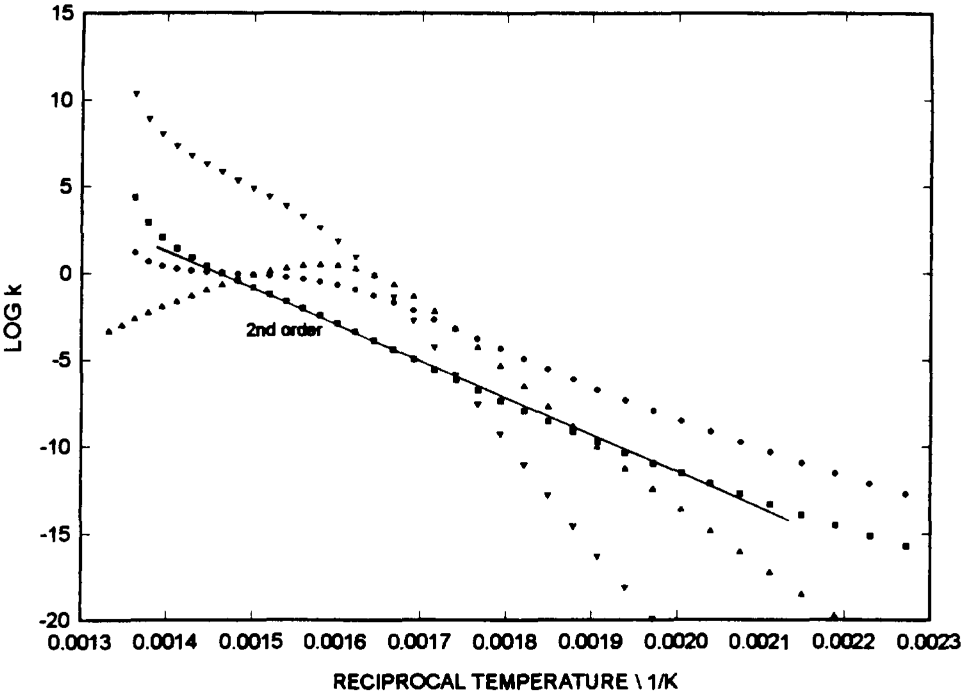

Fig. 5. Arrhenius plot derived from the second of the two peaks obtained by the deconvolution procedure superimposed on the composite peak of O_2 from K_2O/ZnO.

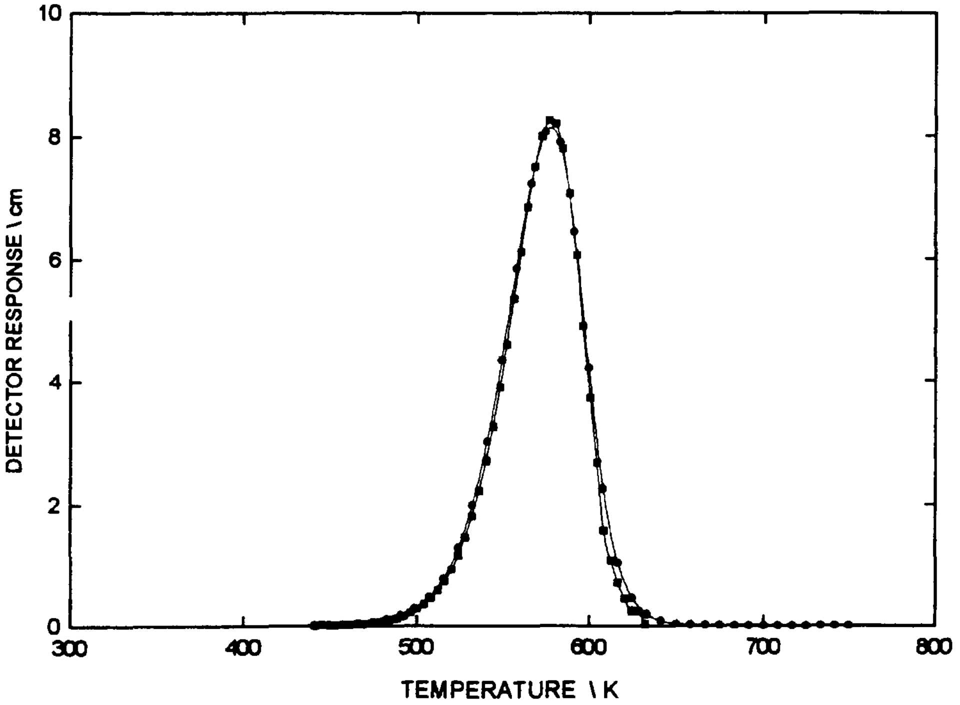

Fig. 6. Comparison of the first peak obtained by the deconvolution with a non linear fitting of the proposed model.

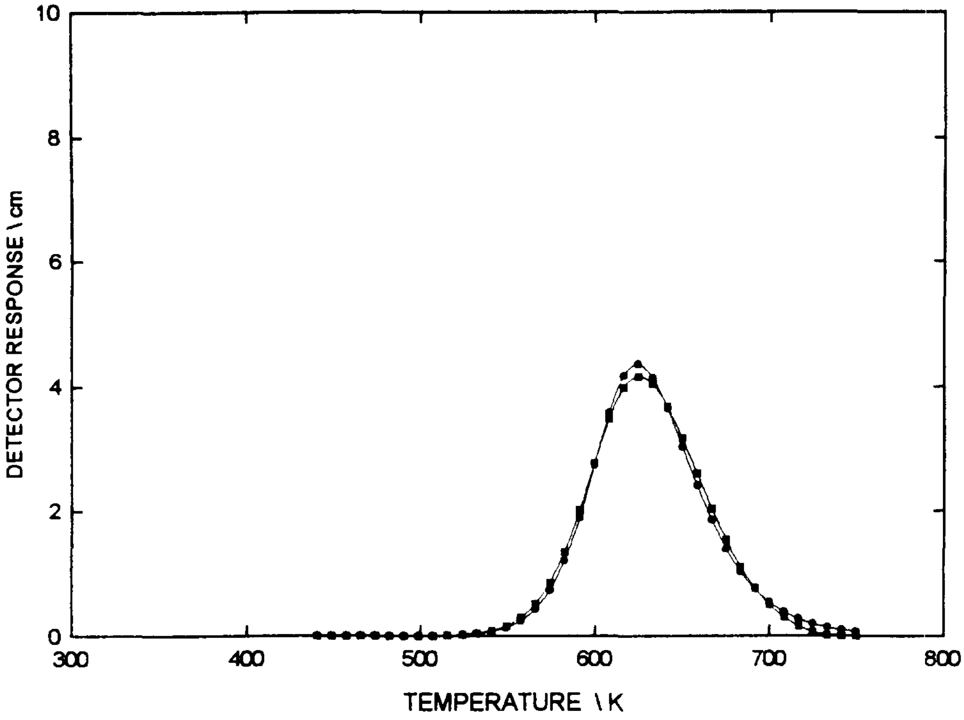

Fig. 7. Comparison of the second peak obtained by the deconvolution with a non linear fitting of the proposed model.

imation values in a procedure of non linear least squares fitting of the kinetic models:

1. $h_t=Z \cdot e\ -^{\Delta H/RT} \cdot((A\text{-}A_t)/A_t)^2$ for the first peak;
2. $h_t=Z \cdot e\ -^{E/RT} \cdot((A\text{-}A_t)/A_t)^2$ for the first peak.

The peaks obtained are shown in Fig. 6 and respectively in Fig. 7 and are in good agreement with the the peak obtained by the deconvolution. The values also of the kinetic parameters are nearly the same obtained from the Arrhenius plots.

3. Conclusions

Temperature programmed desorption is a widespread technique in the heterogeneous catalysis studies which can allow a characterisation of the interactions between gases and solid catalysts: many qualitative informations indeed can be obtained on the stability of the surface species of reactants and products.

If quantitative informations are to be obtained, as for example the activation energy for the desorption processes and therefore a quantitative evaluation of the energetic interactions between adsorbent and adsorbate, much care must be taken.

In many cases the analysis of the same peak obtained in different experiments at different heating rates can offer unreliable results and it is preferable that an analysis of a single peak, eventually accompanied by a deconvolution, if necessary, relating the kinetic parameters obtained to the experimental conditions of pretreatment adsorption, and desorption and comparing them with those obtained in different conditions, in order to obtain informations from this comparison also.

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