A MODEL FOR THE CHARACTERIZATION OF SUPPORTED
CATALYSTS BY TEMPERATURE-PROGRAMMED DESORPTION WITH
READSORPTION AND HETEROGENEITY

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A model has been developed in which the thermogram is
the net balance of the overall desorption-adsorption
process. The equations necessary for its application are
proposed and the model is tested using a simulation
program.

INTRODUCTION

Currently, temperature-programmed desorption (TPD) is a
technique used in the characterization of supported catalysts
since apart from its simplicity, it affords considerable infor-
mation about the adsorption and catalysis processes. The shape
of the thermogram, the position of its maximum, its displace-
ment as a function of the initial coverage or the heating rate
are sufficient to obtain knowledge of the catalyst and of the
adsorbate. However, the spectrum is often affected by diffu-
sional resistance, readsorption phenomena, surface heterogeneity,
etc., which hinder correct interpretation of the results. The
literature describes many methods that can be applied to the
determination of the kinetic parameters of TPD. Despite this,
most of them attempt to avoid or minimize undesirable effects
through the experimental conditions employed. In this sense,

Cvetanovic and Amenomiya [1] have proposed high flow rates of the carrier gas to avoid readsorption phenomena. Brenner and Hucul [2] state that errors due to diffusion can be minimized by using low heating rates. The applications of this techniques to studies of supported catalysts have been reviewed in depth by Falconer and Schwarz [3].

Among the most commonly employed methods is that of Redhead [4] and the method involving variation of the position of the maximum as a function of the heating rate [1, 4-6], although in both cases, readsorption is either not considered or is assumed to be negligible. Readsorption has only recently been included in the analysis of TPD data, and even then under the assumption of free readsorption (equilibrium-state) [7-11]. Despite this, as mentioned by Ungarish and Schmidt [12], the degree of approximation to equilibrium-state varies throughout the heating step, such that a situation of non-free readsorption would be expected in most experiments.

Another complication that may appear in the analysis of thermodesorption curves is the heterogeneity of the catalyst surface, either due to variation in the nature of adsorption sites or to interactions among the molecules of adsorbate.

In the present work we propose and check by simulation a model that permits rigorous treatment of the TPD experimental data in which readsorption is considered in general, without the need to contemplate free adsorption. It also considers the possibility of surface heterogeneity.

MODEL

From the kinetic point of view, the thermogram is composed of the net balance of the desorption process minus that of readsorption. That is, as shown in Fig. 1, the TPD curve is a composition of the pure desorption rate curve minus the pure adsorption curve ($v=v_\alpha-v_a$).

According to the Langmuir postulates, one has:

$$v_a = (1-\theta)\, c\, A_a\, e^{-\frac{E_a}{RT}} \qquad (1)$$

$$v_d = \theta\, A_d\, e^{-\frac{E_d}{RT}} \qquad (2)$$

where c is the concentration of desorbed species in the carrier gas and $\theta = N/N_o$ where N represents the moles adsorbed per unit of surface and N_o the total moles corresponding to the monolayer.

If one considers three TPD curves obtained under the same experimental conditions with the exception of the initial coverage (Fig. 2), eqs 1 and 2 for a constant value of θ allow one to relate the pure rates of the different thermograms among each other:

$$v_{a_1} = \frac{c_1}{c_2}\, v_{a_2}\, e^{-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \qquad (3)$$

$$v_{d_1} = v_{d_2}\, e^{-\frac{E_d}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \qquad (4)$$

The net rate will be:

$$v_1 = v_{d_2}\, e^{-\frac{E_d}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} - \frac{c_1}{c_2}\, v_{a_2}\, e^{-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \qquad (5)$$

A total of six equations similar to this can be written.

From eq. 6 substituting $v_{d2} = v_2 + v_{a2}$, and according to a simple mass balance $(v = c\, F/N_o)$, where F is the flow rate, one obtains:

$$v_{a_2} \frac{N_o}{F} = \frac{c_1 - c_2\, e^{-\frac{E_d}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}}{e^{-\frac{E_d}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} - \frac{c_1}{c_2}\, e^{-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}} = \frac{c_3 - c_2\, e^{-\frac{E_d}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right)}}{e^{-\frac{E_d}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right)} - \frac{c_3}{c_2}\, e^{-\frac{E_a}{R}\left(\frac{1}{T_3} - \frac{1}{T_2}\right)}} \qquad (6)$$
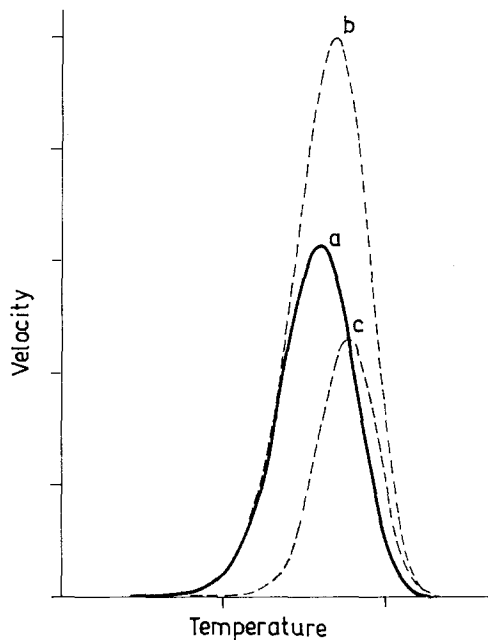
Fig. 1. a) Desorption thermogram; b) pure desorption
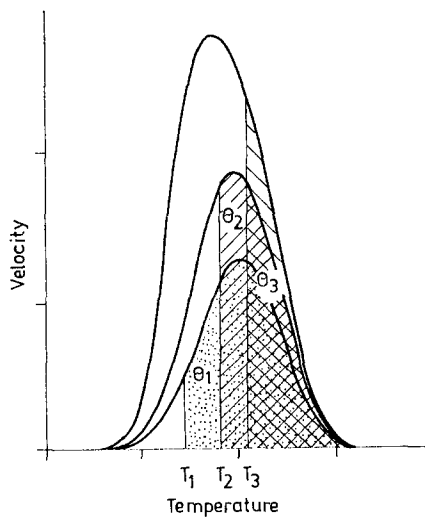rate curve; c) pure adsorption rate curve

Fig. 2. Desorption thermograms at different initial cov-
erages. $\Theta_{01} < \Theta_{02} < \Theta_{03}$; $\Theta_1 = \Theta_2 = \Theta_3$

$N_0 = 1\,10^{-1}\,\text{mol}$ $E_a = 4.0\,\text{kcal mol}^{-1}$

$F = 3.5\,\text{cm}^3\,\text{min}^{-1}$ $A_a = 2.5\,10^{-5}\,\text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1}$

$\beta = 5.0\,°\text{C min}^{-1}$ $E_d = 10.0\,\text{kcal mol}^{-1}$

$A_d = 6.0\,10^{-5}\,\text{min}^{-1}$
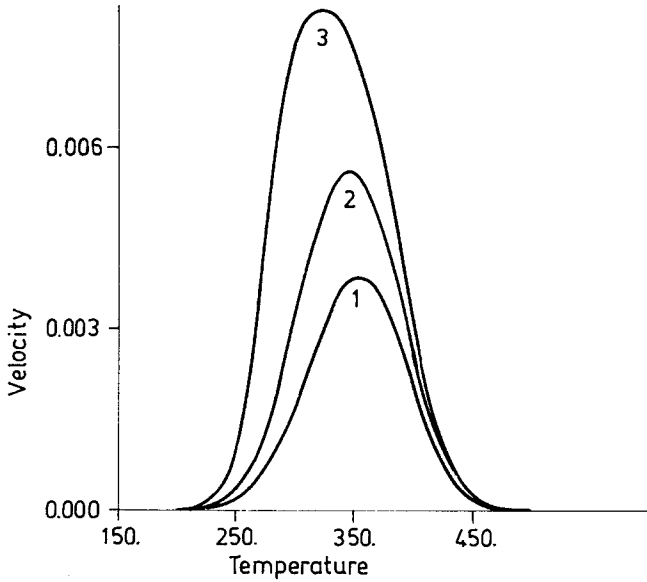

Fig. 3. Simulation of three TPD thermograms at different
initial coverages.

$\theta_{01} = 0.40$; $\theta_{02} = 0.60$; $\theta_{03} = 0.99$

Using the same procedure, from eq. 5, now substituting $v_{a2} = v_{d2} - v_2$, one obtains a three further equalities as a function of desorption rates.

It should be noted that eq. 6 relate concentrations and temperatures, which are experimental data, with the activation parameters of adsorption and desorption. These parameters can be determined as follows:

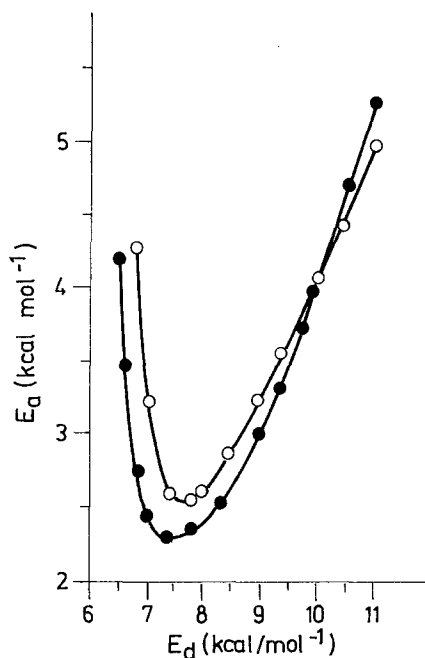1. One selects a first coverage that is common to all three

Fig. 4. E_d and E_a plot for two constant coverages.
● $\Theta_1=0.15$;   o $\Theta_2=0.35$

thermograms (Fig. 2) and calculates the corresponding values of c_1, c_2, c_3 and T_1, T_2 and T_3 (experimental data).

2. Using a trial and error procedure (Newton-Raphson) a scan is made of one of the parameters to be determined, for example E_d, obtaining the corresponding value of E_a that fulfils eq. 6.

3. The set of values of E_a and E_d thus obtained are plotted against each other. The plot gives a curve Fig. 4.

4. By selecting a second coverage common to the three thermograms and following the same steps as above, one obtains another curve to plot E_d against E_a, that will have a point in common with the previous one. This point will be the pair of values E_a, E_d solution. In the case of the curves not showing any point in common, this would indicate that the activation ener-

gies depend on coverage. It would then be necessary to obtain
a fourth thermogram. These would be grouped in threes (four com-
binations) and any two of the possible four combinations would
be selected. One would then choose a common coverage for both,
plotting E_a against E_d according to the above process. The cut-
off point will give the values of the energies for this cover-
age. The way to obtain the dependence of the activation ener-
gies with coverage is to repeat the same procedure for other
coverages.

RESULTS

The method was tested for three simulated desorption ther-
mograms obtained with different initial coverages $\Theta_{01}=0.40$;
$\Theta_{02}=0.60$; $\Theta_{03}=0.99$ (Fig. 3). The plot of E_a against E_d is shown
in Fig. 4 for the following coverages: $\Theta_1=0.35$ and $\Theta_2=0.15$. The
cut-off point between the two curves affords values of 4.0 and
10.0 kcal mol^{-1} for the activation energies of adsorption and
desorption, respectively. These values are in complete agree-
ment with those used to simulate the thermograms.

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