Journal of Thermal Analysis, Vol. 40 (1993) 1347-1356

TEMPERATURE-PROGRAMMED SURFACE REACTIONS (TPSR) ON HETEROGENEOUS SURFACES

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On the basis of calculations using a simple model of the energetic heterogeneity of a solid surface (assuming linear dependence of activation energy of desorption of the reactant on the degree of coverage), it is shown that both the degree of conversion and the course of desorption of the reactants are strongly influenced by the degree of heterogeneity assuming non-isothermal conditions. In contrast to a homogeneous solid surface, the degree of conversion for a heterogeneous surface depends strongly on the initial coverage of a catalyst by reactant. Possibilities for kinetic evaluation are indicated from the modelling calculations.

Keywords: heterogeneous surfaces, temperature-programmed surfaces reactions

Introduction

Temperature-programmed desorption (TPD) is a method frequently used for characterization of adsorption and surface-chemical properties of porous solids [1, 2]. Caused by different states of binding of an adsorptive (intrinsic heterogeneity) or by a differently strongly developed adsorbate–adsorbate interaction (induced heterogeneity), complex desorption curves can result for relatively simple desorption processes. When carrying out kinetic evaluations this factor is usually taken into consideration by a dependence of the pre-exponential factor A and of the activation energy of desorption (E) on the degree of coverage [3–6]:

$$r_d = -d\Theta / dt = \Theta^n A\,(\Theta) \exp\,[-E\,(\Theta) / RT] \tag{1}$$

Recently methods have also been used which are based on a distribution function of desorption energy [6, 7, 8]:

$$r_d = A \int_{E_{min}}^{E_{max}} [\Theta(E,T)]^n \exp\,[-E(\Theta) / RT]\, f(E) dE \tag{2}$$

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$\Theta(E,T)$ = fractional adsorbate coverage at E and T, n = order of desorption, $f(E)$ = distribution function of desorption activation energy

For calculation of the distribution function of desorption energy, $f(E)$, the order of desorption and the pre-exponential factors should be known, or should be determined by other methods. If, however, the desorption of a gas from a porous solid is connected with a surface reaction (TPSR: temperature-programmed surface reaction), it is usually assumed for a kinetic evaluation that the surface reaction occurs on a catalyst with a homogeneous surface [9–11].

Therefore, it is the intention of this paper to derive statements about the influence of surface heterogeneity of a catalyst on the degree of conversion and on the course of desorption of the components of the reaction, and from this to explore the possibilities for kinetic evaluation.

Model formulation

The following irreversible first-order surface reactions serve as model reactions:

$$A_{\mathrm{ads}} \xrightarrow{k_{\mathrm{dA}}} A_{\mathrm{gas}}$$

$$A_{\mathrm{ads}} \xrightarrow{k_{\mathrm{r}}} B_{\mathrm{ads}}$$

$$B_{\mathrm{ads}} \xrightarrow{k_{\mathrm{dB}}} B_{\mathrm{gas}}$$

Adsorption or desorption of A and B are also considered first-order steps (e.g. molecular adsorption and desorption). Moreover, it is assumed that no influence of diffusion exists and no re-adsorption plays a role. Adsorption of A and B are considered independent of each other. Taking into account these assumptions for alteration of degree of coverage with time, the following equations are valid:

$$-\mathrm{d}\Theta_{\mathrm{A}} / \mathrm{d}t = (k_{\mathrm{dA}} + k_{\mathrm{r}})\,\Theta_{\mathrm{A}} \tag{3}$$

$$-\mathrm{d}\Theta_{\mathrm{B}} / \mathrm{d}t = -k_{\mathrm{r}}\Theta_{\mathrm{A}} + k_{\mathrm{dB}}\Theta_{\mathrm{B}} \tag{4}$$

In the case of the temperature-dependence of k_{r} and k_{dB} the validity of the Arrhenius equation is assumed.

$$k_{\mathrm{r}}(T) = A_{\mathrm{r}} \exp(-E_{\mathrm{r}} / RT) \tag{5}$$

$$k_{\mathrm{dB}}(T) = A_{\mathrm{dB}} \exp(-E_{\mathrm{dB}} / RT) \tag{6}$$

The dependence of the activation energy of desorption of the reactant A on the degree of coverage serves as a model for energetic heterogeneity of the solid. In this case both a linear and a logarithmic dependence are considered:

$$E_{dA} = E_o - \beta\Theta_A \tag{7}$$

$$E_{dA} = E_1 - \gamma\ln\Theta_A \tag{8}$$

E_o: activation energy at $\Theta_A = 0$, E_1: activation energy at $\Theta_A = 1$, β and γ: constants.

The model assumptions discussed here correspond to a catalytic reaction where a reactant is adsorbed at centres of different strength, but where only some of these are catalytically active. For these, the surface reaction should occur with constant activation energy. The main aim of the calculations is the determination of the influence of heterogeneity; therefore in most of the cases it has been assumed that the reaction product would be only weakly adsorbed ($k_{dB} >> k_r$).

For desorption of B the following approximation should be valid

$$r_{dB} = k_r\Theta_A \tag{9}$$

A value of 1×10^{13} s^{-1} was used for the pre-exponential factor for all three partial steps. Calculations were carried out for a linear temperature programme ($T = 300 + \alpha t$; $\alpha = 1 \ldots 25$ deg·min^{-1}). Numerical solution of the system of differential equations for calculation of the desorption curves of A and B was based on the Euler-Chauchy procedure or a fourth order Runge-Kutta procedure.

Results and discussion

In Fig. 1 desorption curves of A and B are shown for both different dependences of activation energy of desorption of A on the degree of coverage together with the desorption curves of A where no reaction of A to B occurs. It is clearly

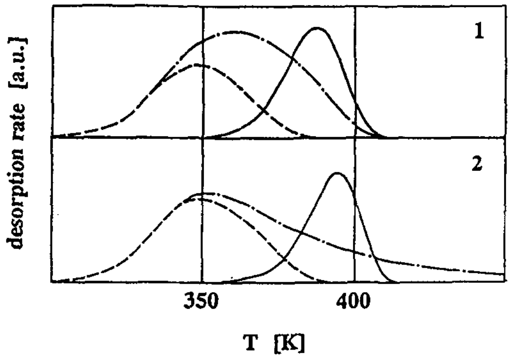

Fig. 1 Desorption curves of A (– – – – with reaction, – · – · – without reaction) and B (——) for different dependences of desorption activation energy of A on the degree of coverage ($T = 300 + 10t$): 1: $E_{dA} = 110 - 10\Theta_A$ [kJ/mol], $E_r = 105$ kJ/mol, $E_{dB} = 110$ kJ/mol, conversion=49.2%; 2: $E_{dA} = 110 - 10\ln\Theta_A$ [kJ/mol], $E_r = 110$ kJ/mol, $E_{dB} = 110$ kJ/mol, conversion=40.7%

that in both cases of running surface reaction the shape of the desorption curve strongly changes compared to the desorption curve without reaction. For middle conversion degrees, desorption curves of approximately equal shape result for different dependences of E_{dA} on degree of coverage.

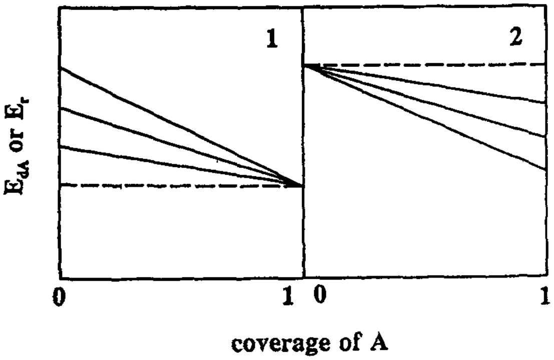

Fig. 2 Dependence of desorption activation energy of A on degree of coverage (— $E_{dA} = E_0 - \beta\Theta_A$, ---- E_r)

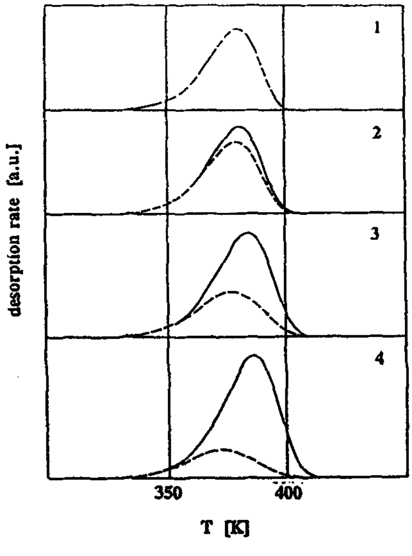

Fig. 3 Desorption curves of A (– – – –) and B(——) for case 1 of Fig. 2 (E_r = 110 kJ/mol, $T = 300 + 10t$): 1: E_{dA} = 110 kJ/mol, conversion = 50.0%; 2: $E_{dA} = 111 - \Theta_A$ [kJ/mol], conversion = 53.9%; 3: $E_{dA} = 115 - 5\Theta_A$ [kJ/mol], conversion = 67.8%; 4: $E_{dA} = 120 - 10\Theta_A$ [kJ/mol], conversion = 79.3%

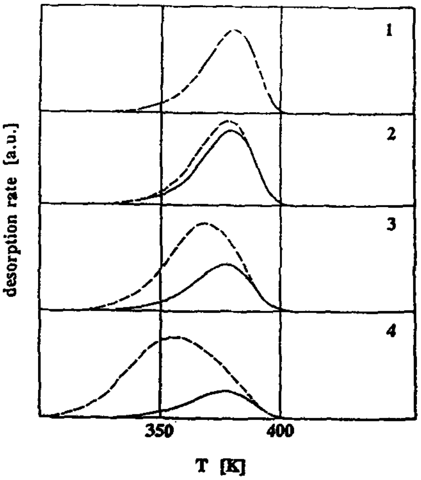

Fig. 4 Desorption curves of A (– – – –) and B (—) for case 2 of Fig. 2 (E_r = 110 kJ/mol, T = 300 + 10t): 1: E_{dA} = 110 kJ/mol, conversion = 50.0%; 2: E_{dA} = 110 – Θ_A [kJ/mol], conversion = 45.9%; 3: E_{dA} = 110 – 5Θ_A [kJ/mol], conversion = 31.2%; 4: E_{dA} = 110 – 10Θ_A [kJ/mol], conversion = 19.5%

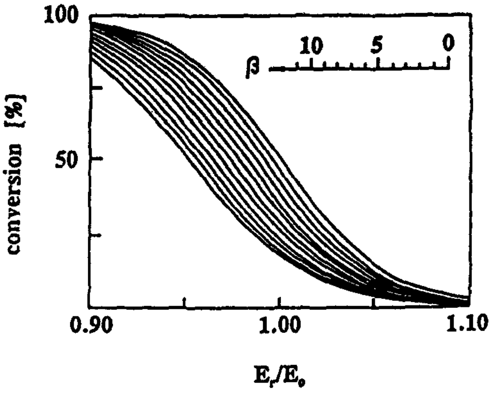

Fig. 5 Dependence of degree of conversion on β and E_r/E_0 (E_r = 110 kJ/mol, T = 300 + 10t)

In order to estimate the influence of the degree of heterogeneity of the catalyst surface, several models were used for linear dependence of coverage (β in Eq. 7). These are distinguished by the fact that the activation energy of surface reaction at different strong alteration of activation energy of desorption of A corresponds to the value of E_{dA} at complete coverage ($\Theta_A = 1$) or at $\Theta_A = 0$ (Fig. 2). The appropriate desorption curves are shown in Figs 3 and 4. It can be clearly seen that the strength of heterogeneity not only strongly influences the degree of conversion but also substantially changes the course of desorption. When the activation energy of the reaction corresponds to the value of the activation energy of desorption at $\Theta = 1_A$, the degres of conversion rises with increasing β and the desorption curve of A shifts to lower temperatures. When, however, $E_r = E_o$, the conversion degree decreases with increasing β and the desorption curve of A also shifts to lower temperatures. In Fig. 5, in addition to this dependence of the degree of conversion, the influence is also shown of the ratio of E_r/E_o. From this it is clear that the degree of conversion changes markedly in dependence on β at different values of E_r/E_o. The influence is larger if $E_r / E_o < 1$.

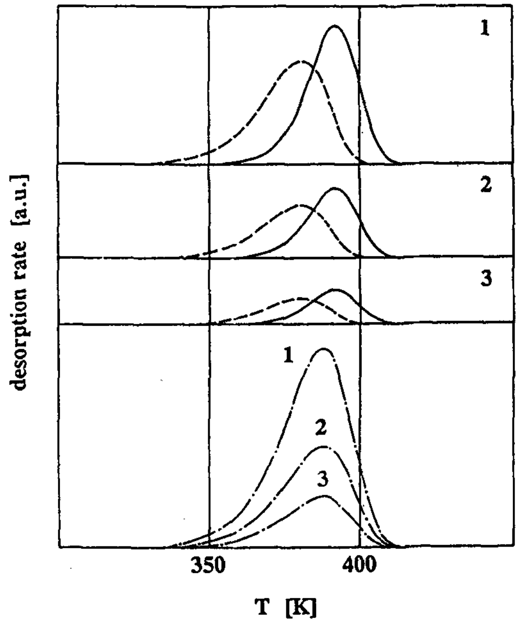

Fig. 6 Desorption curves of A (– – – – with reaction, – · – without reaction) and B (——) for different initial degrees of coverage of A ($E_{dA} = E_r = E_{dB} = 110$ kJ/mol, $T = 300 + 10t$): 1: $\Theta_A^o = 1.00$, conversion = 50.0%; 2: $\Theta_A^o = 0.50$, conversion = 50.0%; 3: $\Theta_A^o = 0.25$, conversion = 50.0%

In contrast to a catalytic reaction at a homogeneous surface [9], the degree of conversion depends, in the case of a heterogeneous surface, on the initial coverage of the catalyst by reactant (Figs 6 and 7). This influence is differently strongly developed in dependence on the ratio E_r/E_o as shown for several model cases in Fig. 8. Thus the experimental determination of this dependence provides a suitable means of obtaining initial indications of the existence of a heterogeneous surface. However, in the range of heating rates suitable for porous solids (about 1–25 deg·min^{-1}) the degree of conversion changed only marginally, as shown in Fig. 9.

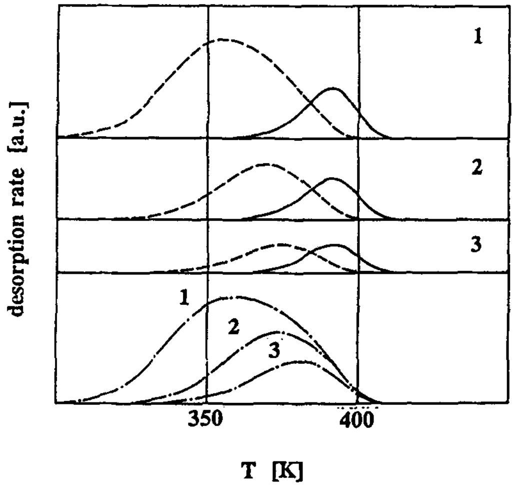

Fig. 7 Desorption curves of A (– – – – with reaction – · – without reaction) and B (—) for different initial degrees of coverage of A ($E_r = E_{dB}$ = 110 kJ/mol, $E_{dA} = 110 - 10\Theta_A$ [kJ/mol], $T = 300 + 10t$): 1: $\Theta_A^0 = 1.00$ conversion = 19.5%; 2: $\Theta_A^0 = 0.50$, conversion = 31.2%; 3: $\Theta_A^0 = 0.25$, conversion = 39.9%

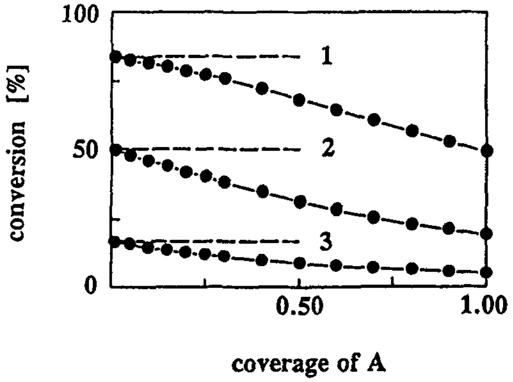

Fig. 8 Dependence of degree of conversion on initial degree of coverage of A ($E_{dA} = 110 - 10\Theta_A$ [kJ/mol], $T = 300 + 10t$): 1: E_r = 105 kJ/mol; 2: E_r = 110 kJ/mol; 3: E_r = 115 kJ/mol

The activation energy of desorption can be determined relatively well at the degree of coverage of the desorption-curve maximum using the method of variation of heating rate for desorption from an energetically heterogeneous surface without a running surface reaction, if the activation energy of desorption depends to only a small extent on the degree of coverage [12, 13]. From this the dependence of the activation energy of the degree on coverage is calculable, e.g. using a normalized desorption curve [6, 14]. Moreover, it can be shown for a surface reaction at a homogeneous surface that the corresponding activation energy can be estimated from the change of the curve-maximum temperature in dependence on the heating rate, depending on the ratio of the activation energies of desorption of reactant and of the surface reaction [11]. Thus, the use of the method discussed seems to be qualified also for the more complex case discussed here when studies with different initial coverage are considered.

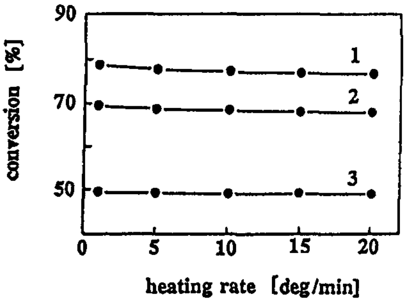

Fig. 9 Dependence of degree of conversion on heating rate for different initial degrees of coverage of A ($E_{dA} = 110 - 10\Theta_A$ [kJ/mol], $E_r = 105$ kJ/mol, $T = 300 + 10t$): 1: $\Theta_A^0 = 0.25$; 2: $\Theta_A^0 = 0.50$; 3: $\Theta_A^0 = 1.00$

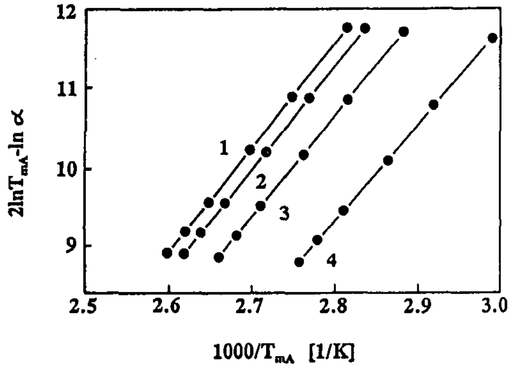

Fig. 10 Plots of $2\ln T_{mA} - \ln\alpha$ vs. $1/T_{mA}$ for different initial degrees of coverage of A ($E_{dA} = 110 - 10\Theta_A$ [kJ/mol], $E_r = 110$ kJ/mol): 1: $\Theta_A^0 = 0.125$; 2: $\Theta_A^0 = 0.25$; 3: $\Theta_A^0 = 0.50$; 4: $\Theta_A^0 = 1.00$

In Fig. 10 the corresponding plot ($2\ln T_{mA} - \ln\alpha$) vs. $f(1/T_{mA})$ is shown for a selected model case using average degrees of conversion and varying initial

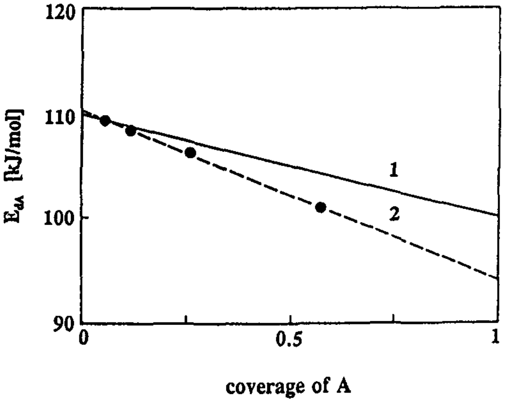

Fig. 11 Dependence of desorption activation energy of A on degree of coverage: 1: theoretical: $E_{dA} = 110 - 10\Theta_A$ [kJ/mol]; 2: calculated: $E_{dA} = 110 - 16\Theta_A$ [kJ/mol]

coverages of A. In each case a good linear correlation results. If the corresponding degree of coverage at the maximum of the desorption curve of A can be determined also, an estimate of the dependence of E_{dA} on coverage is possible. The calculated dependence for the model case is shown in Fig. 11. Agreement with the assumed linear dependence of E_{dA} on the degree of coverage is relatively good. Only at higher degrees of coverage are large differences seen. The activation energy of the surface reaction resulting from the dependence of the maximum temperature of the desorption curve of B on the heating rate is to be expected, corresponding to the theoretical value (110 kJ/mole) for all initial coverages. Also, in more unfavourable cases (e.g. at larger conversion degrees) a worse accordance with the assumed dependence of E_{dA} on the coverage degree resulted so the use of this non-isothermal method should provide a suitable means to obtain not only information about activity and selectivity of a catalyst but also additional statements about its adsorption properties or about the energetic heterogeneity of the surface of the catalyst. Very little information about these problems can be obtained from isothermal catalytic investigations. Moreover, the advantage of non-isothermal studies is increased by the fact that, although significant diffusional influences on the desorption from a porous solid can exist, a kinetic evaluation should provide information about adsorption properties [15]. More extensive modelling calculations are, however, necessary to obtain detailed information about the course of a catalytic surface reaction and other possibilities of a kinetic evaluation.

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Zusammenfassung — Für eine irreversible Oberflächenreaktion 1. Ordnung wird anhand von Rechnungen mit einem einfachen Modell für die energetische Heterogenität einer Festkörperoberfläche (lineare Abhängigkeit der Aktivierungsenergie der Desorption des Ausgangsstoffes vom Bedeckungsgrad) gezeigt, daß der Grad der Heterogenität den Umsatz und den Desorptionsverlauf der Reaktanten unter nichtisothermen Bedingungen entscheidend beeinflußt. Im Gegensatz zu einer homogenen Festkörperoberfläche ist der Umsatz bei Annahme einer heterogenen Oberfläche relativ stark von der Anfangsbelegung des Katalysators mit dem Ausgangsstoff abhängig. Aus den Modellrechnungen werden Möglichkeiten für eine kinetische Auswertung abgeleitet.