STUDY OF COMPLEX DESORPTION PROCESSES ON POROUS CATALYSTS BY MEANS OF TEMPERATURE-PROGRAMMED DESORPTION (TPD) WITH NON-LINEAR TEMPERATURE PROGRAMMES

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Through simulation of TPD model curves for desorption from adsorption sites of different strength could be shown that the use of non-linear temperature programmes influences the complex desorption process in such a manner that the appearing desorption maxima are better visible.

Because in case of using non-linear temperature programmes the overlapping of different desorption processes is smaller it is possible to evaluate approximately the activation parameters for the single steps from the complex desorption curve.

The temperature-programmed desorption of NH_3 and H_2O from variously modified X and Y zeolites in most cases provides complex desorption spectra resulting from the presence of adsorption sites of different strengths [1, 2]. When a linear temperature schedule is used, single desorption maxima are often difficult to perceive.

In the case of NH_3 and H_2O desorption from HY zeolites, it could be shown that the use of a hyperbolic temperature programme led to a better distinction of different adsorption sites [3].

The aim of this work was therefore to test the suitability of non-linear temperature programmes of the common form

$$\frac{dT}{dt} = Q_n \cdot T^n \tag{1}$$

(Q_n = constant, $n = 1, 2, 3, \ldots$) for a simple model by simulation of the desorption curves with respect to the improvement of the resolution of variously occurring desorption processes from porous catalysts.

Kinetic modelling and simulation procedure

According to Cvetanović and Amenomiya [4], the amount of gas desorbed per unit time is proportional to the decrease in the degree of coverage if all the adsorption sites are of equal strength:

$$C = \frac{v_s \cdot v_m}{F} \left(-\frac{d\Theta}{dt}\right) \tag{2}$$

where v_s = volume of catalyst, v_m = volume of the adsorbed gas at a degree of coverage of one, C = gas concentration, F = flow rate of the carrier gas, and Θ = degree of coverage.

If it is assumed that desorption from two sites of different strengths occurs independently, it holds that:

$$C = \lambda_1 \left(-\frac{d\Theta_1}{dt}\right) + \lambda_2 \left(-\frac{d\Theta_2}{dt}\right) \tag{3}$$

where λ_i = proportionality factors. Furthermore, assuming a first-order process without readsorption, it follows that:

$$-\frac{d\Theta_i}{dt} = \Theta_i A_i \exp\left(-\frac{E_i}{RT}\right) \quad (i = 1, 2) \tag{4}$$

Simulation of the TPD model curves $C(t)$ was carried out by means of a step procedure [5] with Eqs (3) and (4) for the following non-linear programmes:

$$n = 2, \quad \frac{1}{T} = \frac{1}{300} - Q_2 t \tag{5}$$

$$n = 4, \quad \frac{1}{T^3} = \frac{1}{300^3} - 3Q_4 t \tag{6}$$

$$n = 5, \quad \frac{1}{T^4} = \frac{1}{300^4} - 4Q_5 t \tag{7}$$

the step width being chosen very small (0.002 and 0.01 min).

Results and discussion

Figure 1 shows desorption curves calculated for several temperature programmes according to Eqs (3) and (4) using

$E_1 = 80$ kJ/mole, $\quad A_1 = 6 \cdot 10^6$ min^{-1}, $\quad \lambda_1 = 1$,

$E_2 = 95$ kJ/mole, $\quad A_2 = 1.24 \cdot 10^7$ min^{-1}, $\quad \lambda_2 = 0.5$.

All desorption processes based on the above data occur at dT/dt value which are usual in the case of real TPD experiments. It can be seen clearly that the desorption
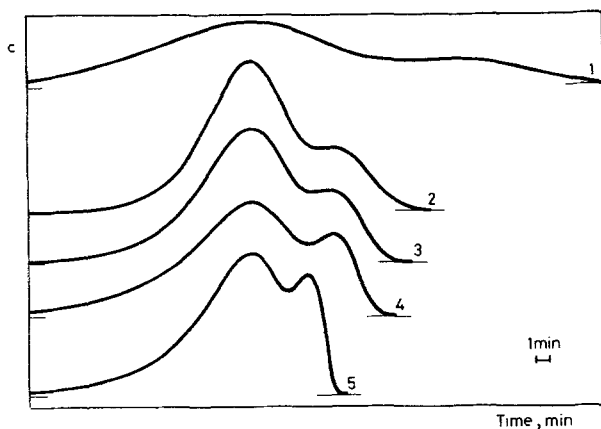
Fig. 1 Desorption curves for $E_1 = 80$ kJ/mole, $A_1 = 6 \cdot 10^6$ min^{-1}, $\lambda_1 = 1$, and $E_2 = 95$ kJ/mole, $A_2 = 1.24 \cdot 10^7$ min^{-1}, $\lambda_2 = 0.5$. 1: $T = 300 + 4t$, 2: $T = 300 + 10t$, 3: $1/T = 1/300 - 3 \cdot 10^{-5}t$, 4: $1/T^3 = 1/300^3 - 2.6 \cdot 10^{-10}t$, 5: $1/T^4 = 1/300^4 - 7.7 \cdot 10^{-13}t$

maximum at the higher temperature becomes better visible with increasing non-linearity of the temperature programme. However, even at low non-linearity (hyperbolic programme), which allows an approximation-free integral kinetic evaluation [6, 7], this desorption maximum is also better perceptible than in the case of linear heating.

When the same temperature function is used but at different heating rates, Q_n, the shape of the desorption curve hardly changes, bringing about an equally percep-
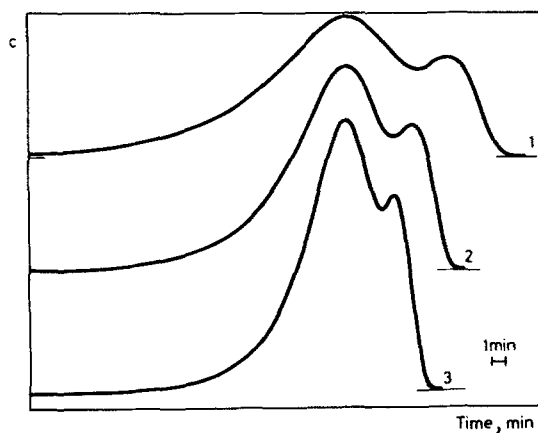

Fig. 2 Desorption curves for $E_1 = 80$ kJ/mole, $A_1 = 6 \cdot 10^6$ min^{-1}, $\lambda_1 = 1$, and $E_2 = 95$ kJ/mole, $A_2 = 1.24 \cdot 10^7$ min^{-1}, $\lambda_2 = 0.5$ with $1/T^3 = 1/300^3 - 3Q_4t$. 1: $Q_4 = 0.87 \cdot 10^{-10}$, 2: $Q_4 = 1.2 \cdot 10^{-10}$, 3: $Q_4 = 1.53 \cdot 10^{-10}$

tibility in all cases. Figure 2 shows this fact for the case with

$$E_1 = 80 \text{ kJ/mole}, \qquad A_1 = 6 \cdot 10^6 \text{ min}^{-1}, \qquad \lambda_1 = 1,$$

$$E_2 = 95 \text{ kJ/mole}, \qquad A_2 = 1.24 \cdot 10^7 \text{ min}^{-1}, \qquad \lambda_2 = 0.5,$$

using a temperature programme $1/T^3 = 1/300^3 - 3Q_4 t$.

For a hyperbolic temperature programme, Anderson, Witte and Haberland [8] showed that the shape index of the desorption curve should be independent not only of E and A, but also of the parameter Q_n.

The maximum for the desorption at the higher temperature is relatively well perceptible even when the desorption at the higher temperature occurs with lower activation energy and there is therefore a stronger overlapping of the two processes, as shown in Fig. 3 for the example with

$$E_1 = 80 \text{ kJ/mole}, \qquad A_1 = 6 \cdot 10^6 \text{ min}^{-1}, \qquad \lambda_1 = 1,$$

$$E_2 = 70 \text{ kJ/mole}, \qquad A_2 = 1.134 \cdot 10^5 \text{ min}^{-1}, \qquad \lambda_2 = 1.$$
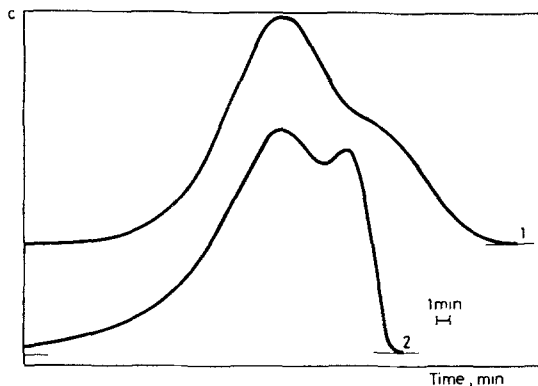
Fig. 3 Desorption curves for $E_1 = 80 \text{ kJ/mole}$, $A_1 = 6 \cdot 10^6 \text{ min}^{-1}$, $\lambda_1 = 1$, and $E_2 = 70 \text{ kJ/mole}$, $A_2 = 1.134 \cdot 10^5 \text{ min}^{-1}$, $\lambda_2 = 1$. 1: $T = 300 + 10t$, 2: $1/T^4 = 1/300^4 - 7.7 \cdot 10^{-13} t$

The reason for the different courses of desorption for the two examples of a complex desorption process using non-linear temperature programmes should be the change of the asymmetry of the desorption curves for the single steps of the process.

Várhegyi [9] and Anderson, Witte and Haberland [8] demonstrated the desorption vs. time curve exhibits a different shape for a hyperbolic than for a linear temperature programme. Calculation of the shape index from modelling curves [8] resulted in lower values for the hyperbolic programme than for the linear one, which means that the falling side of the desorption curve is steeper in the non-linear case.

A simple measure of the asymmetry of a desorption curve is the ratio of the widths of the decreasing and increasing sides at one-tenth of the maximum height of the

Table 1 Factor $S_{0.1}$ for the desorption with $E_1 = 80$ kJ/mole and $A_1 = 6 \cdot 10^6$ min^{-1} for different temperature programmes

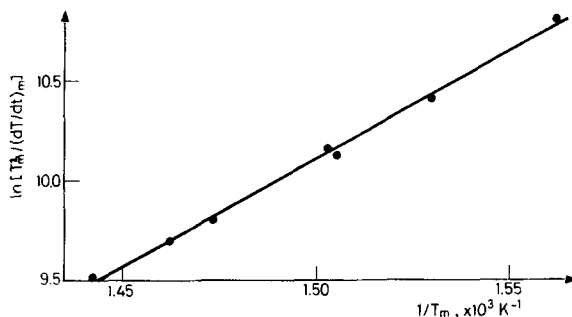| Temperature programme	$S_{0.1}$
$T = 300 + 4t$	0.638
$T = 300 + 10t$	0.602
$1/T = 1/300 - 3 \cdot 10^{-5}t$	0.459
$1/T^3 = 1/300^3 - 2.6 \cdot 10^{-10}t$	0.374
$1/T^4 = 1/300^4 - 7.7 \cdot 10^{-13}t$	0.322

desorption curve. In Table 1 these values are listed for the temperature programmes of Fig. 1, using $E_1 = 80$ kJ/mole and $A_1 = 6 \cdot 10^6$ min^{-1}. The decrease in this ratio with increasing non-linearity of the temperature function clearly shows the change in the asymmetry of the desorption curve: the increasing side becomes progressively less steep and the decreasing side more steep. This means the weaker overlapping of the two desorption processes, and therefore the better visibility of the high-temperature maximum.

The activation energy of the high-temperature process can be calculated relatively simply because of the smaller overlapping of the two desorption processes in the case of non-linear temperature schedules, by considering the position of the desorption maximum as a function of the temperature programme and of the heating rate at the maximum in the desorption curve.

Similarly as given by Cvetanović and Amenomiya [4], for the maximum temperature we have

$$\ln T_m^2 - \ln \left(\frac{dT}{dt}\right)_m = \ln \left(\frac{E}{AR}\right) + \frac{E}{RT_m} \tag{8}$$

Figure 4 shows this linear relation for the desorption process with $E = 95$ kJ/mole. The maximum temperature has been calculated from the complex desorption curve.

Fig. 4 Linear relation according to Eq. (8) for $E_2 = 95$ kJ/mole and $A_2 = 1.24 \cdot 10^7$ min^{-1}

The activation energy value calculated by linear regression, 89.6±2.6 kJ/mole (corr. coeff. = 0.9979), can be considered relatively good. When a linear temperature programme is used, this possibility of calculation of E does not exist because of the stronger overlapping of the two processes.

To summarize, it can be stated that the use of non-linear temperature programmes influences the complex desorption process: the desorption maxima which can be assigned to the desorption from different sites are better visible.

Moreover, TPD studies should be carried out by means of non-linear temperature programmes, because of the additional possibility of the approximate evaluation of the activation energy. The experimental realization of several non-linear programmes is easy by using a microprocessor and a suitable heating system.

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Zusammenfassung — Durch Simulationsrechnungen für ein einfaches Modell der Desorption von Adsorptionsplätzen verschiedener Stärke kann gezeigt werden, daß bei Verwendung nichtlinearer Temperaturprogramme auftretende Desorptionsmaxima der komplexen Desorptionskurve besser erkennbar sind. Da bei nichtlinearer Temperaturführung die Überlagerung mehrerer Prozesse geringer ist, können die Aktivierungsparameter der einzelnen Prozesse näherungsweise aus der komplexen Desorptionskurve ermittelt werden.

Резюме — Посредством моделирования ТПД модельных кривых десорбции для адсорбционных участков различной силы, было показано, что использование нелинейных температурных программ затрагивает сложный адсорбционный процесс таким образом, что появляющиеся десорбционные максимумы становятся более видимыми. Использование нелинейных температурных программ приводит к меньшему перекрыванию различных десорбционных процессов, вследствии чего представляется возможным, исходя из комплексной кривой десорбции, приблизительно оценить активационные параметры отдельных стадий реакции.