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PARAMETRIC SENSITIVITY OF COMPLEX TEMPERATURE-PROGRAMMED DESORPTION, REACTION AND REDUCTION

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Through simulation of the temperature-programmed desorption, reaction and reduction in a system of parallel reactions. it is shown that the experimental conditions influence the simultaneous or consecutive occurrence of the individual reactions of the system. Adjustment of the concentration of a gaseous reaction component or optimization of the temperature program results in a shift to the desired consecutive occurrence of the reactions. Therefore, a better resolution of the individual reactions can be achieved through a judicious choice of the experimental conditions of the temperature-programmed methods.

Temperature-programmed desorption (TPD), reaction (TPR) and reduction (TPRD) can be used to estimate the kinetic parameters of the desorption of gases from solid surfaces, of surface catalytic reactions and of reactions of gases with solids [1, 2]. These methods consist in monitoring the concentration of a gaseous reaction component at the outlet of a reactor packed with a solid catalyst/adsorbent, whose temperature is gradually raised. In the evaluation of the experimental concentration profiles, each point is regarded as an independent measurement of the concentration of the gaseous component at the given temperature and at corresponding concentrations of the other reaction components. These data are fitted by the TPD, TPR or TPRD models formed by the kinetic equations for the individual reactions of the system, the balance of the components in the reactor and the time-dependence of temperature. The kinetic parameters of the individual reactions are sought.

In the case of simple TPD, TPR and TPRD, only one reaction takes place. Therefore, only one kinetic equation and one set of parameters are evaluated. In complex TPD, TPR and TPRD, several reactions take place simultaneously and a set of kinetic equations for individual reactions and their parameters are sought.

In complex TPD, the concentration of a gaseous component A, desorbing, for

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example, from different types of adsorption centers $X_1, X_2, \ldots, X_m$ is evaluated:

$$\begin{aligned} AX_1 &= A(g)+X_1 \\ AX_2 &= A(g)+X_2 \\ &\vdots \\ AX_m &= A(g)+X_m \end{aligned} \tag{1}$$

An example of this system is the desorption of hydrogen from a nickel surface [3].

In complex TPR, a decrease in the concentration of gaseous reaction component C between the reactor inlet and outlet is followed, or the concentration of product A formed by concurrent reactions of C with surface components $B_1X, B_2X, \ldots, B_mX$ is monitored:

$$\begin{aligned} B_1X+C(g) &= A(g)+X \\ B_2X+C(g) &= A(g)+X \\ &\vdots \\ B_mX+C(g) &= A(g)+X \end{aligned} \tag{2}$$

In complex TPRD, the concentration of reacting component C or product A in the reaction of C with different solid components $B_1, B_2, \ldots, B_m$ is recorded:

$$\begin{aligned} B_1+C(g) &= A(g)+D_1 \\ B_2+C(g) &= A(g)+D_2 \\ &\vdots \\ B_m+C(g) &= A(g)+D_m \end{aligned} \tag{3}$$

System 2 (complex TPR) corresponds to reactions of hydrogen with different types of surface carbon deposited on a Ni catalyst [4]. As to reactions 3 (complex TPRD), the reduction of Co and Mo sulphides in $CoMo/Al_2O_3$ catalyst by hydrogen was studied [5].

From the above examples, the common feature of complex TPD, TPR and TPRD is obvious; the concentration of only one reaction component (either A or C) is always measured, even though a system of m reactions takes place. If only one reaction takes place in a certain range of conditions (Fig. 1, peak 1), the determination of its kinetic equation and parameters does not make difficulties in principle [5, 6]. However, it is more usual that individual reactions take place simultaneously and their peaks coincide (Fig. 1, peaks 2 and 3). The overall kinetic model can then hardly be evaluated [7, 8]. This situation might be avoided by reducing the extent of simultaneous occurrence of the individual reactions.

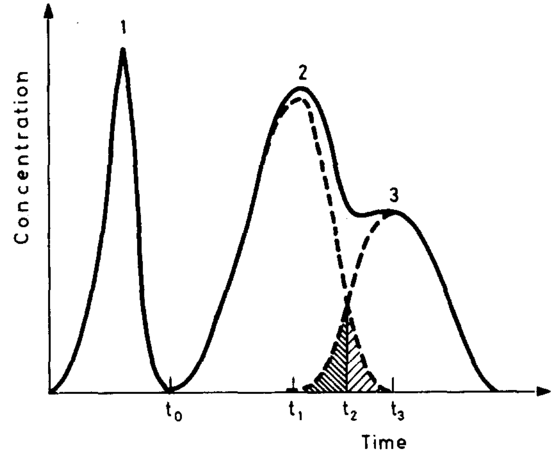

Fig. 1 Complex TPD, TPR and TPRD profiles in a system of three reactions

This work is aimed at determining whether the design of the experimental conditions of TPD, TPR and TPRD can help towards better resolution of the individual reactions. Analysis of this kind of parametric sensitivity includes investigation of the influence of space velocity, surface and gaseous reactant concentrations, temperature program, and of the reaction kinetics. The influence of the simultaneous occurrence of individual reactions on the estimation of the kinetic parameters in TPD, TPR and TPRD will be analyzed in the next paper [8].

Theory

The simulations were carried out for the TPR, TPR and TPRD taking place in a non-isothermal, continuously stirred tank reactor (CSTR), with uniform composition in both gas and solid phases, without the influence of transport effects inside or outside the particles of the solid adsorbent or reactant.

Complex TPR and TPRD were described by the same model. During TPR and TPRD, an increase in reaction temperature results in the consumption of reaction component C and the release of component A by reactions 2 and 3. The rates of these reactions can be described by simple first-order kinetics with respect to the surface concentration, q_1, of the i-th surface component (B_iX or B_i) and to the concentration c_c of reacting gaseous component C:

$$R_i = A_i \cdot \exp(-E_i/R_gT) \cdot q_i \cdot c_c \cdot i = 1, 2, \ldots, m \tag{4}$$

The amount of component A released in unit time from the sample of mass W in the i-th reaction is

$$W \cdot \mathrm{d}q_i/\mathrm{d}t = R_i \tag{5}$$

and the total amount of A released in m reactions is obviously

$$R = \sum_{i=1}^{m} R_i \tag{6}$$

Reaction mixture enters the reactor with volumetric flow rate F_0, temperature T_0 and pressure P. The total molar flow remains constant through the reactor (see Eqs 2 and 3). The reactor temperature changes with time according to

$$\mathrm{d}T/\mathrm{d}t = a \cdot T^b \tag{7}$$

and therefore the volumetric flow rate at the reactor outlet, F, is

$$F = F_0 \cdot T/T_0 \tag{8}$$

The mass balance of component A in the i-th reaction can be written as

$$\mathrm{d}c_{Ai}/\mathrm{d}t = W/V \cdot R_i - F/V \cdot c_{Ai} \tag{9}$$

During TPD, component A is desorbed as a result of the rising adsorbent temperature by the reactions in Scheme 1. The rate of desorption can be described by simple first- or second-order kinetics with respect to the surface concentration, q_i, of the i-th surface component, AX_i:

$$\vec{R}_i = \vec{A}_i \cdot \exp(-\vec{E}_i/R_gT) \cdot q_i^n \cdot i = 1, 2, \ldots, m; \qquad n = 1, 2 \tag{10}$$

If readsorption of A takes place, its rate is given by Eq. (11):

$$\overleftarrow{R}_i = \overleftarrow{A}_i \cdot \exp(-\overleftarrow{E}_i/R_gT) \cdot (q_i^0 - q_i)^n \cdot c_A \tag{11}$$

and for the net rate of formation of A in the i-th reaction, we have

$$R_i = \vec{R}_i - \overleftarrow{R}_i \tag{12}$$

In TPD, component A is released into the stream of carrier leaving the reactor with the volumetric flow rate F. The total flow rate at the reactor outlet is therefore higher by the amount of A evolved:

$$F_{\mathrm{TPD}} = F + WR_gT/P \cdot R \tag{13}$$

Equations (7) and (9) are complemented by initial conditions:

$$t = 0,\ T = T_0,\ q_i = q_i^0,\ c_{Ai} = 0,\ c_c = c_c^0 \tag{14}$$

Procedure

The time profiles of molar concentration c_{Ai} were calculated for the reactor outlet and for the reactions in Schemes 1–3, for various combinations of the kinetic parameters (n, A_i, E_i) and experimental conditions (F_0, W, q_i^0, c_c^0, $f(T)$; see Table 1). The system of ordinary differential equations, Eqs (7) and (9), was integrated by using the 4th-order Runge–Kutta method.

Table 1 Parameters used in simulations

Catalyst mass, W	0.025–0.250 g
Volumetric flow rate, F_0	10–300 cm^3/min
Void volume of reactor, V	0.25–5 cm^3
Total pressure, P	100 kPa
Initial concentration of surface (solid) component, q_i^0	10–300 μmol/g
Inlet concentration of gaseous reacting component, c_c^0	0.446–44.6 μmol/cm^3
Activation energy, E_i	70–150 kJ/mol
Pre-exponential factor*, A_i	10^4–10^{13}
Coefficients of temperature function**	
a	10^{-7}–10^4
b	−1, 0, 1, 2, 3

* The dimension of A_i depends on the kinetics.

** The dimension of a depends on the value of b.

The areas under the calculated profiles c_{Ai} were numerically integrated by means of the trapezoidal rule to describe the extent of simultaneous occurrence of the individual TPD, TPR and TPRD reactions. This extent was characterized by criterion S_{ij}, which gives the relative amount of surface component AX_i, B_iX or B_i which reacted simultaneously with the component j (Fig. 1):

$$S_{ij} = \frac{\int_{t_1}^{t_2} c_j \, dt + \int_{t_2}^{t_3} c_i \, dt}{\int_{t_0}^{t_3} c_i \, dt} \tag{15}$$

i.e. $S_{ij} \in (0, 1)$. In the case that $S_{ij} = 0$, the i-th and the j-th reactions take place consecutively; if $S_{ij} = 1$, they proceed simultaneously.

Results and discussion

As many as several tens of individual reactions may take place during complex TPD, TPR and TPRD [1, 2]. Owing to the loss of physical significance of the parameters in fitting more complicated profiles, we assumed that only three of them proceed simultaneously at any moment. More than one hundred simulation experiments were carried out under various experimental conditions. The generated concentration profiles of gaseous component A are illustrated in Fig. 2. The dashed peaks correspond to individual reactions; the observed profile of A is drawn with a solid line. The hatched areas correspond to the amounts of surface (solid) components which react simultaneously and determine the value of criteria S_{ij}. On change of the TPR, TPR and TPRD conditions, a shift of the individual peaks along the time axis and a change of their shape was observed (the curves in Figs 2a and 2b). At the same time, the degree of peak overlapping changed.

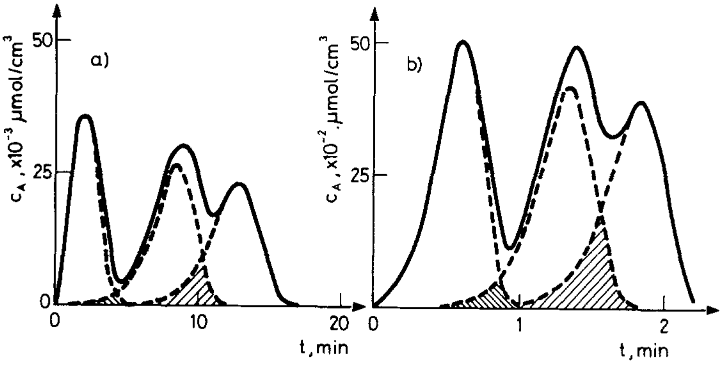

Fig. 2 Complex TPR and TPRD profiles of the evolved gaseous component A: $c_c^0=4.46$ μmol/cm^3, $q_i^0=100$ μmol/g, $F_0=50$ cm^3/min, $V=1$ cm^3, $W=0.2$ g. $A_i=1\cdot10^{10}$ cm^3/μmol min, $E_1=75$, $E_2=85$, $E_3=95$ kJ/mol. Fig. 2a: $a=5$ deg/min, $b=0$. Fig. 2b: $a=100$ deg/min, $b=0$

Effect of the kinetics. The simultaneous or consecutive course of the reactions depends on the differences between the pre-exponential factors (A_i) and activation energies (E_i) of the individual reactions, on their orders (n), and on the presence or absence of readsorption. For small differences between the A_i and E_i values, the individual reactions can not be uncoupled through the choice of temperature program $T(t)$; hence, the resulting profiles consist of one peak only. This situation does not necessarily correspond to $S_{ij}=1$. For the equal starting concentrations of surface components, S_{ij} should not exceed a value of about 0.4 (i.e. the simultaneous course from 40%) for the detection of several peaks.

For different activation energies, overlaps S_{ij} depend not only on the differences in E_i, but also on their absolute values. This follows from the exponential dependence of the reaction rate on temperature. It can be seen from Fig. 2 that, for differences in E_i of 10 kJ/mol, the overlaps between the first and second and the second and third peaks are quite different: whereas the value of S_{12} amounted to

0.03, S_{23} was 0.19. In other word, the higher the activation energies, the higher must be the difference between them to get the same S_{ij}.

For the same reaction orders, peak overlapping can be influenced significantly only if a sufficient difference exists in the activation energies of the individual reactions. An increase in reaction order causes an increase in S_{ij}. The extent of simultaneous occurrence of the reactions can increase severalfold when passing from $n=1$ to $n=2$ (Table 2).

Table 2 Influence of desorption order and of readsorption on S_{ij}. $q_i^0=50$ µmol/g, $F_0=100$ cm³/min, $V=0.5$ cm³, $W=0.1$ g, $a=50$ deg/min, $b=0$. $\vec{A}_1=5\cdot 10^{11}$, $\vec{A}_2=\vec{A}_3=1\cdot 10^{10}$, $\overleftarrow{A}_1=\overleftarrow{A}_2=\overleftarrow{A}_3=1\cdot 10^7$ cm³(g)/µmol min; $\vec{E}_1=80$, $\vec{E}_2=85$, $\vec{E}_3=95$, $\overleftarrow{E}_1=\overleftarrow{E}_2=\overleftarrow{E}_3=2$ kJ/mol

Kinetics	1st-order	2nd-order	1st-order, readsorption
S_{12}	0.11	0.25	0.20
S_{13}	0.01	0.05	0.04
S_{23}	0.26	0.38	0.34

When the presence of readsorption (low activation energy [9]) was assumed, an increase in the peak overlapping was discovered as well (Table 2). Both an increase in the reaction order and the presence of readsorption cause peak broadening, i.e. higher S_{ij}.

Effect of the carrier gas flow rate and the amount of sample. The flow rate of the carrier gas and the amount of sample influence the concentration and conversion of the reaction components. If readsorption does not take place during TPD, the values of S_{ij} remain constant (Table 3), because the rate of formation of component A does not depend on the concentration of C. We expected that, in the presence of readsorption, an increase of the carrier gas flow rate and a decrease of the amount of catalyst would lead to a decrease in the concentration of desorbing component A, which would reduce the rate of readsorption. The net effect should be a decrease in

Table 3 Influence of carrier gas flow rate (F_0) and amount of sample (W) on S_{ij}. $c_c^0=0.446$ µmol/cm³, $q_i^0=100$ µmol/g, $V=2$ cm³, $a=50$ deg min, $b=0$. $A_1=5\cdot 10^9$, $A_2=5\cdot 10^{10}$, $A_3=1\cdot 10^7$ cm³(g)/µmol min, $E_1=80$, $E_2=100$, $E_3=90$ kJ/mol

Method	TPd, 2nd order	TPR, TPRD		
W (g)		0.05	0.1	0.5
F_0 (cm³/min)	200	25	250	20
S_{12}	0.26	0.26	0.12	0.14
S_{13}	0.02	0.02	0.01	0.01
S_{23}	0.11	0.11	0.07	0.09

peak overlapping. However, when the parameters from Table 2 were used, this effect proved to be of little significance.

In the simulation of TPR and TPRD, at low flow rate, high amount of sample, and low concentration of gaseous component C, a shift towards the simultaneous occurrence of the individual reactions was observed (Table 3). The reason was the decrease in reaction rate owing to the decreased concentration of C.

Effect of concentration of gaseous reacting component. This effect plays a role only in TPR and TPRD. When the temperature is raised, the rate of reaction increases, but it is limited by the low kinetic constant at first. When the first inflexion point of the TPR or TPRD peak is passed, the reaction rate falls due to the decreasing concentration of surface component, even though the rate constant is already high. It now depends on A_i and E_i whether the increase in concentration of the gaseous component C will increase or decrease S_{ij}. Provided that the reaction with lower activation energy takes place at a lower temperature than that with higher activation energy, the S_{ij} values will decrease with increasing concentration of C (Fig. 3). This is because the reaction with lower E_i is finished sooner. If the reaction with lower E_i takes place at a higher temperature than that with higher E_i, S_{ij} will increase (Fig. 3).

Effect of concentration of surface component. When the relative concentrations of different surface species can be changed by the sample preparation method, the S_{ij} values can be changed as well. This method was employed in resolving the individual reduction reactions of Cr^{6+} in CrO_3/SiO_2 catalyst [10]. By adjusting the Cr^{6+} concentration in the sample, a change of the relative concentrations of

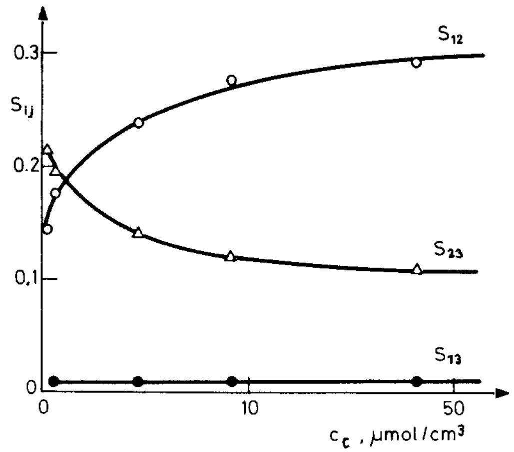

Fig. 3 Influence of concentration of the gaseous reacting component C on S_{ij}: $q_i^0=100$ μmol/g, $F_0=100$ cm³/min, $V=2$ cm³, $W=0.1$ g, $a=25$ deg/min, $b=0$. $A_1=1\cdot10^{13}$, $A_2=1\cdot10^{9}$, $A_3=1\cdot10^{10}$ cm³/μmol min, $E_1=100$, $E_2=80$, $E_3=100$ kJ/mol

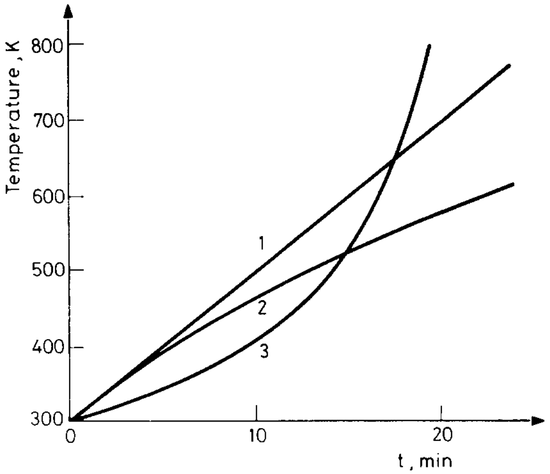

Fig. 4 Time dependence of temperature as a function of parameters of Eq. (7). Curve 1: $a=20$ deg/min, $b=0$. Curve 2: $a=6\cdot 10^3$ 1/min, $b=-1$. Curve 3: $a=5\cdot 10^{-7}$, $b=3$

hexavalent chromium was achieved, and hence a better resolution of the individual reactions. If the concentrations of the surface species remain in constant ratios (regardless of their absolute values), changes in q_i^0 do not induce any shift in S_{ij}.

Effect of temperature program. When the reaction temperature is increased in the presence of reactions with different activation energies, the reaction with higher E_i is favored. If the reaction with lower E_i takes place at a lower temperature than that with higher E_i, an increase of the rate of temperature rise causes the first reaction to be delayed and the second one to proceed sooner. The net effect is an increase in S_{ij} (Table 4). In contrast, S_{ij} decreases when the reaction with lower E_i takes place later than that with higher E_i (Table 4).

Some results on the use of non-linear temperature programs are also given in Table 4. Changes in the extent of the simultaneous occurrence of the reactions can be explained here in the same way as in the case of a linear program. The results

Table 4 Influence of temperature program on S_{ij}. $c_c^0=4.46$ µmol/cm³, $q_i^0=100$ µmol/g, $F_0=50$ cm³/min, $W=0.05$ g, $V=1$ cm³. $A_1=4\cdot 10^9$, $A=7\cdot 10^{10}$, $A_3=5\cdot 10^7$ cm³/µmol min, $E_1=80$, $E_2=100$, $E_3=90$ kJ/mol

a*	$7.5\cdot 10^3$	5	100	$1\cdot 10^{-3}$	$1\cdot 10^{-6}$
b	1	0	0	2	3
S_{12}	0.18	0.14	0.25	0.27	0.21
S_{13}	0.02	0.01	0.01	0.01	0.01
S_{23}	0.17	0.07	0.05	0.05	0.05

* The dimension of a depends on the value of b.

indicate that the most suitable temperature program (S_{ij} is minimal) can be proposed on using an optimization procedure.

The results obtained by modelling complex TPD, TPR and TPRD in systems of parallel reactions reveal that, for certain combinations of kinetic parameters, it is possible to change the extent of the simultaneous occurrence of the individual reactions. A sufficient difference between the activation energies of the reactions is a necessary condition. A shift towards the desired consecutive course of the reactions can be attained by adjusting the concentration of the gaseous component in TPR and TPRD, and by optimizing the temperature program in TPD, TPR and TPRD. The question should now be addressed of the influence of the experimental design on the estimation of kinetic parameters from TPD, TPR and TPRD data [8].

List of symbols

a, b = coefficients of temperature function*,
A_i = pre-exponential factor**,
c_A = concentration of gaseous component released, µmol/cm^3,
c_c = concentration of reacting gaseous component, µmol/cm^3,
c_c^0 = inlet concentration of C, µmol/cm^3,
c_{Ai} = concentration of gaseous component released in the i-th reaction, µmol/cm^3,
E_i = activation energy, kJ/mol,
F = reactor outlet flow rate, cm^3/min,
F_{TPD} = reactor outlet flow rate (TPD), cm^3/min,
F_0 = reactor inlet flow rate (TPR and TPRD), cm^3/min,
i, j = reaction indices,
m = number of reactions,
n = adsorption and desorption orders,
P = total pressure, kPa,
R = net rate of formation of a component, µmol/g min,
R_i = rate of formation of a component in i-th reaction, µmol/g min,
R_g = gas constant, kJ/mol K or kPa cm^3/µmol K,
t = reaction time, min,
t_0 = time of start of i-th reaction, min,
t_1 = time of start of j-th reaction, min,
t_2 = time when $c_{Ai} = c_{Aj}$, min,

* The dimension of a depends on the value of b.
** The dimension of A_i depends on the kinetics.

t_3 = time when $c_{Ai}=0$, min,
T_0 = initial reaction temperature, K,
T = reaction temperature, K,
V = void volume of reactor, cm^3,
W = catalyst mass, g.

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Zusammenfassung — Durch Simulierung temperaturprogrammierter Desorption, Reaktion und Reduzierung in einem System von Parallelreaktionen konnte gezeigt werden, daß die experimentellen Bedingungen die Simultanität bzw. Konsekutivität der Einzelreaktionen des Systems beeinflussen. Durch eine Einstellung der Konzentration der gasförmigen Reaktionsprodukte oder durch Optimalisierung des Temperaturprogrammes kann eine gewünschte Folge der Einzelreaktionen erreicht werden. Somit kann durch eine geschickte Wahl der experimentellen Bedingungen bei temperaturprogrammierten Verfahren eine bessere Separierung der Einzelreaktionen erreicht werden.

Резюме — Путем моделирования температурно-программированной десорбции, реакции и воостановления в системе с параллельно протекающими реакциями, установлено, что экспериментальные условия оказывают влияние на одновременное или последовательное протекание отдельных реакций в системе. Регулировка концентрации газообразной реакционной компоненты или оптимизация температурной программы вызывает смещение к желаемой последовательности протекания реакций. В связи с этим, хорошее разделение индивидуальных реакций может быть достигнуто посредством разумного выбора экспериментальных условий температурно-программных методов.