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KINETIC ANALYSIS OF TEMPERATURE-PROGRAMMED SURFACE REACTIONS ON POROUS CATALYSTS

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By means of model calculations it could be shown for an irreversible surface reaction of 1st order that the determination of the activation energy of the desorption of the reactant or, respectively, of the surface reaction is possible by application of the method of variation of the heating rate to the desorption curve of the reactant, according to circumstances whether the ratio of the activation energy of the surface reaction and of the desorption of the reactant is greater or smaller than one.

The possibilities of the kinetic evaluation are applied to the isomerization of cyclopropane on a NaX-zeolite catalyst. The resulting heat of adsorption of cyclopropane and the activation energy of the reaction agree well with the values of literature obtained by isothermal measurements in a pulse reactor.

Keywords: kinetic analysis, NaX-zeolite catalyst, surface reactions

Introduction

The temperature programmed desorption (TPD) of probe molecules represents a method frequently used to characterize the surface chemical properties of porous catalysts [1, 2]. In case that the desorption process is connected with a surface reaction (temperature programmed surface reaction: TPSR), usually only a qualitative interpretation was carried out in order to characterize the reactivity of the catalyst or, respectively, its surface chemical properties (see e.g. [2–4].

Therefore, in this paper an attempt was made to find possibilities for a kinetic evaluation by means of modelling calculations on the base of a simple kinetic model, respectively, to find out whether the evaluation method proposed for flash desorption experiments on solids with low surfaces by Gorte and Schmidt [5] is applicable to porous solids. The isomerization of cyclopropane on a NaX-zeolite was used as a test reaction.

Model calculations

An irreversible surface reaction of the first order served as a model reaction:

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

$$A_{ads} \xrightarrow{k_r} B_{ads}$$

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

It is assumed that there is no diffusional influence and no readsorption occurs. Further on, adsorption of A and B are considered as independent of each other.

Moreover the Arrhenius equation should be valid to describe the temperature dependence of the rate constants and the Arrhenius parameters should not depend on the degree of ceverage (θ_A and θ_B):

$$-\frac{d\theta_A}{dt} = \theta_A A_{dA} \exp\left(-\frac{E_{dA}}{RT}\right) + \theta_A A_r \exp\left(-\frac{E_r}{RT}\right) \tag{1}$$

$$-\frac{d\theta_B}{dt} = \theta_B A_{dB} \exp\left(-\frac{E_{dB}}{RT}\right) - \theta_A A_r \exp\left(-\frac{E_r}{RT}\right) \tag{2}$$

The numerical solution of the system differential equations was carried out for case of a linear temperature programme ($T = 300+\alpha t$) using the Euler–Cauchy procedure. The parameters were chosen so that the desorption of A and B and the surface reaction occur simultaneously at increasing temperature.

Figure 1 shows desorption curves of A and B for various activation energies of the surface reaction while the other parameters are kept constant. It is clear that the temperature of the maxima as well as the degree of conversion change relatively strongly. In the variation range of the heating rate for porous solids (about 1...25 deg/min) the conversion only a little depends on the heating rate (see Fig. 2). This means, as also shown in Fig. 2 that the degree of conversion assuming equal preexponential factors for desorption and surface reaction is almost determined only by the ratio of the activation energies of desorption of A and of the surface reaction. However, an evaluation of the desorption curve on the base of the differential rate equation is not possible because the degree of coverage in dependence on the temperature cannot be directly determined by usual methods. Assuming no reaction occurs another possibility of kinetic evaluation is the determination of the Arrhenius parameters from the dependence of

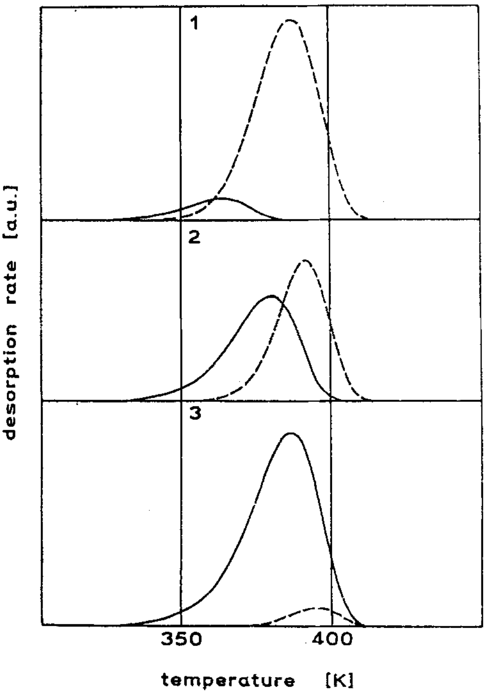

Fig. 1 Calculated desorption curves (—— A, – – – B) for different activation energies of the surface reaction
($A_{dA}=A_r=A_{dB}=1\cdot10^{13}$ s^{-1}, $E_{dA}=E_{dB}=110$ kJ/mol, heating rate=10 deg/min)
1: $E_r=103.4$ kJ/mol, conversion=90.1%, 2: $E_r=110.0$ kJ/mol, conversion=50.0%, 3: $E_r=118.8$ kJ/mol, conversion=5.9%

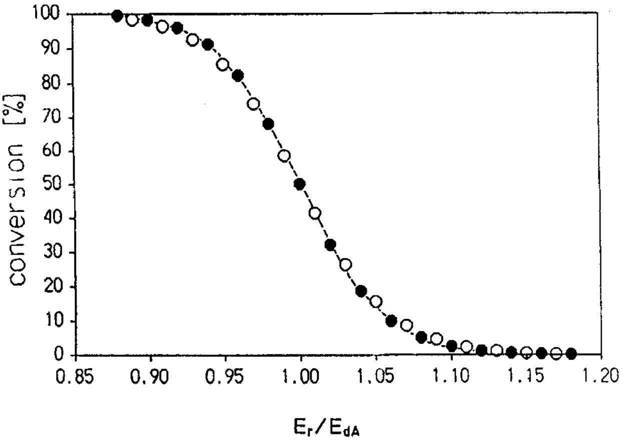

Fig. 2 Dependence of the conversion on the ratio E_r/E_{dA} for different heating rates ($A_{dA}=A_r=A_{dB}=1\cdot10^{13}$ s^{-1}, $E_{dA}=E_{dB}=110$ kJ/mol), ●: 1 deg/min, o: 25 deg/min

the temperature of the maximum of the desorption curve on the heating rate [1, 2, 6–9]. For $d(k_{dA}\theta_A/dt = 0$ results from Eq. (1) [5]:

$$\frac{E_{dA}\,\alpha}{RT_{mA}^2} = A_{dA}\exp\left(-\frac{E_{dA}}{RT_{mA}}\right) + A_r\exp\left(-\frac{E_r}{RT_{mA}}\right) \qquad (3)$$

Therefore, the maximum of the desorption curve of A is determined more or less by the desorption process or by the surface reaction depending on the quantity of the Arrhenius parameters. Using the method of variation of heating rate for the desorption of A shows that the plot $(2\ln T_{mA} - \ln\alpha = f(1/T_{mA}))$leads to a good linear relation for various model cases (see Fig. 3). In case that ratio is $E_r/E_{dA} < 1$, the activation energy of the surface reaction is well calculable from the slope and the preexponential factor more or less incorrect from the intercept. When, however, $E_r/E_{dA} > 1$, the activation energy of the desorption of A is determinable. With the help of this, the activation energy of the surface reaction can be estimated when the degree of conversion is known. The initial range of desorption of A is, however, also at relatively high conversion almost not influenced by the surface reaction, as shown in Fig. 4 for some examples. Therefore, the method for the determination of the activation energy without knowing the degree of coverage proposed by Habenschaden and Küppers [10] can be used additionally.

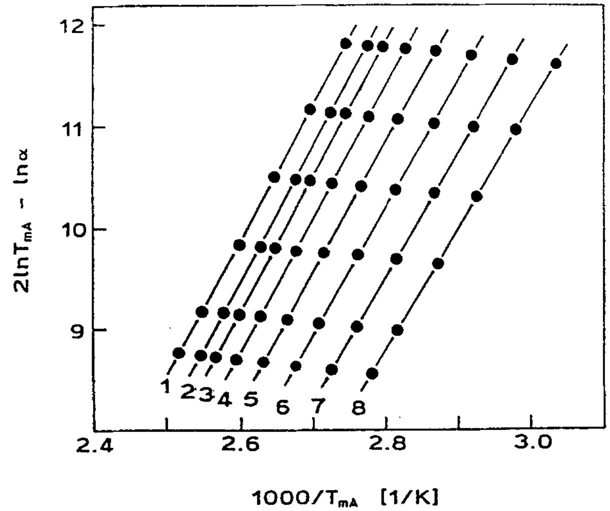

Fig. 3 Plots of $2\ln T_{mA} - \ln\alpha$ against $1/T_{mA}$ for the desorption of A
1: $E_r/E_{dA} = 1.18$, 2: $E_r/E_{dA} = 1.02$, 3: $E_r/E_{dA} = 1.00$, 4: $E_r/E_{dA} = 0.98$, 5: $E_r/E_{dA} = 0.96$, 6: $E_r/E_{dA} = 0.94$, 7: $E_r/E_{dA} = 0.92$, 8: $E_r/E_{dA} = 0.90$

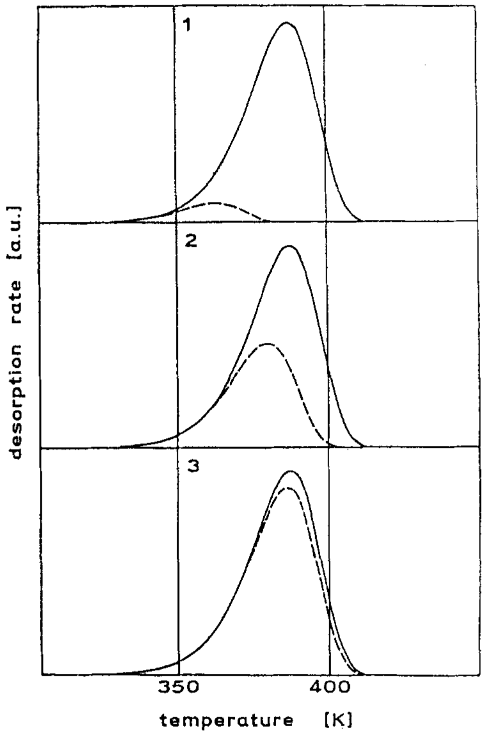

Fig. 4 Calculated desorption curves of A for different activation energies of the surface reaction (– – –) in comparison with the desorption curve of A without reaction (——) ($A_{dA}=A_r=A_{dB}=1\cdot10^{13}$ s^{-1}, $E_{dA}=E_{dB}=110$ kJ/mol, heating rate=10 deg/min)
1: $E_r=103.0$ kJ/mol, conversion=91.3%, 2: $E_r=110.0$ kJ/mol, conversion=50.0%, 3: $E_r=117.0$ kJ/mol, conversion=9.9%

The assumption of different preexponential factors for the desorption of A and for the surface reaction leads to a parallel shift of the dependence of the conversion on the ratio of the activation energies (Fig. 2) along to the abscissa (see Fig. 5). The possibility for the determination of the preexponential factor of the surface reaction developed from this by Gorte and Schmidt [5] is in case of porous solids only restricted applicable because the heating rate necessary for the obtainment of a conversion of 50 per cent can be so large that considerable gradients of temperature and, respectively, concentration in the porous solid cannot be avoided, which uncontrollably influence the course of the whole process. Therefore, for a detailed evaluation additional investigations are necessary.

Isomerization of cyclopropane

Experimental

The isomerization of cyclopropane on a NaX-zeolite catalyst (Si/Al = 1.18) was studied in a flow system using helium as a carrier gas (3 l per h). The continuous analysis of the gas stream at the exit of the reactor was carried out by a heat conductivity detector. Additionally, the composition of the gas stream was studies by gas chromatographic analysis (2 m column, 15 per cent dimethylsupholane on Chromosorb P-NAW, carrier gas: hydrogen, flame ionization detector). For each attempt 0.1 g of the zeolite diluted by 1 g quartz of equal grain size (0.2...0.4 mm) were used. The catalyst was heated in a helium stream of 3 l per h up to 673 K using a heating rate of 10 deg/min, then cooled down to room temperature and saturated by cyclopropane (2 ml-pulse or continuous stream of cyclopropane).

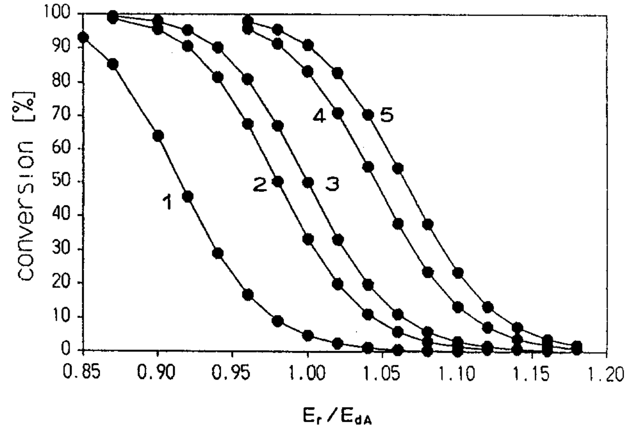

Fig. 5 Dependence of the conversion on the ratio E_r/E_{dA} for different values of A_r ($A_{dA}=A_{dB}=1\cdot10^{13}$ s^{-1}, $E_{dA}=E_{dB}=110$ kJ/mol, heating rate=10 deg/min)
1: $A_r=5\cdot10^{11}$ s^{-1}, 2: $A_r=5\cdot10^{12}$ s^{-1}, 3: $A_r=1\cdot10^{13}$ s^{-1}, 4: $A_r=5\cdot10^{13}$ s^{-1}, 5: $A_r=1\cdot10^{14}$ s^{-1}

This was followed by the isothermal desorption of excess cyclopropane at room temperature. After that the sample was heated using a linear temperature programme with a heating rate of 2...20 deg/min.

Results and discussions

Figure 6 shows a typical desorption curve of cyclopropane, respectively, of the reaction product propene after adsorption of 0.054 mmol/g cyclopropane at room temperature. Within the experimental error no systematic dependence of the degree of conversion on the heating rate (2...20 deg/min) could be estimated. The conversion amounted to 3.3±0.4 per cent. The use of the method of variation of heating rate on the desorption of cyclopropene led to a good linear relation (see Fig. 7). The energy value resulting from the slope of 45±5 kJ/mol (preexponential factor $1.2\cdot10^{6}$ min^{-1}), which is in good agreement with the evaluation of the initial range of desorption according to Habenschaden and Küppers [10] (52 kJ/mol, see Fig. 8). The degree of conversion is relatively small, and so this value should correspond to the activation energy of desorption of cyclopropane, because one can assume that the activation energy of the surface reaction is much greater (see Fig. 2 and Table 1). In case that a diffusional influence exists the predicted energy has the meaning of the apparent desorption energy [11] comparable with the heat of adsorption. The good agreement with adsorption heats of cyclopropane on NaX zeolites measured with gas chromatographic methods by Bassett and Habgood [12] (42.7 kJ/mol) and Benn *et al.* [13] (45.1 kJ/mol) should support this interpretation. The activation energy of the isomerization of cyclopropane to propene was estimated by numerical solution of the system of differential equations (Eqs (1) and (2)) assuming a preexponen-

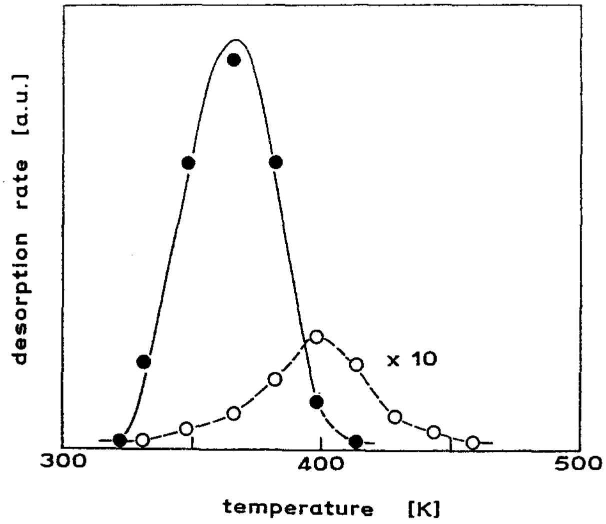

Fig. 6 Desorption curves for cyclopropane (—— :detector response, ● : GC analysis) and propene (o: GC analysis) (heating rate = 7.8 deg/min)

tial factor of $1 \cdot 10^{13}$ s^{-1}. With a value of about 120 kJ/mol comparable with literature data [12, 13] the temperature of maximum of the desorption curve of propene (10 deg/min, 400±5 K) and the degree of conversion (3.3 per cent) can be described well. In order to determine the parameters more exactly (e.g. by fitting of a kinetic model with non-linear regression [14]) measurements would be

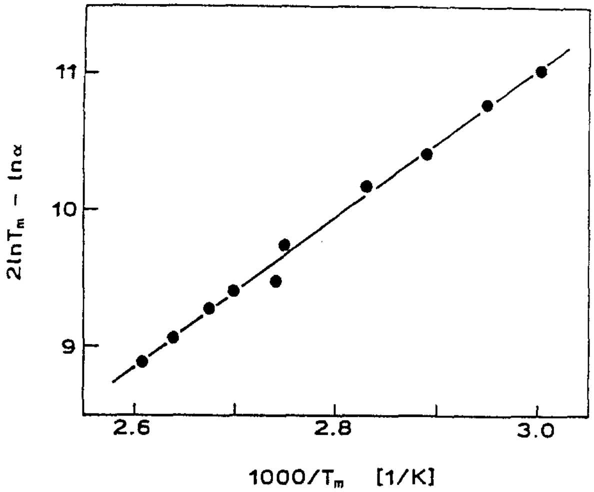

Fig. 7 Plot of $2 \ln T_m - \ln \alpha$ against $1/T_m$ for the desorption of cyclopropane

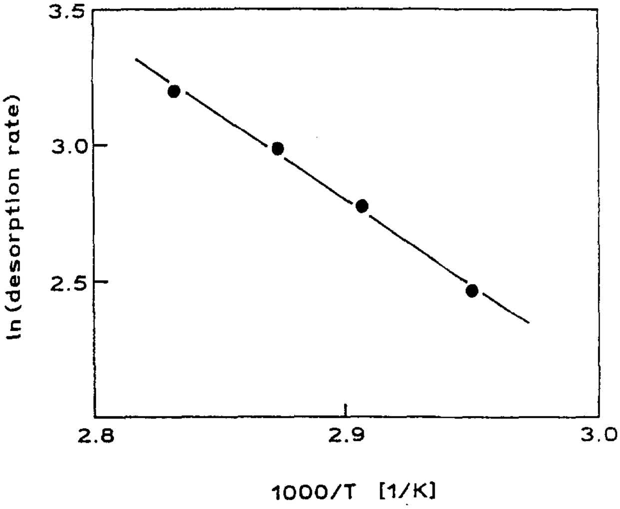

Fig. 8 Plot of ln(desorption rate) against $1/T$ for the desorption of cyclopropane (heating rate = 7.8 deg/min)

Table 1 Results of kinetic evaluation

Model parameter		$2\ln T_{mA} - \ln\alpha = f(1/T_{mA})$	
E_r/E_{dA}	E_r/ kJ·mol^{-1}	E / kJ·mol^{-1}	$A\cdot 10^{-13}$ / s^{-1}
0.90	99.0	99.3	1.02
0.92	101.2	101.6	1.11
0.94	103.4	104.0	1.28
0.96	105.6	106.5	1.61
0.98	107.8	108.5	1.84
0.99	108.9	109.4	1.96
1.00	110.0	110.1	2.06
1.01	111.1	110.4	1.91
1.02	112.2	110.8	1.92
1.04	114.4	110.9	1.68
1.06	116.6	110.7	1.39
1.08	118.8	110.6	1.28
1.10	121.0	110.4	1.18
1.12	123.2	110.2	1.09
1.14	125.4	110.2	1.07
1.16	127.6	110.0	0.99
1.18	129.8	110.2	1.06

E_{dA}=110 kJ/mol, A_{dA}=A_r=1·10^{13} s^{-1}

necessary which should enable a very exact determination of the course of desorption of propene because of the small degree of conversion.

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Zusammenfassung —Mit Modellrechnungen für eine irreversible Oberflächenreaktion 1. Ordnung konnte gezeigt werden, daß durch Anwendung der Methode der Variation der Heizgeschwindigkeit auf die Desorptionskurve des Ausgangsstoffes die näherungsweise Bestimmung der Aktivierungsenergie der Desorption des Ausgangsstoffes bzw. der Oberflächenreaktion möglich ist, je nachdem ob das Verhältnis der Aktivierungsenergien für die Oberflächenreaktion und der Desorption des Ausgangsstoffes größer oder kleiner als eins ist.

Die Möglichkeiten der kinetischen Auswertung werden auf die isomerisierung von Cyclopropan an einem NaX-Zeoliten angewendet. Die erhaltene Adsorptionswärme für Cyclopropan und die Aktivierungsenergie für die Reaktion stimmen gut mit Literatur-werten von isothermen Messungen im Impulsreaktor überein.