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TEMPERATURE-PROGRAMMED DESORPTION (TPD) STUDIES OF THE DEAMMONIATION KINETICS OF NH_4NaY ZEOLITES USING A HYPERBOLIC TEMPERATURE PROGRAMME

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TPD studies on the kinetics of deammoniation of an NH_4NaY zeolite showed that the use of a hyperbolic temperature programme led to kinetic parameters agreeing with those resulting from a linear heating process. Because of the progressive increase of the heating rate in the case of hyperbolic heating schedules, the parameters can be considered as independent of the heating rate within certain limits. The better resolution of complex desorption spectra with hyperbolic programmes is an additional reason for their use.

The thermal activation of NH_4NaY zeolites is connected with the desorption of water and ammonia, the latter occurring in the temperature interval from 473 to 673 K and resulting in two overlapping peaks [1–3]:

$$NH_4NaY \longrightarrow HNaY + NH_3 \nearrow$$

Desorption of the high-temperature form of the sorbed NH_3 can be well described over a relatively large range of coverage by a rate equation of first order without readsorption [3]. The activation energies of the desorption process on zeolites with different ammonium contents are very suitable for characterizing the acidity of the appropriate H forms [3], provided, however, that the activation energies calculated are widely independent of the experimental conditions and of the method of evaluation.

On the other hand, besides other influences, the literature reports on the dependence of the kinetic parameters on the heating rate in thermoanalytical studies on other desorption processes by means of linear heating schedules [4–6].

The application of non-linear, especially hyperbolic, temperature programmes could be very useful to obtain information about the influence of the heating rate:

$$\frac{1}{T} = \frac{1}{T_0} - \beta \cdot t \qquad (1)$$

Furthermore, this kind of temperature guidance would permit a correction-free integral evaluation [7, 8]. In comparison with linear heating schedules, the shape index would advantageously be a function of reaction order only or of the mechanism of the desorption process in the case of hyperbolic temperature programmes [9, 10], thereby offering an opportunity for the fast and exact determination of the concentration function of undisturbed desorption curves using the shape index.

The subject of these studies using a hyperbolic temperature programme therefore was the checking of the kinetic parameters obtained for the deammoniation process by means of a linear temperature programme.

Experimental

The apparatus used was reported elsewhere [11, 12]. A thermal conductivity cell (TCC), followed by a flame ionization detector (FID), were used as detectors, in this was permitting the separate recording of concentration curves of water and ammonia by forming the difference of the two detector signals.

The flow rate of dry helium used as carrier gas was 3 l per hour.

The hyperbolic temperature programme was realized by means of a special programmer and a thermocouple of extremely low inertia. The hyperbolic heating constant was $\beta = 1 \cdot 10^{-5} - 3 \cdot 10^{-5}$ $K^{-1}min^{-1}$. In each case 50 mg of 0.88 NH_4NaY zeolite (Si/Al ratio 2.6), pelleted to grains 0.2–0.4 mm in diameter, water-equilibrated over a saturated $Ca(NO_3)_2$ solution and diluted with 1 g of quartz of equal pellet size, was used.

In order to separate the peak of the high-temperature form of the desorbing ammonia, the temperature programme was stopped at the peak maximum of the low-temperature form and the ammonia desorption was continued until the zero-line of the recorder was reached. The temperature programme was then started again.

Results and discussion

Figure 1 shows TPD curves of water and ammonia resulting from the use of different temperature programmes. The heating constant of the hyperbolic temperature programme was chosen so that the complex desorption curve developed in about the same time as for a linear heating schedule of 10 deg/min. Application of the hyperbolic programme led to a substantially better resolution, which was obviously brought about by the progressive increase of the heating rate in the case; it likewise led to a shift to other temperature ranges of the desorption of molecules relating to different surface conditions (as compared with experiments at constant heating rate).

It is necessary to mention here that an improvement in the resolution of complex desorption spectra is also possible to a certain degree when using a relatively slow heating programme of linear type. However, in this case the amount of gas desorbed per unit time is low and it may therefore be difficult to detect the desorbed substances quantitatively (e.g. in curve 2 of Fig. 1 the two maxima are

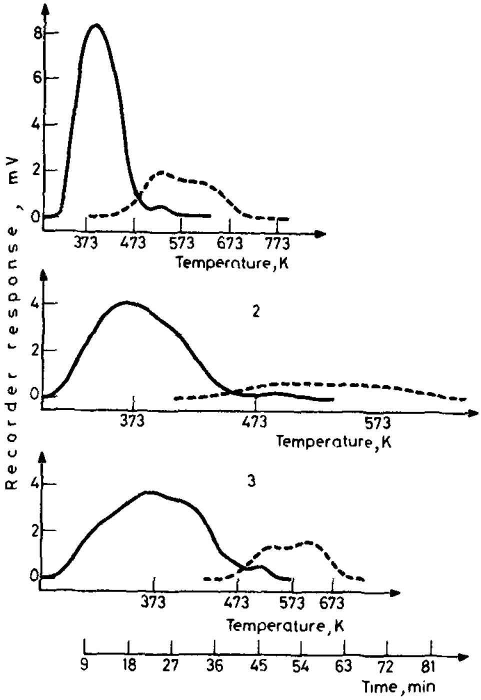

Fig. 1 TPD curves of water and ammonia for different temperature programmes. 1: $T = T_0 + 10t$; 2: $T = T_0 + 4t$; 3: $1/T = 1/T_0 - 3 \cdot 10^{-5}t$; solid line: water; dashed line: ammonia

nearly inperceptible). Furthermore, the duration of one experiment is substantially longer.

Kinetic evaluation of the separated high-temperature peak of the deammoniation process was carried out on the basis of a rate equation of first order without readsorption:

$$-\frac{d\Theta_{NH_3}}{dt} = \Theta_{NH_3} \cdot A \cdot \exp(-E/RT) \qquad (2)$$

Θ_{NH_3} being the coverage degree, A the pre-exponential factor and E the activation energy.

In the case of the hyperbolic temperature programme the evaluation was performed by various methods:

1. by means of the differential rate equation:

$$\ln\left[\left(-\frac{d\Theta_{NH_3}}{dt}\right)\frac{1}{\Theta_{NH_3}}\right] = \ln A - E/RT \qquad (3)$$

2. by means of the integrated rate equation:

$$\ln\left(\ln\frac{\Theta^0_{NH_3}}{\Theta_{NH_3}}\right)=\ln\frac{AR}{\beta E}-E/RT \tag{4}$$

3. by means of the method of Freeman and Carroll [13]:

$$\frac{\Delta\ln\left(-\frac{d\Theta_{NH_3}}{dt}\right)}{\Delta\ln\Theta_{NH_3}}=-\frac{E}{R}\,\frac{\Delta\left(\frac{1}{T}\right)}{\Delta\ln\Theta_{NH_3}}+n \tag{5}$$

For the purpose of comparison, experiments using linear temperature programmes were also carried out. In these cases the activation energy of desorption was calculated either on the basis of the differential rate equation (Eq. (3)) or by using the relationship between the peak-maximum temperature and the heating rate α (Eq. (6)) [14]:

$$2\ln T_m-\ln\alpha=\frac{E}{RT_m}+\ln\frac{E}{AR} \tag{6}$$

Results of the evaluation are shown in Table 1. A statistical comparison of the activation energies (t test with regression coefficients; significance level = 2 per cent) showed the calculated values not to be significantly different.

Table 1 Results of kinetic evaluation

Temperature programme	Method of evaluation	Range of coverage	E, kJ/mol	ln A	Corr. coeff.
$T = T_0 + 10t$	equation (3)	0.85–0.36	88.4 ± 1.7	15.44 ± 0.24	0.9995
$T = T_0 + \alpha t$ $\alpha = 1 \ldots 20$ K/min	equation (6)	–	90.5 ± 3.6	16.42 ± 1.65	0.9984
	equation (4)	0.43–0.10	88.0 ± 1.0	15.40 ± 0.17	0.9997
$1/T = 1/T_0 - 1.88 \cdot 10^{-5}t$	equation (3)	0.85–0.35	80.7 ± 1.8	14.06 ± 0.26	0.9984
	equation (5)	0.73–0.15	82.8 ± 2.2	–	0.9980

With the exception of the use of the integrated rate equation, the optimum adaption to the appropriate linear equation was possible in almost identical ranges of coverage. A reason for deviation could be the somewhat different sensitivity of the method.

As the entire desorption peak could not be described by means of a single rate equation in any case, the use of the shape index to calculate the dependence of the coverage degree involves relatively great difficulties. This method of evaluation was therefore not used here.

Evaluation according to Freeman and Carroll resulted in a reaction order of 1.09 ± 0.03, supporting the assumption of a rate equation of first order.

To summarize, it can be stated that the kinetic studies on the deammoniation of

NH_4NaY zeolites, using a hyperbolic temperature programme on the one hand and a linear one on the other, led to identical findings. However, hyperbolic programmes have the advantage of the relative non-dependence of the kinetic parameters on the heating rate, resulting from the progressive increase of the latter.

The correction-free use of the integrated rate equation as an additional possibility of evaluation of TPD results should permit more certain findings with respect to the correct model. By reason of the better resolution of complex desorption spectra, hyperbolic temperature guidance should also be of advantageous when used to study complex desorption processes. In particular, the use of stronger non-linear heating schedules gives reason to expect greater effects with respect to the resolution of overlapping peaks. The advantages of hyperbolic programmes should in each case justify the higher experimental expense.

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Zusammenfassung — Bei TPD-Untersuchungen zur Kinetik der Deammonisierung eines NH_4NaY-Zeolithen konnte gezeigt werden, dass die Verwendung eines hyperbolischen Temperaturprogrammes zu mit der linearen Temperaturführung übereinstimmenden kinetischen Parametern führt. Wegen der progressiven Zunahme der Aufheizgeschwindigkeit bei diesem Temperaturprogramm können somit die Parameter als in gewissen Grenzen unabhängig davon betrachtet werden.

Und nicht zuletzt sollte die beobachtete bessere Auflösung komplexer Desorptionsspektren Grund dafür sein, diese nichtlineare Temperaturführung bei TPD-Untersuchungen mit zu berücksichtigen.

Резюме — В исследованиях методом термодесорбции кинетики десорбции аммиака с NH_4NaY-цеолита было показано, что применение гиперболической температурной программы приводит к кинетическим параметрам, соответствующим линейной программе. Из-за прогрессирующего роста скорости прогрева при такой температурной программе, параметры могут быть рассмотрены в определенных пределах независимыми от вида программы. Наблюдаемое лучшее разрешение комплексных десорбционных спектров, не в последнюю очередь, является поводом, чтобы обратить внимание на такой нелинейный температурный режим при исследованиях методом термодесорбции.