TEMPERATURE PROGRAMMED DESORPTION (TPD) ON ZEOLITES BY MEANS OF NON-LINEAR TEMPERATURE PROGRAMMES

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On the examples of the temperature programmed desorption of water from a NaA and a 0.45 NiNaX zeolite, it is shown that, through the use of non-linear temperature programmes with increasing heating rate, the individual desorption steps at higher temperatures of a complex desorption process are better recognizable, or can be distinguished almost completely from desorption at lower temperatures. This type of temperature processing therefore offers a suitable means of improving the finding on complex desorption processes relating to porous catalysts and other systems.

Temperature programmed desorption (TPD) is a method frequently used to characterize the surface-chemical properties of porous catalysts [1, 2]. For the most part, the thermal desorption of suitable probe molecules preadsorbed in a stream of carrier gas is studied during linear heating of the sample, using for example NH_3, H_2 or CO. However, this method can also be used for the study of surface processes occurring during the thermal activation of catalysts (e.g. dehydration, deammoniation and dehydroxylation). In both cases, however, typical structured desorption curves are obtained because of the overlapping of several desorption processes, and single desorption maxima are not often observed. A quantitative evaluation with regard to the number of different desorption processes, to desorbed amounts of single steps and to kinetic calculations is often very difficult, because of the low amounts of desorbed compounds at higher temperatures, frequently with strong overlapping with the desorption of greater amounts at lower temperatures. An improvement of the resolution of structured desorption curves is possible if low linear heating rates are applied, but this often leads to detector responses which are not evaluable because of the accompanying decrease of the desorption rate. When larger amounts of sample are used additional problems appear (e.g. heat transfer, back-mixing, chromatographic regime); this is therefore not a suitable way to obtain evaluable desorption curves at low linear heating rates.

It seems possible to carry out a kinetic evaluation for relatively strongly overlapping desorption steps [3–8], but this is connected with relatively large uncertainties in any case [3, 7, 8]. Therefore, an experimental separation of the terms of a complex desorption curve seems to be of advantage for a quantitative evaluation. Possibilities for this are a combination of isothermal and non-isothermal desorption [9, 10], or, in the case of reversible processes, the adsorption of definite amounts [7, 10, 11]. Because of the difficulties connected with the choice of the temperature for isothermal desorption and with the fixing of amounts of preadsorbed compounds, it appears reasonable to look for further experimental possibilities which allow a better recognizability of the individual desorption processes which occur at higher temperatures or which can be separated satisfactorily as such processes are especially interesting for the characterization of porous catalysts.

By simulation of the desorption curve for a simple model of two independently occuring overlapping desorption processes [12], it could be shown that through the use of non-linear temperature programmes of the common form:

$$dT/dt = Q_n \cdot T^n \quad (Q_n = \text{const.}, n = 1, 2, 3, \ldots) \tag{1}$$

the desorption maximum at the higher temperature is better recognizable with increasing non-linearity (n). For porous catalysts, however, a good description of the desorption course by means of such a simple model is possible in only a few cases, because of the heterogeneity of the surface or/and the complexity of the desorption process (diffusion, desorption and readsorption).

Therefore, the aim of this work is to demonstrate the advantages of the use of temperature programmes of higher non-linearity as compared to the usual linear heating programmes, using the first results of water desorption from several zeolites. Previously, only a hyperbolic temperature programme $(n=2)$ has been used [13, 14].

Experimental

All experiments were carried out in a conventional flow apparatus. Water desorption was registered by a heat conductivity detector. The carrier gas was well-dried helium (3 l per h). For each experiment, 0.1 g of zeolite diluted with 1 g of quartz of equal grain size (0.2–0.4 mm) was used. To guarantee a constant water content, the zeolites (NaA, 0.45 NiNaX Si/Al = 1.18) were stored over saturated $Ca(NO_3)_2$ solution. A home-made apparatus for temperature programming, containing a U880–K1520 microprocessor system (VEB Robotron-Elektronik

Zella-Mehlis, GDR) and two Ni/CrNi thermocouples, was used to control the temperature [15]. The relatively low thermal inertia of the heating furnace allowed heating rates up to 50 deg per min.

Results and discussion

Figure 1 shows the TPD curves for water desorption from a NaA zeolite using several temperature programmes. In each case, three different desorption ranges are recognizable (in the cases of curves 5 and 6, the first part of the curves is not shown) as typical for water desorption from A zeolites containing monovalent cations [7, 8, 16]. When a linear temperature programme is used (curves 1 and 2), the desorption of the low water amount at higher temperatures occurs in a very broad and flat peak, which is relatively strongly overlapped by the desorption of the main amount of water at lower temperatures. A quantitative evaluation of this peak, which is attributed to water desorption from the sodalite cage of the zeolite [16], is therefore very difficult. When the desorption is carried out under non-linear heating programmes with increasing heating rate (curves 3–6), the desorption course changes so that the peak in the higher temperature region is always better visible. Moreover, when the heating parameter is chosen to be relatively low (programmes
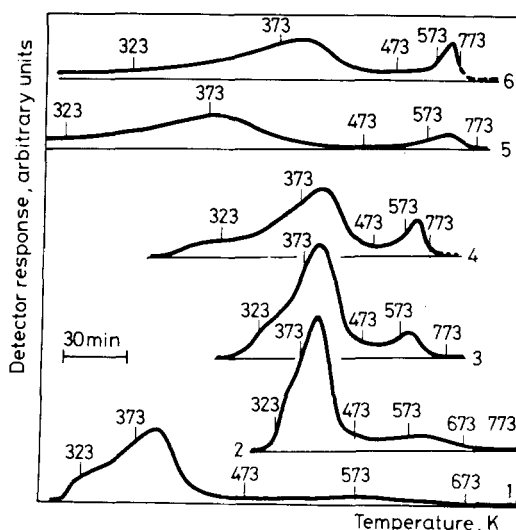

Fig. 1 TPD curves of water desorption from NaA zeolite: 1: $n=0$, $Q_0 = 1.9$ deg min^{-1}; 2: $n=0$, $Q_0 = 3.8$ deg min^{-1}; 3: $n=2$, $Q_2 = 2.0 \cdot 10^{-5}$ deg^{-1} min^{-1}; 4: $n=4$, $Q_4 = 9.1 \cdot 10^{-11}$ deg^{-3} min^{-1}; 5: $n=4$, $Q_4 = 4.4 \cdot 10^{-11}$ deg^{-3} min^{-1}; 6: $n=5$, $Q_5 = 1.4 \cdot 10^{-13}$ deg^{-4} min^{-1}; − − − isothermal desorption
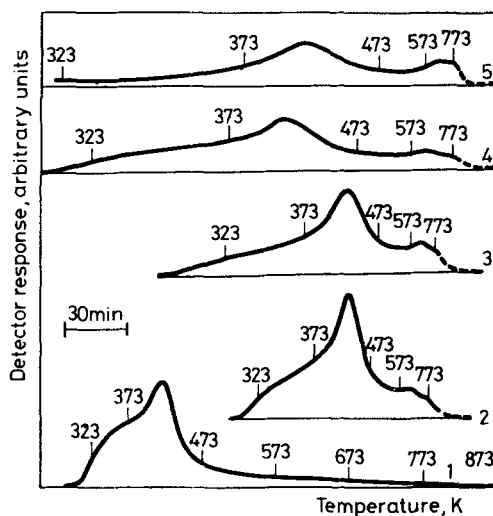
Fig. 2 TPD curves of water desorption from 0.45 NiNaX zeolite: 1: $n=0$, $Q_0 = 2.9$ deg min^{-1}; 2: $n=3$, $Q_3 = 5.0 \cdot 10^{-8}$ deg^{-2} min^{-1};   3: $n=4$, $Q_4 = 9.1 \cdot 10^{-11}$ deg^{-3} min^{-1};   4: $n=4$, $Q_4 = 5.3 \cdot 10^{-11}$ deg^{-3} min^{-1};   5: $n=5$, $Q_5 = 1.2 \cdot 10^{-13}$ deg^{-4} min^{-1};   – – – isothermal desorption

with higher non-linearity), an almost complete separation of this peak is possible (curve 5). Since the same desorption ranges are obtained when different temperature programmes are used, the individual desorption steps can be considered to be relatively independent of each other.

Figure 2 shows TPD curves for the desorption of water from a 0.45 NiNaX zeolite. With a linear temperature programme of 3 deg per min (curve 1), but also at other heating rates, the water desorption at higher temperatures is visible only as a slowly falling flank of the peak at about 423 K. However, as this water desorption is a result of the dehydroxylation of the zeolite [17, 18], a quantitative evaluation of this desorption is of great interest for the characterization of the surface-chemical properties of this catalytically active zeolite. In each case, a distinct structuring is recognizable for this desorption when non-linear temperature programmes are used (curves 2–5), pointing to different dehydroxylation processes, as found in combined isothermal/non-isothermal desorption experiments [18]. A complete separation of the dehydroxylation cannot be expected, because of the relatively strong overlapping by the dehydration at lower temperatures. In this case, the use of non-linear temperature programmes provides an opportunity of obtaining an indication of the number of different desorption steps at higher temperatures from the course of the complex desorption curve. Moreover, the use of other techniques for the

separation of individual desorption steps (e.g. the determination of temperature for an isothermal desorption) can be facilitated.

Since temperature programmes according to Eq. (1) represent only a certain type of non-linear temperature programmes, it is conceivable that, through the application of other temperature *vs.* time functions, a further improvement can be obtained with respect to findings about complex desorption processes for the demonstrated possibilities of applications and of the advantages of special non-linear temperature programmes for kinetic evaluation [19–23], non-linear heating programmes should be used more widely, even if the determination of the optimum temperature course is difficult for a certain problem.

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Zusammenfassung — Am Beispiel der Temperatur-Programmierten Desorption von Wasser von einem NaA- und einem 0,45 NiNaX-Zeolithen wird gezeigt, daß durch Anwendung von nichtlinearen Temperaturprogrammen mit zunehmender Heizgeschwindigkeit einzelne Desorptionsschritte bei

höheren Temperaturen eines komplexen Desorptionsprozesses besser erkennbar sind, bzw. von der Desorption bei niedrigeren Temperaturen fast völlig abgetrennt werden können. Diese Art der Temperaturführung stellt somit eine geeignete Möglichkeit dar, um die Aussagemöglichkeiten bei der Untersuchung von komplexen Desorptionsprozessen an porösen Katalysatoren und anderen Systemen zu verbessern.

Резюме — На примерах температурной программированной десорбции воды из NaA и цеолита 0,45 NiNaX показано, что благодаря использованию нелинейных температурных программ с увеличивающейся скоростью нагрева, каждые отдельные высокотемпературные стадии десорбции сложного десорбционного процесса лучше определяются и могут быть полностью отделены от десорбции при низких температурах. Поэтому такой тип температурной обработки предлагает удобный метод улучшения нахождения сложных десорбционных процессов на пористых катализаторах и других системах.