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# CHARACTERIZATION OF THE ACIDIC PROPERTIES OF ZEOLITES WITH TEMPERATURE PROGRAMMED DESORPTION (TPD) OF VARIOUS BASES INCLUDING NON-LINEAR TEMPERATURE PROGRAMMES

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## ABSTRACT

By means of tpd studies of $NH_3$ from HY zeolites it could be shown that the use of non-linear temperature programmes influences the complex desorption process in such a manner that appearing desorption maxima are better visible. When using bases which only are able to enter the supercage of HY zeolites so one obtains information about catalytically active acid centres.

## INTRODUCTION

One of the most important properties concerning catalytic activity of zeolites is their acidity /1/. In order to characterize it beside titration by n-butylamine /2/ and ir spectroscopic studies of pyridine adsorption /3, 4/ tpd of $NH_3$ is used frequently /5-9/. In case of HY zeolites it could be shown that the activation energy of $NH_3$ desorption /9/ but also desorption of other bases /10/ can serve as a quantitative measure of acid strength of the "HF" OH groups. Moreover in case of $Me^{2+}$HY zeolites tpd of $NH_3$ allows decision between $NH_3$ splitting from Brönsted centres (OH groups) and Lewis centres (coordinatively unsaturated $Me^{2+}$ ions) /11/. Interpretation of results or kinetic evaluation, respectively, are often difficult because of the formation of strongly structured desorption curves with poorly perceptible maxima resulting from the desorption from centres of different acid strength. Moreover, in every case it is necessary to check whether the activation parameters obtained are independent of the experimental conditions and the method of evaluation, respectively.
The apparatus used and the measuring method were described elsewhere /9, 10, 12, 13/.

## RESULTS AND DISCUSSION

Fig. 1 shows tpd curves of $NH_3$ desorption from a HNaY zeolite (Si/Al ratio 2.6, degree of exchange 88 %) for several temperature programmes with $NH_3$ amounts according to the OH group con-

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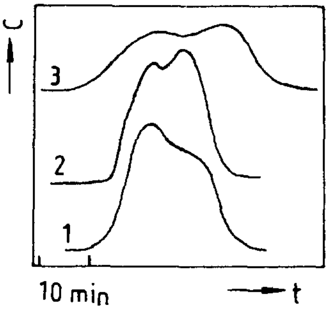

**Fig. 1** tpd curves for $NH_3$
1: $T = T_o + 10 \cdot t$
2: $1/T = 1/T_o - 3 \cdot 10^{-5} \cdot t$
3: $1/T = 1/T_o - 2 \cdot 10^{-5} \cdot t$

tent of the zeolite. In every case two overlapping peaks result which can be attributed to the $NH_3$ desorption from "LF" OH groups (low temperature peak) and from the "HF" OH groups (high temperature peak), respectively /9, 14/. Only if a hyperbolic temperature schedule is used the desorption maximum of the higher temperature is visible clearly /15/. With the activation energy of the first peak estimated approximately and the activation energy of peak 2 calculated by several methods /9, 15/ and the $NH_3$ amount according to the both peaks /9/ calculation of the complex desorption curve for several non-linear temperature programmes of the common form

$$dT/dt = Q_n \cdot T^n \qquad Q_n = \text{const.} \qquad n = 1, 2, \ldots$$

is possible assuming additionally the existence of two 1st order desorption steps without readsorption /16/. In fig. 2 calculated desorption curves for several temperature programmes are shown ($E_1$ = 39 kJ/mole, $A_1$ = $1.4 \cdot 10^3$ $min^{-1}$, $E_2$ = 88 kJ/mole, $A_2$ = $8.1 \cdot 10^6$ $min^{-1}$, ratio of $NH_3$ amount peak 1 to peak 2 = 1 : 0.5). In case of linear and hyperbolic heating desorption curves result which show good qualitative agreement with the experiments. Moreover, it can be seen clearly that on increase of the non-linearity of the temperature programme ($n = 3, 4$) the maximum of peak 2 becomes better visible that means the desorption process is less influenced by the desorption according peak 1. This is of advantage for kinetic evaluation (use of half wide for calculation of the activation energy). Besides, in case of exponential heating one can see that the heating parameter $Q_n$ is only of low influence on the desorption course /17/ therefore the maximum of peak2 is better visible at lower heating rates. At increasing non-linearity ($n > 1$) this influence does not exist any longer /16, 17/ and so the course of desorption only depends on n. For other examples of overlapping of two desorption steps it could be shown that the use of temperature schedules with n = 4 or 5 allows a

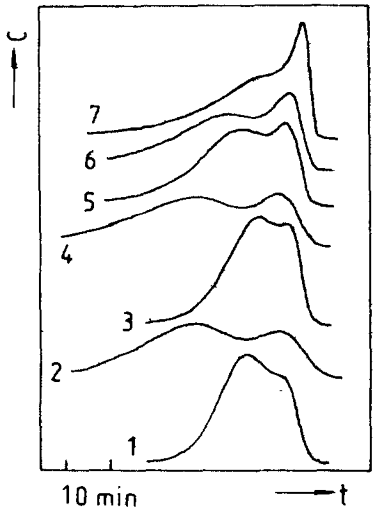

Fig. 2 Calculated tpd curves for

1: $T = T_o + 10 \cdot t$
2: $T = T_o \exp(0.01 \cdot t)$
3: $T = T_o \exp(0.02 \cdot t)$
4: $1/T = 1/T_o - 2 \cdot 10^{-5} \cdot t$
5: $1/T = 1/T_o - 3 \cdot 10^{-5} \cdot t$
6: $1/T^2 = 1/T_o^2 - 1 \cdot 10^{-7} \cdot t$
7: $1/T^3 = 1/T_o^3 - 3.6 \cdot 10^{-10} \cdot t$

good visibility of the desorption maxima of both steps /16/. Therefore it is necessary in every case to check which temperature programme is best suitable for a special problem.

When characterizing acidic properties of HY zeolites by bases which are able to enter the supercage of the zeolites by reason of their diameter so one obtains information about catalytically active acid centres. Fig. 3 shows desorption of N-methylpyrrolidine for a linear temperature programme with different heating rates. The amount of desorbed base in this case corresponds to the "HF" OH group content of the HNaY (88 %) (OH groups in the supercage). The relatively unique peak is describable well by a $1^{st}$ order rate equation without readsorption for a relatively large range of coverage degree. In tab. 1 the activation energies are summarized obtained by different methods. When the heating rate is changed one obtains somewhat different values, but changing only in the range of errors and not representing a significant dependence. Thus the obtained activation energy (together with tpd results of different sample amounts and arrangement of the sample) can be considered as independent of the experimental conditions and therefore represents a suitable measure for the

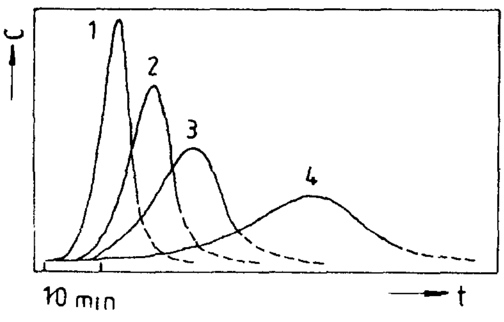

Fig. 3 tpd curves for N-methylpyrrolidine
1: 10 K/min, 2: 6 K/min,
3: 4 K/min, 4: 2 K/min

strength of interaction of bases with OH groups.

Tab. 1 Results of kinetic evaluation

| heating rate (K/min) | method | range of coverage | E (kJ/mole) | corr. coeff. |
|---|---|---|---|---|
| 2 | 1 | 0.98-0.29 | 225.0±12.3 | 0.99949 |
| | 2 | 0.98-0.41 | 227.2±19.7 | 0.99701 |
| | 3 | - | 223.3 | - |
| 4 | 1 | 0.98-0.35 | 203.2±18.8 | 0.99918 |
| | 3 | - | 203.1 | - |
| 6 | 1 | 0.96-0.34 | 218.0±23.2 | 0.99912 |
| | 3 | - | 218.4 | - |
| 10 | 1 | 0.98-0.27 | 195.7±16.3 | 0.99949 |
| | 2 | 0.97-0.27 | 199.7±10.5 | 0.99902 |
| | 3 | - | 199.7 | - |

method: 1: $\ln(-d\theta/dt \cdot 1/\theta) = \ln A - E/RT$, 2: Freeman and Carroll /18/, 3: Chan, Aris and Weinberg /19/

## REFERENCES

/1/ D. Barthomeuf, "Catalysis by Zeolites" (B. Imelik et al Eds.) Elsevier Sci. Publ. Company, Amsterdam, 1980, p. 55
/2/ H.A. Benesi, J. Phys. Chem. 61 (1957) 970
/3/ E.P. Parry, J. Catal. 2 (1963) 371
/4/ P.A. Jacobs, B.K.B. Theng and J.B. Uytterhoeven, J. Catal. 26 (1972) 175, 191
/5/ H. Itoh, T. Hattori and Y. Murakami, Chem. Lett. 8 (1981) 1147
/6/ N.-Y. Topsoe, K. Pedersen and E.G. Derouane, J. Catal. 70 (1981) 41
/7/ C.V. Hidalgo, H. Itoh, T. Hattori, M. Niwa and Y. Murakami, J. Catal. 85 (1984) 362
/8/ J.G. Post and J.H.C. Hooff, Zeolites 4 (1984) 9
/9/ J. Hoffmann, B. Hunger, U. Streller, Th. Stock, D. Dombrowski and A. Barth, Zeolites in the press
/10/ B. Hunger and J. Hoffmann, React. Kinet. Catal. Lett. in the press
/11/ J. Hoffmann, D. Dombrowski, B. Hunger and B. Staudte, Zeolites 4 (1984) 240
/12/ J. Hoffmann, B. Hunger and A. Barth, Z. Chem. 19 (1979) 389
/13/ D. Dombrowski, J. Hoffmann, B. Hunger and A. Barth, Z. phys. Chemie, Leipzig 261 (1980) 649
/14/ P. Chu, J. Catal. 43 (1976) 346
/15/ B. Hunger and J. Hoffmann, J. Thermal Anal. 27 (1983) 353
/16/ B. Hunger and J. Hoffmann, J. Thermal Anal. in the press
/17/ H. Anderson, E. Witte and D. Haberland, J. Thermal Anal. 21 (1981) 327
/18/ E.S. Freeman and B. Carroll, J. Phys. Chem. 62 (1958) 394
/19/ C.-M. Chan, R. Aris and W.H. Weinberg, Appl. Surf. Sci. 1 (1978) 360