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KINETIC ANALYSIS OF NH_3 TEMPERATURE PROGRAMMED DESORPTION (TPD) ON A HZSM-5 ZEOLITE

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ABSTRACT

By means of a kinetic evaluation using several methods it could be shown that the high-temperature peak of the temperature programmed desorption (TPD) of ammonia (γ-peak) is well described by a rate equation of first order considering a linear dependence of the activation energy on the degree of coverage ($E_d = E_d^0 - \gamma\theta$). The activation energies obtained for different amounts of ammonia agree well with differential heats of adsorption of NH_3 given in the literature.

INTRODUCTION

TPD of ammonia is a useful method for characterizing the acidic properties of HZSM-5 zeolites [1–8]. The kinetics of this desorption process have received little attention up to now [3,4]. For HNaY zeolites it has been shown that the activation energy for the desorption process of ammonia from the acidic OH groups located inside the supercage represented a suitable measure of acid strength of the latter [9]. The aim of the present work was, therefore, to obtain detailed information about the kinetics of ammonia desorption on HZSM-5 by means of more extensive TPD studies.

EXPERIMENTAL

The apparatus used was similar to that of Cvetanovic and Amenomiya [10] and has been described earlier [11,12]. Heat conductivity and flame ionization detectors together served as detectors. Before adsorption of ammonia the HZSM-5 ($H_{3.84}(AlO_2)_{3.84}(SiO_2)_{92.16}$, water content 6%, amount of the sample 0.5 g), mixed with 1 g of quartz of equal grain size (0.2–0.4 mm), was pretreated in He flow ($3\ l\ h^{-1}$) at 820 K for 2 h. The adsorption of NH_3 was carried out at different temperatures with 5 vol% NH_3 in He flow ($3\ l\ h^{-1}$) for 30 min. Finally the zeolite was flushed with He for 1 h at the adsorption temperature. The desorption using He as carrier gas ($3\ l\ h^{-1}$) was

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brought about by various temperature programmes (linear 2–20 K min^{-1}, hyperbolic $1/T = 1/T_0 - 3 \times 10^{-5}\ t$). In order to detect the total ammonia desorbed, the stream of helium was led through 0.2 M H_2SO_4 in some experiments and the content of NH_3 determined by back titration.

RESULTS AND DISCUSSION

As Fig. 1 shows the HZSM-5 zeolite investigated adsorbs NH_3 up to 770 K irreversibly under the conditions described. TPD yields differently structured desorption curves depending upon the amount of NH_3 adsorbed (see Fig. 2), representing three typical ranges of desorption (α-, β- and γ-peaks) in agreement with the literature [2,3,7,8]. These three ranges also result in the case of non-linear heating (see Fig. 3), indicating a desorption from adsorption centres of different strength. The position of the desorption maxima and the amount of NH_3 desorbed at the different ranges strongly depends on the amount preadsorbed. Both desorption maxima, resulting from that amount of ammonia (curve 4 in Fig. 2) which accords closest to the H^+ content of the zeolite (0.66 mmol g^{-1}), are ascribed to the desorption from different strength acid sites (Brönsted and Lewis acid sites) as supported by IR studies [1,3].

The catalytic properties of HZSM-5 zeolites are determined first by acid sites which correspond to the high-temperature bonded form of the NH_3 (γ-peak) [2,4]. In this case a non-structured TPD curve is also obtained when using several linear temperature programmes (Fig. 4). Kinetic evaluation was therefore carried out only in the case of this peak.

Assuming the validity of a first-order desorption process [4], calculation of the activation energy of desorption, E_d, and of the pre-exponential factor, A, is possible in the following ways:

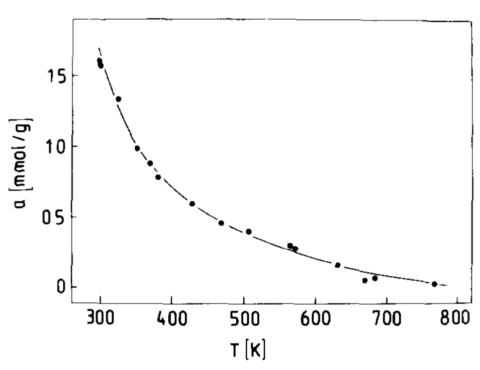

Fig. 1. Irreversibly adsorbed amount of ammonia in dependence on temperature.

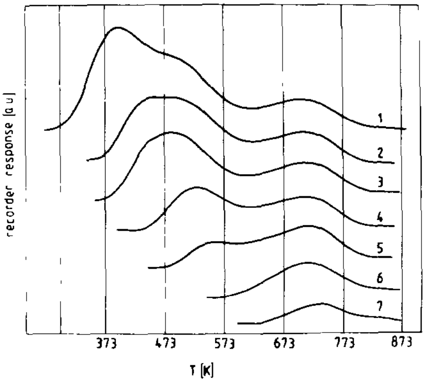

Fig. 2. TPD curves (10 K min^{-1}) for different amounts of ammonia (mmol g^{-1}): (1) 1.70, (2) 1.05, (3) 0.83, (4) 0.63, (5) 0.48, (6) 0.30, (7) 0.16.

(1) Dependence of the peak-maximum temperature T_m on the heating rate α [10]:

$$2 \ln T_m - \ln \alpha = \ln(E_d/AR) + E_d/RT_m \qquad (1)$$

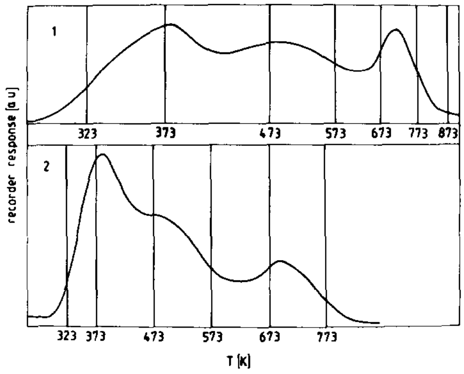

Fig. 3. TPD curves for different heating schedules (1.70 mmol g^{-1} NH_3): (1) $1/T = 1/T_0 - 3 \times 10^{-5}\, t$; (2) $T = T_0 + 10\, t$.

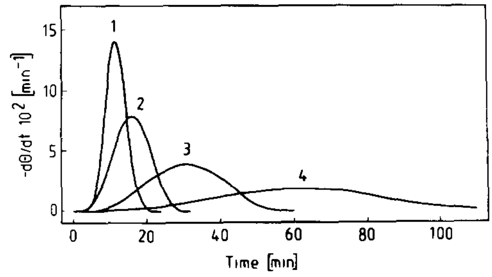

Fig. 4. TPD curves of the γ-peak for different linear heating rates: (1) 20 K min^{-1}, (2) 10 K min^{-1}; (3) 4 K min^{-1}, (4) 2 K min^{-1}.

TABLE 1

Results of kinetic evaluation using $-\mathrm{d}\theta/\mathrm{d}t = \theta A \exp(-E_d/RT)$

Heating rate (K min^{-1})	θ_0	Method of evaluation	E_d (kJ mol^{-1})	A (min^{-1})
2–20	1	eqn. (1)	145.5	2.04×10^{10}
10	1	eqn. (2)	66.4	1.43×10^{4}
10	1	eqn. (3)	73.6	5.42×10^{4}
10	1	eqn. (4)	68.0	1.92×10^{4}
2	1	eqn. (3)	85.8	2.35×10^{5}
2	1	eqn. (4)	77.7	5.00×10^{4}

(2) Linearizing the differential rate equation:

$$\ln[-\mathrm{d}\theta/\mathrm{d}t(1/\theta)] = \ln A - E_d/RT \tag{2}$$

where θ = degree of coverage of the γ-peak, $\theta = 1$ corresponds to 0.30 ± 0.04 mmol g^{-1} NH_3.

(3) Width of the peak at half ($\Delta W_{1/2}$) or, respectively, at three-quarters ($\Delta W_{3/4}$) of the maximum height [13]:

$$\frac{E_d}{RT_m} = \left(1 + \frac{5.832\ T_m^2}{\Delta W_{1/2}^2}\right)^{1/2} - 1 \tag{3}$$

$$\frac{E_d}{RT_m} = \left(1 + \frac{2.353\ T_m^2}{\Delta W_{3/4}^2}\right)^{1/2} - 1 \tag{4}$$

The parameters calculated by these methods (Table 1) depend on the method used and show a systematic change in the case of E_d taken from eqns. (3) and (4). However, in no case is the description of the whole desorption curve possible, as shown in Fig. 5 for the example $\alpha = 10$ K min^{-1}. A reason for this could be that the activation energy depends on the degree of coverage resulting from the desorption from centres of different strength, viz;

$$-\mathrm{d}\theta/\mathrm{d}t = \theta A \exp[-E_d(\theta)/RT] \tag{5}$$

with:

$$E_d(\theta) = E_d^0 + \mathrm{f}(\theta) \tag{6}$$

where E_d^0 = activation energy at $\theta = 0$.

For the dependence of the peak-maximum temperature on the heating rate one obtains, therefore:

$$2 \ln T_m - \ln \alpha = \ln\left(\frac{E_d^0 + \mathrm{f}(\theta)_m}{AR}\right) + \frac{E_d^0 + \mathrm{f}(\theta)_m}{RT_m} - \ln\left(1 - \frac{\theta_m \mathrm{f}'(\theta)_m}{RT_m}\right) \tag{7}$$

and for the slope:

$$\frac{\mathrm{d}[\ln(T_m^2/\alpha)]}{\mathrm{d}(1/T_m)} = \frac{E_d^0 + \mathrm{f}(\theta)_m}{R} - \left(\frac{1}{T_m} - \frac{R}{\theta_m \mathrm{f}'(\theta)_m}\right)^{-1} \tag{8}$$

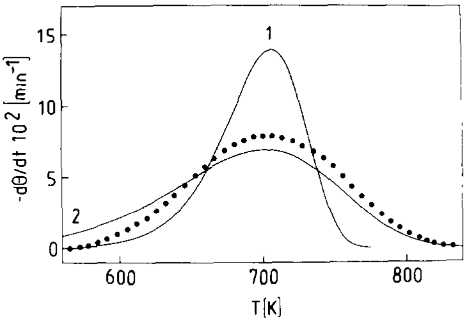

Fig. 5. Calculated TPD curves for the γ-peak (10 K min^{-1}; $\theta_0 = 1$): (1) $-d\theta/dt = \theta \times 2.04 \times 10^{10} \exp(-145500/RT)$, (2) $-d\theta/dt = \theta \times 1.43 \times 10^4 \exp(-66400/RT)$, (●) digitized experimental data.

Assuming θ_m to be independent of T_m and the second term on the right-hand side of eqn. (8) to be relatively small [14], one may calculate $E_d^0 + f(\theta)_m$ and A from the resulting linear relation (see Fig. 6). Using the transposed eqn. (5):

$$-RT\left[\ln\left(-\frac{d\theta}{dt}\frac{1}{A\theta}\right)\right] = E_d^0 + f(\theta) \tag{9}$$

the dependence of the activation energy of the degree of coverage can be determined. In Fig. 7 this relationship is shown for 10 K min^{-1} and the initial degree of coverage $\theta_0 = 1$. A good linear relation in the range $\theta = 0.2$–0.95,

$$E_d^0 + f(\theta) = E_d^0 - \gamma\theta \tag{10}$$

is obtained at other heating rates and, respectively, for lower initial degrees of coverage (see Table 2). An estimation of the second term on the right-hand side of eqn. (8) using the values obtained shows that this term represented only ~ 3% of the slope, and therefore ignoring it seems to be

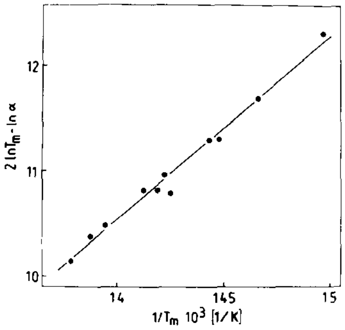

Fig. 6. 2ln T_m − ln α versus $1/T_m$ for the γ-peak.

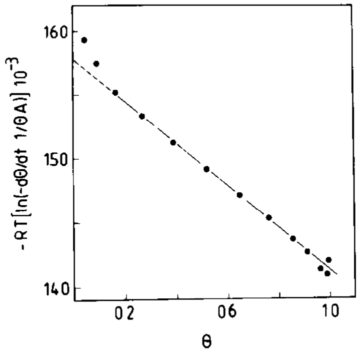

Fig. 7. $-RT[\ln(-\mathrm{d}\theta/\mathrm{d}t(1/A\theta))]$ versus θ for the γ-peak (10 K min^{-1}).

reasonable. The calculation of A from this dependence ($T_m(\alpha)$) by this method is novel.

The calculation of γ is also possible from isothermal desorption experiments [15]. For an isothermal desorption one obtains from eqns. (5) and (10):

$$\ln\left(-\frac{\mathrm{d}\theta}{\mathrm{d}t}\frac{1}{\theta}\right)=\ln A-\frac{E_d^0}{RT}+\frac{\gamma}{RT}\theta=K+\frac{\gamma}{RT}\theta \tag{11}$$

By plotting $\ln[-\mathrm{d}\theta/\mathrm{d}t(1/\theta)]$ against θ the value of γ may be calculated from the slope. The calculation of A and E_d^0 is then possible via TPD experiments, i.e:

$$\ln\left(-\frac{\mathrm{d}\theta}{\mathrm{d}t}\frac{1}{\theta}\right)-\frac{\gamma}{RT}\theta=\ln A-\frac{E_d^0}{RT} \tag{12}$$

From Table 2 one can see that the results of both methods of evaluation agree well. By means of these parameters the description of the whole desorption course is possible (Fig. 8). Therefore, the rate equation obtained

TABLE 2

Results of kinetic evaluation using $-\mathrm{d}\theta/\mathrm{d}t=\theta A\exp(-(E_d^0-\gamma\theta)/RT)$

Heating rate (K min^{-1})	θ_0	E_d^0 (kJ mol^{-1})	γ (kJ mol^{-1})	A (min^{-1})
Method 1: A by eqn. (7), E_d^0 and γ by eqn. (9)				
2	1	154.9	13.7	2.04×10^{10}
10	1	157.8	16.5	2.04×10^{10}
10	0.51	158.8	15.9	2.04×10^{10}
Method 2: γ by eqn. (11) (isothermal desorption at 670 K), E_d^0 and A by eqn. (12)				
2	1	163.7	15.3	8.68×10^{10}
10	1	151.5	15.3	7.73×10^{10}
10	0.51	156.8	15.3	1.52×10^{10}

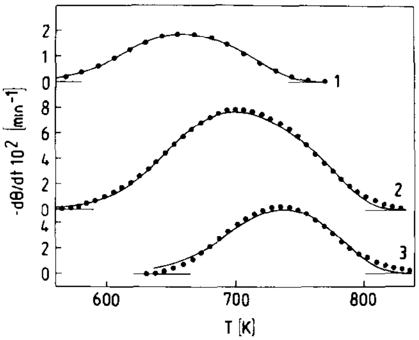

Fig. 8. Calculated TPD curves for the γ-peak: (1) 2 K min^{-1}, $\theta_0 = 1$, $-d\theta/dt = \theta \times 2.04 \times 10^{10} \exp[-(154900 - 13700\theta)/RT]$; (2) 10 K min^{-1}, $\theta_0 = 1$, $-d\theta/dt = \theta \times 2.04 \times 10^{10} \exp[-157800\text{–}16500\theta)/RT]$; (3) 10 K min^{-1}, $\theta_0 = 0.51$, $-d\theta/dt = \theta \times 2.04 \times 10^{10} \exp[-(158800\text{–}15900\theta)/RT]$; (●) digitized experimental data.

by this method could represent a useful relation for the description of the kinetics of the desorption process.

Assuming the activation energy of the adsorption to be very small the calculated activation energies of desorption should be comparable with adsorption energies determined experimentally. Differential heats of adsorption of ammonia on similarly pretreated HZSM-5 zeolites with a Si/Al ratio close to the zeolite used in this work have been determined by Auroux et al. [16,17] by means of microcalorimetric measurements. These adsorption heats decrease nearly linearly in the range of coverage of 0–6.5 ml g^{-1} from about 154 to 138 kJ mol^{-1}, which is in good agreement with the linear decrease of the activation energies from 157.9 ± 5.0 to 141.9 ± 5.0 kJ mol^{-1} obtained in our work. From a coverage of 6.5 ml g^{-1} up to about 14 ml g^{-1} the adsorption heat decreases more strongly. This range of coverage, however, corresponds to the NH_3 amount desorbed in connection with the β-peak, thus it should be reasonable to assign this desorption to less acidic sites which obviously represent a broader spectrum of acid strengths than in the case of the γ-peak. A kinetic analysis of the β-peak, however, involves serious difficulties because of a relatively strong overlapping with the α-peak and was not the object of this work.

REFERENCES

1 C.V. Hidalgo, H. Itoh, T. Hattori, M. Niwa and Y. Murakami, J. Catal., 85 (1984) 362.
2 J.R. Anderson, K. Foger, T. Mole, R.A. Rajadhyaksha and J.V. Sanders, J. Catal., 58 (1979) 114.
3 N.-Y. Topsoe, K. Pedersen and E.G. Derouane, J. Catal., 70 (1981) 41.
4 J.G. Post and J.H.C. van Hooff, Zeolites, 4 (1984) 9.
5 J. Novàkovà, L. Kubelkovà, K. Habersberger and Z. Dolejsek, J. Chem. Soc., Faraday Trans. 1, 80 (1984) 1457.

6 K.F.M.G.J. Scholle, A.P.M. Kentgens, W.S. Veeman, P. Frenken and G.P.M. van der Velden, J. Phys. Chem., 88 (1984) 5.

7 P.A. Jacobs, J.B. Uytterhoeven, M. Steyns, G. Froment and J. Weitkamp, Proc. 5th Int. Conf. on Zeolites, Naples, Italy, 1980, Heyden, London, 1980, p. 607.

8 P.A. Jacobs, J.A. Martens, J. Weitkamp and H.K. Beyer, Discuss. Faraday Soc., 72 (1981) 353.

9 J. Hoffmann, B. Hunger, U. Streller, Th. Stock, D. Dombrowski and A. Barth, Zeolites, 5 (1985) 31.

10 R.J. Cvetanovic and Y. Amenomiya, Advances in Catalysis, Vol. 17, p. 103, Academic Press, New York, 1967.

11 J. Hoffmann, B. Hunger and A. Barth, Z. Chem., 19 (1979) 389.

12 D. Dombrowski, J. Hoffmann, B. Hunger and A. Barth, Z. Phys. Chem. (Leipzig), 261 (1980) 649.

13 C.-M. Chan, R. Aris and W.H. Weinberg, Appl. Surf. Sci., 1 (1978) 360.

14 P.T. Dawson and Y.K. Peng, Surface Sci., 33 (1972) 565.

15 R. Spinicci, J. Therm. Anal., 29 (1984) 1061.

16 A. Auroux, P.C. Gravelle, J.C. Vedrine and M. Rekas, Proceedings, 5th Int. Conf. on Zeolites, Naples, Italy, 1980, Heyden, London, 1980, p. 433.

17 A. Auroux, V. Bolis, P. Wierzchowski, P.C. Gravelle and J.C. Vedrine, J. Chem. Soc., Faraday Trans. 1, 75 (1979) 2544.