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TEMPERATURE-PROGRAMMED DESORPTION (TPD) OF AMMONIA FROM H$^+$-EXCHANGED ZEOLITES WITH DIFFERENT STRUCTURES

B. Hunger and *J. Hoffmann*

DEPARTMENT OF CHEMISTRY, KARL MARX UNIVERSITY,
LEIPZIG, G.D.R. 7010

Curves of the temperature-programmed desorption (TPD) of ammonia from zeolites were evaluated with several kinetic models. An approximately linear correlation was found between the activation energy of desorption or the heat of adsorption of H zeolites with various Si/Al ratios and the intermediate electronegativity of the zeolites, the latter representing a measure of the acid strength.

This result corresponds to the change in the high-frequency infrared band of the OH groups and also to the change in the heat of adsorption, determined by microcalorimetry. Thus, the TPD of NH_3 is a useful technique for quantitative characterization of the acidic properties of several H zeolites.

For characterization of the Brönsted-acidic properties of the H forms of zeolites, ammonia is a suitable probe molecule, because of its molecular dimensions and base strength. Thus, besides IR spectroscopy [1], microcalorimetry [2–7], magic angle spinning magnetic resonance (^{1}H MAS NMR [8], ^{15}N MAS NMR [9]) and other methods [10, 11], temperature-programmed desorption (TPD) is often used to determine the number and strength of acidic OH groups [1, 12–20].

The "high-temperature peak" in the TPD of NH_3 is attributed above all to the desorption of ammonia from acidic OH groups of the zeolites which are characterized by the high-frequency band in the IR spectrum. These OH groups also mainly determine the catalytic properties of these zeolites. In the case of HY zeolites, it could be shown that the variation in the activation energy of NH_3 desorption from the OH groups inside the supercage displays a good linear correlation with the increasing acid strength, depending on the increasing degree of exchange of H$^+$ [17]. However, the literature to date contains almost no information about a quantitative characterization of the acid strength of H zeolites with different Si/Al ratios and different structures through the TPD of NH_3.

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Experimental

All investigations were carried out in a conventional flow apparatus. Desorption products were recorded by means of a heat conductivity detector (H_2O and NH_3) and a flame ionization detector (NH_3). The activation of the zeolites and the experimental performance of NH_3 adsorption have been described previously [17–19].

For each experiment, 0.05 g of zeolite, diluted with 1 g of quartz of equal grain size (0.2–0.4 mm), was used. Desorption was performed in flowing (3 l h^{-1}) helium gas with linear temperature programmes (2–20 deg min^{-1}).

Results and discussion

Figure 1 shows the dependence of the maximum temperature of the high-temperature peak (corresponding to different NH_3 amounts, see Table 1) on the intermediate electronegativity (S_{int}), a measure of the change in the acidic properties with the H^+ content and the Si/Al ratio [21]. The maximum at $S_{int}=4.1$ agrees with literature data [1, 12, 15, 16], but the increase in acid strength with increasing Si/Al ratio [22] is neglected. A reason for this discrepancy could be the different shapes of the desorption curves (see Fig. 2), suggesting that different kinetic models are necessary to describe the desorption. Therefore, a kinetic evaluation was carried out with different rate equations:

1. 1st order without readsorption:

$$-d\theta/dt = \theta \cdot A_d \cdot \exp(-E_d/RT) \tag{1}$$

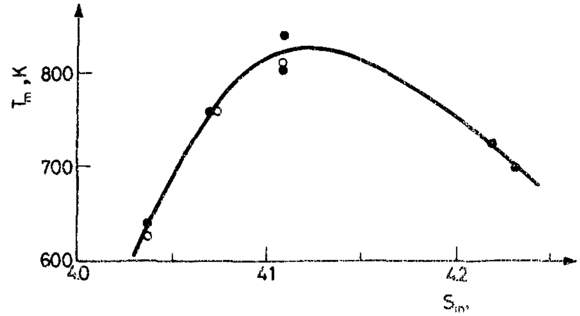

Fig. 1 Temperature of peak maximum vs. intermediate electronegativity of the zeolites: mass of zeolite: ○ 50 mg, ◐ 100 mg, ◒ 200 mg, ● 500 mg, heating rate 10 deg min^{-1}

Table 1 Composition of the zeolites and amount of desorbed NH_3

Zeolite	Si/Al	H^+ content (mmol g^{-1})	Amount of desorbed ammonia		S_{int}[2]
			(mmol g^{-1})	(molecules NH_3 nm^{-3})[1]	
HY	2.6	4.02	1.25	0.96	4.0373
H erionite	3.0	3.83	2.44	2.32	4.0712
H mordenite	5.0	2.34	2.30	2.39	4.1082
HZSM-5 (15)	15.0	1.04	0.59	0.63	4.2190
HZSM-5 (24)	24.0	0.67	0.30	0.32	4.2321

[1] calculated according to the framework density [32]

[2] calculated according to [21]

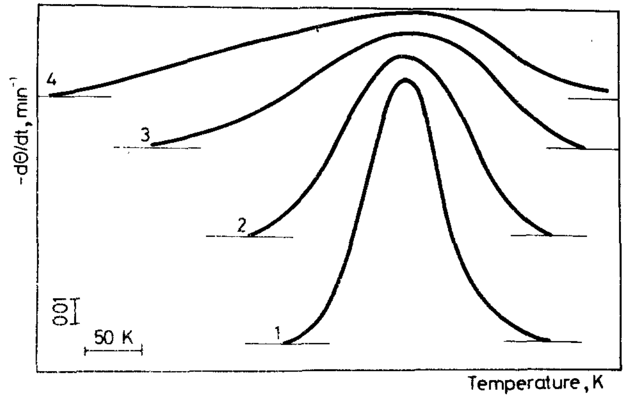

Fig. 2 Normalized TPD curves (area of curves): *1:* HY, *2:* HZSM-5(24), *3:* H mordenite, 4: H erionite, heating rate 10 deg min^{-1}

2. 1st order with readsorption:

$$-d\theta/dt = [\theta/(1-\theta)]\cdot A_{ads}\cdot \exp(-\Delta H_{ads}/RT) \tag{2}$$

3. 1st order without readsorption, with the activation energy depending on the degree of coverage:

$$-d\theta/dt = \theta\cdot A_d\cdot \exp(-E_d(\theta)/RT) \tag{3}$$

The values of A_d, A_{ads}, E_d, ΔH_{ads}, $E_d(\theta)$ and E_{dm} (activation energy at peak maximum) were estimated by various methods:

1. heating rate variation [18, 23, 24];
2. normalized curve treatment [25];

Table 2 Results of kinetic evaluation

Zeolite	Rate equation	Method evaluation	ΔH_{ads}, E_d, E_{dm} (kJ/mol)	Ref.
HY	1	1	90.5	17
		2	107.9	
		3	88.4	17
		4	89.1	
H erionite	2	3	71.6	
		4	74.1	
H mordenite	2	1	130.0	
		3	124.1	
		4	122.4	
HZSM-5 (15)	3 $E(\theta) = E_d^\circ - \gamma\theta$	2	131.0 $E_d^\circ = 142.6$ $\gamma = 21.3$	
		1	145.5	18
		2	136.6	
HZSM-5(24)	3 $E(\theta) = E_d^\circ - \gamma\theta$	3	149.6 $E_d^\circ = 157.8$ $\gamma = 16.5$	18
		4	145.5 $E_d^\circ = 153.7$ $\gamma = 15.9$	

3. linear regression (differential rate equation);
4. non-linear regression (differential rate equation).

The results are shown in Table 2 in each case for the rate equation which yielded agreeing parameters for all methods used. Figure 3 compares the experimental curves and the calculated ones. The course of the curves is described relatively well in all cases, and therefore the use of different rate equations seems to be reasonable. The necessity to take readsorption into account in the case of H erionite and H mordenite can be explained by the essentially larger amount of adsorbed ammonia per volume unit (see Table 1) compared to other zeolites, and therefore by a relatively high probability of freely-occurring readsorption. The dependence of the peak-maximum temperature on the electronegativity (Fig. 1) should not be an expression of the acid strength, because freely-occurring readsorption shifts the desorption towards higher temperatures [26, 27], and in the case of a linear decrease of activation energy with increasing degree of coverage (HZSM-5), a peak maximum results at lower temperatures as compared to the activation energy at a coverage degree of zero [28].

If the activation energy of adsorption is assumed to be very low, the calculated activation energies of desorption should be directly comparable to the heats of

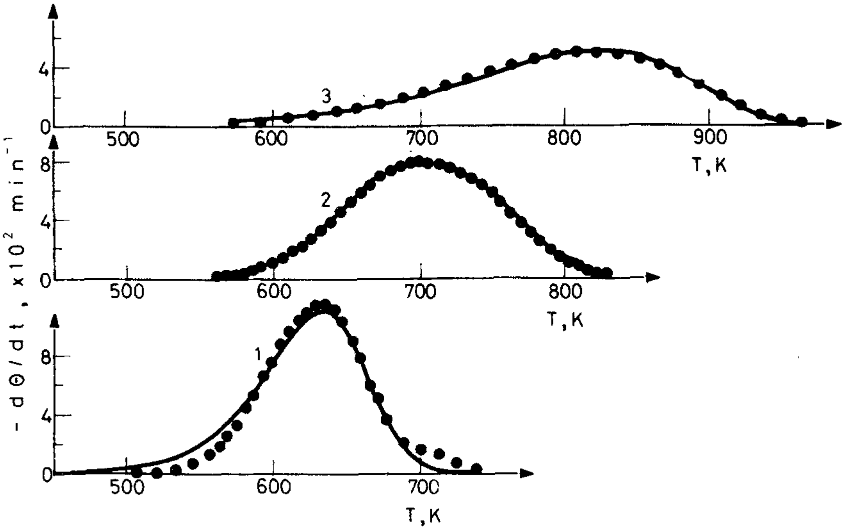

Fig. 3 Calculated TPD curves (10 deg $\min^{-1}$, $\theta_0 = 1$): *1:* HY, $-\mathrm{d}\theta/\mathrm{d}t = \theta \cdot 7.61 \cdot 10^6 \cdot \exp(-(90460/RT)$, *:* HZSM-5(24), $-\mathrm{d}\theta/\mathrm{d}t = \theta \cdot 7.9 \cdot 10^9 \cdot \exp[-(153701 - 15915 \cdot \theta)/RT]$, *3:* H mordenite, $-\mathrm{d}\theta/\mathrm{d}t = [\theta/(1-\theta)] \cdot 5.6 \cdot 10^6 \cdot \exp(-124060/RT)$, ● digitized experimental data

adsorption measured by microcalorimetry. Figure 4 compares the mean values of the parameters obtained at the peak maximum with heats of adsorption taken from the literature, using values which correspond to the degree of coverage at the peak maximum. The relatively low value for H erionite was not considered, because of a possible marked diffusional influence resulting from the lower pore width (0.36 × 0.52 nm, [29]), indicated by the apparent activation energies and heats of adsorption. Moreover, no heats of adsorption of ammonia on this zeolite ar

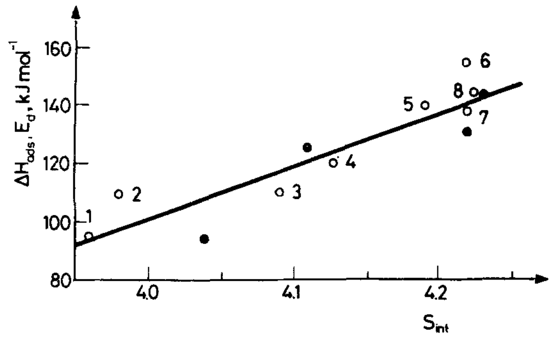

Fig. 4 Results of kinetic evaluation (●) in comparison with literature heats of adsorption: *1:* Ref. [2], *2:* Ref. [3], *3:* Ref. [5], *4:* Ref. [4], *5:* Ref. [3], *6:* Ref. [6], *7:* Refl [7], *8:* Ref. [7]

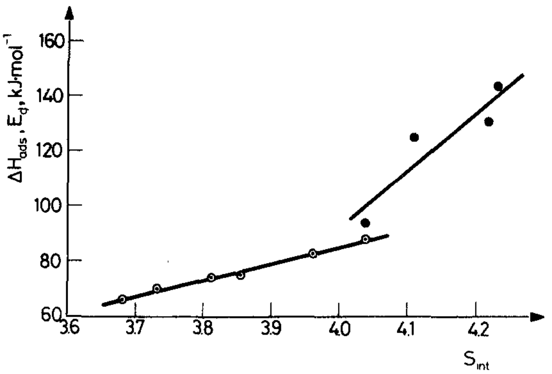

Fig. 5 Energy of activation and heat of adsorption, vs. intermediate electronegativity of the zeolites: ⊙: Ref. [17]

available in the literature. For the other zeolites, the adsorption heats and activation energies estimated by both methods increase approximately linearly with the electronegativity. This can be correlated with the decrease in the frequency of the infrared OH stretching vibration [30], and also with CNDO/2 calculations on the interaction of ammonia with OH groups [31]. A noteworthy finding in this connection is that H erionite does not yield a correlation between the high-frequency band and the electronegativity, likewise explainable by electrostatic or crystal-field effects [30]. Figure 5 shows the approximately linear increase of activation energy or heat of adsorption determined by means of TPD experiments with increasing intermediate electronegativity of the H zeolites. For the zeolites used here, the raise in electronegativity is caused by an increase of the H^+ content of the HY zeolite up to $S_{int} = 4.05$ [17] and then the Si/Al ratio increases (results of this paper). In the case of a raising Si/Al ratio, the increase in acidic strength expressed by the increase in the heat of adsorption and the activation energy is markedly higher than that due to the increase in OH group content at constant Si/Al ratio. Since this result corresponds to the decreasing frequency of the h.f. band in the IR spectrum [22], the TPD results should provide a reasonable quantitative characterization of the acid strength of H zeolites if the pores are not too small.

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Zusammenfassung — Kurven der temperaturprogrammierten Desorption (TPD) des Ammoniak von Zeolith wurden mit verschiedenen Kinetischen Modellen ausgewertet. Ein annähernd linearer Zusammenhang wurde gefunden zwischen der Aktivierungsenergie der Desorption bzw. der Adsorptionswärme von NH_3 an H-Zeolithen mit unterschiedlichem Si/Al-Verhältnis und der intermediären Elektronegativität der Zeolithe, die ein mass für die Säurestärke darstellt. Dieses Ergebnis entspricht der Verschiebung der hochfrequenten IR-Bande der OH-Gruppen und der mikrokalorimetrisch bestimmten Änderungen der Adsorptionswärme. Damit erweist sich die TPD von NH_3 als brauchbare Methode zur quantitativen Charakterisierung der sauren Eigenschaften von H-Zeolithen.

Резюме — С помощью нескольких кинетических моделей проведена оценка кривых температурно-программируемой десорбции аммиака из цеолитов. Установлена приблизительно линейная корреляция между энергией активации процесса десорбции или тепловой адсорбции H-цеолитов с различным соотношением Si/Al и промежуточной электроотрицательностью цеолитов, являющейся мерой их кислотности. Этот результат соответствует изменению высокочастотной ИК полосы поглощения OH групп, а также изменению теплоты адсорбции, найденной с помощью микрокалориметрии. Следовательно, метод температурно-программируемой десорбции аммиака является полезным методом количественной характеристики кислотных свойств некоторых H-цеолитов.