

TEMPERATURE-PROGRAMMED DESORPTION (TPD) OF AMMONIA FROM HZSM-5 ZEOLITES

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The temperature-programmed desorption (tpd) of the amount of ammonia which is preadsorbed at about 373 K at HZSM-5 zeolites yields a complex desorption curve consisting of two overlapped peaks (β and γ peak). Parts of the ammonia desorbed can be attributed to SiOHAl groups considering also ^1H -MAS NMR measurements.

The course of the desorption of both peaks is describable by a rate equation which considers a dependence of the desorption energy on the degree of coverage or an energy distribution, as could be shown by various methods of evaluation. The calculated dependence of the desorption energy on the ammonia amount adsorbed well agrees with data of literature of adsorption heats determined micro-calorimetrically.

Temperature-programmed desorption (tpd) of bases [3, 4-7, 20-31] is, beside of IR spectroscopy [1-9], ^1H -MAS-NMR spectroscopy [10-16] and microcalorimetry [2, 8, 9, 17-20] a method frequently used for the characterization of acidic properties of HZSM-5 zeolites.

Tpd of ammonia adsorbed at low temperature provides 3 peaks more or less strongly overlapped (α , β or LT, and γ or HT peak [7, 20]), which are ascribed to acidic centres of different strength. The α peak is ascribed in this case to the physisorption of ammonia. The reason for the γ peak is the NH_3 desorption from strongly acidic OH groups, which can be characterized in the IR spectrum by the vibration band at about 3600 cm^{-1} . The β peak is explained in different manner by several authors: Topsøe [7] ascribes this peak to desorption from weak acidic centres according to a IR band in the $3720\text{...}3740\text{ cm}^{-1}$ region or to the adsorption on Na^+ and Hidalgo [5] to a broad IR band at $3350\text{...}3650\text{ cm}^{-1}$. Lok [3] interpretes the peak by splitting of physisorbed ammonia and Schnabel *et al.* [6] discuss a desorption from extra-framework aluminium.

About the kinetics of NH_3 desorption with respect to the β peak only a few data are available in literature [7, 20, 29]. The aim of this work therefore was a complex kinetic analysis of the β and γ peak using results of earlier work [30].

Experimental

Tpd

All investigations were carried out using He as carrier gas (3 l/hour). A heat conductivity detector and a flame ionization detector serve as detectors. The NH_3 amount desorbed additionally was analysed in some cases by absorption in 0.05 *m* H_2SO_4 and back titration by NaOH. Desorption of NH_3 occurs by means of several heating schedules ($T = T_0 + \alpha t$, $\alpha = 2\text{...}20$ K per min and $1/T^3 = 1/T_0^3 - 1.03 \times 10^{-10} t$). Two HZSM-5 zeolites of different Si/Al ratio (see Table 1) were used in various amounts (125...500 mg), diluted by 1 g of quartz of the same grain size (0.2...0.4 mm). Pretreatment occurs in a helium stream of 3 l/hour using a heating rate of 10 K per min up to temperatures of 823...1123 K and then holding the system at the corresponding temperature for 1...4 hours. For ammonia adsorption the samples were saturated by a pulse of ammonia at room temperature and then the excess of NH_3 isothermally desorbed at various temperatures by flushing with helium. Moreover, a helium stream of 3 l/hour containing 5 Vol - % of ammonia was used for some experiments in order to preadsorb NH_3 at various temperatures. Both methods of preadsorption resulted in identical tpd curves if considering the same amounts of ammonia. Repeated adsorption/tpd experiments using the same sample did not show any change in the desorption curve.

^1H -MAS NMR

^1H -MAS NMR measurements were carried out at room temperature on a Bruker MSL-300 spectrometer. Sealed samples were spun in a homemade MAS probe at 3 kHz. Using an external standard, the accuracy of concentration is $\pm 10\%$. The samples were pretreated according to shallow-bed activation conditions in a glass tube of 5.5 mm inner diameter and with 10 mm bed-depth of zeolite. The temperature was increased at a rate of 10 K per hour. The samples were kept at the final activation temperature of 670 K under a pressure below 1×10^{-2} Pa for 24 hours, and then cooled and sealed.

Table 1 Composition of the zeolites and desorbed amount of ammonia

	HZSM-5 ₁	HZSM-5 ₂
Si/Al (²⁷ Al MAS NMR)	28	15
Si/Al (ESCA)	13±2	20±2
¹ H-MAS NMR:		
SiOHAl (4.2 ppm), mmol/g	0.55±0.06	0.81±0.08
SiOH (2.1 ppm), mmol/g	0.17	0.10
Tpd:		
desorbed NH ₃ after adsorption at 423 K, mmol/g	0.61±0.06	0.89±0.09
β peak, mmol/g	0.54	0.45
γ peak, mmol/g	0.28	0.60

Results and discussion

Figure 1 shows tpd curves for the HZSM-5₁ zeolite after preadsorption of different amounts of ammonia. The β peak raises and its maximum shifts to lower temperatures with increasing ammonia amount as can be seen from the figure. Curve 4 thereby represents the NH₃ amount where the low-temperature flank shows no shoulder. Thus, this NH₃ amount as well as that of curve 1 and 2 in Fig. 3 for the HZSM-5₂ zeolite can be attributed to the sum of the β and γ peak. The determination of the amounts of the individual peaks (see Table 1) was carried out by stepwise alteration of the pread-

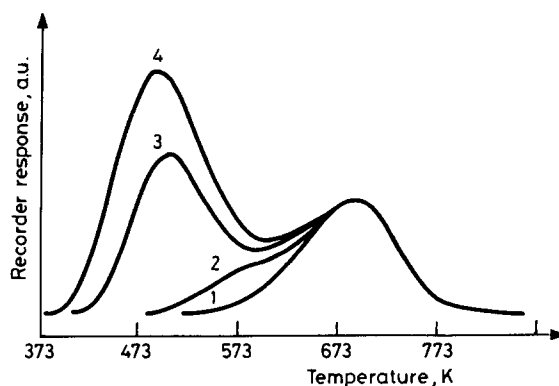


Fig. 1 Tpd curves for different amounts of ammonia on the HZSM-5₁ (250 mg, 10 deg/min):
1: 0.28 mmol/g, 2: 0.42 mmol/g, 3: 0.61 mmol/g, 4: 0.82 mmol/g

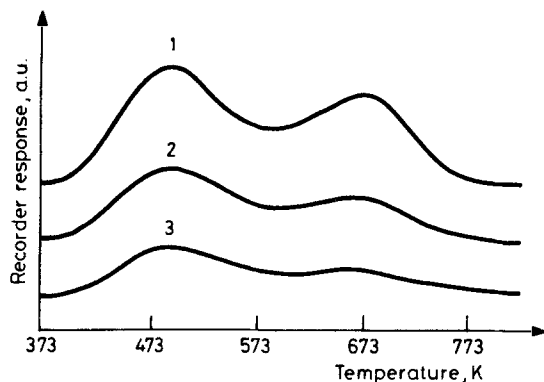


Fig. 2 Tpd curves after different pretreatment temperatures of HZSM-51 (125 mg, 10 deg/min): 1: 2 h, 823 K, 2: 2 h, 1073 K, 3: 6 h, 1073 K

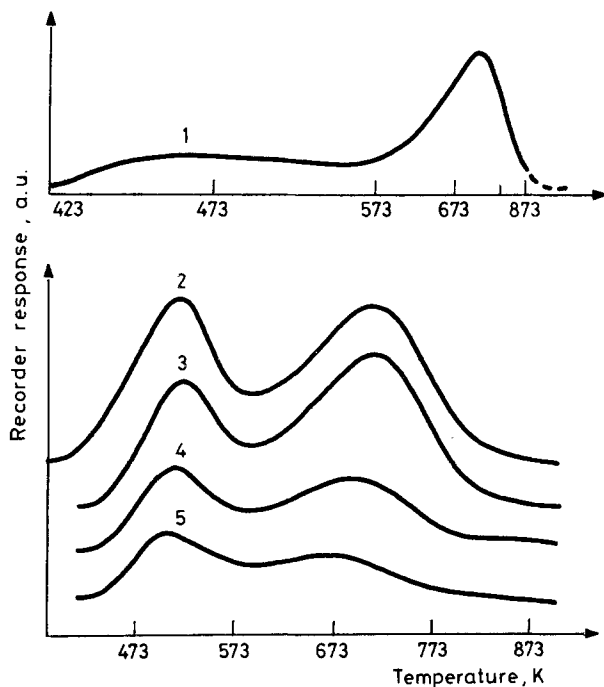


Fig. 3 Tpd curves of the HZSM-52 (200 mg): (pretreatment temperature, NH_3 amount, temperature programme/heating rate) 1: 2 h, 823 K, 1.05 mmol/g, $1/T_3 = 1/T_0^3 - 1.03 \times 10^{-10}$; 2: 2 h, 823 K, 1.05 mmol/g, 10 deg/min; 3: 2 h, 823 K, 0.89 mmol/g, 10 deg/min; 4: 1 h, 1073 K, 10 deg/min; 5: 1 h, 1073 K and 1 h 1123 K, 10 deg/min

sorbed NH_3 amount (about adequate to the γ peak) up to an amount at which at the low-temperature flank of the peak no more shoulder was visible, or, respectively, from the complex desorption curve using a non-linear heating programme (see, for example, curve 1 in Fig. 3).

Figure 4 shows ^1H -MAS NMR spectra for both zeolites. From the intensity (area) of the line at a chemical shift of 4.2 ppm the number of bridging OH groups (SiOHAl) and from that at 2.1 ppm the number of SiOH groups could be estimated [16] (see Table 1).

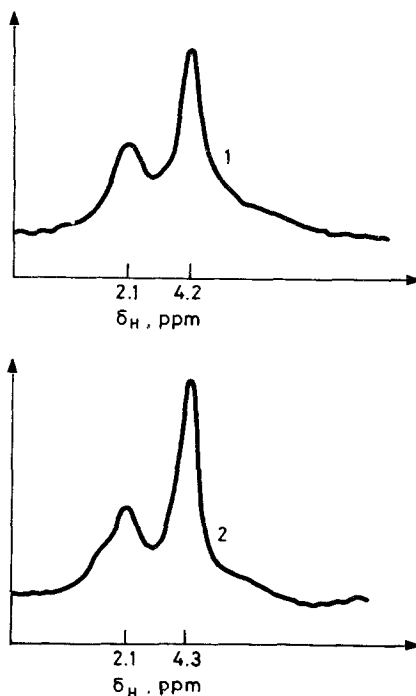


Fig. 4 ^1H -MAS NMR spectra of the zeolites: 1: HZSM-51; 2: HZSM52

Desorption of the ammonia amount corresponding about to the number of SiOHAl groups results for both zeolites in tpd curves which comprise the γ peak and parts of the β peak (Fig. 1, curve 3, and Fig. 3, curve 3), but the portions of both peaks being different (Table 1). Therefore, a part of the β peak should also represent desorption from acidic OH groups of the zeolites. This is in agreement with numerous tpd and microcalorimetric

studies [2, 4, 5, 9, 18, 19, 21, 23] even though the comparison is difficult in some cases.

Moreover, this assumption is supported by the fact that after pretreatment at higher temperatures (dehydroxylation of the zeolite) the intensity of both peaks decreases as shown in Figs 2 and 3 but this effect is lower for both zeolites in case of the β peak. The reason for the fact that in case of the HZSM-5₁ zeolite a greater portion of the acidic OH groups (SiOHA1) corresponds to the ammonia desorption of the β peak could be the more heterogeneous distribution of Al, shown by the large differences in Si/Al ratio when comparing the ²⁷Al-MAS NMR and ESCA results. In order to answer the question why ammonia is bound at the bridging OH groups with different strength further studies are necessary, even though theoretical considerations show that possible different kinds of SiOHA1 groups at HZSM-5 zeolites exist [32].

At first a kinetic analysis of the complex desorption curve (β and γ peak) for the HZSM-5₁ was made assuming a rate equation of 1st order without readsorption by means of the equation of the variation of the peak-maximum temperature in dependence on the heating rate:

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

T_m : temperature of the peak maximum, α : heating rate of the linear temperature programme, A : preexponential factor, E_d : energy of activation.

For all amounts of samples a relatively good linear plot is obtained (see Fig. 5), for the β peak no dependence on the sample amount is perceptible. However, in the case of the γ peak different straight lines result in dependence on the sample amount, but the activation energy calculated from the slope doesn't change systematically in the limits of the experimental error (see Table 2). A reason for the change of the peak-maximum temperature of the γ peak in dependence of the sample amount could be an influence of readsorption as discussed by Kapustin et al. [20]:

$$2 \ln T_m^2 - \ln v_s = \ln [(\alpha \Delta H (1 - \theta_m)^2 v_a) / (RFA_{ads})] + \Delta H / RT_m \quad (2)$$

v_s : sample amount, F : flow rate of the carrier gas, θ_m : degree of coverage at the peak-maximum, ΔH : heat of adsorption, A_{ads} : preexponential factor, v_a : adsorbed amount.

An evaluation using Eq. (2) showed, however, no linear relation and, at low heating rate (2...3 deg/min) indeed a straight line but with an unrealistic high slope. Moreover, the desorption curve using the linearized rate equation for 1st order desorption with readsorption did not provide reasonable results. On the other hand Tronconi and Forzatti [34] could show by means of model calculations that desorption from an energetic heterogeneous surface with readsorption and diffusional influence can be described nearly by a rate equation which was the base of Eq. (1). E_d should be an effective value in this case containing the heat of adsorption and the activation energy of diffusion. Thus an influence of readsorption cannot be excluded even though Eq. (1) is valid.

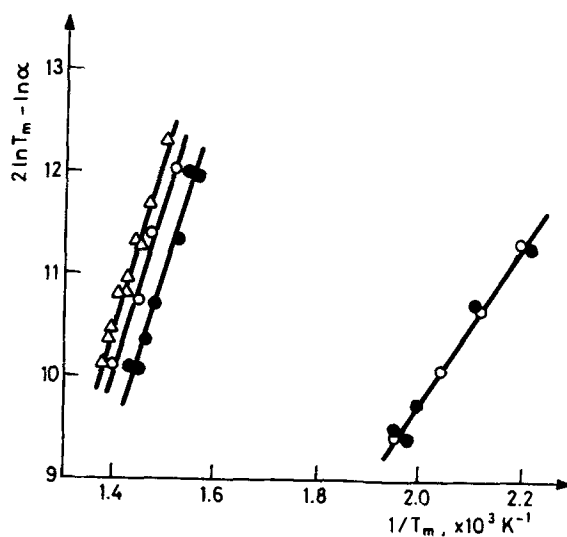


Fig. 5 Plots of $\ln(T_m^2/a)$ against $1/T_m$ for the β and γ peak: Δ : 500 mg; \circ : 250 mg; \bullet : 125 mg

In a previous work [30] we could show that the γ peak of ammonia tpd from a HZSM-5 zeolite is describable with a rate equation of 1st order if a dependence of the desorption energy on the degree of coverage is considered:

$$-d\theta/dt = \theta A \exp[-E(\theta)/RT] \quad (3)$$

In this case an evaluation according Eq. (1) provides the desorption energy at the coverage degree of the peak maximum (E_m) if the dependence

of the coverage degree is not so great [30]. Therefore the determination of the dependence of the desorption energy on the degree of coverage is possible either via approximate estimation of the preexponential factor [30] or from the relation of Forzatti *et al.* [35] for the normalized desorption curve:

$$E(\theta) = RT[E_m / RT_m + \ln(\theta / \theta_m) - \ln(-d\theta / dt) + \ln(-d\theta / dt)_m] \quad (4)$$

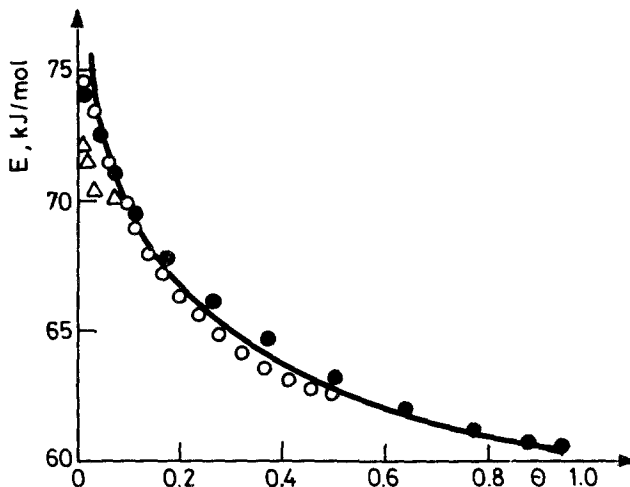


Fig. 6 Energy of desorption in dependence on the degree of coverage of the β peak: \bullet : $\theta_0 = 1$, \circ : $\theta_0 = 0.59$, Δ : $\theta_0 = 0.1$, —: calculated according $E = 60000 - 4100 \ln \theta$

In Figs 6 and 7 the calculated desorption energies are shown in dependence on the degree of coverage for the β peak separated by subtraction of curve 1 from curve 4 (Fig. 1) and for the γ peak in case of different sample amounts, heating rates and initial coverage. For the β peak this dependence can be described by (see Table 2):

$$E(\theta) = E_1 - \beta \ln \theta \quad (5)$$

E_1 : Energy at $\theta = 1$

The course of desorption calculated so (A was estimated from E_m , T_m , θ_m and $(-d\theta/dt)_m$) agrees relatively well with the experimental curve (see Fig. 8). As earlier shown [30] a description of the course of the desorption of the γ peak with a linear dependence of the desorption energy in a range of coverage degree 1...0.2 is well possible:

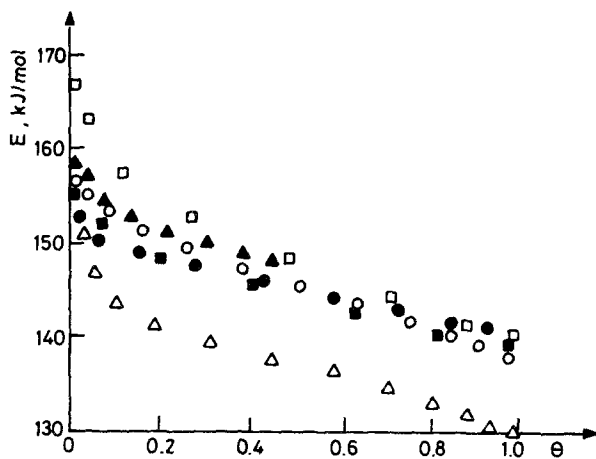


Fig. 7 Energy of desorption in dependence on the degree of coverage of the γ peak: \square : 500 mg, $\theta_0 = 1$, 20 deg/min; \blacksquare : 500 mg, $\theta_0 = 1$, 2 deg/min; \blacktriangle : 500 mg, $\theta_0 = 0.51$, 1 deg/min; \bullet : 500 mg, $\theta_0 = 1$, 4 deg/min; \circ : 500 mg, $\theta_0 = 1$, 1, 10 deg/min; \triangle : 250 mg, $\theta_0 = 1$, 10 deg/min

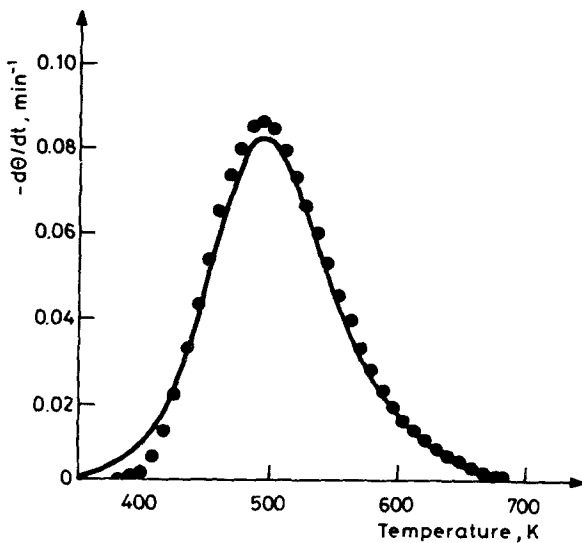


Fig. 8 Calculated β peak in comparison with the experimental data (\bullet):
 $-d\theta/dt = \theta \cdot 6.24 \times 10^5 \exp[-(60000 - 4130 \times \ln \theta) / RT]$

$$E(\theta) = E_0 - \gamma \theta \quad (6)$$

E_0 : energy at $\theta = 0$

The difference of $E(\theta)$ for 250 and 500 mg samples (see Fig. 7) corresponds almost only to the difference of the calculated E_m values (see Table 2), therefore the shape of the peaks doesn't change in dependence of the sample amount.

Table 2 Results of kinetic evaluation

According to Eq. (1)					
Peak	ν_s , mg	E_d/E_m , kJ/mol	A , min^{-1}		
β	125				
	250	62.5±8	1.46x10 ⁶		
γ	125	139.7±9.8	2.25x10 ¹⁰		
	250	137.8±9.2	7.65x10 ⁹		
	500	145.5±15.1	2.04x10 ¹⁰		
β peak: according to Eqs (4) and (5)					
	E_1 , kJ/mol	β kJ/mol	A , min^{-1}		
125, 250 mg θ_0 : 1, 0.59	60.0	4.1	6.24x10 ⁵		
γ peak: according to Eqs (4) and (6)					
ν_s , mg	θ_0	α , K/min	E_0 , kJ/mol	γ , kJ/mol	A , min^{-1}
250	1	10	143.9	13.8	4.89x10 ⁹
500	1	2	151.1	13.0	1.07x10 ¹⁰
500	1	4	150.4	10.6	1.07x10 ¹⁰
500	1	10	153.6	15.7	1.07x10 ¹⁰
500	1	20	157.8	18.8	1.07x10 ¹⁰
500	0.51	10	154.5	14.7	1.07x10 ¹⁰

For further interpretation of the calculated dependence of the desorption energy on the degree of coverage in the sense of desorption from an energetic heterogeneous surface (adsorption centres of different strength) a Monte-Carlo-Simulation of the desorption curves was carried out assuming various energy distributions for a square lattice with 100x100 sites and two kinds of sites [36, 37]. The parameters were chosen according to the results obtained by approximate evaluation. It could be shown that the course of

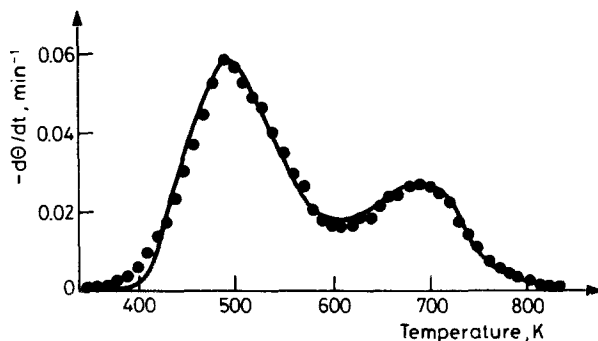


Fig. 9 Simulated tpd curve (●) in comparison with the experimental data (—): β peak: $E_{gm} = 63.5 \text{ kJ/mol}$, $\sigma = 0.08$, $A = 7 \times 10^5 \text{ min}^{-1}$; γ peak: $E = 137.0 \text{ kJ/mol}$, $\sigma = 8.2$, $A = 8 \times 10^9 \text{ min}^{-1}$

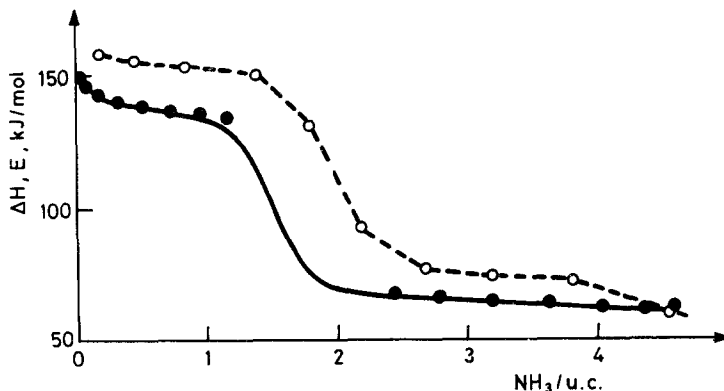


Fig. 10 Calculated energy of desorption in dependence on the adsorbed amount of ammonia: ●: according equation (4), (5) and (6); —: Monte-Carlo-Simulation; - o -: heats of adsorption according ref. [18]

desorption of the β peak is well describable assuming a logarithmic energy distribution:

$$f(E) = 1/[\sigma E(2\pi)^{1/2}] \exp[-(\ln E - \ln E_{gm})^2/\sigma^2] \quad (7)$$

E_{gm} : geometric mean, σ = standard deviation
while in case of the γ peak a normal distribution:

$$f(E) = 1/[\sigma(2\pi)^{1/2}] \exp[-(E - \bar{E})^2/2\sigma^2] \quad (8)$$

\bar{E} mean value, σ : standard deviation

fulfil the desorption results best. Figure 9 shows the simulated curve in comparison with the experimental data. An advantage of Monte-Carlo-Simulation considering an energy distribution is the possibility to calculate the average desorption energy at each degree of coverage very simple. In Fig. 10 the calculated dependence together with the dependence of desorption energy on the degree of coverage according Eqs (5) and (6) is presented. The change of the desorption energy in dependence on the ammonia amount adsorbed agrees relatively well with micro-calorimetrically measured adsorption heats of a similar HZSM-5 zeolite [18]. Therefore the evaluation used here seems to be reasonably. Together with the consideration of a non-negligible influence of physisorption caused by surface curvature effects [38] it seems possible by means of tpd to yield information about the strength of interaction of ammonia with the acidic OH groups.

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Zusammenfassung — Die temperaturprogrammierte Desorption (TPD) einer Menge Ammoniak, die bei 373 K an einem HZSM-5 Zeolithen voradsorbiert wurde, ergibt eine aus zwei einander überlappenden Peaks (γ und β Peak) bestehende komplexe Desorptionskurve. Das desorbierte Ammoniak kann unter Berücksichtigung von ^1H -MAS NMR Messungen auf SiOHAl-Gruppen zurückgeführt werden.

Der Verlauf der Desorption kann für beide Peaks mittels einer Geschwindigkeitsgleichung beschrieben werden, die eine Abhängigkeit der Desorptionsenergie vom Bedeckungsgrad oder eine Energieverteilung berücksichtigt, wie durch verschiedene Wertbestimmungsmethoden gezeigt werden konnte. Die berechnete Abhängigkeit der Desorptionsenergie von der adsorbierten Ammoniakmenge stimmt gut mit Literaturangaben über mikrokalorimetrisch bestimmte Adsorptionswärmen überein.