

CHARACTERIZATION OF THE ACIDIC PROPERTIES OF ZEOLITES BY MEANS OF TEMPERATURE-PROGRAMMED DESORPTION (TPD) OF AMMONIA

Calculation of distribution functions of the desorption energy

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Abstract

Desorption energy distributions were calculated for temperature-programmed desorption (TPD) of ammonia from H zeolites of different type by means of regularization. This method does not require any limiting assumptions about the distribution function. It could be shown that the desorption energy distributions obtained are nearly independent of the experimental conditions and therefore they should represent a suitable measure for the distribution of the strength of acidic sites. The calculated desorption energy distributions for the ammonia desorption from the isolated bridging SiOHAl groups of H zeolites of different type significantly differ from each other in shape. The increase of the desorption energy of the main range of the distribution functions correlates well with the increase of the average acid strength of the SiOHAl groups with decreasing Al content of the zeolites.

Keywords: desorption energy, temperature-programmed desorption, zeolites

Introduction

The importance of zeolites as catalysts for the transformation of hydrocarbons is based on their acidity besides their shape-selective properties. However, in order to obtain more detailed information with respect to the catalytic activity and the selective behaviour a very exact knowledge of the acidic properties of the zeolites is necessary. For the characterization of the acidic sites – the determination of their nature, of their number and localization as well as their strength – various methods are used (see e.g. [1, 2]).

Temperature-programmed desorption (TPD) of basic probe molecules is, besides microcalorimetric measurements, a suitable method for the characterization of the strength or the strength distribution of acid sites [3–5]. In many cases in TPD studies only the temperature of the maximum of the desorption

curves is used as a relative measure for the strength of acid sites. In order to obtain quantitative information about the strength of interaction of the bases with the acidic sites of the zeolites a kinetic analysis of the more or less complex desorption curves is necessary. However, difficulties arise frequently in this case because often a stronger diffusional influence on the overall desorption process might exist originated from the micro-porous structure of the zeolites. Tronconi and Forzatti [6] showed by means of model calculations that in this case the observed desorption rate r_d for a desorption process of first order is well described by the following approximation:

$$r_d = -\frac{d\theta}{dT} \approx k_{\text{eff}} \theta = \frac{\pi^2 D_{\text{eff}}}{\alpha R_p^2} \frac{k_d}{v_m k_a} \theta \quad (1)$$

- θ : average degree of coverage
- α : heating rate
- R_p : mean particle radius of the catalyst pellets
- D_{eff} : effective diffusion coefficient
- k_d : rate constant of desorption
- k_a : rate constant of adsorption
- v_m : initial concentration of the probe molecule adsorbed
- k_{eff} : effective desorption rate constant

If the temperature dependence of the effective diffusion coefficient is relatively low (low activation energy or non-activated diffusion) compared to that of readsorption and desorption as it is typical for chemisorption of probe molecules then the temperature dependence of the effective desorption rate constant k_{eff} is mainly determined by the adsorption heat (in the following designated as desorption energy).

Moreover, in many cases of kinetic evaluation it has to be considered that the observed desorption process represents a superposition of desorption from sites of different energetic strength (acidic sites of different strength). This fact is usually taken into account by a dependence of the desorption energy E and the pre-exponential factor A on the degree of coverage (see e.g. [7–10]):

$$r_d = \theta A(\theta) \exp[-E(\theta) / RT] \quad (2)$$

For that various algorithms of evaluation were developed, resulting from different assumptions or requiring different experimental data (see e.g. [11–14]).

The assumption of a distribution function $f(E)$ for the probability density of the desorption energy is another possibility to describe desorption from an energetically heterogeneous surface (see e.g. [5, 15, 16]):

$$r_d = \frac{A}{\alpha} \int_{E_{\min}}^{E_{\max}} [\theta(E, T)]^n \exp(-E / RT) f(E) dE \quad (3)$$

For the calculation of the desorption energy distribution the pre-exponential factor (assumed to be constant) and the order of desorption (n) must be known or have to be determined by other methods. Only a few examples for evaluation according to Eq. (3) are described in the literature. The calculation of the distribution function is carried out by evaluation of difference-curves [17] using modelled distribution functions and determination of the parameter by means of a fitting program [5, 18], or by MONTE CARLO simulation [19–21]. Moreover, a numerical solution of Eq. (3) by the regularization method can be applied [22, 23]. This method does not require any limiting assumptions about the distribution function, used up to now only for some model cases of temperature-programmed desorption [22, 23].

Therefore, it is the aim of this contribution to obtain quantitative information about the acid strength distribution of the SiOHAl groups of H zeolites of varying type using the regularization method for the kinetic evaluation of temperature-programmed desorption of ammonia. The existence of acidic SiOHAl groups of different strength on zeolites is evident from microcalorimetric studies of ammonia adsorption [24–26] and IR spectroscopic studies [27, 28], but also from TPD measurements [e.g. 5, 14, 18, 20, 21].

Method of evaluation

The general form of Eq. (3) is a FREDHOLM integral equation of the first kind,

$$g(y) = \int K(x, y) f(x) dx \quad (4)$$

in which the kernel $K(x, y)$ is representative of the experimental TPD system and procedure, $g(y)$ denotes the experimentally determined overall desorption rate and $f(x)$ is the unknown distribution function of the desorption energy.

FREDHOLM integral equations are of numerically ill-posed nature. The peculiar behaviour of ill-posed problems consists in a possible transmission of experimental errors to the unknown result in such a way that the result can be completely distorted. To overcome this problem special numerical methods are required. In our calculation the regularization method was used, which in general adds an assumption about the distribution like smoothness or non-negativity in order to obtain a physically meaningful solution within the range of experimental errors.

In case of the use of the distribution function's smoothness, the regularization formalism yields the following form:

$$g(y) = \int_a^b K(x,y)f(x)dx + \gamma \int_a^b \left[\frac{\partial^2 f(x)}{\partial x^2} \right]^2 dx \quad (5)$$

where γ is the so-called regularization parameter, which weighs the terms on the right-hand side against each other. A more detailed description of the mathematical background and the computer program INTEG used for the calculation can be found in [29].

The apparatus used for TPD experiments, the pretreatment of the zeolites studied and the conditions of the desorption experiments have already been described elsewhere [21, 30–32]. The evaluation was carried out for a 0.88NaHY zeolite (Si/Al=2.6) [30], for a H-mordenite (Si/Al=5) [31] and for a HZSM-5 zeolite (Si/Al=28) [21]. In each case only those desorption curves were used which could be attributed to the desorption of ammonia from the isolated bridging SiOHAl groups of the zeolites [21, 30, 31]. Complex desorption curves were separated by means of combination of isothermal and non-isothermal desorption, or ammonia was adsorbed at room temperature only to such an extent as to correspond to the number of SiOHAl groups of the zeolite in question. As mentioned earlier, the knowledge of the pre-exponential factor is necessary for the calculation of the distribution function. For the time being values were used which were approximately determined by other methods [20, 21, 32], since a theoretical estimation, due to the effective character of the desorption rate constant k_{eff} in Eq. (1), seems to be not justified.

Results and discussion

In order to obtain consistent results in case of a kinetic evaluation of desorption studies it is required that the calculated parameters are independent of the experimental conditions. Figure 1 shows the calculated distribution functions of the desorption energy for the desorption of ammonia from HZSM-5 zeolite in case of several heating rates. It can be seen clearly that the position of the maximum of the distribution function is independent of the heating rate (145 ± 1 kJ/mol) and the shape of the distribution function does not change significantly. The good description of the course of desorption (Fig. 2) but also the relatively low negative part of the distribution function found in all cases should be an expression for the adequacy of the evaluation. The desorption energy of the maximum of the distribution function corresponds to the energy of desorption which was obtained for this zeolite by application of the REDHEAD [33]

method [14, 21]. Therefore, this value can be interpreted as a mean desorption energy of an approximately symmetric distribution function.

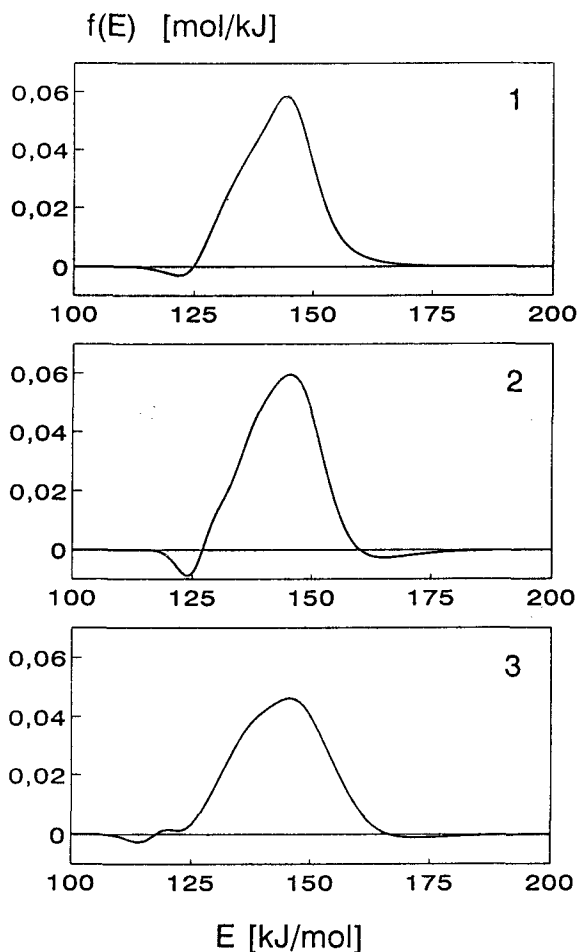


Fig. 1 Calculated desorption energy distributions of ammonia desorption on HZSM-5 for different rates (500 mg zeolite, 0.28 mmol/g ammonia, $A = 1.1 \times 10^{10} \text{ min}^{-1}$); 1: 2 deg·min⁻¹; 2: 4 deg·min⁻¹; 3: 10 deg·min⁻¹

Only small differences are obtained in the calculation of the distribution function of the desorption energy in dependence on the zeolite amount used as shown in Fig. 3. The position of the maximum (500 mg: 146 kJ/mol, 250 mg: 141 kJ/mol) and the width (about 45 kJ/mol) agree well for both samples. For the evaluation of the shoulder appearing somewhat more clearly in the case of the 250 mg zeolite sample it should be considered that the desorption curve used for calculation (so-called γ -Peak [4]) was separated from the complex

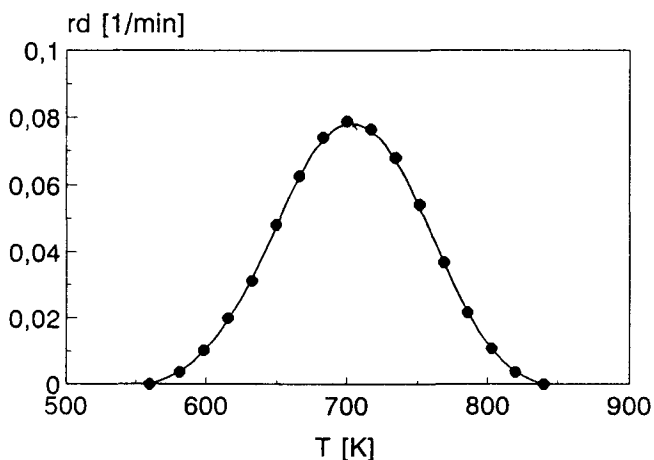


Fig. 2 Calculated desorption curve (—) from the desorption energy distribution of ammonia desorption on HZSM-5 (500 mg zeolite, 0.28 mmol/g ammonia, 10 deg·min⁻¹, $A=1.1 \times 10^{10}$ min⁻¹) •: experimental data

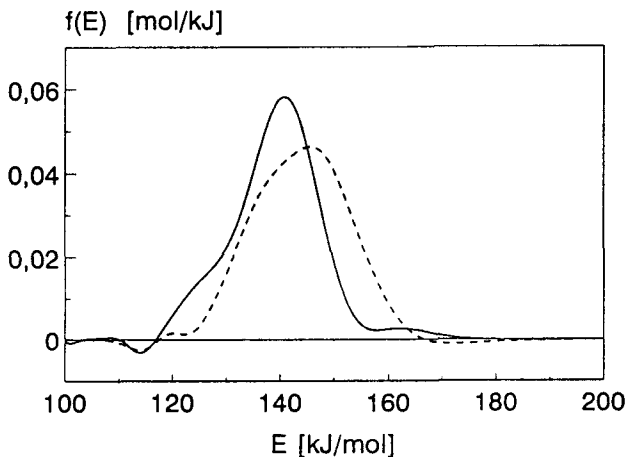


Fig. 3 Calculated desorption energy distributions of ammonia desorption on HZSM-5 for different heating amounts of the zeolite (0.28 mmol/g ammonia, 10 deg·min⁻¹, $A=1.1 \times 10^{10}$ min⁻¹); (—) 250 mg; (---) 500 mg

desorption curve ($\beta + \gamma$ -Peak) by combination of isothermal and non-isothermal desorption. Errors resulting of this separation procedure have serious consequences for the course of desorption initial range of the process at higher temperatures, relatively strongly influencing the calculation of the distribution function.

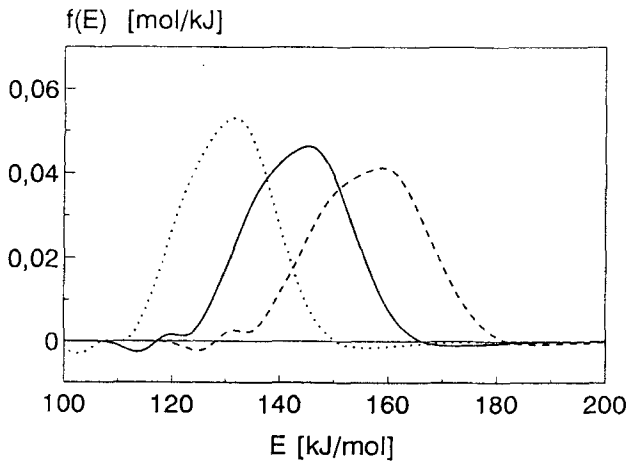


Fig. 4 Calculated desorption energy distributions of ammonia desorption on HZSM-5 for different pre-exponential factors (500 mg zeolite, 0.28 mmol/g ammonia, 10 deg·min⁻¹). (···): $A=1 \times 10^9$ min⁻¹; (—): $A=1 \times 10^{10}$ min⁻¹; (---): $A=1 \times 10^{11}$ min⁻¹

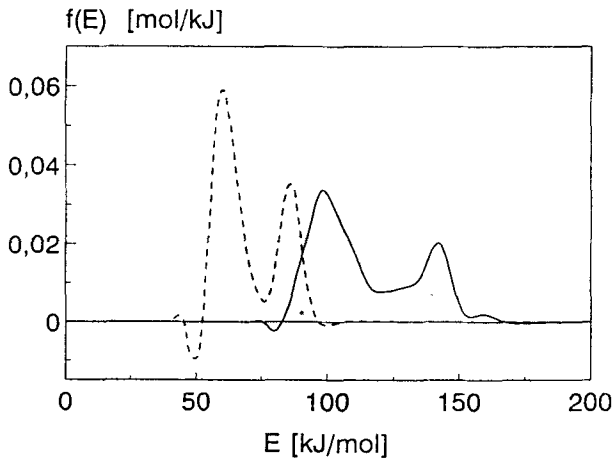


Fig. 5 Calculated desorption energy distributions of ammonia desorption on HZSM-5 from the complex desorption curves (500 mg zeolite, 0.82 mmol/g ammonia, 10 deg·min⁻¹); (—) $A=1.1 \times 10^{10}$ min⁻¹; (---) $A=6.2 \times 10^5$ min⁻¹

The solution of the integral equation for the calculation of the distribution function depends on the value of the pre-exponential factor. Since, however, the calculation of the A factor is only possible approximately, or, with a significant error, its influence on the calculation of the distribution function should be estimated. In Fig. 4 the distribution functions of the desorption energy are shown in case of the HZSM-5 zeolite for different pre-exponential factors.

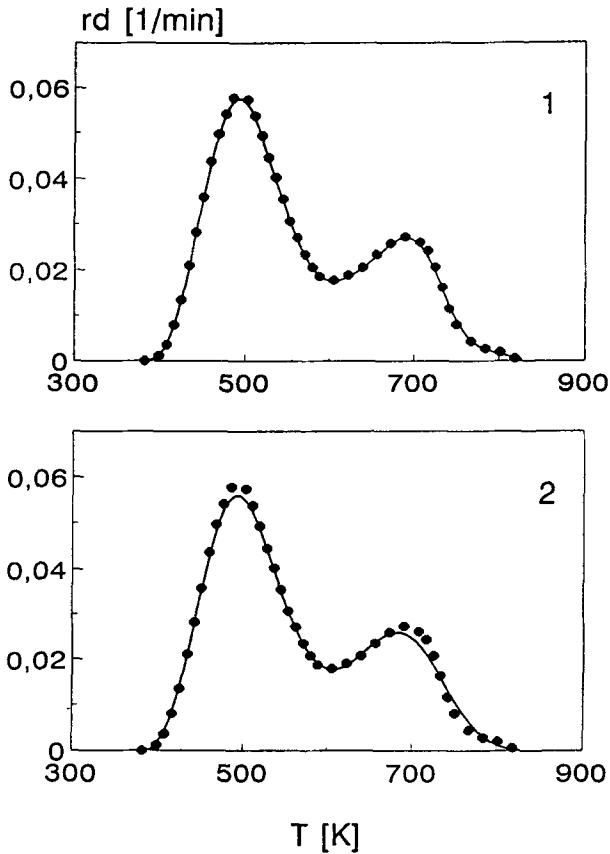


Fig. 6 Calculated desorption curves (—) of ammonia desorption on HZSM-5 (500 mg zeolite, 0.82 mmol/g ammonia, 10 deg·min⁻¹): (•: experimental data).
 1: $A = 1.1 \times 10^{10} \text{ min}^{-1}$; 2: $A = 6.2 \times 10^5 \text{ min}^{-1}$

The range was chosen in a manner to correspond to the error of the determination of the pre-exponential factor. In contrast to the shape of the distribution function the position of the maximum changes relatively strongly (about 14 kJ/mol for the change of A by one order of magnitude). But the deviations correspond to the uncertainty of a kinetic analysis of non-isothermal measurements. However, greater differences result in case of the evaluation of a complex desorption curve with significantly different desorption ranges if a value of A is used which was determined only for a partial range of the desorption curve. In Fig. 5 the desorption energy distributions for ammonia desorption from the HZSM-5 zeolite ($\beta + \gamma$ -Peak) and in Fig. 6 the calculated desorption curves are shown. In each case a distribution function with two distinctly marked maxima results. A satisfactory coincidence with the results of the analysis of the separate

desorption curves [21] is resulting only for the part of a distribution function for which the corresponding pre-exponential factor was determined. Since these desorption energies agree fairly well with the adsorption heat in dependence on the degree of coverage measured by microcalorimetry [21] it should not be allowed to use only one value for the pre-exponential factor in order to calculate the distribution functions for complex desorption curves for greater temperature ranges or with distinctly marked maxima. However, for a separated evaluation of single desorption steps an experimental deconvolution of the complex desorption curve is necessary.

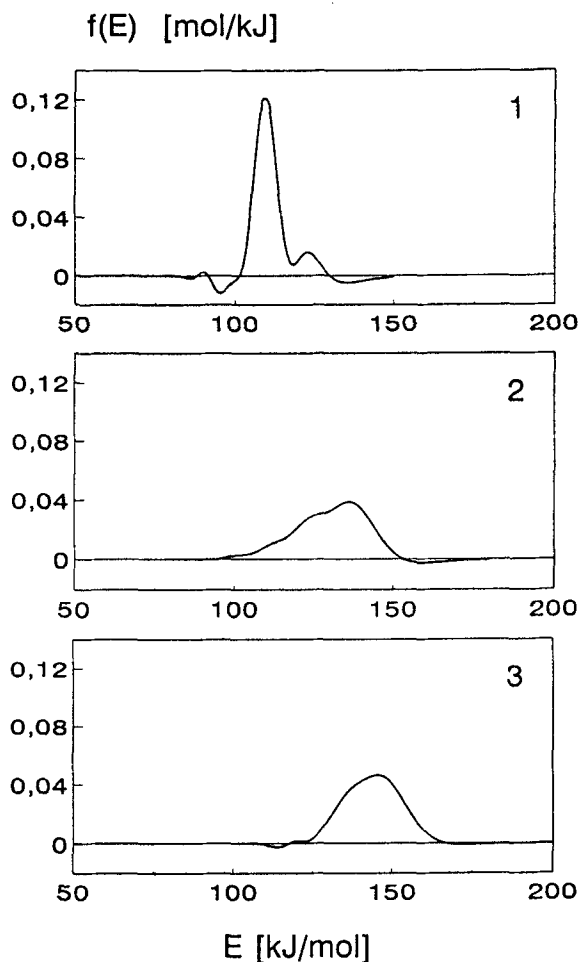


Fig. 7 Calculated desorption energy distributions of ammonia desorption on different zeolites ($10 \text{ deg} \cdot \text{min}^{-1}$): 1: 0.88HNaY, 1.2 mmol/g ammonia, $A=3.5 \times 10^8 \text{ min}^{-1}$; 2: H-mordenite, 2.34 mmol/g ammonia, $A=5.0 \times 10^7 \text{ min}^{-1}$; 3: HZSM-5, 0.28 mmol/g ammonia, $A=1.1 \times 10^{10} \text{ min}^{-1}$

Figure 7 shows the calculated distribution functions of the desorption energy for the ammonia desorption for the three selected H-containing zeolites of different type. The distribution functions obtained are clearly different with respect to their shapes. In case of the HNaY zeolite the distribution function is relatively small and shows only an additional maximum of low intensity at higher energy values which should not have a significant meaning for the characterization of the acid strength of this zeolite. This shape of the distribution function agrees well with the fact that the course of desorption can be described relatively exactly by a rate equation based on constant desorption energy [30, 32] or on a small dependence of the desorption energy on the degree of coverage [20]. In case of the other zeolites essentially broader distribution functions with one maximum result, referring to the existence of OH groups which differ in their acid strength more strongly. This is supported by the fact that the calculated dependence of the desorption energy on the degree of coverage is much greater than in case of the HNaY zeolite [14, 21, 32]. Also microcalorimetric investigations confirm these results [24, 25]. Considering the main range of the distribution function of each zeolite studied it can be seen clearly that the increase of the desorption energy of ammonia corresponds to the increase of the acid strength of the SiOHAl groups with decreasing Al content [32, 34, 35].

However, for a quantitative characterization of the acidic properties of different zeolites by means of TPD the whole distribution function of the desorption energy of ammonia and also of other basic probe molecules should be considered. For this reason the calculation of the distribution function by means of the regularization method seems to be a suitable possibility for the kinetic evaluation of desorption curves without any limiting assumption.

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Zusammenfassung — Mit Hilfe von Regularisation wurden die Desorptionsenergieverteilungen bei der temperaturprogrammierten Desorption (TPD) von Ammoniak aus H-Zeolithen verschiedenen Typs berechnet. Diese Methode bedarf keinerlei einschränkender Annahmen bezüglich der Verteilungsfunktion. Es konnte gezeigt werden, daß die erhaltenen Desorptionsenergieverteilungen von den Versuchsbedingungen nahezu unabhängig sind und somit einen geeigneten Maßstab für die Verteilung der Stärke acidischer Stellen darstellen. Die berechneten Desorptionsenergieverteilungen für die Ammoniakdesorption an den isolierten SiOHAl-Brückengruppen von H-Zeolithen verschiedenen Typs weichen hinsichtlich des Verlaufes eindeutig voneinander ab. Ein Ansteigen der Desorptionsenergie des Hauptbereiches der Verteilungsfunktion korreliert gut mit dem Ansteigen der durchschnittlichen Säurestärke der SiOHAl-Gruppen bei abnehmendem Al-Gehalt der Zeolithe.