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CHARACTERIZATION OF SHORT-TIME DEALUMINED HZSM-5 ZEOLITES

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Abstract

Temperature-programmed desorption (TPD) of water was applied to characterize short-time dealuminated HZSM-5 zeolites. Using a regularization method, distribution functions of the effective desorption energy of water were calculated. The results clearly show that during dealumination a new adsorption site is formed which can be attributed to non-framework or transient aluminium species. The highest concentration of these sites was observed for a dealumination time of 25–30 min. NO adsorption studies support this result. Furthermore, it could be concluded that the heterogeneity and the average acid strength of the remaining Si–OH–Al groups of the dealuminated samples do not change compared to the Si–OH–Al groups of the parent HZSM-5 zeolite.

Keywords: dealumination, HZSM-5 zeolites, NO adsorption, non-framework aluminium, TPD of water

Introduction

Secondary or post-synthesis treatments of zeolites are utilized to produce desired catalytic properties of zeolite catalysts which could not be achieved by direct synthesis. In this context dealumination is an important process in the preparation of catalysts with an enhanced catalytic acid activity, an improved thermal and hydrothermal stability (e.g. [1–3]). The Si/Al ratio of zeolites can be increased by a thermal or hydrothermal treatment of the ammonium exchanged form or by leaching of silicon-rich zeolites with acids [4–11]. Furthermore, framework aluminium can be replaced directly with silicon by the treatment with gaseous silicon tetrachloride, aqueous solution of ammonium hexafluorosilicates or other agents [6, 11–15]. During dealumination part of the tetrahedral coordinated framework aluminium is removed and partially deposited in the pore volume of the zeolite. This non-framework aluminium shows Lewis acid properties and can be detected by EPR spectroscopy using NO as probe molecule [16, 17]. Several authors reported about an enhanced catalytic activity of mild dealuminated zeolites in different hydrocarbon conversion

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reactions (e.g. [6, 9, 11]). An interpretation of this catalytic behavior requires a detailed characterization of the adsorption properties of the modified zeolites.

The present work is a contribution to the characterization of short-time dealuminated HZSM-5 zeolites by means of temperature-programmed desorption (TPD) of water. To our best knowledge, no TPD studies of water on dealuminated ZSM-5 zeolites are reported so far in the literature. For technical purposes zeolite powders have to be granulated by inorganic and organic binders. In most of the cases the properties of the zeolites were influenced by the binder. Therefore, we have studied ZSM-5 zeolite granulates after pelletization.

Experimental

The parent NaZSM-5 zeolite with a Si/Al ratio of 15 was provided by the Chemiewerk Bad Köstritz GmbH (Germany). The granulated samples additionally possess a binder made of Greek bentonite (25 mass%). The granulates were reduced to small pieces and sieved to a grain size of 0.2–0.3 mm. In addition, dealumination was carried out with the NaZSM-5 zeolite without binder.

Dealumination procedure

The dealumination was carried out in a suspension containing 10 g zeolite and 100 mL hexafluorosilic acid/water mixture. For the granulated zeolite a 37.5 vol% and for the binder-free NaZSM-5 samples a 12.5 vol% solution of hexafluorosilic acid in water were used. The dealumination was performed at 343 K with different times (0, 10, 20, 30, 60 and 120 min). After this treatment the samples were washed with water until the pH=7. Then the zeolites was dried and exchanged into the NH_4^+ form by means of a 2 M NH_4NO_3 solution. After that a drying was performed at 393 K. Finally, the samples were calcinated at 673 K for 24 h.

Adsorption studies

For isopiestic adsorption studies one gram of the dehydrated samples was placed in a desiccator filled with ethanol or a saturated aqueous NH_4Cl solution at room temperature. The adsorbed amount was determined gravimetrically after 48 h.

Nitrogen adsorption was performed at 77 K by means of a ASAP 2000 Micropore System (Micromeritics).

The adsorption isotherms of NO at 298 K were determined gravimetrically on a McBain balance fitted to a high-vacuum system. 100 mg of the samples were activated under vacuum at 673 K for 20 h. Blank runs were employed to allow for buoyancy effects.

Temperature-programmed desorption of water

The TPD experiments were carried out in a flow apparatus with helium as carrier gas (50 cm^3 min^{-1}). For evolved gas detection both a thermal conductivity detector (TCD) and a quadrupole mass spectrometer (Leybold, Transpector CIS System) with a capillary-coupling system were used. The samples were equilibrated with water vapor over a saturated NH_4Cl solution in a desiccator. For each experiment 100 mg of the hydrated zeolite were used in a mixture with 1 g quartz of the same grain size (0.2–0.3 mm). At first the samples were flushed with helium at room temperature for 1 h and then heated at 10 K min^{-1} in helium up to 700 K. The desorbed amounts of water were determined by calibration of the TCD signal and the intensity of the 18 amu response.

Results and discussion

The calculated BET surfaces and micropore volumes of the dealuminated samples are given in Table 1. It is obvious that both properties are independent of the dealumination time. However, the total pore volumes are slightly increasing up to a dealumination time of 25 min indicating the formation of a secondary pore system in the binder phase. This result agrees well with the increasing saturation capacity of ethanol adsorption up to this dealumination time, as it is shown in Fig. 1. Since ethanol can occupy the whole pore volume it can be derived from the studies that the dealumination process has no influence on the micropore volume and, therefore, on the crystallinity of the samples. The estimated saturation capacity of water decreases, as expected, with increasing dealumination time indicating the greater hydrophobicity of the dealuminated samples.

Table 1 Sample characteristics

t_{deal}/min	BET surface/m^2 g^{-1}	Micropore volume/cm^3 g^{-1}	Total pore volume/cm^3 g^{-1}
0	299	0.142	0.164
10	293	0.135	0.186
20	280	0.127	0.187
25	310	0.141	0.200
30	299	0.136	0.198
60	301	0.137	0.205
120	284	0.130	0.192

The non-isothermal profiles of water on all samples under study are shown in Fig. 2. The desorbed amount of water, given in Table 2, decreases only to a small extent. All profiles show a pronounced peak at 366±2 K and a shoulder in the temperature range between about 400 and 500 K. Beside that the main peak does not shift in dependence on the dealumination time it is characteristically for the profiles that up to a dealumination of 30 min the intensity of the desorption feature at higher temperatures increases.

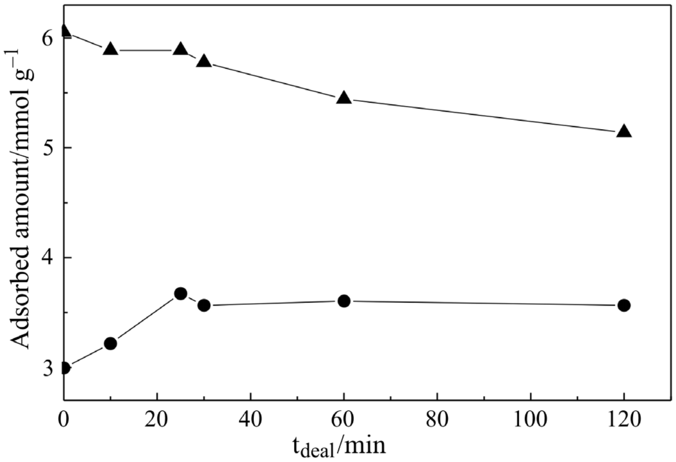

Fig. 1 Water and ethanol adsorption in dependence on the dealumination time: -●- – ethanol, -▲- – water

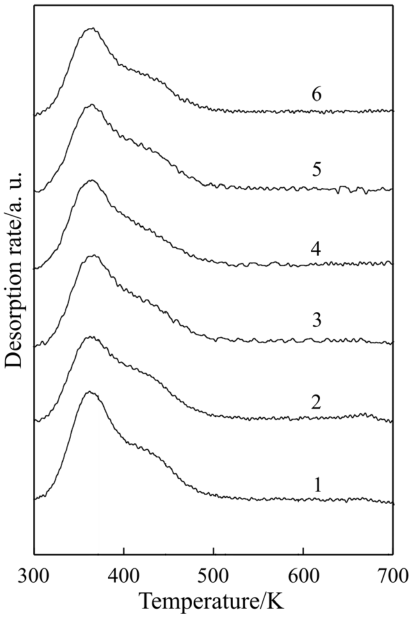

Fig. 2 TPD profiles of water (10 K min^{-1}) in dependence on the dealumination time: 1 – 0 min, 2 – 10 min, 3 – 20 min, 4 – 25 min, 5 – 30 min, 6 – 60 min

The observed desorption profiles $r_d(T)$ were analyzed by considering a first order desorption process with a distribution function $f(E)$ of the effective desorption energy E [18, 19]:

$$r_{\mathrm{d}}(T)=-\frac{\mathrm{d}\theta}{\mathrm{d}t}(T)=A\int_{\mathrm{E}_{\min}}^{\mathrm{E}_{\max}}\theta_{\mathrm{loc}}(E,T)\exp\left(-\frac{E}{RT}\right)f(E)\mathrm{d}E \qquad (1)$$

Table 2 TPD results

t_{deal}/ min	Desorbed amount of water (300–700 K)/mmol g^{-1}	Desorbed amount of water (peak at 55 kJ mol^{-1})/mmol g^{-1}	Si–OH–Al groups per unit cell
0	2.94	1.38	6.1
10	2.78	1.32	5.8
20	2.73	1.13	5.0
25	2.67	1.04	4.6
30	2.72	0.97	4.3
60	2.54	0.87	3.8

Here θ is the average coverage or loading, and A is an effective pre-exponential factor. θ_{loc} is the coverage of adsorption sites with desorption energy E, $E_{\min}$ and $E_{\max}$ are the limits of the desorption energy range. The energy distribution function $f(E)$ was determined from the experimental desorption curves $r_{\mathrm{d}}(T)$ by means of the program INTEG, which involves a regularization method for solving the integral Eq. (1) [18, 19]. The pre-exponential factor A required to solve Eq. (1) was taken from a previous study ($A=2\cdot10^{6}$ min^{-1}) [20]. The calculations were carried out without any assumptions or constraints on the resulting distribution functions. Thus, negative parts in the distributions are possible. They do not have any special physical meaning, but show the degree of adequacy between the desorption model used and the experimental data. Therefore, the negative parts in the calculated distribution will not be a matter of interpretation.

The calculated desorption energy distribution functions are presented in Fig. 3. The peak at about 45 kJ mol^{-1} can be related to physisorbed water. The range of energy (40–50 kJ mol^{-1}) is comparable to the heat of condensation of water vapour (ΔH=43.5 kJ mol^{-1} at 303 K and 40.6 kJ mol^{-1} at 373 K). Similar energy values have been also found for heats of adsorption of water on HZSM-5 zeolites at higher loadings [21]. The part at higher energy values of the desorption energy distributions (peak at about 55 kJ mol^{-1}) corresponds to an interaction of water with stronger adsorption sites. In case of the parent HZSM-5 zeolite this part could be attributed to desorption of water adsorbed on the bridged Si–OH–Al groups by means of a combined TPD and infrared spectroscopic study of water adsorption [20]. The energy value of the maximum (55 kJ mol^{-1}) corresponds to heats of adsorption of water on HZSM-5 zeolites at low loading [22]. But also first principles density functional molecular dynamics calculations result for one water molecule adsorbed on a Si–OH–Al group in an adsorption energy of 50 kJ mol^{-1} [23]. In order to determine the relative contributions of both peaks the distribution functions were fitted by Gaussian functions. Using two Gaussian peaks, a reasonable description of

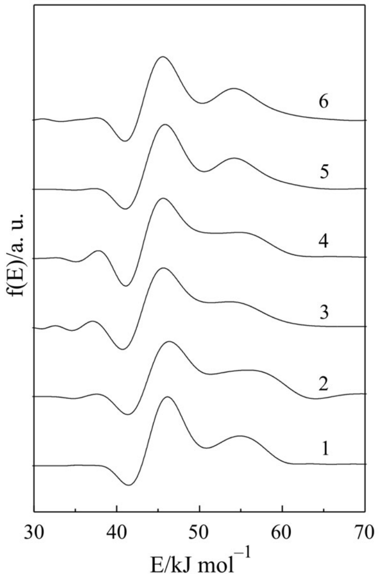

Fig. 3 Desorption energy distribution functions of water in dependence on the dealumination time: 1 – 0 min, 2 – 10 min, 3 – 20 min, 4 – 25 min, 5 – 30 min, 6 – 60 min

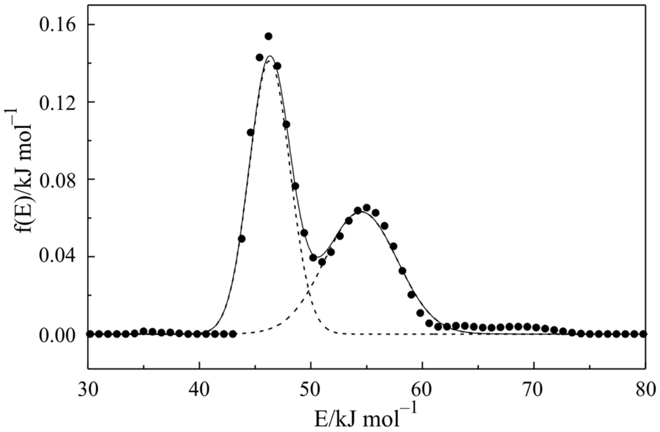

Fig. 4 Desorption energy distribution function of water on the parent HZSM-5: ● – calculated by means of the INTEG program, — – fitted distribution function, --- – individual Gaussian peaks

the desorption energy distribution of the parent HZSM-5 zeolite is possible (Fig. 4). The percentage of the high energy peak yields a water amount which is adsorbed on the OH groups of about 1.4 mmol g^{-1}. This corresponds to about 1.3 water molecules per Si–OH–Al group.

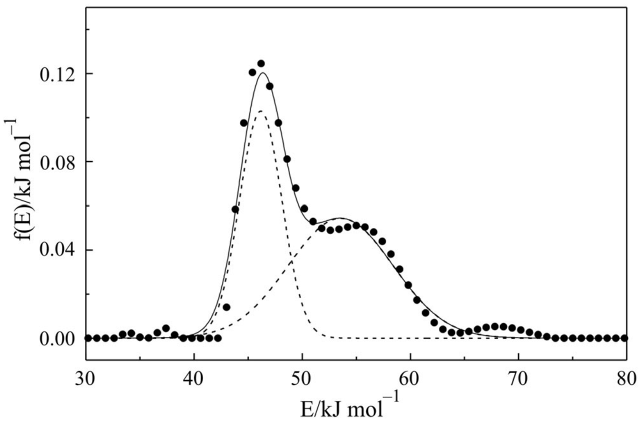

Fig. 5 Desorption energy distribution function of water on the 20 min dealuminated HZSM-5: ● – calculated by means of the INTEG program, — – fitted distribution function, --- – individual Gaussian peaks

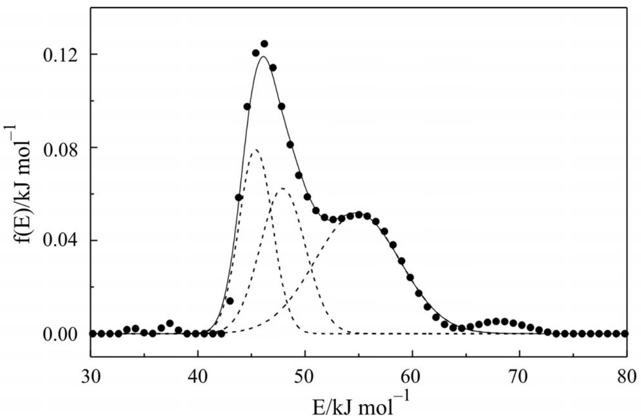

Fig. 6 Desorption energy distribution function of water on the 20 min dealuminated HZSM-5: ● – calculated by means of the INTEG program, — – fitted distribution function, --- – individual Gaussian peaks

However, in case of the dealuminated samples the assumption of two Gaussian peaks does not result in a reasonable approximation of the distribution functions, as it is shown in Fig. 5 for the 20 min dealuminated sample. Therefore, the fit was carried out by means of three Gaussian peaks which allows a adequate description of the desorption energy distributions of all dealuminated samples (Fig. 6).

The appearance of a new peak at about 50 kJ mol^{-1} of the distribution functions of shortly dealuminated samples can be interpreted in the sense that during the dealumination process a new adsorption sites was formed. On these adsorption sites water is weaker bounded than on the remaining OH groups of the zeolites. Using the percentage of this energy peak on the distribution function the corresponding de-

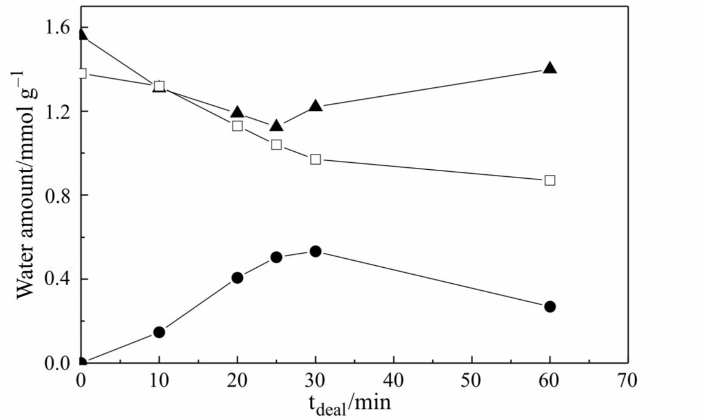

Fig. 7 Desorbed water amounts of the individual peaks of the desorption energy distributions in dependence on the dealumination time: -▲- – peak at 45 kJ mol^{-1}, -●- – peak at 50 kJ mol^{-1}, -□- – peak at 55 kJ mol^{-1}

sorbed amount of water can be calculated. Figure 7 shows that with increasing dealumination time the adsorbed amount of water on this new formed adsorption site increases up to a dealumination time of 30 min. Afterwards a decrease is observed. In order to avoid an influence of the binder dealumination was also carried out with the binder-free NaZSM-5 zeolite. TPD of water on these prepared samples results in agreeing findings indicating that the new formed adsorption site can be related to the dealumination of the HZSM-5 zeolite.

These adsorption sites can be attributed to non-framework aluminium species which were formed during the dealumination procedure but not removed from the samples. But also an interpretation in the sense of a framework-related or transient Al–OH species is possible [10, 24, 25]. These species result from a partial hydrolysis of the framework Al–O bonds due to the interaction of water with OH groups. Additional water molecules can interact coordinatively with the Al–OH species to form a octahedrally coordinated aluminium complex. The observed decrease of the amount of the new adsorption site at longer dealumination times should be support somewhat an assignment to a transient Al–OH species. However, a definite clarification requires further investigations.

The acid strength of Si–OH–Al groups on dealuminated zeolites is a controversially discussed problem in the literature. One interpretation of the enhanced catalytic activity of dealuminated zeolites is the increase of acid strength of the bridging Si–OH–Al group due to an increase in polarization of the O–H bond caused by an interaction with unsaturated non-framework aluminium species [5]. On the other hand, Datka *et al*. [9] found a distribution of the acidic strength of the Si–OH–Al groups in mildly dealuminated HZSM-5 zeolites and suggested that the increase in the average acidic strength of the remaining Si–OH–Al groups is due to the removal of less acidic OH groups in the first order. But other authors did not found OH groups of higher acid strength in dealuminated zeolites [6, 26].

The acid strength of the Si–OH–Al groups of the studied zeolites can be related to the peak at 55 kJ mol^{-1} of the desorption energy distributions of water. The energy value of the maximum can be interpreted in the sense of the average acid strength of the Si–OH–Al groups. With increasing dealumination time this peak does not shift indicating an equal average acid strength of the remaining bridging OH groups. From the constant shape of this energy peak for all studied samples it can be derived that the acidic strength distribution of the residual Si–OH–Al groups does not changed in dependence on the degree of dealumination, as it was found by Datka *et al*. [9] for steamed HZSM-5 zeolites. The desorbed amount of water which results for the energy peak at 55 kJ mol^{-1} decreases with increasing dealumination time (Fig. 7). Taking into account that on the parent HZSM-5 zeolite about 1.3 water molecules interact with one OH groups, the amount of remaining Si–OH–Al groups of the samples can be calculated (Table 2). It is worth mentioning that up to a dealumination time of 30 min a nearly linear decrease of the OH group concentration is observed. The adequacy of the assumption of three Gaussian peaks for the deconvolution of the desorption energy distribution functions of the dealuminated samples is reaffirmed by the fact that the use of two Gaussian peaks results in unrealistic great amounts of Si–OH–Al groups.

Figure 8 shows the NO adsorption isotherms at 298 K of the parent HZSM-5 zeolite and two dealuminated samples. The measured adsorption isotherms were analyzed by considering a combined isotherm equation [16]:

$$N=\frac{nkp}{1+kp}+Kp \tag{2}$$

where N is the total amount of adsorbed NO at equilibrium pressure p. The first term expresses the localized adsorption of NO with the adsorption constant k on sites of concentration n (Langmuir adsorption isotherm). Taking into account that NO is localized adsorbed on the Lewis acid sites, n represents the total amount of these sites

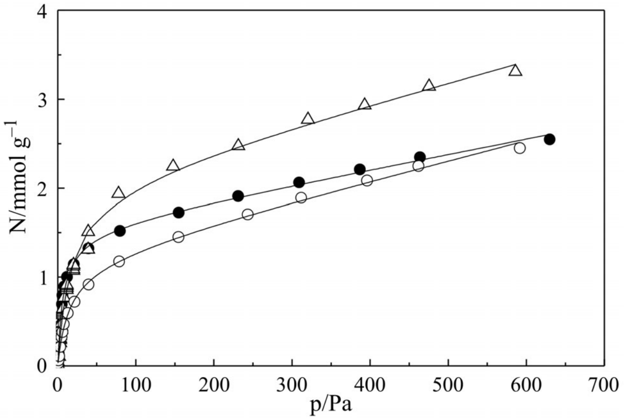

Fig. 8 NO adsorption isotherms at 298 K: ● – parent HZSM-5, △ – t_{deal}=20 min, ○ – t_{deal}=60 min, lines – calculated according to Eq. (2)

Table 3 Adsorption parameters of NO at 298 K

t_{deal}/min	n/mmol g^{-1}	k/Pa^{-1}	$K\cdot 10^3$/mmol g^{-1} Pa^{-1}
0	1.55	0.1390	1.71
20	2.06	0.0584	2.38
60	1.21	0.0671	2.25

in the investigated sample. The second term corresponds to the non-localized adsorption of NO in the remaining pore space with the Henry constant K. Using this equation, the measured adsorption isotherms of NO can be well reproduced by means of non-linear regression (Fig. 8). The obtained parameters are given in Table 3. The sample which was 20 min dealuminated possesses the highest concentration of Lewis acid sites. This fact can be also interpreted in the sense that during short-time dealumination a greater number of new adsorption sites with Lewis acid properties were formed. This result agrees well with the findings of the above discussed temperature-programmed desorption studies of water.

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