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Investigation and Modeling of the Hydrothermal Stability of Technically Relevant Zeolites*

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Abstract. The dense-structured zeolites of types ZSM-5 (MFI) and mordenite (MOR) of different SiO_2/Al_2O_3 moduli are relatively stable under treatment by liquid water for 72 hours up to 513 K. The open-structured zeolites of types Y in dealuminated modification (FAU) and beta (BEA) undergo strong decomposition in the same range. For these two sample types a mathematical model for the decomposition of the zeolite framework is established that takes into account the influence of modulus as well as temperature. Here the kinetic of the solid phase reaction is a superposition of two different mechanisms described by the Monod equation.

Keywords: zeolite, hydrothermal treatment, long-term stability, modeling

Introduction

The interaction of zeolites and water concerns a basic property of these natural or synthetic materials: hydrated zeolites deliver water under heating without destruction of their framework structure. After cooling a renewed hydration takes place. This reversible process of adsorption and desorption is used for selective drying of gases and liquids in laboratory but especially at technical scale (Breck, 1974).

An extensive application of zeolites comprises their use as catalysts in chemical processes where water may be one of the feedstocks or reaction products. Examples are the MTP (Rothaemel and Holtmann, 2002), the MTG (Derouane et al., 1981), and the MTO processes (Kvisle et al., 2003). Extreme hydrothermal stress is imposed on the zeolite structure in oxidation reactions where water acts under relative harsh conditions (regeneration of the FC catalyst (O′Connor et al., 1998)) or in the catalytic treatment of water-loaded waste gas stream (automotive applications (Traa et al., 1999) and waste gas treatment (Schwefer et al., 2001). Comprehensive knowledge of hydrothermal stability of zeolites under such reaction conditions is a mandatory precondition for a successful process layout.

Unlike acid and alkaline solutions which attack preferably Al-rich and Si-rich zeolites, respectively, the water molecules may attack the zeolite framework according to the chemical reactions

$$\begin{aligned} &\mathbf{H}^+ + \mathrm{OH}^- + \mathrm{Na}^+ \equiv \mathrm{Al}^- - \mathrm{O} - \mathrm{Si} \equiv \\ &\quad \leftrightarrow \mathrm{OH}^- + \mathrm{Na}^+ + \equiv \mathrm{Al} + \mathbf{HO} - \mathrm{Si} \equiv \qquad (1) \end{aligned}$$

and

$$\begin{aligned} &\mathrm{H}^+ + \mathbf{OH}^- + \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv \\ &\quad \leftrightarrow \equiv \mathrm{Si} - \mathrm{OH} + \mathbf{HO} - \mathrm{Si} \equiv \qquad (2) \end{aligned}$$

of both types although to a significant lower effect. Thereby, the protons of water molecules attack the —Si—O—Al— bonds over the whole framework whereas the hydroxide ions attack specifically the terminal OH-groups of the surface. The Figs. 1 and 2 give a schematic impression of both processes where water acts like a catalyst (Iler):

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*Dedicated to the late of Wolfgang Schirmer

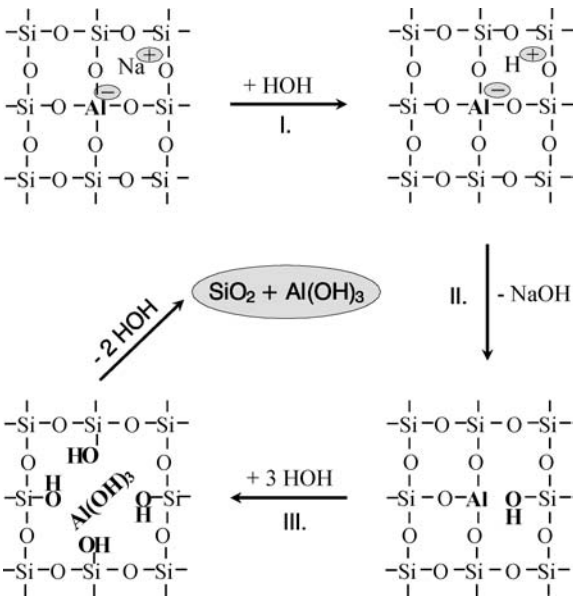

Figure 1. Stepwise decomposition of a low-silica zeolite framework by water.

Because of problems in determination of the hydrothermal long-term stability of zeolites in presence of different concentration of water molecules, one way of estimation of their hydrothermal behavior consists in a treatment in liquid water at elevated temperatures for some days, and the modeling of the properties. Under these experimental conditions the most intensive effect is received because of the highest and a constant water concentration on and in the zeolites. This paper reports the hydrothermal treatment and modeling of the hydrothermal behaviour of industrial zeolites MFI, MOR, BEA, and FAU of different SiO_2/Al_2O_3 moduli.

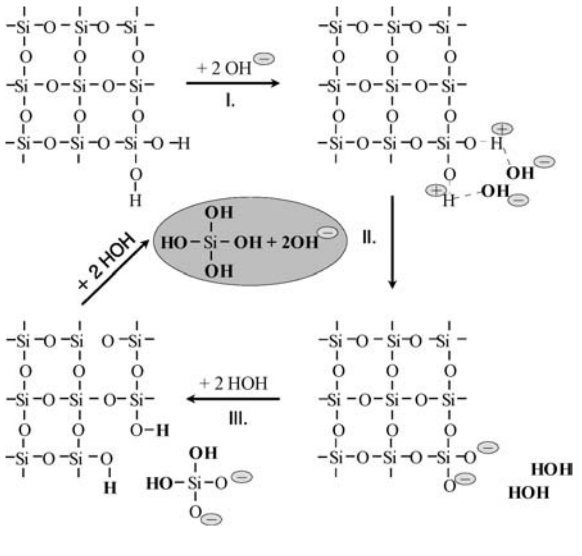

Figure 2. Stepwise decomposition of a high-silica zeolite framework by water.

Experimental

All investigated zeolites were synthesized in industrial processes by Tricat Zeolites GmbH, the Zeosorb GmbH, and Degussa AG, respectively. The template-free MOR zeolites were used in the as-synthesized modification. The templat-containing samples MFI and BEA were calcined at laboratory scale at 873 K for 1 hour in air. The H-modification of zeolite FAU was obtained at laboratory scale, too, by a three-fold ion-exchange (81%) in aqueous solution of 0.1 M ammonium sulphate at room temperature followed by an ammonium decomposition at 533 K for 1 hour in air after drying of the samples at 293 K for 3 hours. The FAU samples of higher moduli were dealuminated at 623 K by a $SiCl_4$-vapour process similar to that described by Beyer et al. (1995). Characteristic data of the samples investigated are summarised in Table 1.

The hydrothermal stability of the zeolites was checked by a treatment in teflon-coated autoclaves in liquid water, free of carbon dioxide at 403–513 K under saturated pressure for 72 hours. The water/solid ratio was 50.

The samples were characterized by XRD measurements on a CUBIX diffractometer of PANALYTICAL (CuK_a radiation), by determination of the BET-surface area on basis of volumetric nitrogen adsorption at $p/p_0 = 0.075$, 0.1, and 0.125 at –77.8 K on a NOVA 1200 of QUANTACHROME Corp., and by the determination of the water sorption capacity at room temperature at $p/p_s = 0.36$. The degree of zeolite decomposition was determined on the basis of a combination of the quantitative analysis of the XRD measurements, the BET analysis, and water uptake.

Results and Discussion

All directly synthesized or dealuminated samples are very pure zeolites with zeolite content more than 95% according to XRD measurements.

A great influence of cations on the hydrothermal stability of A-type (Fichtner-Schmittler et al., 1992) and

Table 1. Characteristic data of zeolites investigated hydrothermally.

SiO_2/Al_2O_3 modulus	Way of preparation	H^+/Me^+ exchange (%)	Water uptake (mg/g)	BET surface (m^2/g)	Relative crystallinity (%)
H-MFI					
24	synthesis	99	130	350	98
47	synthesis	> 99	101	364	99
65	synthesis	> 99	110	358	97
236	synthesis	> 99	36	361	102
608	synthesis	> 99	34	380	100
918	synthesis	> 99	7	344	95
H-MOR					
12	synthesis	97	165	436	98
20	synthesis	98	174	506	93
H-BEA					
21	synthesis	99	293	680	100
36	synthesis	99	257	670	105
48	synthesis	98	244	682	98
200	dealumin$^+$	> 99	255	609	88
H-FAU					
5	synthesis	81	282	705	96
15	dealumin*	97	273	617	85
25	dealumin*	99	270	575	89
56	dealumin*	99	268	614	86
110	dealumin*	98	265	587	83
265	dealumin*	99	262	728	90

$^+$Dealuminated by acid leaching.
*Dealuminated in $SiCl_4$-vapour.

X-type zeolites (Buhl et al., 2004) was found in earlier investigations. This phenomenon was checked in this series that utilizes the sodium and proton modifications of a FAU zeolite. Whereas the Na-modification is nearly unchanged up to its collapse above 513 K (Ehrhardt et al., 1995), the H-modification is decomposed beginning already at 403 K (Fig. 3). The reason for this consists in the basic reaction of Na-FAU (SiO_2/Al_2O_3 = 4,8) in aqueous medium and the inactivity of the protons of water responsible for attacking the Al-rich framework according to the scheme in Fig. 1. Therefore, all samples investigated here were set in as proton-form. Thus, only the properties of the framework determine the hydrothermal behaviour of the different zeolites.

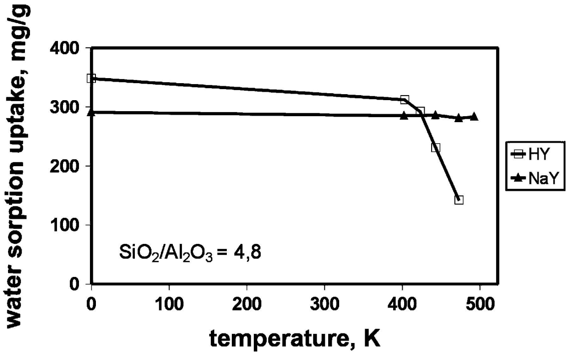

Figure 3. Water sorption uptake of the hydrothermally treated zeolites Na-FAU and H-FAU.

MFI Zeolites

The water-sorption capacity of the MFI zeolites decreases absolutely with increasing modulus, due to the rising hydrophobicity of the samples (Fig. 4). There is, however, a significant difference between the value of water uptake in comparison with those resulted from XRD and BET measurements. Therefore, only these values were used for a characterization of the framework collapse (Fig. 5) that is remarkably smaller than characterized by water sorption. The real structure decomposition of the samples is proportional to

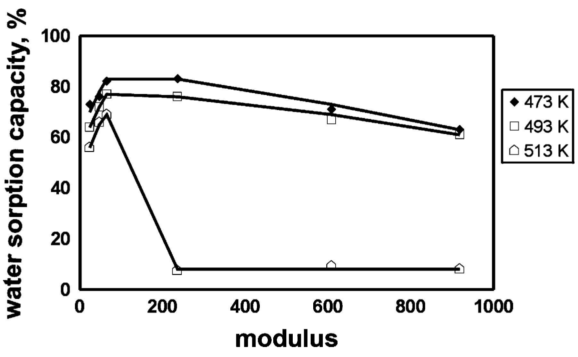

Figure 4. Relative change of the water sorption capacity of MFI zeolites after the hydrothermal treatment at different temperatures.

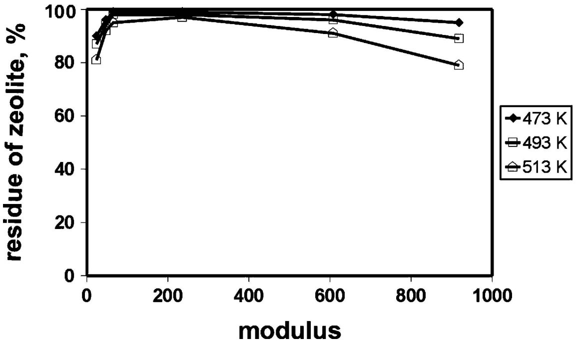

Figure 5. Residue of the zeolitic framework of MFI zeolites after a hydrothermal treatment at different temperatures.

the content of aluminium: stability shows an optimum at medium moduli, decomposition is slightly stronger for samples of low and high moduli, specifically at the highest temperature investigated, viz., of 513 K.

It seems that in case of MFI zeolites the hydrothermal treatment entails an additional healing out of the structure (reduction of terminal OH-groups and defects of the framework) so that hydrophobicity increases and water uptake reduces more than the framework being decomposed by the treatment. The treatment at 513 K is very effective for this process, especially for samples of high moduli.

MOR Zeolites

The hydrothermal treatment of MOR zeolites causes no more healing out of the framework. Therefore, water-sorption uptake, BET and XRD measurements show the same results. The sample with modulus 12 is unchanged whereas the sample with modulus 20 is slightly decomposed at all temperatures (Fig. 6). From

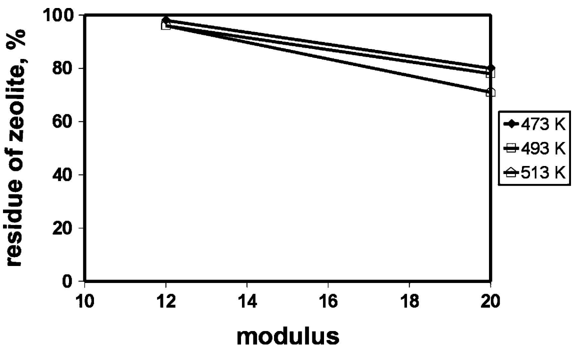

Figure 6. Residue of the zeolitic framework of MOR zeolites after a hydrothermal treatment at different temperatures.

these samples, no clear tendency of the dependence upon modulus can be deduced, but a stronger decomposition like in case of the MFI samples for low moduli does not seem to be actual. Also this zeolite type is stable to a high degree under the strong conditions chosen in this experimental work. Especially, the temperature influence on stability seems to be very small.

BEA Zeolites

In opposite to a weak change in structure of the MFI and MOR samples, the BEA zeolites show a significant loss in framework structure beginning already at 403 K (Fig. 7). At 513 K even more than half of the zeolite framework is damaged. Because of a modulus starting with the relatively high value of 21 as lowest value, the Al content of the framework is low in all samples. Therefore, the dependence of the hydrothermal stability on the modulus is relatively small at each of the

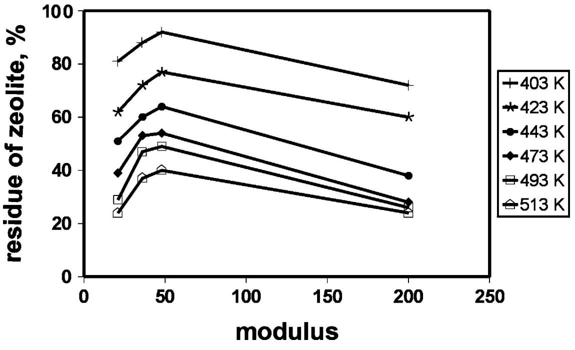

Figure 7. Residue of the zeolitic framework of BEA zeolites after a hydrothermal treatment at different temperatures.

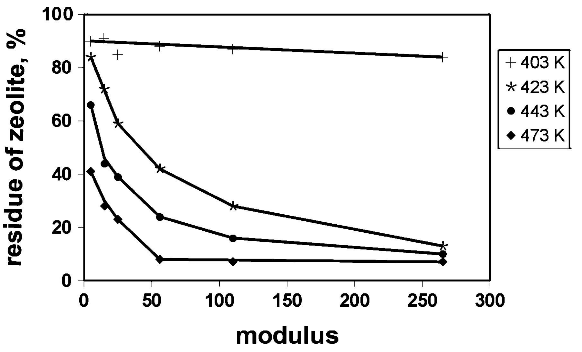

Figure 8. Residue of the zeolitic framework of FAU zeolites after a hydrothermal treatment at different temperatures.

temperatures the process had been investigated at. In analogy to the MFI type, a slightly stronger decomposition takes place in case of the samples with highest and lowest contents of aluminium.

FAU Zeolites

The samples of the FAU type are significantly damaged beginning at 423 K with a remarkable dependence on the modulus at higher temperatures. The loss of framework structure increases linearly with increasing modulus. The high-silica sample (265) is totally damaged already at 423 K and the sample (56) at 473 K (Fig. 8). Water sorption, BET and XRD measurement results correspond well between each other.

A comparison of the four zeolite types shows no systematic tendency in hydrothermal behavior. The dense-structured orthorhombic MFI (17.9 T/nm^3, T = Si or Al atoms) and MOR (17.2 T/nm^3) frameworks are hydrothermally stable under the drastic experimental conditions applied. The activation energy of decomposition seems to be too high to get significant effects up to 513 K, as the highest temperature in our autoclave technique. In opposite, the more open-structured tetragonal BEA (15.1 T/nm^3) and cubic FAU lattices (12.7 T/nm^3) undergo dramatic changes of their framework beginning at 403 K and 423 K, i.e. at relatively mild conditions.

There is a linear decomposition of FAU, the stronger the higher the SiO_2/Al_2O_3 modulus is, and a non-linear dependence of BEA with stronger effects for high-alumina and high-silica samples. It seems that in the last case the "acid" and "alkaline" decomposition mechanism of Figs. 1 and 2 act stronger than for samples of medium moduli. If the zeolite framework contains a high number of aluminium atoms, the protons attack strongly the —Si—O—Al— bonds inside the whole framework. The effect decreases with increasing SiO_2/Al_2O_3 modulus because of a reduction in the absolute number of —Si—O—Al— bonds and, additionally, due to their higher stability. The —Si—O—Al— bonds lose in this range more and more of their proportionate ionic character to change into pure covalent bonds. In samples of medium moduli, the number of negative charges caused by framework aluminium is, however, still high enough to repulse the negatively charged hydroxide ions. Thus, the "alkaline" process acts significantly only in samples of high moduli with only residuals of negative framework charges.

The lower density of the FAU and BEA frameworks favours the decomposition of the zeolites stronger because of the greater free space inside. At this place, the new silica and amorphous aluminosilicate phases, respectively, may be formed as decomposition products. Thereby, a formation of secondary products is the driving force for transformation of the solids if the activation energy of the process is reached by thermal treatment (Iler).

Modeling

Mathematical models for the decomposition of zeolite frameworks under hydrothermal conditions were derived by Suckow et al. (1992) and Ehrhard et al. (1995). The first paper presents a model for dissolution of the Si—O—Si bonds of high-silica zeolites by an "alkaline" mechanism whereas the second one deals with the hydrolysis of the —Al—O—Si— bonds of high-alumina zeolites by "acid" mechanism. All investigations were performed on a fixed type of zeolite. To create a model that accounts for both mechanisms, the degree of destruction of the framework in dependence of the modulus M has to be incorporated.

It is assumed that the crystallinity z of significantly damaged BEA and FAU samples is directly proportional to their water adsorption capacity measured at room temperature at $p/p_s = 0.36$. Thus, the function

$$z(t) = \frac{q(t)}{q_0} \tag{3}$$

can be used to describe the experimental results, where $q(t)$ is the adsorbed amount of water after the treatment time t (in our case at 72 h), and q_0 is the amount of the untreated sample. We assume the destruction of the zeolitic framework to be a reaction catalysed by water

$$Z + W \xrightarrow{k} A + W, \tag{4}$$

where A means the up to a certain extend resulting amorphous material. Utilizing the results of the mentioned papers above, the solid-phase reaction follows a first-order reaction kinetics and can be described by

$$\frac{dz}{dt} = -k \cdot g(w) \cdot z. \tag{5}$$

The function $g(w)$ characterizes the influence of steam pressure in the system, and it is assumed that it can be defined as a n-th order dependency of normalized steam concentration (Ehrhardt et al., 1995)

$$g(w) = \left(\frac{p}{p_s}\right)^n \tag{6}$$

with the saturation pressure p_s and a certain exponent n. Under our experimental conditions, saturation pressure is given in all experiments, and $g(w)$ reduces to

$$g(w) \equiv 1. \tag{7}$$

Consequently, the parameter n could not be determined and not used in our simulation.

The main problem remaining is to find an appropriate description of the reaction rate constant k in dependence of the modulus M and the temperature T. If we assume that water molecules are in surplus, and the two reaction mechanisms are not in competition the overall reaction rate k splits into the sum of the two parallel reactions (according to the "acid" (a) and the "alkaline" (b) mechanisms)

$$k = k_a + k_b\cdot \tag{8}$$

For a determination of k_i $(i = a, b)$, one has to look at the kinetics of enzymatic reactions in the production of biomasses. There, the reaction rate constant for the growth of biomass or the loss of substrate is given by the Monod equation (which has a structural equivalence with the Michaelis-Menton-equation) (Wolf, 1991). If one assumes equivalence between the loss of substrate on the one hand and the loss of Al atoms in the zeolitic framework on the other hand, where the latter results in an increasing modulus, the reaction-rate constants have the form

$$k_i = \mu_i \frac{M}{\varepsilon_i + M}\cdot \tag{9}$$

For the energetic constant ε_i we choose a description by the Arrhenius law

$$\varepsilon_i = \varepsilon_i^0 \cdot e^{\frac{E_i}{R \cdot T}} \tag{10}$$

with the temperature $T(K)$ of treatment, the activation energy E_i (J mol^{-1}), and the universal gas constant R (J mol^{-1} K^{-1}).

The model contains six parameters, three for every reaction mechanism: the energetic parameters ε_i^0, E_i and the maximal reaction rate μ_i (h^{-1}). The parameter estimation was performed by a minimization of the sum of un-weighted least squares of the solution of the model equation

$$z(t) = e^{-k \cdot t} \tag{11}$$

to the experimental data. The data basis comprises measured point matrices for zeolite BEA at six temperatures and four moduli and for zeolite HY at four temperatures and six moduli, respectively. The results for the zeolites BEA and FAU obtained are shown in Figs. 9 and 10.

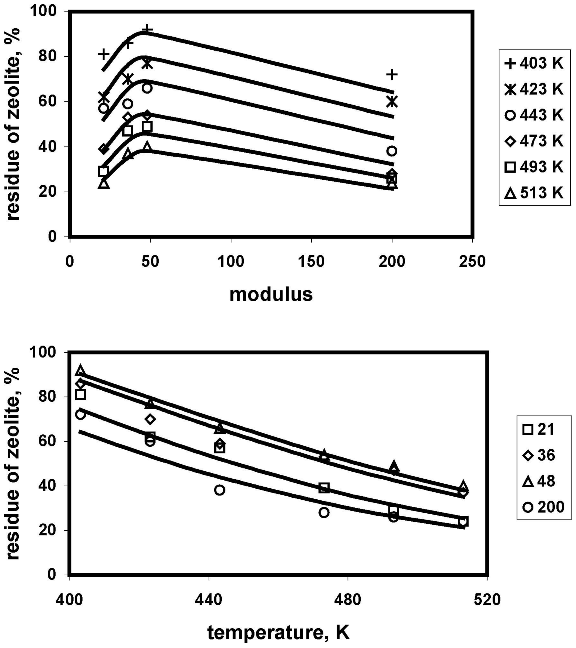

Figure 9. Measured (points) and calculated (lines) decrease of crystallinity in dependence of modulus and temperature for zeolite BEA.

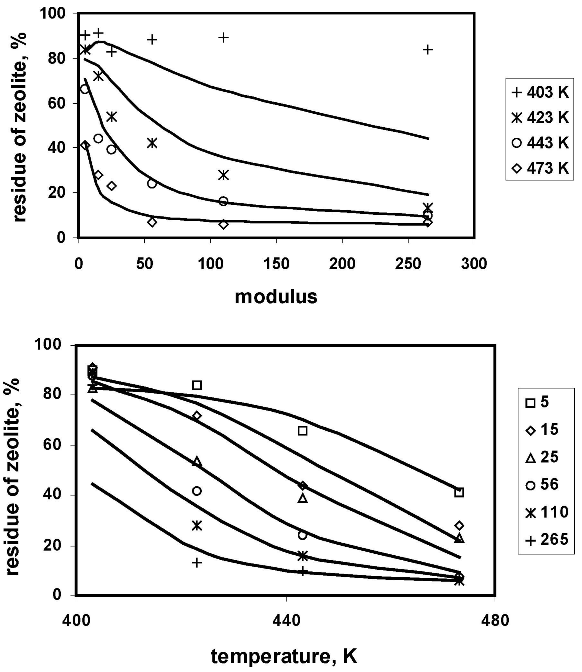

Figure 10. Measured (points) and calculate (lines) decrease of crystallinity in dependence of modulus and temperature for zeolite DAY.

For BEA the measured data could described well with the given model ($r^2 = 0.96$) whereas for the zeolite DAY the description failed for mild conditions at the low temperature $T = 403$ K ($r^2 = 0.92$). This discrepancy can be explained by a failure in the simple assumption of the superposition of the two destruction mechanisms. Furthermore, the influence of the modulus in the model behaviour can be improved by taking into account an exponential dependence M^α. The parameter α stands in the enzyme kinetics for the number of activated centres where substrate molecules can dock. In our equivalence model, one can hardly find an appropriate physical meaning, and, thus, we have done it without exponential dependency.

The different behaviour of the two zeolites BEA and DAY, respectively, can be seen from the dependence of the reaction rate constants k_a for the "acid" decomposition mechanism and k_b for the "alkaline" decomposition mechanism (Figs. 11 and 12).

At the first look it stands out that the constant k_b for the "alkaline" mechanism increases with modulus and k_a for the "acid" mechanism decreases. It is unexpected however, that the data for k_a are negative. This seems to indicate that the "alkaline" mechanism for both zeolites is the dominant one. On the other hand, negative k_a values could mean that the "acid" mechanism acts contrary to the "alkaline" mechanism; the "acid" destruction is weakened by the "alkaline" one. Although this coincides well with observations for zeolites MOR and MFI, this interpretation is in contrast to the assumption made above that both reactions mechanisms do not interact.

While for zeolite BEA k_b grows linearly with modulus at all temperatures, for zeolite DAY it tends to reach a maximum with modulus for high temperatures. On the other hand, for zeolite BEA there is a decrease of the influence of the "acid" mechanism in dependence of temperature. For zeolite DAY this drop takes place in a very small value range and is independent of temperature. Due to the de facto independence of k_a of the modulus the "acid" mechanism alone is responsible for the destruction of the zeolitic framework. The shape of the dependence of k_b on modulus coincides with the monotonous loss of crystallinity. For BEA, the two destruction mechanisms overlap in such a way, that for low modulus the "acid" and for high modulus the "alkaline" mechanism is responsible for the framework decomposition. Between these end points, each mechanism has such a very small influence that the

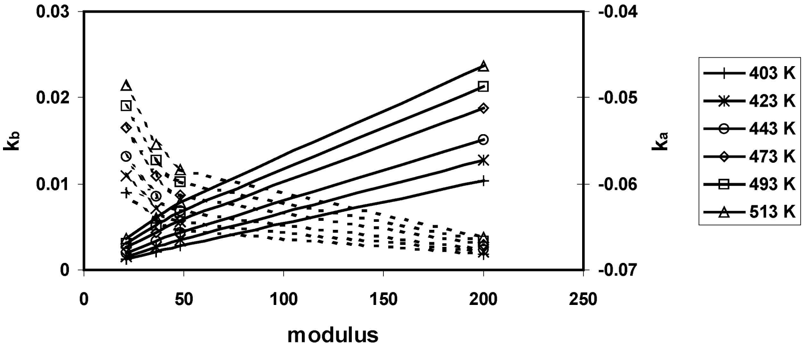

Figure 11. Dependence of reaction rate constants k_b (solid line) and k_a (dotted line) from modulus for different temperatures for zeolite BEA.

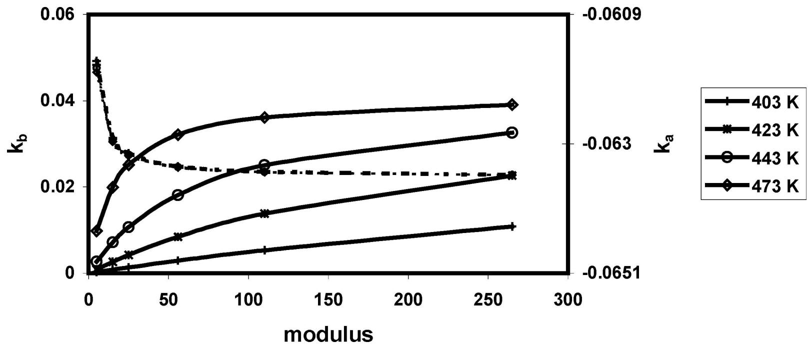

Figure 12. Dependence of reaction rate constants k_b (solid line) and k_a (dotted line) from modulus for different temperatures for zeolite DAY.

superposition of both has a week effect, too. Therefore, a maximum is found for stability at the modulus of 48.

Conclusions

The hydrothermal behaviour of technical relevant zeolites in contact with steam or water produces non-uniform results. Under a treatment in liquid water for 72 h and for different temperatures up to 513 K dense-structured zeolites (MFI) and mordenite (MOR) are relatively stable. They lose a maximum of 20% of their crystallinity in weak dependence on the SiO_2/Al_2O_3 modulus. Unlike this, the destruction of the framework of the open-structured BEA and FAU zeolites is much stronger. Under high temperatures and at a great modulus, 80% of the crystallinity are lost. Differences could be explained by the two destruction mechanisms: on the one hand the attack of the protons of water on the Si—O—Al—bonds over the whole framework (“acid” attack) and on the other hand the attack of the hydroxide ions especially on the terminal OH groups of the zeolite surface (“alkaline” attack).

A mathematical model is presented, that gives insight on the strength of the “acid” and the “alkaline” mechanism as dependence on temperature and modulus. The model is based on the assumption that the two mechanisms of destruction overlap independently of each other. For the zeolite BEA, relevance of both mechanisms is of comparable order of magnitude. Their superposition results in a maximum of stability at inner points of the modulus interval. For FAU zeolites, the acid mechanism seems to play the decisive role, which accords with common knowledge.

Nevertheless, the model is a first attempt to take into account the influence of the modulus. Due to the current data basis the framework decomposition in dependence on the partial pressure of water and in dependence on different treatment times is not taken into account yet. But such data are necessary to perform *a priori* calculations about long-term stability and ageing behavior of zeolites in important technical applications.

In one case – the MFI zeolite – the hydrothermal treatment entails a better structure by healing out the structure without significant damage of the framework, which leads to a product of increased hydrophobicity.

Nomenclature

E	activation energy (J mol^{-1})
$g(w)$	functional dependence of water content w
k	rate constant (h^{-1})
M	modulus (M)
q	adsorbed water amount (mmol g^{-1})
p	pressure (Pa)
R	universal gas constant (J mol^{-1} K^{-1})
t	time (h)
T	temperature (K)
z	residue of zeolite (%)
ε	energy constant(−)
μ	maximal rate constant (h^{-1})

Subscripts

a	“acid” mechanism
b	“alkaline” mechanism
i	$= a, b$
0	initial state

Acknowledgments

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