

Review Article

Zeolite Y: Synthesis, Modification, and Properties—A Case Revisited

Wolfgang Lutz

Brandenburgische Technische Universität Cottbus, Volmerstraße 13, 12489 Berlin, Germany

Correspondence should be addressed to Wolfgang Lutz; lutz@btu-lc.fta-berlin.de

Received 9 October 2013; Revised 21 January 2014; Accepted 23 January 2014; Published 22 May 2014

Academic Editor: Louis-Philippe Lefebvre

Copyright © 2014 Wolfgang Lutz. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Y zeolites dealuminated by steaming were introduced as fluid-cracking catalysts in the year 1970. Extensive research has been done to develop suitable dealumination techniques, to investigate crystal structure, and to characterize catalytic behaviour. However, the origin of the secondary pore system formed in the zeolite structure during dealumination process remained completely obscure over a period of four decades. Open questions concerned also the existence of extraframework siliceous admixture in addition to extraframework aluminium species which can dramatically change the catalytic properties of these zeolites. This paper gives a review on the synthesis of DAY materials and provides some answers to several open questions.

1. Introduction

Commercial synthesis of Y zeolite was claimed by Breck in 1964 [1] after the first industrial manufacturing of A and X types by Milton [2, 3]. Zeolite NaY appears to be topologically analogous with the type X aluminosilicate framework. The cubic unit cell of all these aluminosilicates contains 192 (Si,Al)O₄ tetrahedrons. Breck suggested that the change of X to Y modification occurs at a silicon to aluminium ratio of 1.5 [4]. Zeolites with Si/Al values lower and higher than this critical point characterize X and Y composition, respectively. Because of the instability of Al-rich samples in acids or water at elevated temperatures [5], Rüscher et al. [6] proposed a new definition based on a typical chemical behaviour of the samples—the dealumination by steam treatment [7]. Above Si/Al ratio of 2.2, Y samples may be dealuminated in steam without collapse of its framework. The reason for that arises from long silicate chains with 132 remaining silicate units while 60 aluminate units can be removed.

The new X/Y definition explains the reason why only high-silica modifications of zeolite Y have been used as cracking catalysts [8, 9]. Since zeolite Y can be directly synthesized with maximal Si/Al values of about 3 [10], all catalytically relevant materials must be prepared by postsynthetic removal of framework aluminium. Zhdanov et al. [11] provided an

overview about different techniques of zeolite dealumination such as acid extraction [12], isomorphous Al/Si substitution [13], and thermochemical treatment of NH₄Y [7]. Heating of NH₄Y in dry or wet air brings different dealumination effects and structural features to dealuminated Y samples (DAY) [14]. In each case, framework aluminium will be transformed thereby into extraframework aluminous species (EFAl) [15].

Ambs and Flank [16] explained the thermal stability of DAY over 1273 K as a result of the removal of sodium ions which destabilize the framework due to their mineralizing effect. Peri [17] gave preference to the formation of novel Si–O–Si bonds as a result of dehydroxylation of intermediately formed hydroxyl nests. Kerr et al. [18] explained rising stability of DAY by effect of healing of the Al defects with migrating H₄SiO₄ molecules.

Increasing thermal stability of DAY was one of the reasons why the thermochemical process has been commercially established in a high extent. After discovery of structural fundamentals of steamed zeolites, researchers put more attention on their catalytic behaviors. Thereby, the formation of a secondary pore system in DAY has been found. According to [19], this process was assumed to enhance the molecular transport of starting materials and final products during catalytic conversion. But, in spite of the framework repairing, a significant decrease of the sorption capacity

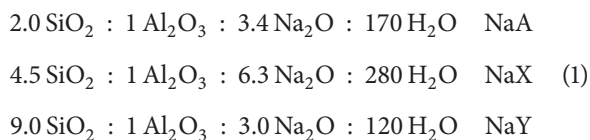
was observed [7]. The nature of this phenomenon is still unclear and problems of mesopores formation and types of mesopores, as well as partial amorphization of the zeolite framework remain open.

Since a direct relationship between the structure of NaY and the specific dealumination behavior of NH_4Y undoubtedly exists, revisiting the problems of synthesis, ion-exchange, and dealumination behaviors of zeolite Y seems to be advisable.

2. Results and Discussion

2.1. Synthesis of Zeolite NaY. Fundamentals of the synthesis of aluminum-rich zeolites of A, X, and Y types were reported by Kerr [20, 21], Breck and Flanigan [22], Zhdanov [23], and McNicol [24]. These and several other authors discussed mainly the crystallization process of zeolites from their primary aluminosilicate gels. Using Molybdate method [25], Fahlke and colleagues [26, 27] investigated in details the mechanism of gel formation and following rearrangement. This method determines the length of silicate chains between aluminate units in dependence on gel maturation. Indeed, prolonged silicate units define the process of gel aging. For measurement, the $\equiv\text{Al}-\text{O}-\text{SiO}_{(n)}-\text{Al}\equiv$ with $n = 1-\infty$ zeolite framework is hydrolyzed in mineral acid and added to molybdic acid. The degradation rate (the measure of the length of silicate chains) is optically followed by formation of the yellowish silica Molybdate complex. This technique characterizes perfectly the Al-rich A and X zeolites, but it fails in the case of Y crystals because the infinite long silicate chains of latters are practically insoluble in acid.

Properties of DAY samples—crystallinity, silicon to aluminium ratio, secondary pore volume, and extraframework species—depend directly on the state of the parent NaY crystals and even on the starting gel. Typical composition of synthesis batches of aluminosilicate zeolites are



with final Si/Al ratios of 1, 1–1.2, and 2.2–3.0, respectively [22]. Basic materials are aqueous solutions of sodium aluminate and sodium silicate for NaA and NaX, silica gel or silica sol for NaY, and, as expected, sodium hydroxide and water. The reaction composition diagram according to Breck [4] or Kostinko [28] shown in Figure 1 demonstrates that the fields of gel compositions from those A, X, or Y zeolites are formed.

As can be seen from Figure 1, the variation of gel composition of X and Y zeolites is significantly smaller than that of zeolite A.

By mixing of raw materials, aluminosilicate gels occur in all zeolite synthesis batches. For example, when pure solutions of aluminate and silicate are mixed, spontaneously silicon-rich hydrogels precipitate. Some of the monomeric aluminate ions are linked to the oligomeric silica molecules. The residual aluminate ions remain at first in the solution. But the gel reorganizes its structure by dissolution and renewed

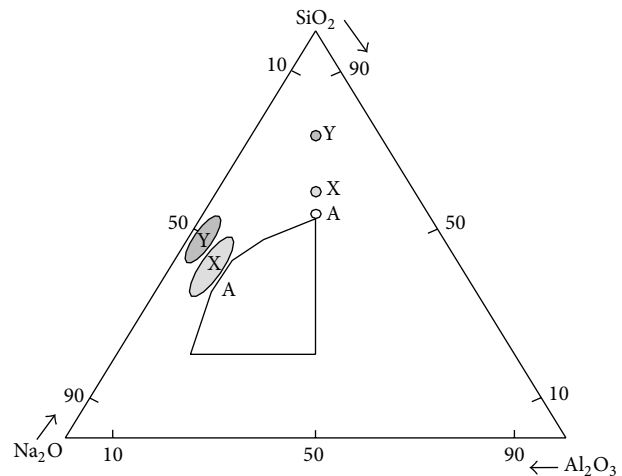


FIGURE 1: Reaction composition diagram of aluminosilicate zeolites A, X, and Y (fields-possible gel composition; points-final zeolite composition) [4].

precipitation up to the equilibrium state. Over an aging period of ten to twenty hours, the gel consumes more and more aluminate in such a way that finally the solids contain silicon and aluminium in equivalent amounts in zeolites A and X batches. The three-dimensional gel structure is stable at ambient temperature in its mother liquid because all alkaline soluble $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds were changed already into chemically stable $\equiv\text{Si}-\text{O}-(\text{Al}^{(-)})\equiv$ bonds. The negative charges of the fourfold coordinated Al atoms protect the gel against further attacks of the likewise negatively charged hydroxyl ions. On the other hand, the negative charges promote the attack of protons for spontaneous degradation of the framework as in the case of Molybdate measurements.

Wieker and Fahlke [27] detected 10% of monomeric $\equiv(\text{Al}^{(-)})-\text{O}-\text{Si}-\text{O}-(\text{Al}^{(-)})\equiv$ silicate building units, in addition to polymeric silicate, in NaY synthesis batches. The NaY gel composition differs thus from that of A and X. Due to these monomeric species, the crystallization of NaY starts with fragments of NaX composition (Si/Al ratio of about 1) at 363–373 K. The crystallization is favored if the batch is seeded by NaX nanocrystals, exactly by the way exploited in industrial zeolite manufacturing. Actually so-called seed-solutions which contains silicate ions in the form of oligomeric chains (length of 10–30 silicon atoms) terminated by aluminate units are used in order to prevent, as much as possible, the formation of Al-rich areas inside the NaY crystals.

With the increasing of time, the crystallization turns gradually into the actual NaY zeolite composition with a Si/Al ratio over 2.2. Then, due to the overproportional consumption of aluminate at the beginning of the process, the crystallization drops off owing to the total consume of aluminate ions being primary building units in the faujasite structure. This is the reason why the crystal surface becomes finally rich in silicon and no secondary crystal growth above $3 \mu\text{m}$ is observed [29, 30]. Frequently, the NaY zeolites are crystallized in polycrystalline particles with smaller actual size [31].

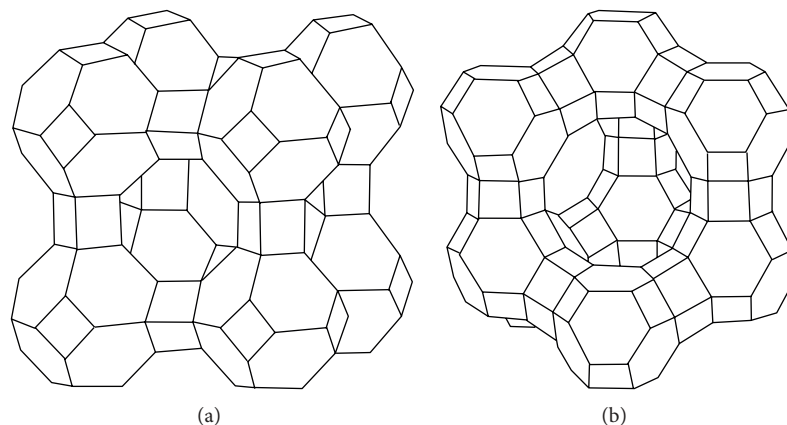


FIGURE 2: Zeolite A (a) and faujasite-type zeolites X and Y (b) formed by sodalite cages.

The synthesis of large faujasite type crystals with diameters $>100\ \mu\text{m}$ was reported by Ferchiche et al. [32, 33] and Berger et al. [29] only for samples with Si/Al ratios below 1.8. It seems very likely that such samples consist of the mixture of both X and Y types [6].

The Si to Al gradients in NaY starting from 1 inside the nuclei and increasing to ∞ at the surface of the zeolite crystals are responsible for several further specific phenomena observed in steamed DAY zeolites. The NaY crystals with Si/Al ratios over 2.2 are unfortunately too small for a characterization of their gradient by physicochemical methods such as ESCA or EDX. Additionally, they tend to collapse during measurements. Therefore, a complex characterization of DAY samples including tests of hydrothermal stability, state of crystallinity, characterization of extraframework species, and pore structure is necessary to describe the actual state of NaY and consecutive products.

2.2. Sodium/Ammonium Ion Exchange of Zeolite NaY. The unit cell of zeolite NaA contains 24 atoms and that of the faujasite-type zeolites NaX and NaY contains 192 SiO_4 and AlO_4 tetrahedrons [34]. They form sodalite cages which are linked to oxygen double 4 rings and 6 rings in NaA, NaX, and NaY, respectively, as seen from Figure 2. In NaA and low-silica NaX frameworks with Si/Al = 1, the SiO_4 and AlO_4 tetrahedrons are arranged in rigorous alternation according to the Loewenstein rule [35].

Cavities with pore diameters of 1.14 nm in NaA and 1.3 nm in NaX, NaY arise. The diameters of pore entrance are equal to 0.42 nm and 0.74 nm, respectively [4].

Due to the negatively charged $\text{AlO}_4^{(-)}$ tetrahedrons, zeolites contain $\text{Na}^{(+)}$ ions in different amounts in their synthesis form –12 in NaA, 96–88 in NaX, 56–53 in NaY (values of X and Y based on the definition of Rüscher et al. in [6]). Different cations may be exchanged for sodium ions, totally or to a high degree, to adjust the entrance pore diameter and specific sorption behaviour of zeolites. Barrer and colleagues published fundamental aspects about this method of zeolite modification, for example, in [36, 37].

Because zeolite NaY is used preferentially in dealuminated state for catalytic processes, the introduction of ammonium ions into this framework is of specific interest. Ammonium ions are decomposed by heating in H^+ and outgoing NH_3 gases thus forming HY modification which is active in the framework dealumination by steaming.

At the laboratory scale, the ammonium ions can be exchanged for sodium ions in 0.1 M solution of ammonium nitrate or sulphate at liquid/solid ratio higher than 10. For an effective and careful exchange, the procedure should be repeated. In this way, 80% of sodium ions are removed from the framework of zeolite Y. Thus, one-fifth of the framework remains inactive in dealumination, for example, by steaming as it will be seen below. The use of a higher concentrated salt solution or/and treatment of the zeolite at 353 K was not successful [38]. But there is a possibility to increase the active framework part if a stepwise way is used: firstly the partially ammonium exchanged sample is heated at 523–543 K then the ion exchange procedure is repeated once more. Intermediately produced protons displace the residual sodium ions from their position inside the sodalite cages and double-six rings which are removed in the second ammonium exchange from the large cavities. Partial dealumination of the framework already takes place at each treatment step.

2.3. Dealumination. Dealumination is a method of chemical and structural modification of zeolites. But not each synthetic zeolite framework preserves structural arrangement and stability after removing some Al atoms. Thus, NaA and NaX zeolites are completely collapsed after any dealumination procedure. NaY zeolite with Si/Al < 2.2 also loses, at least partially, its crystallinity [39]. But only with this treatment, Y aluminosilicates with definite Si to Al ratios that guarantee their specific properties such as thermal stability, hydrophobicity, or catalytic activity can be directly prepared.

The simplest dealumination method consists of the treatment of samples in inorganic or organic acid [12] where decationation takes place. Under action of the introduced protons, $\equiv\text{Si}-\text{O}-\text{Al}^{(-)}\equiv$ bonds became hydrolyzed and changed firstly into more stable $\equiv\text{Si}-\text{O}-\text{H}$ units plus $\text{H}-\text{O}-\text{Al}\equiv$ splitted

structure. At the second step, all the other bindings with Al ions are broken off. Utilizing the natural clinoptilolite, firstly, Barrer and Makki [40] were successful in the treatment of the zeolite with 1 M hydrochloric acid at 373 K. The aluminium content decreased down to 40% without a significant loss of crystallinity of samples. Aluminium atoms removed from the framework were found as EFAl species in the solution. The disadvantage of this method for zeolite NaY lies in remaining structural defects involving formation of hydroxyl groups inside the silicon framework [41].

A more sensitive extraction process includes a treatment of the zeolite with complex agent of ethylene-diamine-tetra-acetic acid (EDTA). By use of this method Kerr [12] removed the half of the framework aluminium atoms in NaY zeolite without a greater amorphization of the crystals but with a high density of structural defects. One can get more intact structures if zeolite NaY is treated in a vapor of silicon-tetra-chloride as it was shown by Beyer and coworkers [13, 42, 43]. In the resulting structure, Al atoms are replaced by silicon atoms at elevated temperature. But rigid control over this exothermic process and technological demand on the resistance against the aggressive medium appears to be too complex so that industrial production was restricted only to the semi-industrial scale. Therefore, the calcination of NH_4Y zeolites in steam [7] has been established worldwide as technical dealumination process.

2.3.1. Thermochemical Treatment of NH_4NaY in Steam. Generally, dealumination of NH_4NaY in steam has not been changed since the introduction of this procedure by McDaniel and Maher in 1971 [15]. Samples are treated in an open furnace or rotary kiln through which steam of 1 bar water pressure is going. Steam is generated by evaporation of liquid water with one bar of water pressure or saturation of gas with water vapor of lower partial pressure. The actual concentration of water molecules inside the oven reaction zone depends on heating and is reduced with increasing temperature of sample treatment. The extent of dealumination is limited by the degree of ammonium exchange of the starting material and depends on the temperature and partial pressure of steam [44, 45].

Salman and colleagues [46] have investigated the dealumination of zeolite $(\text{NH}_4)_{39}(\text{Na})_{10}[(\text{AlO}_2)_{49}(\text{SiO}_2)_{143}]$ with a Si/Al ratio of 2.9 over a wide field of variable parameters. Figure 3 shows increasing removal of framework Al with rising the temperature and period of treatment.

Small and slightly higher dealumination with Si/Al values of 3.2 and 3.5 was found at 573 K and 673 K, respectively. The evolution of Si/Al at 773 K and 873 K indicates a typical saturation behaviour towards values of 4.4 and 5.4. Saturation effects have also been reported earlier by Wang et al. [39], Engelhardt et al. [44], and Lohse et al. [47]. Due to a limitation of sodium/ammonium exchange in the used one-step strategy, 20% of the $\text{Na}^+/\text{AlO}_4^-$ charge complexes remained stable under steam. The equilibrium Si/Al ratios obtained in [46] correspond to 36% (773 K), 49% (873 K), and 64% (973 K) of the total content of Al atoms removed from the framework. Further removal could be increased by a renewed ammonium exchange followed by a second steaming

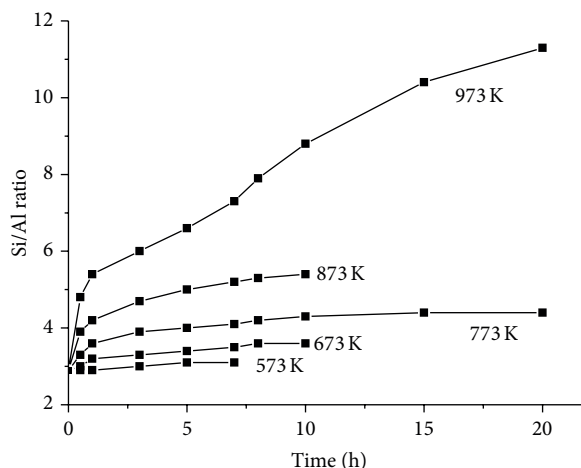


FIGURE 3: Si/Al ratio of DAY zeolites in dependence on steaming temperature and time [46].

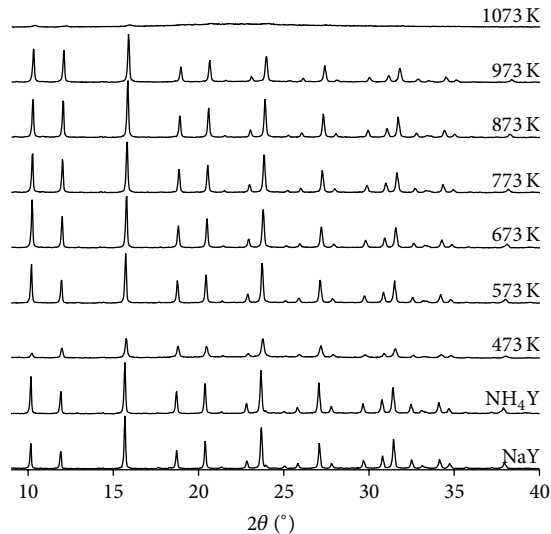


FIGURE 4: Selected XRD patterns of DAY zeolites steamed 3 hours in dependence on temperature [46].

process. Following this two-step strategy, the Si/Al ratio of DAY steamed at 873 K for 5 hours changed from 5.4 to 10.3, with a twofold increase of the dealumination effect without significant sample amorphization [38].

Significantly higher values of Si/Al ratio (up to 11) have been obtained directly for steaming at 973 K. However, this result was accompanied by a partial or strong amorphization of the final product. The sample became completely amorphous at 1073 K because of a thermal collapse at the beginning of steaming. At the lowest temperature investigated (473 K), drastic framework damage has occurred, too. In this case, a sour hydrolysis of the framework owing to the high concentration of water molecules in the reaction zone took place.

X-ray diffraction (XRD) patterns in Figure 4 indicate a moderate decrease in signal intensity for NH_4NaY and DAY

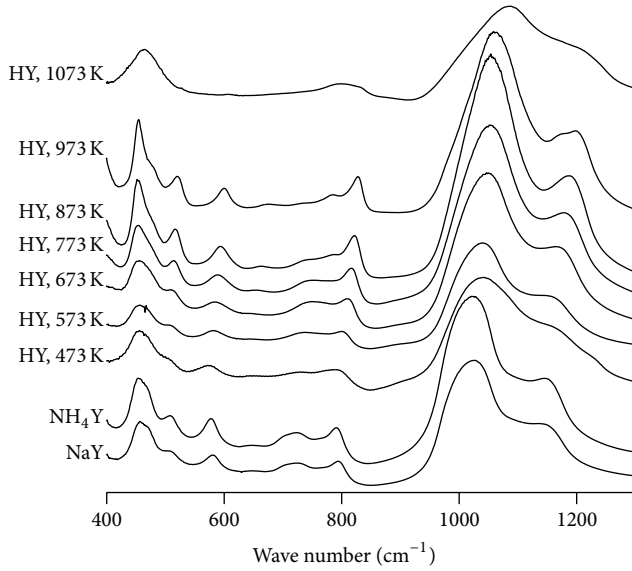


FIGURE 5: IR spectra of parent NaY zeolite and DAY samples steamed for 3 hours in dependence of temperature.

samples. This observation will be discussed below, along with the results on the formation of extraframework species.

Removal of Al atoms results in the shrinking of the total zeolite framework because of the different $-\text{Al}-\text{O}-$ and $-\text{Si}-\text{O}-$ bond lengths of 191 pm and 169 pm [48], respectively. The lattice constant a_0 decreases from 2.463 nm in NaY to 2.438 nm in DAY treated at 973 K for 1 h. This sample shows the highest dealumination state, without a significant structural amorphization.

IR spectra of DAY samples obtained by Salman et al. [46] are given in Figure 5 and support the data of XRD measurements. The framework sensitive double-ring vibration band w_{DR} [49] shifts from 574 cm^{-1} to 610 cm^{-1} with increasing steaming temperature up to 973 K. The signal completely disappeared in the sample dealuminated at 1073 K.

Apart from w_{DR} signal, systematic changes in the shape of spectra, particularly bending, symmetrical and asymmetrical stretching vibration of the TO_4 building units at $450\text{--}550 \text{ cm}^{-1}$, $700\text{--}900 \text{ cm}^{-1}$, and $900\text{--}1200 \text{ cm}^{-1}$, have been additionally observed. Optimal conditions of steaming appear to be at 873 K as evident from the shape and intensities of characteristic peaks in the dealuminated framework seen in Figure 5. The framework became more regular in respect to the former Si/Al gradient resulting from NaY synthesis.

At lower temperature, the shape of peaks becomes broader indicating a higher nonuniform distribution of the Si/Al ratio in the framework and a relative stronger contribution of the extraframework species formed. But, as we will see below, lower steaming temperatures lead to a reduced mesopore formation.

One can suggest that all spectra in Figure 5 are superimposed by extraframework species of aluminosilicate and silica gel [50] formed by some corrosion of the framework. The aluminosilicate may be extracted together with the extraframework aluminium by acid treatment [51]. It is

known that highly dealuminated and acid leached DAY, frequently called US-EX (ultrastable extracted zeolite Y), shows very sharp vibration bands because of homogenisation of the pure SiO_2 framework [52].

In samples treated at 473 K, w_{DR} signal does not shift from its characteristic place. In this case, due to the low thermal activation no dealumination occurs inside the framework but the dissolution of the zeolite takes place.

2.3.2. Determination of the Si/Al Ratio of DAY Samples. The tuning of framework properties of DAY zeolites requires an exact determination of the Si/Al ratio. Dealumination effect can be proved by chemical analysis of the acid solution and washing water in the samples prepared through acid leaching [12] and Al/Si substitution [13], respectively. However, such approach requires certainty that all extraframework aluminium is completely washed out in the samples. Therefore, investigation of the solid state by physicochemical methods like XRD, IR, and NMR seems to be the better way. These methods are even indispensable for characterization of steamed DAY samples because these zeolites still contain the whole amount of EFAl and chemical analysis data appear as contradictory.

Breck [4] has presented the relationship between the unit cell constant, a_0 , and Al atom density per unit cell for hydrated NaX and NaY zeolites on basis of 37 synthesized samples. Rüscher and colleagues [53] extended this mode upon series of DAY samples prepared by steaming as well as Al/Si substitution. They additionally proposed a thorough study of evolution of the IR double-ring vibration w_{DR} for determination of Si/Al ratios inside the zeolite framework and compared these calculation methods [50] with empirical equations of Fichtner-Schmittler et al. [52] using the infrared asymmetrical TOT valence vibration ($T = \text{Si, Al}$) and ^{29}Si MAS NMR data obtained by Engelhardt and Michel [54].

XRD_{Rüscher}

$$x = 5.348 a_0 - 12.898 \quad (2)$$

(with $\text{Si/Al} = (1 - x)/x$ and $x = \text{Al molar fraction}$ by use of the cell parameter a_0).

IR_{Rüscher}

$$x = 3.857 - 0.00619 w_{\text{DR}} \text{ (cm}^{-1}\text{)} \quad (3)$$

(with $\text{Si/Al} = (1 - x)/x$ and $x = \text{Al molar fraction}$ by use of w_{DR}).

IR_{Fichtner}

$$x = 4.766 - 0.00439 w_{\text{TOT}} \text{ (cm}^{-1}\text{)} \quad (4)$$

(with $\text{Si/Al} = (1 - x)/x$ and $x = \text{Al molar fraction}$ by use of w_{TOT}).

NMR_{Engelhardt}

$$\frac{\text{Si}}{\text{Al}} = \frac{\sum_n I_n}{(I_4 + 0.75 I_3 + 0.5 I_2 + 0.25 I_1)} \quad (5)$$

($I_n = \text{intensity of } Q^4/n\text{Al signals in } ^{29}\text{Si MAS NMR spectra, } n = 0\text{--}4, \text{ without consideration of the signals of the nonzeolitic admixtures}$).

TABLE 1: Si/Al values of zeolites NaY, HY, and DAY dealuminated for 5 h in steam.

| Sample | Temperature K | Si/Al ratio | | | NMR (5) |
|--------|---------------|-------------|--------------|---------------|---------|
| | | a_0 (2) | w_{DR} (3) | w_{TOT} (4) | |
| NaY | — | 2.8 | 2.8 | 2.8 | 2.9 |
| HY | 543 | 2.8 | 2.9 | 2.8 | 2.8 |
| DAY | 773 | 3.8 | 4.0 | 7.9 | 8.2 |
| DAY | 873 | 4.4 | 5.0 | 8.9 | 8.7 |
| DAY | 973 | 5.2 | 6.7 | 10.8 | 11.8 |

In analogy to the results of Breck [4], Fichtner and coworker [52] have shown the correlation between unit cell parameters, skeletal stretching vibrations, and molar fraction of aluminium ($x = (1 + \text{Si}/\text{Al})^{-1}$) for a series of X and Y zeolites and found an ideal solid solution behaviour for these materials. The lattice constant a_0 as well as the infrared modes w_{TOT} and w_{DR} vary linearly on molar aluminium fraction which provides a rather easy method for calculating the Si/Al ratio of DAY samples independently on their synthetic type. However, differences in the level of Si/Al values have been reported in dependence on applied relations of (2) to (5). Significantly higher Si/Al values seen in Table 1 were calculated according to w_{TOT} and the NMR [50, 55].

The Si/Al ratios obtained with XRD data should characterize the actual state of the framework. These values were assumed to be not affected by extraframework species in the samples. Within each series of steaming temperature, the infrared mode w_{DR} closely coincides with the a_0 value because the double-ring vibration that characterizes only the pure faujasite framework [52]. In contrast, higher values have been calculated using NMR as well as w_{TOT} data. Results from both methods seemed to be influenced by admixtures of DAY samples. To clarify this phenomenon, a detailed phase analysis of framework and extraframework products in DAY specimens should be performed.

2.3.3. Extraframework Species in Steamed Y Zeolites. First observation of extraframework aluminium was published for natural zeolites after their acid treatment [40, 56]. Dealuminated samples obtained thereby [12] or by Al/Si substitution in SiCl_4 vapor [13] are usually free of EFAl if samples have been intensively washed out. Residues may be analyzed by ^{27}Al MAS NMR measurements [54] since the signal of Al atoms tetrahedrally coordinated in the zeolite framework and the signal characteristics of $\text{Al}^{(3+)}$ cations and AlCl_3 salt differ from each other by their spectral positions. The chemical shift of the former is situated at 60 ppm, whereas that of the latter lies at about 0 ppm. Extraframework silicon (EFSi) which can be detected by ^{29}Si MAS NMR measurements appears only in the case of partial amorphization of samples after their chemical treatment.

More complicated situation appears during calcination and steaming of NH_4NaY zeolites since all EFAl remains in the solid state [57, 58]. Baran et al. [59] considered that tetrahedrally coordinated Al is not transformed into exchangeable $\text{Al}^{(3+)}$ cations. Breck and Skeels [60, 61] suggested the formation of precipitated $\text{Al}(\text{OH})_3$ which can be

extracted by leaching with solutions of sodium chloride or potassium fluoride. The remaining defects (hydroxyl nests) of the zeolite framework can be identified by measurement of the infrared stretching vibration of isolated $\equiv\text{Si}-\text{OH}$ hydroxyl groups at 3745 cm^{-1} [11].

Different studies on EFAl have reported their possible location on the surface of crystal and/or mesopores [62, 63], revealed their role in the catalytic behavior [64] and, in particular, analyzed their nature by means of ^{27}Al MAS NMR spectroscopic measurements [65]. EFAl has been characterized as closely related to aluminium-oxo-hydroxo cations of polymeric arrangement described first by Bertram et al. [51] with the help of Ferron method [66]. Their chemical behavior in organic and mineral acids was intensively investigated by Scherzer [67]. An increase of the catalytic selectivity of DAY after extraction of the extraframework aluminium has been reported by Rhodes and Rudham [68]. Disadvantages after treatment in acid consist in the risk of further dealumination of the zeolite with remaining $\text{Al}^{(3+)}$ cations which could act as Lewis active sites in catalysis [69].

In some papers, EFAl has been described as not isolated but incorporated with EFSi and called therefore as silica-alumina species [70–72]. Strong interaction between both types of extraframework species was quantitatively analyzed with X-ray photoelectron spectroscopy [73]. Using specific Molybdate measurements [74], the silica-alumina was later characterized in samples of low-temperature steaming as Al aluminosilicate [75]. Therefore, Siantar et al. [76] and Lutz et al. [77] have performed detailed analysis of EFSi species. The dealumination behavior of NH_4NaY samples in the steam was demonstrated using two commercial and three laboratory NaY zeolite samples. Figures 6 and 7 show ^{27}Al and ^{29}Si MAS NMR spectra of initial and dealuminated zeolites.

Independent of the origin of zeolite samples, extraframework species appeared to be of the same type. The aluminium spectra in Figure 6 show a signal for tetrahedrally coordinated framework Al at 60 ppm [50] (NaY). After dealumination, additional two broader signals for extraframework species near 0 ppm and 30 ppm have been ascribed to octahedrally and pentahedrally coordinated Al, respectively. The signal at 0 ppm characterizes the polymeric oxo-hydroxo-aluminium cations [51] whereas the broad shoulder centered at 30 ppm is assigned to the distorted extraframework octahedra and/or aluminium tetrahedra of the framework [78, 79].

After deconvolution (II), the ^{29}Si MAS NMR spectra of NaY samples (I) in Figure 7 show the five signals typical for the faujasite framework with $\text{Si}(n\text{Al})$ building units ($n = 0-4$)

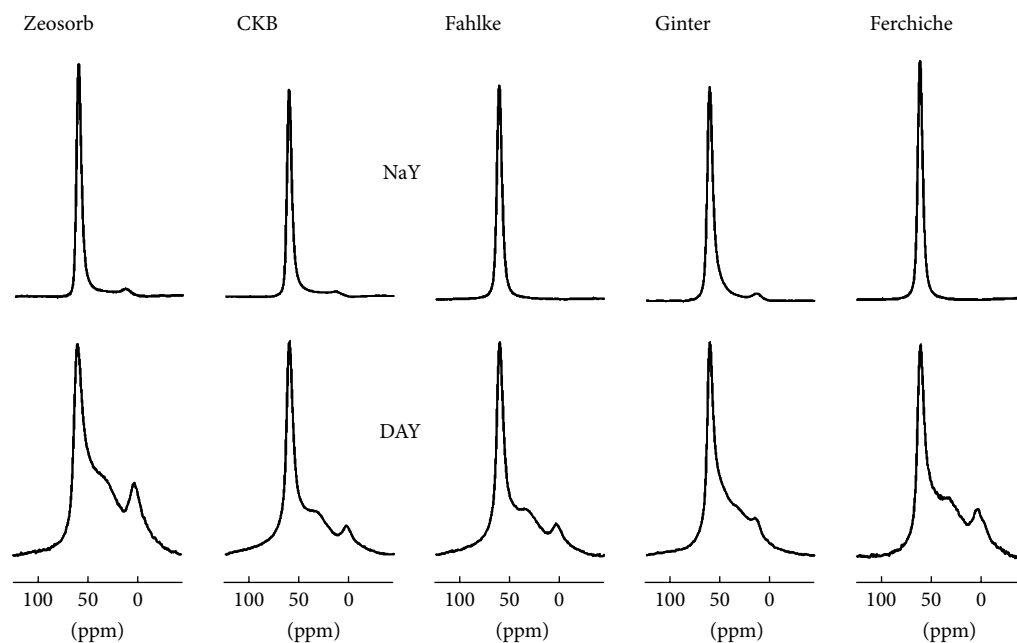


FIGURE 6: ^{27}Al MAS NMR spectra of commercially and laboratory synthesized zeolites before (NaY) and after dealumination for 7 hours at 873 K (DAY) (recipes of laboratory synthesized samples according to Fahlke et al. [26], Ginter et al. [80], and Ferchiche et al. [33]) [50].

at chemical shifts between -84 ppm and -108 ppm [77]. Simulation of the ^{29}Si MAS NMR spectra was performed by the use of a set of single lines with Gaussian line shape. This calculation reveals the lack of siliceous extraframework species (III) in the spectra of parent zeolites. But steaming results in a drastic change in shape and intensity of the NMR signals (I). All peak positions are shifted to higher ppm values. The decrease of the Si(4-2Al) and increase of the Si(1-0Al) structure units confirm the removal of framework aluminium. The significant shoulders between -80 and -90 as well as 112 ppm indicate an internal change of the framework structure and the presence of siliceous extraframework species (III). Contributions of aluminosilicate and silica gel are marked with the symbols *a* and *s*. In earlier investigations, these additional signals have been attributed to in-homogeneously dealuminated high-alumina and high-silica regions inside a disturbed zeolite framework [81, 82].

Content of extraframework species in steamed DAY samples [77] amounted to 0.6–4.9% for the aluminosilicate (*a*) and 4.3–14.7% for silica gel (*s*). It has been shown [83, 84] that the intensity of the peaks assigned to *a* and *s* at low-temperature steaming could be reduced by successive chemical dissolution in hydrochloric acid and solution of potassium hydroxide. Acid treatment caused the decomposition of the Al aluminosilicate with formation of silica gel. Alkaline treatment revealed a light loss of the silica gel admixture. In high-temperature samples, for example, at 873 K, the Al aluminosilicate decomposes into silica gel and clay. In such a case not the aluminosilicate *a* but the silica gel *s* is determined in a higher portion.

The occurrence of extraframework silica-gel *s* is the reason why Si/Al ratios calculated in DAY samples with w_{TOT}

mode (4) and NMR data (5) (see *italics* in Table 1) appear to be principally too high. Both IR and NMR signals are strongly superimposed by contributions of those characteristic of Si(0Al) and Si(1Al) species [85–87].

The strong deviation of Si/Al ratios determined with asymmetrical TOT infrared vibration band results from the great difference between the wave numbers of the zeolite and the silica gel. Wave numbers between 1080 and 1120 cm^{-1} have been observed for silica gels in dependence on their framework state [88]. The higher the portion of Q^4 building $\text{Si}(\text{OSi})_4$ units, the higher the energy for the activation of their framework. For “pure” DAY samples, w_{TOT} values from 1024 to 1040 cm^{-1} should be measured. But, owing to the superposition of the nonresolved signals of both zeolite and silica gel, the actually measured values of DAY vary between 1047 and 1061 cm^{-1} [87].

The Si/Al ratios calculated with ^{29}Si MAS NMR are too high since the $\text{Q}^3(\text{Si}(\text{OSi})_3\text{OH})$ and $\text{Q}^2(\text{Si}(\text{OSi})_2(\text{OH})_2)$ signals of the extraframework silica gel superimpose with those assigned to Si(0Al) and Si(1Al) in the zeolite [85, 87]. In order to get real values, deconvolution of the spectra becomes the essential step of the zeolite analysis with NMR technique [77]. Therefore, more realistic Si/Al ratios should be obtained using the XRD lattice constant a_0 or the infrared w_{DR} mode according to (2) and (3), respectively.

2.3.4. Origin of Siliceous Extraframework Species. Zeolite NaY is stable in dry or wet air up to 923 K. After this temperature, the crystalline framework transforms into the amorphous state. Clay (Al_2O_3) and silica (SiO_2) are formed. Then, with the rising temperature, carnegiite and nepheline occur above 1123 K [4, 10]. In water or steam of autogenous

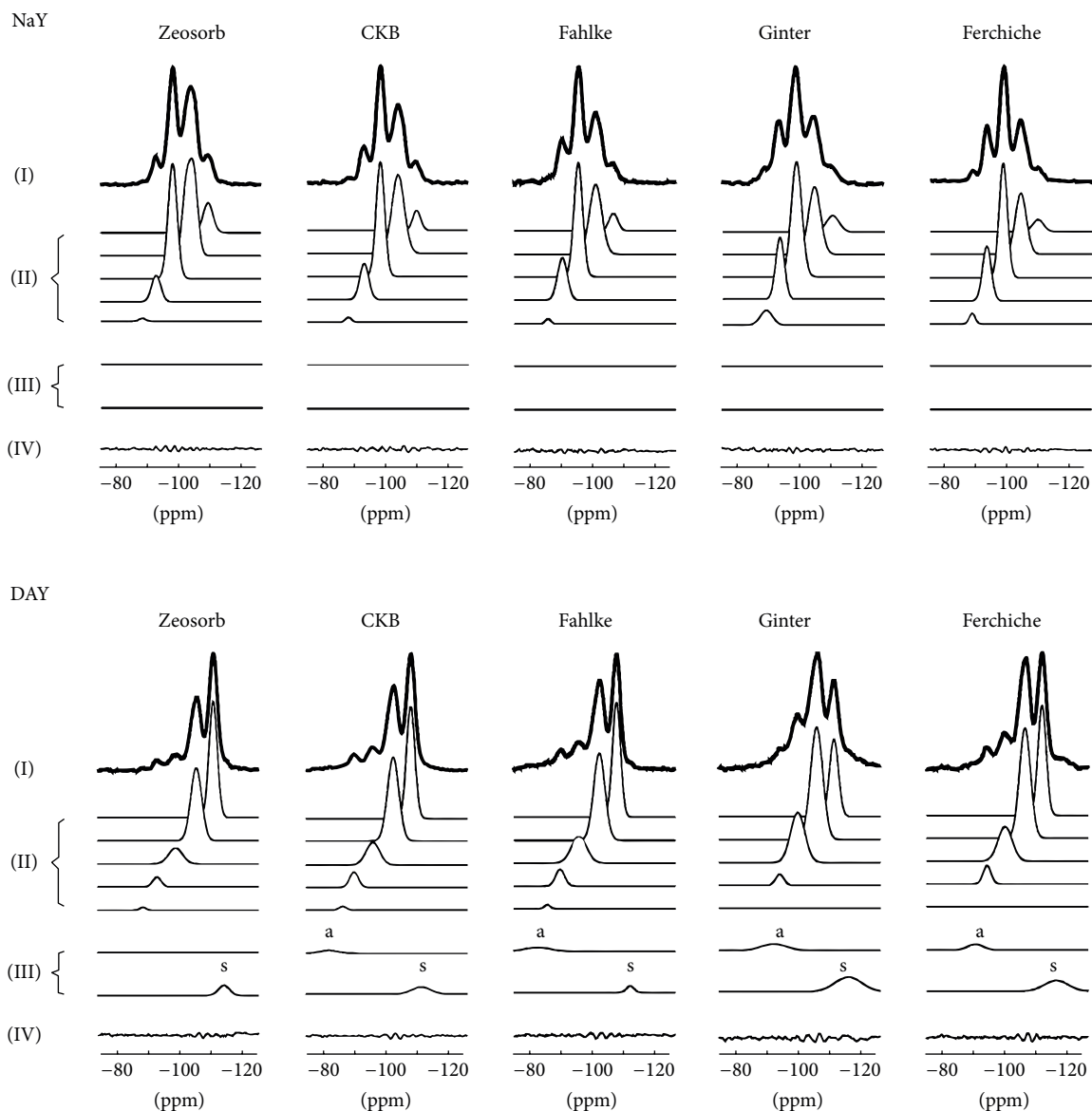


FIGURE 7: ^{29}Si MAS NMR spectra of commercially and laboratory synthesized zeolites before (NaY) and after dealumination for 7 hours at 873 K (DAY) [50].

pressure, NaY is stable up to 513 K [83]. It will be decomposed into an amorphous phase followed by transformation into hydroxysodalite or zeolite P [89, 90]. The containing sodium ions act as mineralizer. Buhl et al. [91] demonstrated their influence on the hydrothermal stability of faujasite type zeolites 13X (Si/Al = 1.2) and LSX (Si/Al = 1.0).

The proton modification of zeolite Y is of interest concerning the application of faujasites as DAY catalyst. According to Rüscher et al. [6] zeolite HY (Si/Al > 2.2) becomes dealuminated above 573 K under the formation of extraframework species. Infinite $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ chains inside the framework prevent the zeolite decomposition and only a small part of the structure is transformed into aluminium hydroxide/-oxide, aluminium aluminosilicate, and silica gel. But in the case of lower Si/Al ratios and finite $\equiv\text{Si}-\text{O}-\text{Si}\equiv$

chains, the structure is hydrolyzed partially or completely. In this sequence, zeolite HX with Si/Al = 1.0–1.2 is particularly instable. In contrary, silicon rich faujasites with Si/Al over 100 manufactured by Al/Si substitution [13] or steaming and acid leaching [92] are instable during steam treatment [93, 94].

Two chemical processes run simultaneously in the same crystal of Y zeolite since the Al–Si gradients between aluminium-rich nuclei and silicon-rich surface of the zeolite appear in this material [89, 95], independent of the origin of NaY or steaming conditions. Consequently, the center of the crystal is transformed into X-ray amorphous aluminosilicate and then, with rising temperature, to clay and silica while the pure silica gel tends to form on the surface.

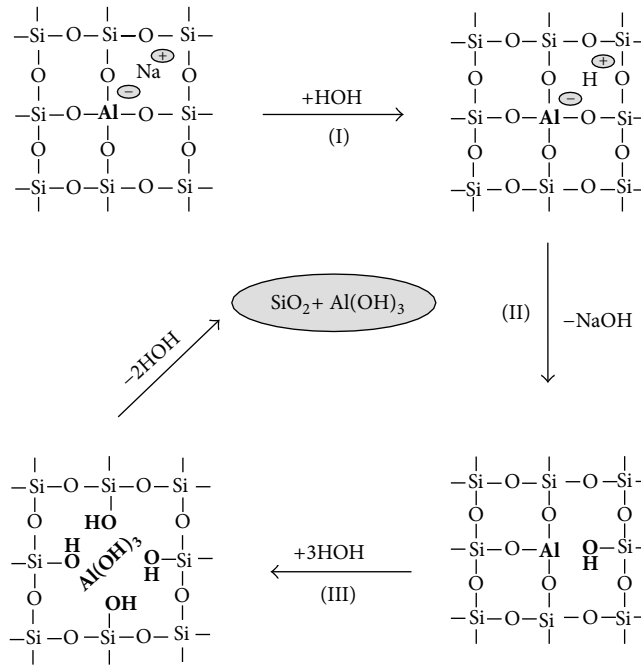
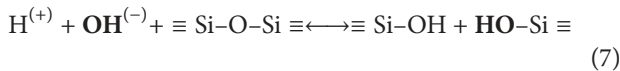
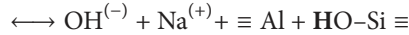
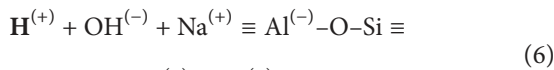


FIGURE 8: Stepwise decomposition of a low-silica zeolite framework by water [96].

Water molecules attack the zeolite framework according to the chemical reactions



with the rising temperatures. Thereby, the protons of the water molecules attack the $\equiv\text{Si-O-(Al}^{(-)})\equiv$ bonds over the whole framework whereas the hydroxide ions attack especially the terminal $\equiv\text{Si-OH}$ groups of the surface. Figures 8 and 9 give a schematic impression of both processes [96] where water acts like a catalyst [74].

In addition to the steaming procedure, a treatment in liquid water is helpful for the understanding of the hydrothermal chemistry of faujasite type zeolites. Dimitrijevic et al. [97] investigated the behavior of NaY and HY with Si/Al 2.7 in water of autogenous pressure between 403 K and 473 K. Figure 10 shows the sorption capacity of both samples after the hydrothermal process. The uptake of water in NaY remains unchanged, but that of HY decreases significantly above 423 K. The proton form is drastically damaged under treatment. The reason for this different behavior consists in the alkaline reaction of NaY in aqueous medium suppressing thus the attack of protons formed by water dissociation.

In addition to extraframework silica and alumina, traces of kaolinite occurred. The formation of a new crystalline phase below 473 K was detected for the first time. It is due to the incomplete sodium/ammonium ion exchange of the progenitor of the HNaY modification which was obtained by careful heating at 523 K.

Surprisingly, the silicon-rich DAY samples obtained by Al/Si substitution are found to be stronger attacked by liquid water as compared with the low-silica samples generated by steaming. Figure 11 shows the corresponding behavior of hydrothermally treated DAY in dependence on the module ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio).

At one hand, appearance of EFAL brings a stabilizing effect to the zeolite framework [98] and a more regular structure in the steamed DAY samples. Some observations indicated that the structure of these zeolites heals during dealumination [99, 100]. Orthosilicic acid (H_4SiO_4) migrates from the crystal surface into free framework vacancies generated due to removal of aluminium atoms. Migration of H_4SiO_4 takes place too, if silica gel obtained by precipitation is hydrothermally treated in analogy to the preparation procedure of DAY zeolites [88]. All defects—sorption centers for gases or liquids—are repaired by reorganization of the framework. Because the framework becomes more regular with rising of time and temperature the silica gel loses its sorption behavior. The asymmetrical TOT (T = Si) valence vibration in infrared spectra shifts into the region of wave numbers characteristic of pyrogenic silica at $1100\text{--}1120\text{ cm}^{-1}$.

An important observation gives another explanation for the different behavior of low-silica and high-silica DAY samples. The degradation of silicon-rich surfaces according to (7) proceeds fast. But if the surface of such a sample is aluminated again [75], stabilization of the structure takes place [101]. The stabilizing effect of the surface layer consisting of sodium aluminosilicate may be associated with the elimination of the terminal silanol $\equiv\text{Si-OH}$ groups and a blocking of the energy-rich $\equiv\text{Si-O-Si}\equiv$ bonds near the crystal surface, where water molecules attack the framework. Contrary to the polymeric silica in the dealuminated framework, this aluminium-rich

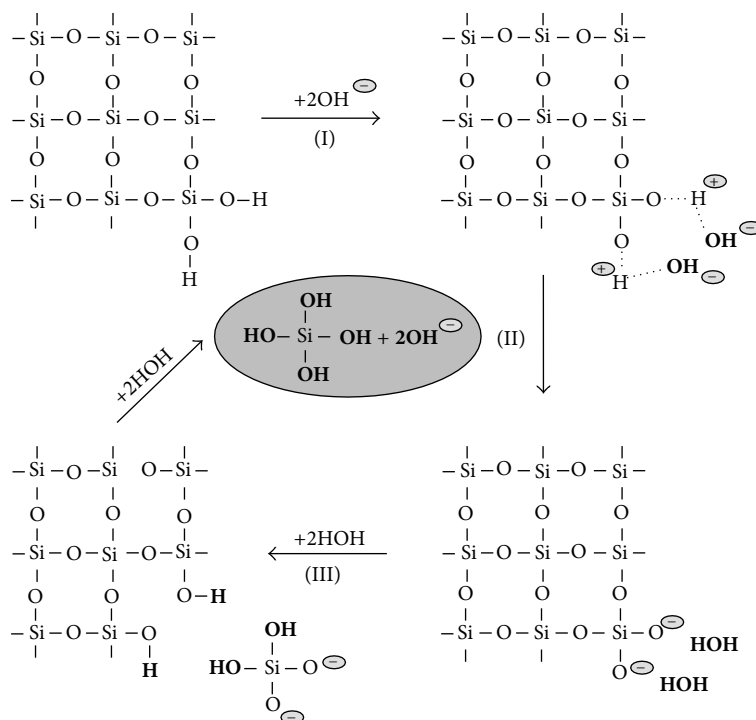


FIGURE 9: Stepwise decomposition of a high-silica zeolite framework by water [96].

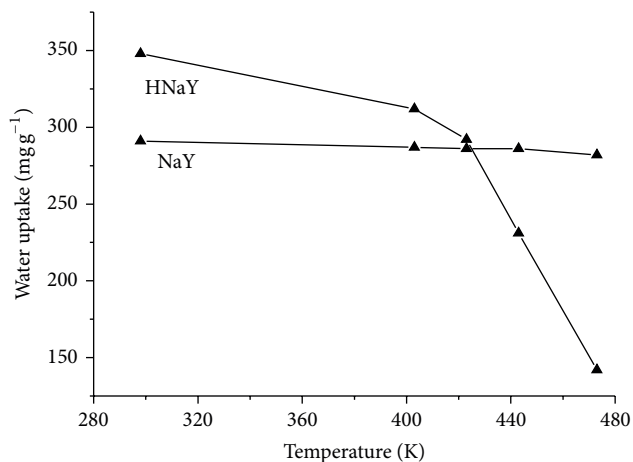


FIGURE 10: Water sorption uptake of zeolites NaY and HNaY after hydrothermal treatment in water of autogenous pressure for 72 hours in dependence on temperature [97].

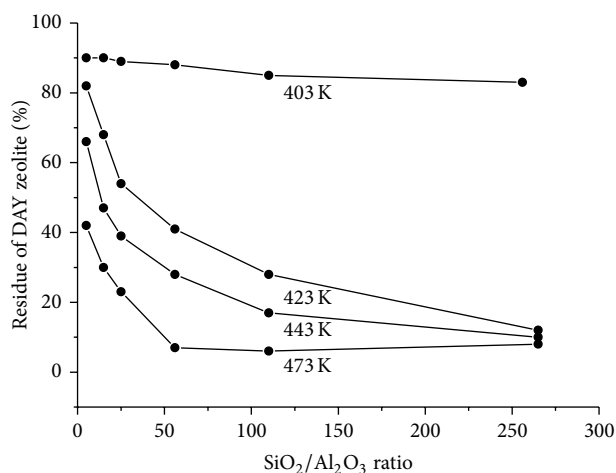


FIGURE 11: Residue of DAY zeolites after hydrothermal treatment in liquid water in dependence on module and temperature [96].

layer contains only monomeric and dimeric silicate units which are detected by Molybdate measurement. Using such an approach, high-silica zeolites may be stabilized against a hydrothermal or alkaline attack [93]. Lutz et al. [102] reported in detail on the external introduction of extraframework sodium aluminosilicate species through an alkaline and combined acid/alkaline pathways using sodium aluminate as well as aluminium-oxo-hydroxo cations [103] or $(\text{Al}, \text{SiO}_x)$ species into faujasite type zeolite [104]. Aluminations in solutions of sodium or potassium aluminate was reported also for other

high-silica zeolites such as silicalite [105], MCM-41 [106], and zeolite Beta [107].

The sodium aluminosilicate surface layer can be functionalized as wafer for catalytically active ingredient. The obtained adsorber/catalyst composites were successfully tested in the conversion of several organics and applied for waste water purification.

2.3.5. Adsorber/Catalyst Composites. Active ingredients in adsorber/catalyst composites on the basis of high-silica DAY zeolites are exclusively localized on the crystal surface while

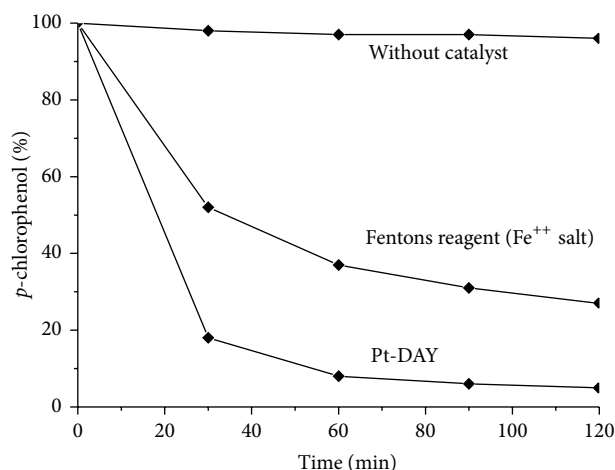


FIGURE 12: Degradation of 1 g per L p-chloro-phenol in water by adding of 4 g H₂O₂ on 10 g of Fenton's reagent, respectively, zeolite Pt-DAY loaded with 5 mg/g platinum [109].

the bulk remains free for adsorption. Thus, high conversion of acetone on an H-DAY composite with Si/Al = 150 or such one of *n*-butane on a Ni-DAY or Pt-DAY analogues has been found [108]. But the specific application of the composites remains in the purification of waste waters. Pollutants such as halogenated hydrocarbons must be removed up to a few nanogram. At the first step of cleaning, the pollution will be separated from liquid phase by adsorption and at the second step it is decomposed by chemical reaction, for example, by oxidation with hydrogen peroxide. Because of the degradation of the toxic agent any regeneration of the composite is not provided.

The decomposition of p-chloro-phenol in water on Pt-DAY was tested comparing to Fenton's reagent (FeSO₄) [109]. The zeolite was loaded by 5 mg, 12 mg, 23 mg, and 47 mg of Pt per g composite. The best effect was obtained with 5 mg/g because of an optimized activation of the admixed hydrogen peroxide. Figure 12 shows the significant advantage of the new composite compared with the classical FeSO₄ using a one-step strategy. In a semitechnical plant, pureness degree lower than 1 ppm has been achieved. Details of preparation and application of adsorber/catalyst composites are discussed in a series of patents [110–114].

2.3.6. Reinsertion of Extraframework Aluminium into Framework Positions. The catalytic activity of zeolites is determined mainly by their framework aluminium. The aluminium content may be varied directly in the synthetic process (zeolite ZSM-5) or, as has been reported here, by subsequent framework dealumination (zeolite Y). The subsequent insertion of external aluminium into zeolites frameworks has been highly discussed from the beginning of eighties. In this case, aluminium chloride [105], clay [115], and alkali aluminate [116] have been suggested as aluminium sources.

For steamed DAY samples, Breck and Skeels [117] have proposed a reinsertion of the extraframework aluminium back into the faujasite framework by treatment of samples

in alkaline solution. Liu and colleagues [118] confirmed this approach by interpretation of ²⁹Si MAS NMR spectra and termed this process as “fine tuning of performance of zeolitic catalysts.” Hamdan et al. [119] saw in the “secondary synthesis,” a method of achieving an optimal number of Brønsted acid sites responsible for the crack activity for hydrocarbons within the zeolite framework. But reexamination of the process by Engelhardt and Lohse [120] did not confirm this hypothesis. Their doubts concerned especially the interpretation of measured ²⁹Si MAS NMR spectra. Nevertheless, a series of NMR studies supported the reinsertion concept of Klinowski et al. [121–128]. The signals of Si(*n*Al) building units shift to a higher values by framework dealumination. While the peaks of the Si(4Al) and Si(3Al) units in Figure 13 decrease in intensity, and the signals assigned to Si(1Al) and Si(0Al) increase.

Lutz et al. reexamined the concept proposed by Liu et al. [118] using steamed DAY samples with varying Si/Al ratio [129], different conditions of alkaline leaching [130], and acid leached samples before the alkaline treatment in KOH solution [84]. The authors reported the drastic decrease of the Si(0Al) and the increase of the Si(1Al–4Al) peaks which indicates actually an Al enrichment inside the zeolites framework. However, this phenomenon was also observed when the extraframework aluminium was eliminated by acid extraction [84, 131] (see Figure 13). Since in alkaline treated DAY samples, the newly formed alkali aluminosilicates contribute especially to the Si(3Al) and Si(4Al) signals; the decrease of the Si(0Al) signal should be ascribed to a yet unknown phenomenon.

Bezmann [132], using the Liu approach, studied the mass balance after KOH treated Y samples and found 5% of the silicon and 2% of the aluminium in the filtrate of the batch. Furthermore, the crystallinity of sample decreased to 80%. Lutz et al. [133] provided a detailed mass balance with a similar tendency. The treatment of aluminosilicates and, particularly, metastable zeolites in alkaline solution gives rise to the change in their crystal structure [10]. The effect of increasing solubility of zeolites framework with increasing Si/Al ratio and the formation of Al-rich gels during alkaline treatment of zeolites have already been reported by Zhdanov and Egorova [134] and Stach et al. [135].

Aouali et al. [136] observed desilication and partial decomposition of highly dealuminated zeolite Y framework resulting in Al enrichment. This is the reason why the amorphization of DAY samples increases by treatment in alkaline solution with the rising of Si/Al ratio seen in badly resolved ²⁹Si MAS NMR spectra [129]. Thereby, 39% silicon of the framework with Si/Al = 23 was migrated into newly formed extraframework aluminosilicate or into alkaline solution.

Dessau et al. [137] observed a strong corrosion of the large crystals of silicalite by a treatment in alkaline solution. Groen et al. [138] and Verbroekend and Pérez-Ramirez [139] generated thus controlled mesoporosity in zeolites. Lutz et al. [140] have treated this zeolite on a frit, separating the formed aluminosilicate in the filtrate. Mirodatos and Barthemeuf [141] assumed the participation of extraframework silicon in the formation of the aluminosilicate.

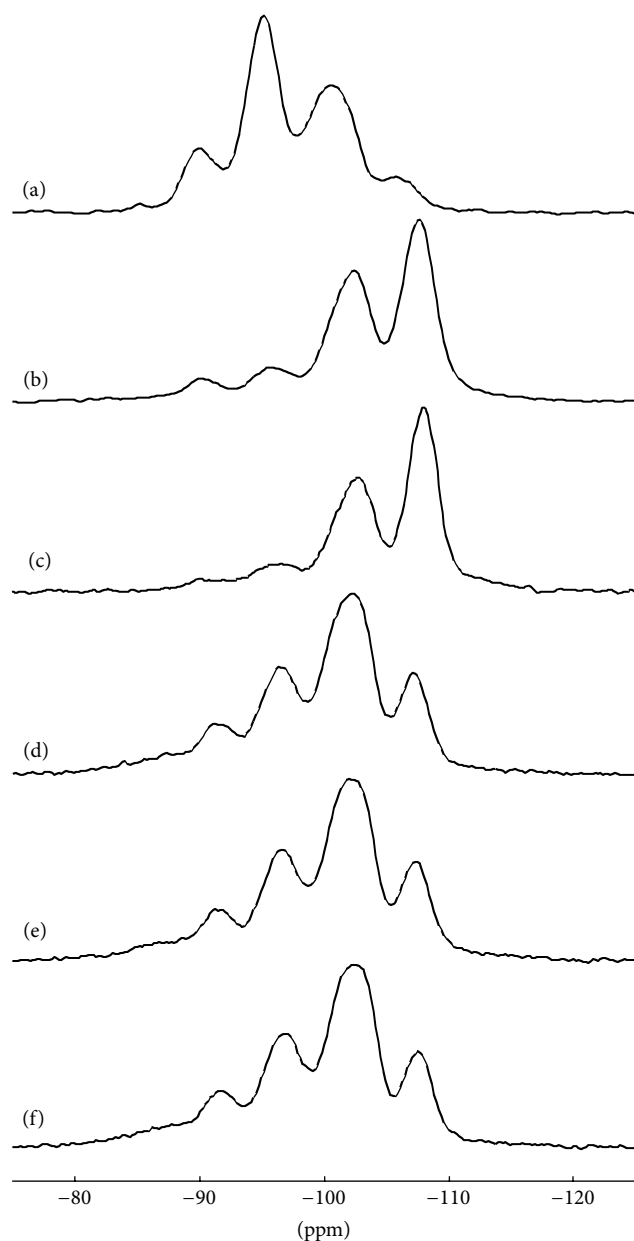


FIGURE 13: ^{29}Si MAS NMR spectra of zeolites NaY (a), steamed DAY (b), acid leached DAY (c), alkaline leached DAY (d), and alkaline leached DAY after acid extraction of the extraframework aluminium with moderate (e) and intensive stirring (f) [130].

In a detailed study on the alkaline reactivity of extraframework species Lutz et al. [87] have shown that EFSi—silica gel at the crystal surface and, in dependence on the steaming conditions, aluminosilicate or clay and silica in the nuclei—contributes to the sample transformation only at a low extent. The aluminosilicate admixture is protected against the attack of sodium or potassium hydroxide by its negative charge and silica gel formed at steaming temperature of 773 K or more is lowly soluble. The observed newly formed sodium or potassium aluminosilicate is generated exclusively from $\text{Al}^{(3+)}$ cations and silicon removed

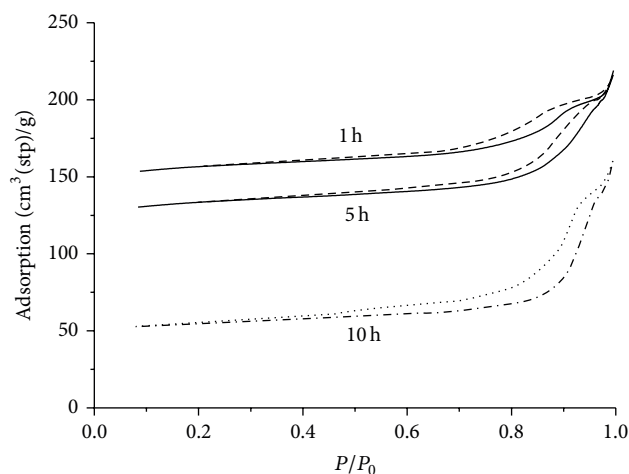


FIGURE 14: Nitrogen isotherms measured at 77 K on DAY steamed at 973 K and 1 bar water pressure in dependence on time [148].

from the dealuminated framework. This means that the “re-insertion” of extraframework aluminium consists in a desilication of the zeolites framework and a formation of additional X-ray amorphous alkali aluminosilicate.

Because of the exchange of protons against alkali metal cations, the Brønsted activity, for example, in conversion of *n*-pentane [142], breaks totally down by use of DAY samples prepared according to “re-insertion” concept given by Liu et al. [118].

2.3.7. Secondary Pore Volume in Steamed Y Zeolites. Much work has been done to characterize the transition of bulk micropores of DAY zeolites into a secondary pore volume [143–147]. Formed mesopores were attributed to reorganization of the framework after removal of aluminium followed by generation of structural defects. The healing of the framework by migrating of orthosilicic acid (H_4SiO_4) into defect positions was discussed too [99, 100, 148]. Formation and healing can be followed by infrared analysis of the formed internal hydroxyl groups [149].

First investigations of the interaction of DAY samples with gases and vapors related to their catalytic behaviors have been performed [150–152] and followed later by systematic studies of their sorption capacity [143]. After the characterization of sorption centers by hydrocarbons, the investigation of the pore structure using nitrogen at 77 K came into the focus of interest. A typical sign of the mesopores in DAY is the hysteresis between the adsorption and desorption loop of the nitrogen isotherm above a relative pressure at p/p_s over 0.5. Nitrogen liquefies in the secondary pore volume and needs, therefore, more energy for evaporation than adsorbed nitrogen molecules. Figure 14 shows typical nitrogen isotherms with such a hysteresis loop.

Using nitrogen uptake techniques, Lutz and colleagues [148] detected a formation of various bulk mesopores in dependence on the conditions of steaming. Framework defects tend to be occupied by migrating H_4SiO_4 , especially at temperatures of 573 K and 673 K. Corresponding diffusion

of orthosilicic acid was described in detail by Iler [74, 153]. Insertion goes down at temperatures above 873 K since the dehydroxylation of the hydroxyl nests accompanied by a rearrangement of the framework and the reduced concentration of offered water takes place.

Mesopores were unquestionably assumed to be the result of pure dealumination of the microporous bulk. Using texture analysis and 3D-TEM measurements, Jansen et al. [154] visualized large mesopores of 0.2–0.4 nm not only within the nuclei but also near to the surface of the DAY crystals. Similar morphology was observed also by Lynch et al., who reported on a secondary pore system without direct connection to the exterior of the crystals [155].

The origin of the closed nuclei and open surface mesopores must be attributed to the inhomogeneous silicon/aluminium contribution over the Y zeolite crystallites [31, 156, 157]. The semiempirical approaches, which describe the Si/Al ratio of faujasite-type zeolites by use of ^{29}Si MAS NMR [158] or X-ray data [159], did not take into account possible effect of such Si/Al gradients [81, 160]. Due to the fine size of the crystallites, a direct proof of the gradient presence is difficult, for example, using EDX analysis. But a hydrothermal instability of the aluminum-rich nuclei and the silicon-rich surface of DAY crystals can be deduced from investigation of faujasite-type zeolites with analogous composition [6].

Kortunov et al. [161] reported on molecular transport in DAY samples. The diffusion measurements have been performed by use of PFG NMR technique with 1,3,5-triisopropylbenzene and *n*-octane as probe molecules. The critical diameters are, respectively, larger and smaller than the inlet of the zeolite micropores. It was found that *n*-octane molecules entered the whole crystal whereas 1,3,5-triisopropylbenzene could not enter the microporous bulk and thus the nuclei mesopores. The idea that the secondary pore system improves the molecular transport of starting materials and products in catalytic conversion processes [19, 55] must be corrected.

One should furthermore assume that DAY samples used by Kortunov contained no or only small amounts of bulk mesopores because of healing of the microporous bulk at 773 K. It seems likely that stronger dealuminated DAY samples steamed, for example, at 973 K, contain such amount of bulk mesopores that traffic of large molecules through the mesoporous network becomes possible [162–164].

Based on current results, one can propose, complementary to the review on mesoporosity in [165, 166], a model containing three types of mesopores with closed mesopores in the crystal nuclei, open mesopores at the crystal surface, and bulk mesopores within microporous bulk. This model is shown schematically in Figure 15.

Generally speaking, even a fourth type of mesopores may occur in the steamed zeolite as a result of nonuniform packing of crystallites with different size in the polycrystalline DAY material. The variation in average crystallite size has been found for a series after dealumination at 773 K, 873 K, and 973 K [55]. It was shown here and in [41] that the average diameter determined by XRD measurements using the Scherrer equation does not vary significantly at 773 K

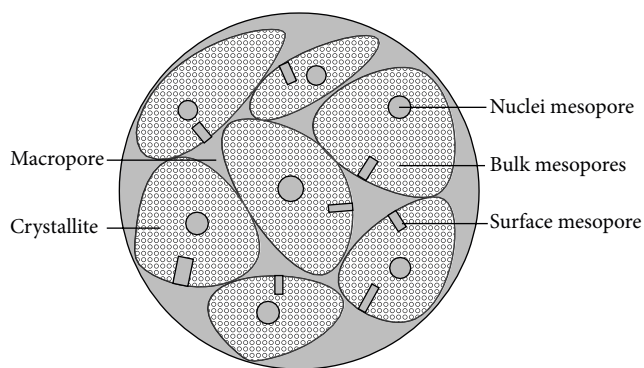


FIGURE 15: Types of mesopores in steamed DAY crystals [31].

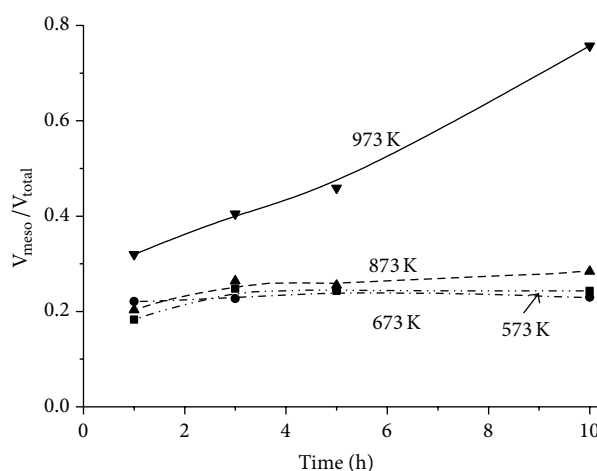


FIGURE 16: Relative mesopore volume ($V_{\text{meso}}/V_{\text{total}}$) of DAY samples in dependence on temperature and steaming time [148].

and 873 K but decreases from 100 nm to 85 nm after 5 hours of steaming at 973 K in sample with zeolite particles of 1000 nm in size. If crystallites become smaller in this way, their package density increases. Therefore, macropores of the intracrystalline space may shrink into larger mesopores which can be detectable by nitrogen measurements at 77 K. However, this assumption cannot be proved actually.

Formation of the secondary pore system leads to a pronounced loss of crystallinity, sorption capacity, and catalytic activity of the zeolite materials. It would be helpful to reduce the mesoporous volume. The first possibility lies in the moderate steaming of samples to guarantee the healing of the framework defects in the microporous bulk (hydroxyl nests) [148]. Performing a gentle and homogeneous dealumination with KY zeolite of higher framework cell which possesses rather equilibrium distribution of ammonium ions inside the structure could provide another solution of this problem. And a third way is associated with minimizing the Si/Al gradient by seeding of NaY synthesis batches with seed solution [156, 167] instead of an insertion of nanoseeds of X zeolite [26].

For an investigation of moderate steaming, commercial NaY zeolite with a Si/Al ratio of 2.7 was exchanged with

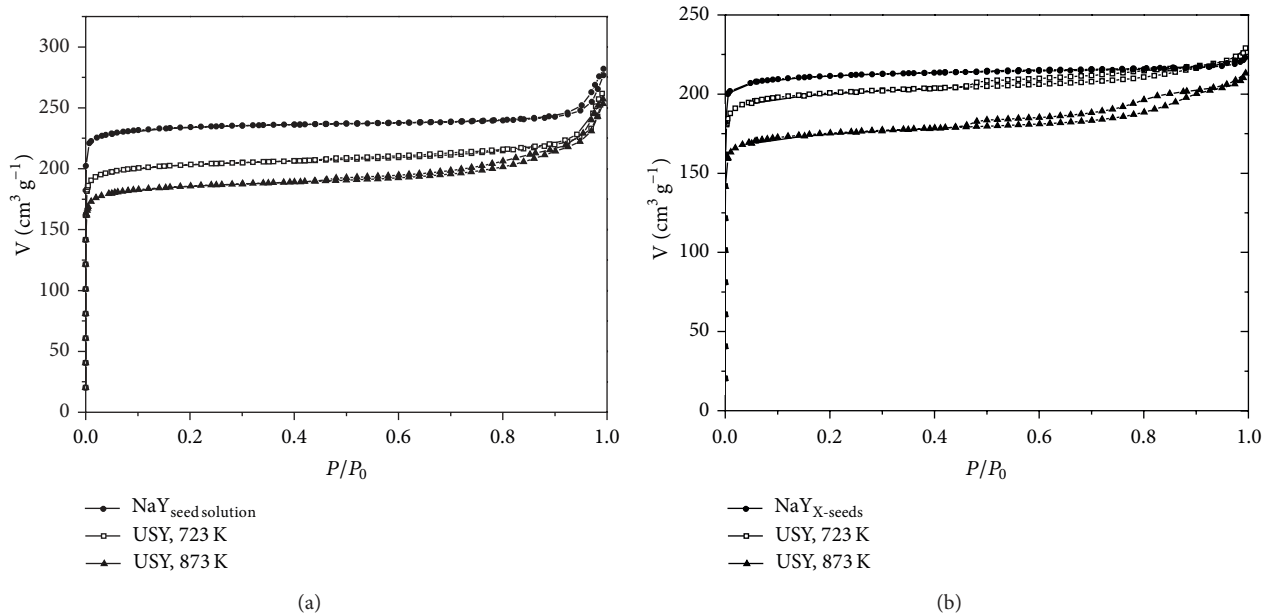


FIGURE 17: Nitrogen isotherms of the initial NaY_{seed-solution} (a) and NaY_{X-seeds} (b) zeolites and the corresponding DAY samples steamed for 7 hours at 723 K and 873 K, respectively [169].

ammonium ions up to 81%. The formation and healing of the bulk mesopores in dependence on temperature were detected by the presentation of the relative change of the pore volume $V_{\text{meso}}/V_{\text{total}}$ during the steaming time [148]. Figure 16 shows that the contribution of mesopores to the total volume is constant at 573 K and 673 K. Only the mesopore surface S_a changes slightly with the time. It seems likely that V_{meso} is dominated by the volume of the closed nuclei mesopores while the mesopore surface S_{meso} characterizes mainly the open surface mesopores.

As we know, a silicon-rich surface acts as source of orthosilicic acid [74, 153] in silica gel as well as in the steamed DAY samples. Incorporation of H_4SiO_4 into the defects inside bulk framework runs better at low temperature of 573 K–673 K because water is available under these conditions in a sufficient amount for healing procedure. With temperature rise, the portion of bulk mesopores grows slightly at 873 K and significantly at 973 K. At these temperatures nonhealed bulk mesopores contribute mainly to the total mesopore/macropore volume. But healing cannot compensate the framework collapse because of the strong thermal activation of the framework and the drastically reduced concentration of water in the reaction zone.

Synthesis of the ammonium form of zeolite Y from a KY modification followed the idea to get a homogeneous dealumination with a reduced mesopore formation. Owing to a bigger size of potassium ions, the framework of Y zeolite is expanded from 2.468 nm (NaY) to 2.473 nm (KY) and the exchange process should run easier. However, exchange of ammonium for potassium ions succeeded surprisingly only to 80%, similar to NaY zeolite. But steaming of KY zeolite at 873 K where a certain healing of bulk mesopores still takes

place demonstrated an unexpected result [168]. The micropore volume of K-DAY was reduced stronger than that of Na-DAY. It appears that residual $\text{Na}^{(+)}$ ions, localized mainly in the aluminum-rich center of crystals, stabilize the sensitive $\equiv\text{Si}-\text{O}-(\text{Al}^{(-)})\equiv$ bonds stronger than $\text{K}^{(+)}$ ions. The latter was more homogeneously distributed over the framework while protons resulting from ammonium complex show a tendency to occupy positions within the nuclei. Due to a repeated ion exchange and steaming procedure, the mesopore volume did not change significantly for both samples but the Si/Al ratio increased gradually from 2.4 (parent NaY and KY) to 4.7 (first steaming) and to 8.4 for both (second steaming).

Modification of the seeding procedure in NaY synthesis looks more attractive in order to decrease the amount mesopores inside the zeolite nuclei [169]. NaY_{seed-solution} and NaY_{X-seeds} samples of same chemical composition were dealuminated in their ammonium form at 723 K and 873 K. Dealumination changed the framework ratios to 3.3 and 4.2, respectively.

The mesoporous area A_{meso} of both series determined by nitrogen adsorption at 77 K differs significantly. Values of DAY_{seed-solution} were smaller than those of DAY_{X-seeds}. This observation gives the hint to the absence of nuclei mesopores in DAY_{seed-solution}. The corresponding nitrogen isotherms in Figure 17 show no hysteresis loop at both temperatures investigated. The weak hysteresis for DAY_{seed-solution} prepared at 873 K is only responsible for emptying the surface mesopores which inevitably appear during steaming.

The occurrence of nuclei mesopores can be reduced by starting the crystallization of NaY with oligomeric aluminosilicate that hinders the appearance of a strong Si/Al gradient typical of seeding procedures with NaX nanocrystals.

3. Conclusion

The fine-tuning of the Si/Al ratio in zeolite Y framework is achieved by a subsequent steam treatment of NH_4NaY samples at temperatures between 573 K and 973 K in dependence on time. At lower and higher temperatures, decomposition occurs due to acid hydrolysis in steam or the thermal collapse of the framework, respectively. But a certain degree of the decomposition is observed in all other steamed DAY products too. This effect results from a corrosion of the Al-rich nuclei and the Si-rich surface of crystallites which are both hydrothermally instable. The Si/Al gradient inside the framework resulting from the specific synthesis of the parent NaY zeolite can be diminished if the synthesis batch is seeded by a so-called seed solution rather than with NaX nanocrystals.

Due to the framework corrosion, inner and outer mesopores occur in addition to bulk mesopores which appear after removal of framework aluminium. Concentration of inner and outer mesopores can only be reduced decreasing the Si/Al framework gradient. In contrast, bulk mesopores are healed by the migration of orthosilicic acid (H_4SiO_4) into vacancies of the framework at steaming temperatures of 573 K and 673 K, especially. All observed nuclei mesopores are closed therefore they cannot contribute to the transport of greater molecules.

In addition to extraframework aluminium, extraframework siliceous species occur as Al aluminosilicate and silica gel. With increasing steaming temperature, the aluminosilicate is decomposed into clay and silica gel. With the rising temperature, all extraframework components become inactive in alkaline treatment. Therefore, the process of Al enrichment of the zeolite framework during alkaline leaching is associated actually not with migrating of extra framework Al species back into the lattice but it results from the fact that the DAY framework becomes desilicated after such alkaline treatment.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

References

- [1] D. W. Breck, "Crystalline zeolite Y," U.S. Patent 3130007, 1964.
- [2] R. M. Milton, "Molecular sieve adsorbents," U.S. Patent 2882243, 1959.
- [3] R. M. Milton, "Molecular sieve adsorbents," U.S. Patent 2882244, 1959.
- [4] D. W. Breck, *Zeolite Molecular Sieves*, John Wiley & Sons, New York, NY, USA, 1974.
- [5] E. M. Flanigan, "Molecular sieve zeolite technology: the first twenty-five year," in *Proceedings of the 5th International Conference on Zeolites*, pp. 760–780, Naples, Italy, June 1980.
- [6] C. H. Rüscher, N. Salman, J.-C. Buhl, and W. Lutz, "Relation between growth-size and chemical composition of X and Y type zeolites," *Microporous and Mesoporous Materials*, vol. 92, no. 1–3, pp. 309–311, 2006.
- [7] C. W. McDaniel and P. K. Maher, in *Molecular Sieves*, p. 186, Society of Chemical Industry, London, UK, 1968.
- [8] P. B. Venuto and E. T. Habib Jr., "Catalyst-feedstock-engineering interactions in fluid catalytic cracking," *Catalysis Reviews: Science and Engineering*, vol. 18, no. 1, pp. 1–150, 1978.
- [9] D. J. Rawlence and K. Gosling, "FCC catalyst performance evaluation," *Applied Catalysis*, vol. 43, no. 2, pp. 213–237, 1988.
- [10] R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, UK, 1978.
- [11] S. P. Zhdanov, S. S. Khvoshchev, and N. N. Feoktistova, *Synthetic Zeolites*, vol. 1, Gordon & Breach Science Publishers, New York, NY, USA, 1990.
- [12] G. T. Kerr, "Chemistry of crystalline aluminosilicates. V. Preparation of aluminum-deficient faujasites," *The Journal of Physical Chemistry*, vol. 72, no. 7, pp. 2594–2596, 1968.
- [13] H. K. Beyer, I. M. Belenykaja, F. Hange, M. Tielen, P. J. Grobet, and P. A. Jacobs, "Preparation of high-silica faujasites by treatment with silicon tetrachloride," *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 81, no. 11, pp. 2889–2901, 1985.
- [14] J. W. Ward, "Thermal decomposition of ammonium Y zeolite," *Journal of Catalysis*, vol. 27, pp. 157–161, 1972.
- [15] P. K. Maher, F. D. Hunter, and J. Scherzer, "Crystal structures of ultrastable faujasites," in *Advances in Chemistry*, vol. 101, chapter 21, pp. 266–278, 1971.
- [16] W. J. Ambs and W. H. Flank, "Thermal behavior of synthetic faujasite," *Journal of Catalysis*, vol. 14, no. 2, pp. 118–125, 1969.
- [17] J. B. Peri, "The nature of ultrastable faujasite," in *Proceedings of the 5th International Congress on Catalysis*, J. W. Hightower, Ed., pp. 329–338, North-Holland, Miami Beach, Fla, USA, 1972.
- [18] G. T. Kerr, A. W. Chester, and D. H. Olson, "Preparation of ultrahigh silicon faujasite by controlled-rate aluminium removal," in *Proceedings of the Symposium on Zeolites*, Jozsef Attila University, 1978, published in *Acta Physica et Chemica, Nova Series*, vol. 24, pp. 169–174, 1978.
- [19] A. Corma and V. Fomés, "Delaminated zeolites as active catalysts for processing large molecules," in *Zeolites and Mesoporous Materials at the Dawn of the 21st Century: Proceedings of the 13th International Zeolite Conference, Montpellier, France, 8–13 July 2001*, A. Galarneau, F. di Renzo, F. Fajula, and J. Védrine, Eds., vol. 135 of *Studies in Surface Science and Catalysis*, pp. 73–82, Elsevier, Amsterdam, The Netherlands, 2001.
- [20] G. T. Kerr, "Chemistry of crystalline aluminosilicates. I. Factors affecting the formation of zeolite A," *The Journal of Physical Chemistry*, vol. 70, pp. 1047–1050, 1966.
- [21] G. T. Kerr, "Chemistry of crystalline aluminosilicates. IV. Factors affecting the formation of zeolites X and B," *The Journal of Physical Chemistry*, vol. 72, no. 4, pp. 1385–1386, 1968.
- [22] D. W. Breck and E. M. Flanigan, "Synthesis and properties of union carbide zeolites L, X and Y," in *Molecular Sieves*, pp. 47–60, Society of Chemical Industry, London, UK, 1968.
- [23] S. P. Zhdanov, "Some problems of zeolite crystallization," in *Molecular Sieve Zeolites-I*, E. M. Flanigan and L. B. Sand, Eds., vol. 101 of *Advances in Chemistry*, chapter 2, pp. 20–43, 1971.
- [24] B. D. McNicol, G. T. Pott, and K. R. Loos, "Spectroscopic studies of zeolite synthesis," *Journal of Physical Chemistry*, vol. 76, no. 23, pp. 3388–3390, 1972.
- [25] E. Thilo, W. Wieker, and H. Stade, "Chemische Untersuchungen von Silicaten. I. Über Beziehungen zwischen dem Polymerisationsgrad silicatischer Anionen und ihrem Reaktionsvermögen mit Molybdänsäure," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 340, no. 5–6, pp. 261–276, 1965.

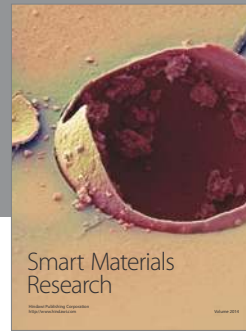
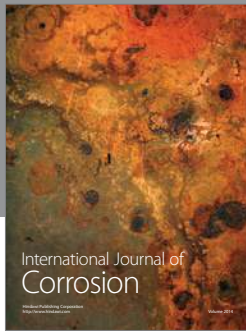
- [26] B. Fahlke, W. Wieker, H. Fürtig, W. Roscher, and R. Seidel, "Untersuchungen zum Bildungsmechanismus von Molsieben," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 439, pp. 95–102, 1978.
- [27] W. Wieker and B. Fahlke, "On the reaction mechanism of the formation of molecular sieves and related compounds," in *Zeolites Synthesis, Structure, Technology and Application: Proceedings of an International Symposium, Organized by the "Boris Kidrič" Institute of Chemistry, Ljubljana, on Behalf of the International Zeolite Association*, B. Držaj, S. Hocevar, and S. Pejovnik, Eds., vol. 24 of *Studies in Surface Science and Catalysis*, pp. 161–181, Elsevier, Amsterdam, The Netherlands, 1985.
- [28] J. A. Kostinko, "Intrazeolite chemistry," in *Factors Influencing the Synthesis of Zeolites A, X, and Y*, G. D. Stucky and F. G. Dwyer, Eds., ACS Symposium Series 218, pp. 3–19, American Chemical Society, Washington, DC, USA, 1983.
- [29] C. Berger, R. Gläser, R. A. Rakoczy, and J. Weitkamp, "The synthesis of large crystals of zeolite Y re-visited," *Microporous and Mesoporous Materials*, vol. 83, no. 1–3, pp. 333–344, 2005.
- [30] N. Salman, *Crystal chemical studies on the growth size problem of Y zeolites [Ph.D. thesis]*, Institute for Mineralogy, University of Hannover, Hannover, Germany, 2006.
- [31] W. Lutz, R. Kurzhals, G. Kryukova, D. Enke, M. Weber, and D. Heidemann, "Formation of mesopores in USY zeolites: a case revisited," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 636, no. 8, pp. 1497–1505, 2010.
- [32] S. Ferchiche, M. Valcheva-Traykova, D. E. W. Vaughan, J. Warzywoda, and A. Sacco Jr., "Synthesis of large single crystals of templated Y faujasite," *Journal of Crystal Growth*, vol. 222, no. 4, pp. 801–805, 2001.
- [33] S. Ferchiche, J. Warzywoda, and A. Sacco Jr., "Direct synthesis of zeolite Y with large particle size," *International Journal of Inorganic Materials*, vol. 3, no. 7, pp. 773–780, 2001.
- [34] Ch. Baerlocher, L. B. McCusker, and D. H. Olson, *Atlas of Zeolite Framework Types*, Elsevier, Amsterdam, The Netherlands, 2007.
- [35] W. Loevenstein, "The distribution of aluminum in the tetrahedra of silicates and aluminates," *American Mineralogist*, vol. 39, no. 1–2, pp. 92–96, 1954.
- [36] R. M. Barrer and J. D. Falconer, "Ion exchange in feldspaths as a solid-state reaction," *Proceedings of the Royal Society A*, vol. 236, pp. 227–249, 1956.
- [37] R. M. Barrer and W. M. Meier, "Structural and ion sieve properties of a synthetic crystalline exchanger," *Transactions of the Faraday Society*, vol. 54, pp. 1074–1085, 1958.
- [38] W. Lutz, non-published results.
- [39] Q. L. Wang, G. Giannetto, M. Torrealba, G. Perot, C. Kappenstein, and M. Guisnet, "Dealumination of zeolites II. Kinetic study of the dealumination by hydrothermal treatment of a NH_4NaY zeolite," *Journal of Catalysis*, vol. 130, no. 2, pp. 459–470, 1991.
- [40] R. M. Barrer and M. V. Makki, "Molecular sieve sorbents from clinoptilolite," *Canadian Journal of Chemistry*, vol. 42, no. 6, pp. 1481–1487, 1964.
- [41] U. Lohse, E. Löffler, M. Hunger, J. Stöckner, and V. Patzelová, "Hydroxyl groups of the non-framework aluminium species in dealuminated Y zeolites," *Zeolites*, vol. 7, no. 1, pp. 11–13, 1987.
- [42] P. Fejes, I. Kiricsi, I. Hannus, A. Kiss, and G. Schöbel, "A novel method for the dealumination of zeolites," *Reaction Kinetics and Catalysis Letters*, vol. 14, no. 4, pp. 481–488, 1980.
- [43] B. M. Lok and T. P. J. Izod, "Modification of molecular sieves—direct fluorination," *Zeolites*, vol. 2, no. 2, pp. 66–67, 1982.
- [44] G. Engelhardt, U. Lohse, A. Samoson, M. Mägi, M. Tarmak, and E. Lippmaa, "High resolution ^{29}Si n.m.r. of dealuminated and ultrastable Y-zeolites," *Zeolites*, vol. 2, no. 1, pp. 59–62, 1982.
- [45] U. Lohse, I. Pitsch, E. Schreier, B. Parlitz, and K.-H. Schnabel, "Cubic and hexagonal faujasites with varying Si/Al ratios I. Synthesis and characterization," *Applied Catalysis A: General*, vol. 129, no. 2, pp. 189–202, 1995.
- [46] N. Salman, C. H. Rüscher, J.-C. Buhl, W. Lutz, H. Toufar, and M. Stöcker, "Effect of temperature and time in the hydrothermal treatment of HY zeolite," *Microporous and Mesoporous Materials*, vol. 90, no. 1–3, pp. 339–346, 2006.
- [47] U. Lohse, E. Alsdorf, and H. Stach, "Dealuminierte Molekularsieve vom Typ Y. Herstellung und Charakterisierung durch IR-Spektren, DTA/DTG-Messungen und Adsorptionsdaten," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 447, no. 1, pp. 64–74, 1978.
- [48] K. P. Schröder and J. Sauer, "Preferred stability of aluminum-oxygen-silicon-oxygen-aluminum linkages in high-silica zeolite catalysis: theoretical predictions contrary to Dempsey's rule," *The Journal of Physical Chemistry*, vol. 97, no. 25, pp. 6579–6581, 1993.
- [49] E. M. Flanigan, H. Khatami, and H. A. Szymanski, "Infrared structural studies of zeolite frameworks," in *Molecular Sieve Zeolites-I*, E. M. Flanigan and L. B. Sand, Eds., vol. 101 of *Advances in Chemistry*, chapter 16, pp. 201–229, 1971.
- [50] W. Lutz, C. H. Rüscher, and D. Heidemann, "Determination of the framework and non-framework $[\text{SiO}_2]$ and $[\text{AlO}_2]$ species of steamed and leached faujasite type zeolites: calibration of IR, NMR, and XRD data by chemical methods," *Microporous and Mesoporous Materials*, vol. 55, no. 2, pp. 193–202, 2002.
- [51] R. Bertram, U. Lohse, and W. Gessner, "Zur Charakterisierung des Extragitter-Aluminiums in Y-zeolithen mittels der Ferronmethode," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 567, no. 1, pp. 145–152, 1988.
- [52] H. Fichtner-Schmittler, U. Lohse, H. Mießner, and H. E. Maneck, "Correlation between unit-cell parameter, skeletal stretching vibrations and molar fraction of aluminium of faujasite type zeolites for Si/Al = 1.1–1000," *Zeitschrift für Physikalische Chemie*, vol. 271, pp. 69–79, 1990.
- [53] C. H. Rüscher, J.-C. Buhl, and W. Lutz, " ^{13}P - ^{15}P -determination of the Si/Al ratio of faujasite-type zeolites," in *Zeolites and Mesoporous Materials at the Dawn of the 21st Century: Proceedings of the 13th International Zeolite Conference*, A. Galarneau, F. di Renzo, F. Fajula, and J. Védrine, Eds., vol. 135 of *Studies in Surface Science and Catalysis*, p. 343, Elsevier, Amsterdam, The Netherlands, 2001.
- [54] G. Engelhardt and D. Michel, *High Resolution Solid State NMR of Silicates and Zeolites*, John Wiley & Sons, New York, NY, USA, 1987.
- [55] W. Lutz, C. H. Rüscher, T. M. Gelsing et al., "Investigations of the mechanism of dealumination of zeolite Y by steam: tuned mesopore formation versus the Si/Al ratio," in *Recent Advances in the Science and Technology of Zeolites and Related Materials Part B: Proceedings of the 14th International Zeolite Conference*, E. van Steen, L. H. Callanan, and M. Claeys, Eds., vol. 154 of *Studies in Surface Science and Catalysis*, pp. 1411–1417, Elsevier, London, UK, 2004.
- [56] R. M. Barrer and D. L. Peterson, "Intracrystalline sorption by synthetic mordenites," *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 280, no. 1383, pp. 466–485, 1964.

- [57] G. T. Kerr, "Intracrystalline rearrangement of constitutive water in hydrogen zeolite Y," *The Journal of Physical Chemistry*, vol. 71, no. 12, pp. 4155–4156, 1967.
- [58] G. T. Kerr, "Chemistry of crystalline aluminosilicates: VII. Thermal decomposition products of ammonium zeolite Y," *Journal of Catalysis*, vol. 15, no. 2, pp. 200–204, 1969.
- [59] B. A. Baran, I. M. Belenkaya, and M. M. Dubinin, "Formation and properties of the hydrogen form of mordenite," *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, vol. 4, pp. 742–749, 1973 (Russian).
- [60] D. W. Breck and G. W. Skeels, *Molecular Sieves II*, vol. 40 of ACS Symposium Series, American Chemical Society, Washington, DC, USA, 1977.
- [61] D. W. Breck and G. W. Skeels, "The role of aluminium in the thermal treatment of ammonium exchanged zeolite Y," in *Proceedings of the 6th International Congress on Catalysis*, G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds., pp. 645–659, The Pitman Press, 1976.
- [62] J. Dwyer, F. R. Fitch, G. Qin, and J. C. Vickerman, "Study of the surface composition of zeolites by fast atom bombardment mass spectrometry," *Journal of Physical Chemistry*, vol. 86, no. 23, pp. 4574–4578, 1982.
- [63] T. Gross, U. Lohse, G. Engelhardt, K.-H. Richter, and V. Patzelová, "Surface composition of dealuminated Y zeolites studied by X-ray photoelectron spectroscopy," *Zeolites*, vol. 4, no. 1, pp. 25–29, 1984.
- [64] D. Freude, H. Ernst, and I. Wolf, "Solid-state nuclear magnetic resonance studies of acid sites in zeolites," *Solid State Nuclear Magnetic Resonance*, vol. 3, no. 5, pp. 271–286, 1994.
- [65] J. Jiao, J. Kanellopoulos, W. Wang et al., "Characterization of framework and extra-framework aluminum species in non-hydrated zeolites Y by ^{27}Al spin-echo, high-speed MAS, and MQMAS NMR spectroscopy at $B_0 = 9.4$ to 17.6 T," *Physical Chemistry Chemical Physics*, vol. 7, no. 17, pp. 3221–3226, 2005.
- [66] R. Bertram, W. Gessner, D. Müller, and M. Danner, "Characterization of Al(III) species in basic aluminium chloride flocculants by means of Ferron method and ^{27}Al nuclear magnetic resonance," *Acta Hydrochimica et Hydrobiologica*, vol. 22, no. 6, pp. 265–269, 1994.
- [67] J. Scherzer, "Dealuminated faujasite-type structures with $\text{Si}_2/\text{Al}_2\text{O}_3$ ratios over 100," *Journal of Catalysis*, vol. 54, no. 2, pp. 285–288, 1978.
- [68] N. P. Rhodes and R. Rudham, "Catalytic studies with dealuminated Y zeolite. Part 1.—Catalyst characterisation and the disproportionation of ethylbenzene," *Journal of the Chemical Society, Faraday Transactions*, vol. 89, no. 14, pp. 2551–2557, 1993.
- [69] D. Freude, T. Fröhlich, M. Hunger, and G. Scheler, "NMR studies concerning the dehydroxylation of zeolites HY," *Chemical Physics Letters*, vol. 98, no. 3, pp. 263–266, 1983.
- [70] M. Stockenhuber and J. A. Lercher, "Characterization and removal of extra lattice species in faujasites," *Microporous Materials*, vol. 3, no. 4–5, pp. 457–465, 1995.
- [71] J. Sanz, V. Fornes, and A. Corma, "Extraframework aluminium in steam- and SiCl_4 -dealuminated Y zeolite. A ^{27}Al and ^{29}Si nuclear magnetic resonance study," *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 84, pp. 3113–3119, 1988.
- [72] W. E. E. Stone, G. M. S. El Shafei, J. Sanz, and S. A. Selim, "Association of soluble aluminum ionic species with a silica-gel surface. A solid-state NMR study," *Journal of Physical Chemistry*, vol. 97, no. 39, pp. 10127–10132, 1993.
- [73] I. Gromann and Th. Gross, "Quantitative analysis of X-ray photoelectron spectroscopy intensities for dealuminated zeolites and supported catalysts where the promoter-forming elements also occur in the support," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 53, no. 3, pp. 99–106, 1990.
- [74] R. K. Iler, *The Chemistry of Silica*, John Wiley & Sons, New York, NY, USA, 1979.
- [75] W. Lutz, E. Löffler, and B. Zibrowius, "Non-framework aluminium in highly dealuminated Y zeolites generated by steaming or substitution," in *Progress in Zeolite and Microporous Materials: Proceedings of the 11th International Zeolite Conference*, H. Chon, S. K. Ihm, and Y. S. Uh, Eds., vol. 105 of *Studies in Surface Science and Catalysis*, pp. 439–446, Elsevier, Amsterdam, The Netherlands, 1995.
- [76] D. P. Siantar, W. S. Millman, and J. J. Fripiat, "Structural defects and cation exchange capacity in dealuminated Y zeolites," *Zeolites*, vol. 15, no. 6, pp. 556–560, 1995.
- [77] W. Lutz, H. Toufar, D. Heidemann et al., "Siliceous extra-framework species in dealuminated Y zeolites generated by steaming," *Microporous and Mesoporous Materials*, vol. 104, no. 1–3, pp. 171–178, 2007.
- [78] K. U. Gore, A. Abraham, S. G. Hegde, R. Kumar, J. Amoureux, and S. Ganapathy, " ^{29}Si and ^{27}Al MAS/3Q-MAS NMR studies of high silica USY zeolites," *Journal of Physical Chemistry B*, vol. 106, no. 23, pp. 6115–6120, 2002.
- [79] H. Hamid and M. A. Ali, *Handbook on MTBE and Other Gasoline Oxygenates*, Marcel Dekker, New York, NY, USA, 2004.
- [80] D. M. Ginter, A. T. Bell, and C. J. Radke, "The chemistry of NaY crystallization from sodium-silicate solution," in *Symposium on Synthesis of Microporous Materials*, M. L. Occelli and H. E. Robson, Eds., vol. 1, pp. 6–30, Van Nostrand, New York, NY, USA, 1992.
- [81] A. Corma, F. V. Melo, and D. J. Rawlence, "Effect of the nonuniform dealumination on the acidity and catalytic activity of faujasite," *Zeolites*, vol. 10, no. 7, pp. 690–694, 1990.
- [82] G. Engelhardt, U. Lohse, E. Lippmaa, M. Tarmak, and M. Mägi, " ^{29}Si -NMR-Untersuchungen zur Verteilung der Silicium- und Aluminiumatome im Aluminosilikatgitter von Zeolithen mit Faujasit-Struktur," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 482, no. 11, pp. 49–64, 1981.
- [83] K. Ehrhardt, M. Suckow, and W. Lutz, "Hydrothermal decomposition of aluminosilicate zeolites and prediction of their long-term stability," in *Catalysis by Microporous Materials: Proceedings of ZEOCAT '95*, H. K. Beyer, H. G. Karge, I. Kiricsi, and J. B. Nagy, Eds., vol. 94 of *Studies in Surface Science and Catalysis*, pp. 179–186, Elsevier, 1995.
- [84] W. Lutz, E. Löffler, M. Fechtelkord, E. Schreier, and R. Bertram, "Non-framework aluminium in highly dealuminated Y zeolites generated by steaming or substitution," in *Progress in Zeolite and Microporous Materials: Proceedings of the 11th International Zeolite Conference*, H. Chon, S.-K. Ihm, and Y. S. Uh, Eds., vol. 105 of *Studies in Surface Science and Catalysis*, pp. 439–446, Elsevier, 1997.
- [85] W. Lutz, D. Heidemann, C. Hübert, and W. Wieker, "Contribution of silica gels to superimposed ^{29}Si MAS NMR spectra of Y zeolites dealuminated by steaming," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 627, no. 11, pp. 2559–2564, 2001.
- [86] W. Lutz, W. Wieker, D. Müller, M. Schneider, C. H. Rüscher, and J.-C. Buhl, "Phase transformations in alkaline and acid leached Y zeolites dealuminated by steaming," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 626, no. 6, pp. 1460–1467, 2000.

- [87] W. Lutz, R. Bertram, D. Heidemann, R. Kurzhals, C. H. Rüscher, and G. Kryukova, "Reactivity of extra-framework species of USY zeolites in alkaline medium," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 637, no. 1, pp. 75–82, 2011.
- [88] W. Lutz, D. Täschner, R. Kurzhals, D. Heidemann, and C. Hübner, "Characterization of silica gels by ^{29}Si MAS NMR and IR spectroscopic measurements," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 635, no. 13–14, pp. 2191–2196, 2009.
- [89] J. Felsche and S. Luger, "Phases and thermal decomposition characteristics of hydro-sodalites $\text{Na}_{6+x}[\text{AlSiO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$," *Thermochimica Acta*, vol. 118, pp. 35–55, 1987.
- [90] G. Engelhardt, J. Felsche, and P. Sieger, "The hydrosodalite system $\text{Na}_{6+x}[\text{SiAlO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$: formation, phase composition, and de- and rehydration studied by ^1H , ^{23}Na , and ^{29}Si MAS-NMR spectroscopy in tandem with thermal analysis, X-ray diffraction, and IR spectroscopy," *Journal of the American Chemical Society*, vol. 114, no. 4, pp. 1173–1182, 1992.
- [91] J.-C. Buhl, M. Gerstmann, W. Lutz, and A. Ritzmann, "Hydrothermal stability of the novel zeolite type LSX in comparison to the traditional 13X modification," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 630, no. 4, pp. 604–608, 2004.
- [92] U. Lohse, *Zur Struktur und zu den Adsorptionseigenschaften von siliciumreichen Molekularsieben [Ph.D. thesis]*, Academy of Sciences of GDR, Berlin, Germany, 1981.
- [93] W. Lutz, B. Zibrowius, and E. Löffler, "Hydrothermal and alkaline stability of high-silica Y-type zeolites in dependence on the dealumination procedure," in *Zeolites and Related Microporous Materials: State of the Art 1994—Proceedings of the 10th International Zeolite Conference, Garmisch-Partenkirchen, Germany, 17–22 July 1994*, J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Hölderich, Eds., vol. 84 of *Studies in Surface Science and Catalysis*, pp. 1005–1012, Elsevier, 1994.
- [94] W. Lutz, B. Zibrowius, and E. Löffler, "Hydrothermal and alkaline stability of high-silica Y zeolites generated by combining substitution and steaming," in *Zeolites: A Refined Tool for Designing Catalytic Sites: Proceedings of the International Zeolite Symposium*, L. Bonneviot and S. Kaliaguine, Eds., vol. 84 of *Studies in Surface Science and Catalysis*, pp. 327–334, Elsevier, 1995.
- [95] W. Lutz, D. Heidemann, R. Kurzhals, and G. Kryukova, "Characterisation of siliceous extra-framework species in day zeolites by ^{29}Si MAS NMR and IR spectroscopic measurements," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 636, no. 7, pp. 1361–1367, 2010.
- [96] W. Lutz, H. Toufar, R. Kurzhals, and M. Suckow, "Investigation and modeling of the hydrothermal stability of technically relevant zeolites," *Adsorption*, vol. 11, no. 3–4, pp. 405–413, 2005.
- [97] R. Dimitrijevic, W. Lutz, and A. Ritzmann, "Hydrothermal stability of zeolites: determination of extra-framework species of H-Y faujasite-type steamed zeolite," *Journal of Physics and Chemistry of Solids*, vol. 67, no. 8, pp. 1741–1748, 2006.
- [98] W. Lutz, "Stabilizing effect of non-framework AL on the structure of dealuminated y zeolites under hydrothermal conditions," *Crystal Research and Technology*, vol. 25, no. 8, pp. 921–926, 1990.
- [99] A. T. Steel and E. Dooryhee, "Time dependence of the structural changes occurring in NH4-Y zeolite on dealumination: a preliminary study using energy-dispersive X-ray diffraction," *Zeolites*, vol. 13, no. 5, pp. 336–340, 1993.
- [100] U. Lohse and M. Mildebrath, "Dealuminierte Molekularsieve vom Typ Y zur Porosität dealuminiertes Molekularsieve," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 476, no. 5, pp. 126–135, 1981.
- [101] W. Lutz, E. Löffler, and B. Zibrowius, "Increased hydrothermal stability of highly dealuminated Y zeolites by alumination," *Zeolites*, vol. 13, no. 8, pp. 685–686, 1993.
- [102] W. Lutz, W. Gessner, R. Bertram, I. Pitsch, and R. Fricke, "Hydrothermally resistant high-silica Y zeolites stabilized by covering with non-framework aluminum species," *Microporous Materials*, vol. 12, no. 1–3, pp. 131–139, 1997.
- [103] S. Schönherr, H. Görz, W. Gessner, and R. Bertram, "Protolysevorgänge in wäßrigen Aluminiumchloridlösungen," *Zeitschrift für Chemie*, vol. 23, no. 12, pp. 429–434, 1983.
- [104] I. Pitsch, U. Kürschner, D. Müller et al., "Synthesis, characterization and catalytic activity of amorphous Al_2SiO_5 gels from weakly acidic aqueous solutions," *Journal of Materials Chemistry*, vol. 7, pp. 2469–2476, 1997.
- [105] M. W. Anderson, J. Klinowski, and X. Liu, "Alumination of highly siliceous zeolites," *Journal of the Chemical Society, Chemical Communications*, no. 23, pp. 1596–1597, 1984.
- [106] H. Hamdan, S. Endud, H. He, M. N. M. Muhid, and J. Klinowski, "Alumination of the purely siliceous mesoporous molecular sieve MCM-41 and its hydrothermal conversion into zeolite Na-A," *Journal of the Chemical Society, Faraday Transactions*, vol. 92, no. 12, pp. 2311–2315, 1996.
- [107] C. Yang and Q. Xu, "Aluminated zeolites β and their properties part 1.-Alumination of zeolites β ," *Journal of the Chemical Society, Faraday Transactions*, vol. 93, pp. 1675–1680, 1997.
- [108] W. Lutz, D. L. Hoang, G. Lischke, and B. Parltitz, "Extra-framework aluminium in DAY zeolites as carrier for catalytic ingredients," in *Proceedings of the 3rd Polish-German Zeolite Colloquium*, M. Rozwadowski, Ed., pp. 205–214, Nicolaus Copernicus University Press, 1998.
- [109] W. Lutz, R. Bertram, W. Wieker, and M. Jank, "Adsorber-Katalysator-Komposite für Umweltprozesse," in *Neue Entwicklungen zur adsorptiven Gas- und Wasserreinigung*, W. Henschel, Ed., vol. 859 of *Freiberger Forschungshefte A: Verfahrenstechnik/Umwelttechnik*, p. 256, Bergakademie Freiberg, Freiberg, Germany, 2000.
- [110] W. Lutz, P. Kleinschmit, and E. Roland, "Removing organic substances from aq. soln. for sepn. of harmful or useful organic substances," DE Patent 4406776, 1994.
- [111] W. Lutz, "Verfahren zum Entfernen von Stoffen aus wäßrigen Lösungen und Adsorptionsmittel," DE Patent 19531933, 1995.
- [112] W. Lutz, D. Hoang, R. Fricke, and H. Lieske, "Asorber/catalyst composite," DE Patent 19708746, 1997.
- [113] W. Lutz, W. Gessner, and R. Bertram, "Hydrothable catalytically active composites for separating organics from fluid phase," DE Patent 19718929, 1997.
- [114] B. Schlicht, H. J. Redlich, G. Höhne, and W. Lutz, "Verfahren zum Entfernen von problembehafteten Schadstoffen aus Abwasser," DE Patent 10114739, 2001.
- [115] C. D. Chang, S. D. Helling, J. N. Miale, P. W. Schmitt, and E. L. Wu, "Insertion of aluminium into high-silica-content zeolite frameworks. Part 3.-Hydrothermal transfer of aluminium from Al_2O_3 into [Al]ZSM-5 and [B]ZSM-5," *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 81, pp. 2215–2224, 1985.
- [116] H. Hamdan and J. Klinowski, "Isomorphous substitution of framework silicon by aluminium in silicalite: factors determining resolution of ^{29}Si magic-angle-spinning NMR spectra of pentasil zeolites," *Chemical Physics Letters*, vol. 139, no. 6, pp. 576–580, 1987.

- [117] D. W. Breeck and G. W. Skeels, "Zeolite chemistry IV-evidence for the elimination and subsequent reinsertion of framework aluminum during the stabilization of NH_4^+ -Exchanged zeolite X," in *Proceedings of the 5th International Conference on Zeolites*, L. V. C. Rees, Ed., pp. 335–343, London, UK, 1980.
- [118] X. Liu, J. Klinowski, and J. M. Thomas, "Hydrothermal isomorphous insertion of aluminium into the framework of zeolite Y: a convenient method of modifying the siting of Al and Si in faujasitic catalysts," *Journal of the Chemical Society, Chemical Communications*, no. 8, pp. 582–584, 1986.
- [119] H. Hamdan, B. Sulikowski, and J. Klinowski, "Hydrothermal isomorphous substitution of aluminum in faujasitic frameworks: second-generation zeolite catalysts," *Journal of Physical Chemistry*, vol. 93, no. 1, pp. 350–356, 1989.
- [120] G. Engelhardt and U. Lohse, "A reexamination of the hypothesis of Breeck and Skeels concerning the reinsertion of aluminum in the framework of dealuminated Y zeolites," *Journal of Catalysis*, vol. 88, no. 2, pp. 513–515, 1984.
- [121] J. Klinowski and P. J. Barrie, "Recent advances in zeolite science," in *Proceedings of the Meeting of the British Zeolite Association*, B. Delmon and J. T. Yates, Eds., Cambridge, UK, April 1989.
- [122] Z. Zhang, X. Liu, Y. Xu, and R. Xu, "Realumination of dealuminated zeolites Y," *Zeolites*, vol. 11, no. 3, pp. 232–238, 1991.
- [123] M. Nayarana and B. D. Murray, "Process for realuminating zeolites," U.S. Patent 5118482, 1992.
- [124] P. J. Barry, L. F. Gladden, and J. Klinowski, "Neutron diffraction studies of realuminated zeolite Y," *Journal of the Chemical Society, Chemical Communications*, no. 8, pp. 592–594, 1991.
- [125] V. Calsavara, E. F. Sousa-Aguiar, and N. R. C. Fernandes-Machado, "Reactivity of USY extraframework alumina in alkaline medium," *Zeolites*, vol. 17, no. 4, pp. 340–345, 1996.
- [126] B. Sulikowski, J. Datka, B. Gil, J. Ptaszynski, and J. Klinowski, "Acidity and catalytic properties of realuminated zeolite Y," *Journal of Physical Chemistry B*, vol. 101, no. 35, pp. 6929–6932, 1997.
- [127] W. Wang and S. J. Hwang, "Effect of treatment conditions on Y-zeolite," *Chinese Journal of Chemical Engineering*, vol. 25, pp. 337–339, 1994.
- [128] D.-S. Liu, S.-L. Bao, and Q.-H. Xu, "Studies on realumination of dealuminated zeolite Y," *Acta Chimica Sinica*, vol. 54, no. 8, pp. 764–771, 1996.
- [129] W. Lutz, U. Lohse, and B. Fahlke, "Chemical reactions during alkaline treatment of dealuminated Y zeolites—impossibility of aluminium reinsertion into the framework," *Crystal Research and Technology*, vol. 23, no. 7, pp. 925–933, 1988.
- [130] W. Lutz, D. Heidemann, C. H. Rüscher, and J.-C. Buhl, "Formation of alkali-aluminosilicate layers on thermochemically dealuminated Y zeolites by alkaline leaching," *Crystal Research and Technology*, vol. 36, no. 1, pp. 9–14, 2001.
- [131] M. Fechtelkord, J.-C. Buhl, W. Lutz, and B. Zibrowius, "Realuminierung von Zeolith DAY infolge Si-Abreicherung," *Zeitschrift für Kristallographie, Supplement*, vol. 9, p. 154, 1995.
- [132] R. D. Bezman, "On the efficiency of insertion of aluminium into the framework of Y-type zeolite by the hydrothermal process of Liu, Klinowski, and Thomas," *Journal of Chemical Society, Chemical Communications*, pp. 1562–11563, 1987.
- [133] W. Lutz, W. Gessner, and D. Müller, "Formation of Al-rich aluminosilicate by alkaline treatment of DAY zeolite dealuminated by steaming," *Zeolites*, vol. 19, no. 2-3, pp. 209–212, 1997.
- [134] S. P. Zhdanov and E. N. Egorova, *Chimija Ceolitov*, Izd. Nauka, Leningrad, Moscow, Russia, 1968.
- [135] H. Stach, U. Lohse, H. Thamm, and W. Schirmer, "Adsorption equilibria of hydrocarbons on highly dealuminated zeolites," *Zeolites*, vol. 6, no. 2, pp. 74–90, 1986.
- [136] L. Aouali, J. Teanjan, A. Dereigne, P. Tougne, and D. Delafosse, "Structural evolution of dealuminated Y zeolites during various chemical treatments," *Zeolites*, vol. 8, no. 6, pp. 517–522, 1988.
- [137] R. M. Dessau, E. W. Valyocsik, and N. H. Goeke, "Aluminum zoning in ZSM-5 as revealed by selective silica removal," *Zeolites*, vol. 12, no. 7, pp. 776–779, 1992.
- [138] J. C. Groen, J. A. Moulijn, and J. Pérez-Ramirez, "Desilication: on the controlled generation of mesoporosity in MFI zeolites," *Journal of Materials Chemistry*, vol. 16, pp. 2121–2131, 2006.
- [139] D. Verbroekend and J. Pérez-Ramirez, "Design of hierarchical zeolite catalysts by desilication," *Catalysis Science & Technology*, vol. 1, no. 6, pp. 879–890, 2011.
- [140] W. Lutz, A. Grossmann, M. Bülow, and Th. Gross, "Questioning Klinowski's concept of isomorphous substitution of silicon by aluminium in the framework of silicates," *Crystal Research and Technology*, vol. 25, no. 2, pp. 135–138, 1990.
- [141] C. Mirodatos and D. Barthèmeuf, "Superacid sites in zeolites," *Journal of the Chemical Society, Chemical Communications*, no. 2, pp. 39–40, 1981.
- [142] W. Lutz, U. Kürschner, and E. Löffler, "Fine-tuning of the catalytic activity of dealuminated faujasites by subsequent chemical treatment," in *Proceedings of the 2nd Polish-German Zeolite Colloquium*, M. Rozwadowski, Ed., pp. 165–170, Nicolas Copernicus University Press, 1995.
- [143] U. Lohse, H. Stach, H. Thamm et al., "Dealuminierte Molekularsieve vom Typ Y Bestimmung des Mikro- und Sekundärporenvolumens durch Adsorptionsmessungen," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 460, no. 1, pp. 179–190, 1980.
- [144] G. Weber and M. Simonot-Grange, "Characterization of the dealumination effect into H faujasites by adsorption: part 2. The hexane molecule as a pore volume probe," *Zeolites*, vol. 14, no. 6, pp. 433–438, 1994.
- [145] A. Corma, "From microporous to mesoporous molecular sieve materials and their use in catalysis," *Chemical Reviews*, vol. 97, no. 6, pp. 2373–2419, 1997.
- [146] C. S. Triantafyllidis, A. G. Vlessides, and N. P. Evmiridis, "Dealuminated H-Y zeolites: influence of the degree and the type of dealumination method on the structural and acidic characteristics of H-Y zeolites," *Industrial & Engineering Chemistry Research*, vol. 39, no. 2, pp. 307–319, 2000.
- [147] K. Sato, Y. Nishimura, N. Matsubayashi, M. Imamura, and H. Shimada, "Structural changes of Y zeolites during ion exchange treatment: effects of Si/Al ratio of the starting NaY," *Microporous and Mesoporous Materials*, vol. 59, no. 2-3, pp. 133–146, 2003.
- [148] W. Lutz, R. A. Shutilov, and V. Y. Gavrilov, "Pore structure of USY zeolites in dependence on steaming condition," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 640, no. 3-4, pp. 577–581, 2014.
- [149] S. P. Zhdanov, L. S. Kosheleva, T. I. Titova, and M. A. Shubaeva, "IR study of the peculiarities of the stabilization of the NH_4NaY zeolite structure during its hydrothermal dealumination," *Russian Chemical Bulletin*, vol. 42, no. 4, pp. 619–623, 1993.
- [150] D. Barthèmeuf and B.-H. Ha, "Adsorption of benzene and cyclohexane on faujasite-type zeolites. Part 1.-Thermodynamic properties at low coverage," *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, vol. 69, pp. 2147–2157, 1973.

- [151] P. D. Hopkins, "Adsorption of hydrocarbons on sodium and demetallated synthetic faujasites," *Journal of Catalysis*, vol. 29, no. 1, pp. 112–119, 1973.
- [152] V. Bosáček, V. Patzelová, C. Hýbl, and Z. Tvarůžková, "Sorption properties of $\text{Na}_x\text{H}_{1-x}\text{Y}$ zeolites," *Journal of Catalysis*, vol. 36, no. 3, pp. 371–378, 1975.
- [153] R. K. Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, NY, USA, 1955.
- [154] A. H. Jansen, A. J. Koster, and K. P. de Jong, "Three-dimensional transmission electron microscopic observations of mesopores in dealuminated zeolite Y," *Angewandte Chemie International Edition*, vol. 40, no. 6, pp. 1102–1104, 2001.
- [155] J. Lynch, F. Raatz, and P. Dufresne, "Characterization of the textural properties of dealuminated HY forms," *Zeolites*, vol. 7, no. 4, pp. 333–340, 1987.
- [156] B. Sarkar, K. Arya, G. Ravichandran et al., "Ready-to-use seed composition and process thereof," USP 20080182744, 2008.
- [157] G. J. Ray and A. Samonson, "Double rotation and variable field ^{27}Al n.m.r. study of dealuminated Y zeolites," *Zeolites*, vol. 13, no. 6, pp. 410–413, 1993.
- [158] D. Ding, B. Li, P. Sun, Q. Jin, and J. Wang, "A simulated annealing study of Si,Al distribution in the faujasite framework," *Zeolites*, vol. 15, no. 6, pp. 569–573, 1995.
- [159] V. Jorik, "Semiempirical approach to determination of framework aluminum content in faujasite-type zeolites by X-ray powder diffraction," *Zeolites*, vol. 13, no. 3, pp. 187–191, 1993.
- [160] E. Merlen, J. Lynch, M. Bisiaux, and F. Raatz, "Surface modifications during Y zeolite dealumination," *Surface and Interface Analysis*, vol. 16, no. 1–12, pp. 364–368, 1990.
- [161] P. Kortunov, S. Vasenkov, J. Kärger et al., "The role of mesopores in intracrystalline transport in USY zeolite: PFG NMR diffusion study on various length scales," *Journal of the American Chemical Society*, vol. 127, no. 37, pp. 13055–13059, 2005.
- [162] L. Gueudré, M. Milina, S. Mitchell, and J. J. Pérez-Ramirez, "Superior mass transfer properties of technical zeolite bodies with hierarchical porosity," *Advanced Functional Materials*, vol. 24, no. 2, pp. 209–219, 2014.
- [163] J. Kärger and R. Valiullin, "Mass transfer in mesoporous materials: the benefit of microscopic diffusion measurement," *Chemical Society Reviews*, vol. 42, no. 9, pp. 4172–4197, 2013.
- [164] K. Li, J. Valla, and J. Garcia-Martinez, "Realizing the commercial potential of hierarchical zeolites: new opportunities in catalytic cracking," *ChemCatChem*, vol. 6, no. 1, pp. 46–66, 2014.
- [165] K. Möller and Th. Bein, "Mesoporosity—a new dimension for zeolites," *Chemical Society Reviews*, vol. 42, pp. 3689–3707, 2013.
- [166] M.-Ch. Silaghi, C. Chizallet, and P. Raybaud, "Challenges on molecular aspects of dealumination and desilication of zeolites," *Microporous and Mesoporous Materials*, vol. 191, pp. 82–96, 2014.
- [167] G. Clet, J. C. Jansen, and H. van Bekkum, "Synthesis of a zeolite Y coating on stainless steel support," *Chemistry of Materials*, vol. 11, no. 7, pp. 1696–1702, 1999.
- [168] W. Lutz, D. Enke, W.-D. Einicke, D. Taschner, and R. Kurzhals, "Mesopores in USY zeolites II," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 638, pp. 2189–2192, 2012.
- [169] W. Lutz, D. Enke, W. Einicke, D. Täschner, and R. Kurzhals, "Mesopores in USY zeolites," *Zeitschrift für Anorganische und Allgemeine Chemie*, vol. 636, no. 15, pp. 2532–2534, 2010.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

