

Characterization and removal of extra lattice species in faujasites

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Abstract

The acidic properties of dealuminated Y-type zeolites were characterized by infrared (IR) spectroscopy, microcalorimetry, ²⁹Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy and temperature-programmed desorption (TPD). Microcalorimetric measurements exhibited a uniform heat of adsorption (140 kJ/mol) of ammonia on the strong Brønsted acid sites. The differences in the acid site concentrations measured by adsorption of ammonia from the gas phase and by decomposition of ammonium-exchanged zeolites are discussed. The results indicate that parts of the extra lattice material consisting of cationic aluminium oxide species or silica alumina species are removed by ion exchange with aqueous solutions of ammonium hydroxide. Based on this, a method for the controlled removal of extra lattice material was developed.

Keywords: Faujasites; Characterization; Microcalorimetry; Infrared spectroscopy; Extra lattice species

1. Introduction

At present, dealuminated Y-type zeolites are extensively used as catalytically active components of cracking catalysts. The catalytic behavior of the catalyst is strongly influenced by the concentration, strength and type of the acid sites [1] as well as by the amount of extra framework aluminium (EFAL) species [2]. Thus, the characterization of the strength and concentration of the active sites of these zeolites is of considerable industrial interest.

Generally, the adsorption and desorption of bases are the most widely accepted methods for the evaluation of the acid site concentration of these materials [3–5]. However, a significant

difference between the concentration of acid sites determined by the adsorption of ammonia from aqueous solutions and from the gas phase was reported in previous studies [6,7]. In order to account for these differences, the two methods were systematically compared on a series of dealuminated faujasite-type zeolites.

Our preliminary studies suggested that the EFAL species formed by dealumination were the major cause for the observed differences. These species were partly removed from the lattice by treatment of the zeolites with NH₄OH solutions. In contrast, adsorption of the NH₃ from the gas phase did not change the concentration of the extra lattice alumina. This is of particular importance, as these extra lattice species seem to influence the catalytic behaviour of zeolites [8,9]. Acid leaching [10] for removal of the extra framework

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species partly destroys the lattice and reduces the concentration of Brønsted acid sites by removing part of the tetrahedrally coordinated Al [10]. This was not observed after treatment of the dealuminated Y samples with an aqueous NH_4OH solution to remove the extra lattice species.

The present paper focuses, thus, on the characterization of the acid sites prior and subsequent to NH_4OH leaching. The main experimental means employed are thermogravimetry–differential scanning calorimetry (TG–DSC), IR and ^{29}Si MAS NMR spectroscopy.

2. Experimental

The adsorption, desorption and surface chemistry of ammonia on several FAU samples, dealuminated by SiCl_4 , were investigated by TG, DSC, TPD, in situ IR and ^{29}Si MAS NMR spectroscopy. In order to probe the surface chemistry in aqueous solutions of ammonia, the samples were treated in aqueous NH_4OH solutions of concentrations varying from 0.01 to 24 mol/l at 300 K. The overall Al concentration of the samples was determined by energy dispersive X-ray absorption spectroscopy (EDAX).

2.1. Infrared spectroscopic measurements

For the IR spectroscopic measurements the samples were pressed into self-supporting wafers with a compact pressure of approximately 10^8 N/cm^2 . The wafers were placed in a sample holder in the center of a furnace and heated in situ to temperatures between 750 and 820 K with increments of 10 K/min. The IR spectra were recorded on a Bruker IFS 88 spectrometer using a spectral resolution of 4 cm^{-1} . A detailed description of the system is given elsewhere [11].

2.2. Calorimetric measurements

A modified Setaram TG–DSC 111 instrument was used for measuring the heat of ammonia adsorption. The sample was pressed into thin wafers (in the same way as for IR spectroscopic measurements) and placed in a small quartz cruci-

ble suspended on quartz glass suspension wires. The crucibles were hanging without physical contact with the quartz tubes in the most sensitive region of the calorimeter. The calibration of the calorimeter was performed over the whole temperature range (380–1060 K) by phase transitions of different inorganic samples. The calorimeter was connected to a vacuum system with a base pressure of $<10^{-4} \text{ Pa}$ equipped with a Balzers QMG420 mass spectrometer. Typically, 10 mg of the sample were heated to 800 K with increments of 10 K/min. During the activation, the change in the gas phase and the calorimetric and the gravimetric signals were recorded simultaneously. The sample was cooled to 475 K at which the adsorption was carried out by introducing small amounts of ammonia into the calorimeter.

3. Results

The acid site concentration of the parent dealuminated FAU (HY-5) and the sample treated with 1 N NH_4OH solution (HY-5-1.0) was compared by means of TPD of ammonia. The TPD curves normalized to the mass of the catalyst are plotted in Fig. 1. The integrated area of the desorption peak at 600 K, which is attributed to the desorption of ammonia from strong Brønsted acid sites [12,13], is significantly larger for the samples treated with aqueous ammonia solutions than for the same sample after adsorption of ammonia from the gas phase.

Fig. 2 shows the normalized IR spectra of the sample treated with an aqueous 1 N NH_4OH solution for 23 h at room temperature and of the same sample in contact with 10^{-1} Pa NH_3 from the gas phase. In both cases a strong absorption band at 3615 cm^{-1} , attributed to OH stretching vibration bands of extra framework species [14,15], was observed. In addition, bands at 1975 and 1865 cm^{-1} (which are assigned to the overtones of the zeolite lattice deformation vibrations [16], bands between 3500 and 2500 cm^{-1} (attributed to N–H stretching vibrations) and a band at 1460 cm^{-1} (NH_4^+ deformation vibrations) were detected. The IR spectra indicate a higher concentration of NH_4^+ in the NH_4OH ion-exchanged

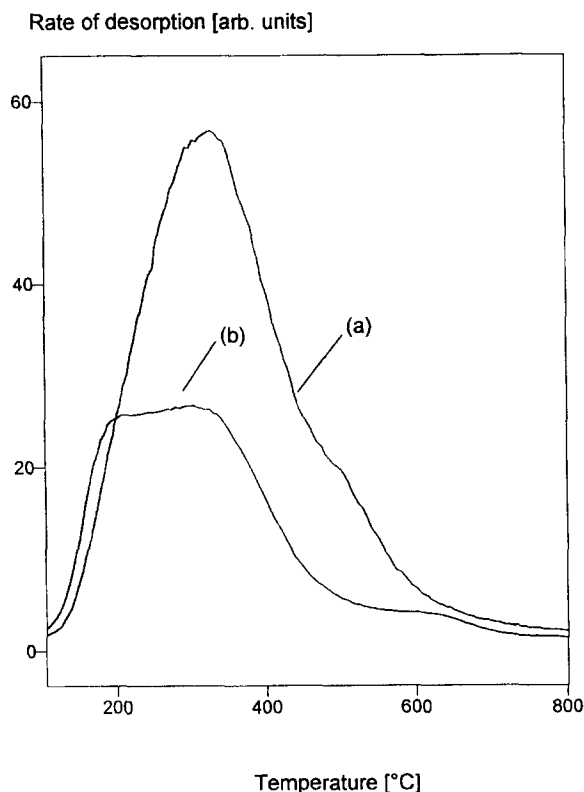


Fig. 1. Comparison of the temperature-programmed desorption from HY-5 (b) after adsorption of 10^{-1} Pa NH_3 and (a) after ion exchange with 1 N NH_4OH solution.

zeolites than in zeolites with NH_3 adsorbed from the gas phase. This is in perfect agreement with the TPD results.

In order to probe whether the variations in the concentration of ammonium ions are caused by the mode of introduction of the ions or are due to a modification of the zeolite and its acid sites, the parent dealuminated Y-type zeolites were treated with aqueous ammonia solutions of concentrations varying from 0.01 to 24 mol/l. HY-5-0.01, HY-5-0.1A and HY-5-1.0 correspond to materials treated with 0.01, 0.1 and 1.0 mol/l NH_4OH , respectively. The physicochemical characteristics of these materials together with those of the parent material and HZSM5 are compiled in Table 1.

The overall aluminium concentration was determined by EDAX spectroscopy, the lattice Al concentration was assessed by ^{29}Si MAS NMR and for some samples by the unit cell dimensions

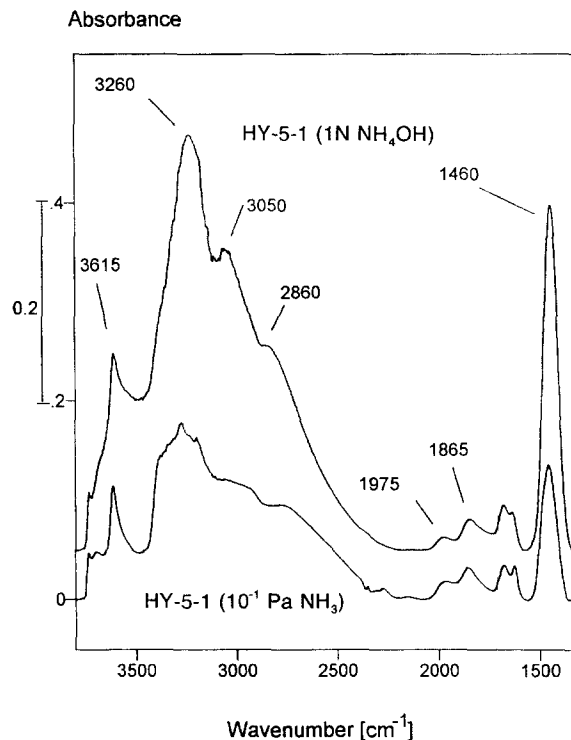


Fig. 2. IR spectra of HY-5 in contact with 10^{-1} Pa NH_3 and HY-5 after ion exchange with 1 N NH_4OH solution.

derived from X-ray diffraction (XRD) measurements [17]. The concentration of strong Brønsted acid sites was measured by acid site titration with ammonia followed by TG-DSC. The Brønsted acid site concentrations given in Table 1 equal the concentrations of adsorbed ammonia liberating a heat of adsorption higher than 120 kJ/mol. In Fig. 3, the evolved heat of adsorption is plotted versus the concentration of ammonia adsorbed. The maximum concentration of ammonia that is strongly adsorbed is indicated by lines A and B. The position of these lines was chosen at the concentration where the heat of adsorption starts to decrease.

The effect of the treatment with aqueous ammonia solutions on the intensity of the bands due to OH stretching vibrations are compared in Fig. 4. In agreement with the literature, the IR spectra of dealuminated zeolite Y shows at least five different OH bands [15,18,19]. The main bands of the activated samples are observed at 3630 cm^{-1} ,

Table 1
Concentrations of aluminium and acid sites and relative fractions of different extra lattice phases

Zeolite	Concentration (mol/g)				Relative fraction of EFAL-OH ^c	Relative fraction of silica in amorphous aluminosilicate ^d
	Aluminium		Acid sites			
	Total (EDAX)	Tetrahedrally (²⁹ Si NMR)	NH ₃ desorption ^a	NH ₃ adsorption ^b		
HY-5	$2.7 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	—	$6.6 \cdot 10^{-4}$	1.04	$5.5 \cdot 10^{-2}$
HY-5-0.01	$3.6 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$8.6 \cdot 10^{-4}$	0.85	$1.1 \cdot 10^{-1}$
HY-5-0.1A	$3.7 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	0.49	$6.7 \cdot 10^{-2}$
HY-5-0.1B	$3.6 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$7.4 \cdot 10^{-4}$	0.90	$9.4 \cdot 10^{-2}$
HY-5-0.1C	$3.7 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$8.9 \cdot 10^{-4}$	0.67	$7.2 \cdot 10^{-2}$
HY-5-1.0	$3.4 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$8.2 \cdot 10^{-4}$	0.68	$6.8 \cdot 10^{-2}$
HZSM5	$4.4 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$	—	—

^a Concentration of ammonia desorbed during heating the NH₄⁺-exchanged samples.

^b Concentration of ammonia strongly adsorbed at 475 K determined by TG–DSC measurements.

^c Fraction of the intensity of the IR band at 3615 cm⁻¹ and the intensities of the Brönsted OH stretching bands: $I_{3615} / \sum I_{\text{SiOHAl groups}}$.

^d Fraction of the ²⁹Si MAS NMR band at 112 ppm and the sum of all Si bands: $I_{\delta_{112}} / \sum I_{\text{Si}}$.

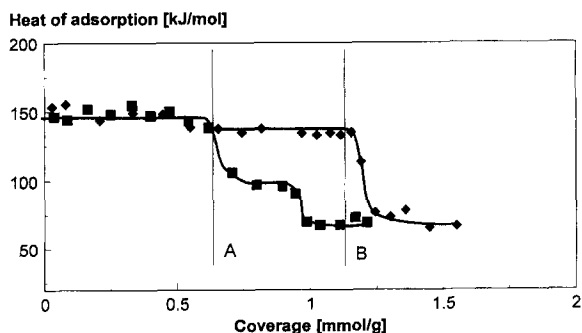


Fig. 3. Heat of adsorption versus amount of ammonia adsorbed for samples HY-5 (■) and HY-5-0.1-A (◆).

attributed to SiOHAl groups in the supercages [high-frequency (HF) band], 3560 cm⁻¹, attributed to SiOHAl groups in the sodalite cages [low-frequency (LF) band], and 3602 cm⁻¹, attributed to OH groups disturbed by extra framework species [20–22]. Comparison with Fig. 2 shows that the band at 3602 cm⁻¹ is superimposed by a strong band at 3615 cm⁻¹. The intensities of the HF and LF bands increase by the treatment with 0.1 N NH₄OH solution and the intensity of the band at 3602 cm⁻¹ (3615 cm⁻¹) decreases (Fig. 4). This suggests that the concentration of extra framework material is reduced and the concentration of the Brönsted acid sites is increased.

This conclusion is supported by comparison of

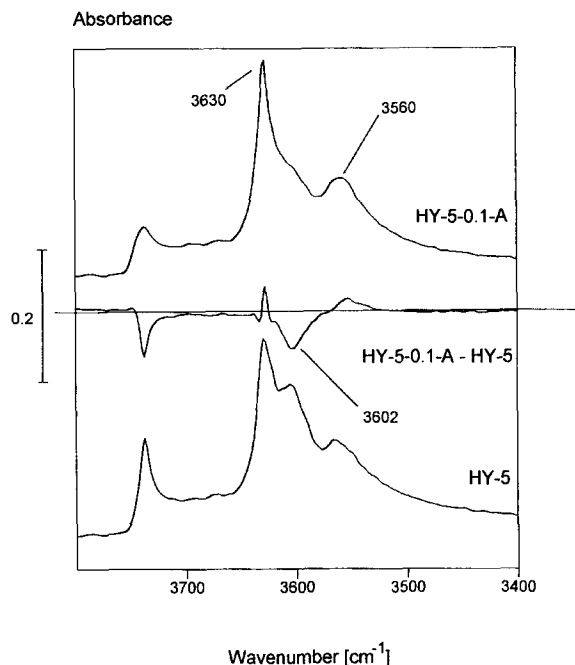


Fig. 4. IR spectra of the activated sample HY-5 and HY-5-0.1-A in the OH stretching vibration region.

the IR spectra of samples HY-5 and HY-5-0.1-A before and after adsorption of 10⁻¹ Pa ammonia at 300 K (Fig. 5). The increase in the intensity of the band at 1460 cm⁻¹ indicates that the concentration of ammonia bound to Brönsted acid

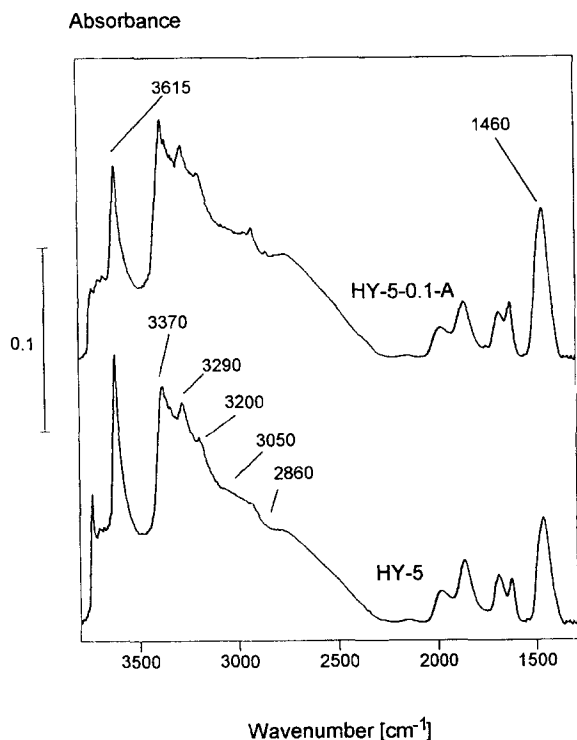


Fig. 5. IR spectra of sample HY-5 and HY-5-0.1-A after adsorption of 10^{-1} Pa NH_3 .

sites is larger for HY-5-0.1-A than for HY-5. Additionally, the band at 3615 cm^{-1} , which is attributed to non-acidic OH groups related to extra framework species [20–22], is substantially reduced after NH_4OH treatment.

Two explanations for these observations are conceivable. (i) The treatment with NH_4OH causes a reinsertion of aluminium from the extra framework phases into the zeolite framework. (ii) The extra framework phases act partially as counter cations for the $\text{SiO}^- \text{Al}$ groups which are replaced by NH_4^+ ions and subsequently washed out by the treatment with a basic solution.

To differentiate between these two models, the Al concentrations derived from ^{29}Si MAS NMR spectra of the different samples are compared in Table 1. The data indicate that the concentration of Al in the lattice after the modification procedure with aqueous ammonia solutions is nearly identical with that of the parent material supporting the second model.

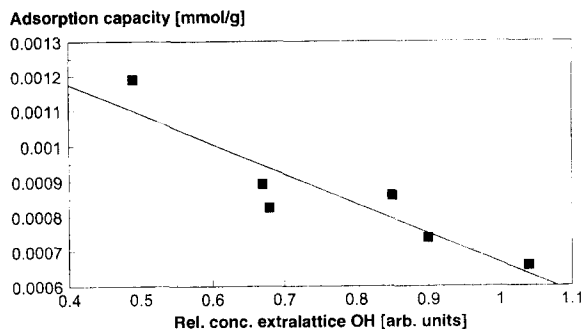


Fig. 6. Relationship between the adsorption capacity for ammonia and the relative intensity of the remaining IR band at 3615 cm^{-1} after adsorption of 10^{-1} Pa NH_3 (normalized to the sum of the intensities of the bridged OH groups).

For a more quantitative description of the extra lattice material present in the different zeolites, the relative fractions of the different extra lattice phases derived by the two methods are also compared in Table 1. The fraction of cationic EFAL species was calculated by the relative intensity of the IR band at 3615 cm^{-1} after adsorption of 10^{-1} Pa ammonia, and the concentration of the aluminosilicate was calculated by the relative intensity of the ^{29}Si MAS NMR peak at 112 ppm, attributed to amorphous aluminosilicates [23]. The numbers given are based on the ratio of the integrals of the remaining band at 3615 cm^{-1} after ammonia adsorption to the integrals of the bridged OH groups as well as on the ratio between the integrals of the aluminosilicate signal and the sum of the ^{29}Si MAS NMR signals. The samples HY-5-0.1-A, HY-5-0.1-B and HY-5-0.1-C were slurried for 138, 19 and 118 h in 0.1 N NH_4OH at 300 K, respectively.

Fig. 6 illustrates the linear decrease of the adsorption capacity for strongly adsorbed ammonia with increasing relative intensity of the band at 3615 cm^{-1} .

4. Discussion

4.1. Characterization of the acid sites

Assuming a stoichiometry of one molecule of ammonia adsorbed per SiOHAl group, the ^{29}Si

MAS NMR data and the amount of ammonia desorbed from the samples during activation (see Table 1) suggest that all strong Brønsted acid sites are accessible for ammonium ions in aqueous solution. In contrast, after adsorption of NH_3 from the gas phase (after the first activation) a significant lower amount of ammonia desorbed from the zeolite (see Fig. 1). It reached only one third to one half of the concentration of NH_3 of the samples after ion exchange in aqueous solution measured with TPD. Previously, this was explained by partial dehydroxylation of the samples during the temperature treatment [6] accompanied by partial removal of aluminium from the zeolite lattice. The ^{29}Si MAS NMR measurements, however, clearly indicate that this is not the case in the present study.

As both approaches led to nearly identical values of NH_4^+ concentration in the case of HZSM5 (see Table 1), we are able to rule out the possibility of an inherent difference in the values measured by aqueous ion exchange and by ammonia adsorption from the gas phase. Thus, ion exchange caused at least partially the replacement of aluminium oxide or hydroxide species, which assumed the role of charge-compensating metal cations. Because the concentration of tetrahedrally coordinated aluminium (as estimated from ^{29}Si MAS NMR) perfectly agrees with the concentration of NH_4^+ ions after ion exchange, we conclude that by the treatment with 1 N NH_4OH all cationic alumina species were replaced by NH_4^+ . After aqueous exchange and thermal treatment, some of the EFAL species still present in the zeolite are able to block again some of the acid sites. Thus, if the EFAL species are not completely removed, a decreased adsorption capacity for ammonia from the gas phase is found.

The acid sites that were able to adsorb NH_3 from the gas phase were quite uniform in strength. The heat of ammonia adsorption at 473 K was 140 ± 10 kJ/mol as long as one NH_3 molecule was adsorbed per acid site. This value agrees perfectly well with previous reported values [24–27].

The IR spectra (see Fig. 7) clearly indicate that adsorption did not take place on SiOH (band at 3737 cm^{-1}) and on AlOH groups of the extra lattice material (band at 3615 cm^{-1}). The NH deformation vibrations indicate that most of the ammonia molecules were adsorbed as NH_4^+ ions.

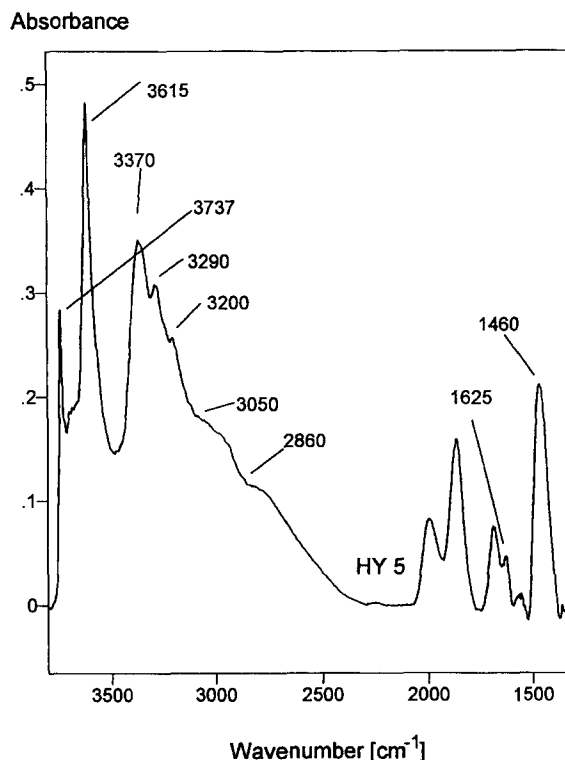


Fig. 7. IR spectrum of 10^{-1} Pa ammonia in contact with HY-5 at 473 K.

Only a small fraction was adsorbed on accessible Lewis acid sites (13% of the integrated areas of the bands at 1625 and 1460 cm^{-1}).

Thus, we conclude that (for characterization purposes) the aqueous ion exchange will provide the total concentration of tetrahedrally coordinated Al in the lattice. Adsorption of ammonia from the gas phase, on the other hand, will provide the concentration of the strong Brønsted acid sites in the zeolite which are accessible for reactant molecules.

In the following we will outline the possibilities to use the NH_4OH treatment for controlled removal of the extra lattice alumina from the channels of the samples studied.

4.2. Removal of the extra framework aluminium species

The increase in the concentration of ammonia adsorbed from the gas phase and the decrease in

the intensity of the IR band at 3615 cm^{-1} after treatment of the zeolite with NH_4OH solution (see Fig. 6) suggest that EFAL oxides are removed during the modification procedure. Because adsorption of ammonia from the gas phase occurs quantitatively on all strong Brönsted acid sites for the samples studied (concluded from the complete disappearance of the HF and LF IR band after adsorption of ammonia), we rule out that EFAL reduces the concentration of acid sites in the parent material by physical blocking. Thus, we propose that most of the EFAL in the parent material is present as cationic aluminum oxide species, which is then partially removed during the NH_4OH treatment. The inverse linear dependence between the chemisorption capacity for ammonia and the concentration of EFAL further indicates that the cationic extra framework species in the zeolite channels is uniform in size and nature.

Although we have clear evidence that EFAL is removed from the zeolite pores, the overall aluminum concentration increased by some 30% during the treatment (see Table 1). Because the concentration of the tetrahedrally coordinated aluminum in the lattice remained constant throughout all modification procedures reported here, we conclude that neither aluminum insertion into [28,29] nor aluminum removal from [10] the lattice occurs. The increase in the overall aluminum concentration thus indicates that SiO_2 (present in the

extra lattice material of the parent zeolite) was also removed during the ion-exchange procedure. This conclusion is supported by the decrease of the SiOH band at 3737 cm^{-1} (suggesting a decrease of the concentration of the SiOH groups) after ion exchange. The SiCl_4 treatment that was used to produce the parent material is speculated to be the source for this silica material outside the zeolite crystals, because the relative intensity of the band at 3737 cm^{-1} in the parent zeolite is remarkably high compared with steam-dealuminated or as-synthesized faujasites [14]. The remaining silica outside the zeolite crystals seems to react in part with aluminum that is removed by the ion-exchange procedure. This is concluded from the increasing ^{29}Si MAS NMR peak at 112 ppm, which is characteristic for amorphous aluminosilicate [23]. The pure silica does not seem to contribute to that signal. A semiquantitative estimate of the relative amount of aluminum in the two extra lattice phases is given in Fig. 8.

It should be especially noted that the aluminum concentration in the lattice remained unaffected throughout all treatments with diluted NH_4OH solutions. The use of concentrated NH_4OH solutions, however, led to the partial destruction of the zeolite (the decrease in the reflection intensities and scattering from amorphous material was detected by XRD). This suggests an approximately equal stability of the Si–O–Si and Si–O–Al bonds with respect to hydrolysis in a basic environment.

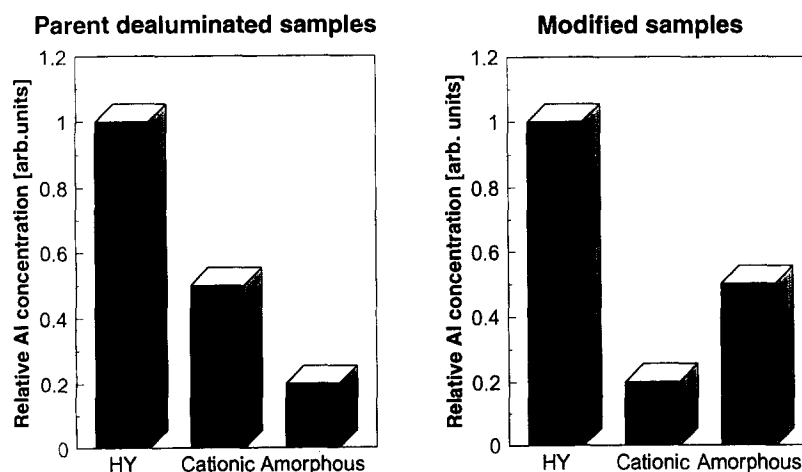


Fig. 8. Schematic presentation of the Al concentration in the phases of the dealuminated zeolites.

The uniform and identical strength of the acid sites in the presently investigated samples contradicts the attribution of high acid strength to OH groups perturbed by EFAL IR band at 3602 cm^{-1}) as proposed by Lunsford et al. [20]. Not even a small fraction of the acid sites of the presently investigated dealuminated samples showed an enhancement in acid strength. The strength of all acid sites, however, decreased slightly ($\Delta q = 10\text{ kJ/mol}$) after removal of the EFAL from the zeolite pores. Thus, we conclude that weak long-range interactions between EFAL and the zeolite lattice exist.

5. Conclusions

The main difference between the adsorption capacity of dealuminated FAU for ammonia adsorbed from aqueous solutions and from the gas phase is concluded to be due to the leaching of EFAL species from the zeolite pores in aqueous ammonia solutions. This procedure enhances the adsorption capacity up to 100%. The extent of adsorption capacity enhancement depends subtly on the concentration of the NH_4OH solutions, the time of treatment and the washing procedures. It is concluded that two extra framework species exist: (i) one that is rich in alumina, has cationic character and balances the charge of tetrahedrally coordinated aluminium in the zeolite lattice; (ii) one that is rich in silica and is located mainly outside the zeolite channels. The strength of the acid sites is not changed during the modification procedure. There is a slight decrease in the overall heat of adsorption of the modified compared with the parent samples, which implies a long-range interaction between the extra lattice phases and the OH groups of the zeolites. The aluminium concentration in the lattice is not significantly altered by that procedure. With respect to the characterization of zeolites, our results show that ammonia TPD after aqueous ion exchange indicates the concentration of tetrahedrally coordinated aluminium framework atoms (i.e. the maximum concentration of strong Brønsted acid sites available). Adsorption of ammonia from the gas phase, on the other hand will yield the concen-

tration of the Brønsted acid sites accessible to a gaseous reactant.

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