Nature of Enhanced Brønsted Acidity Induced by Extraframework Aluminum in an Ultrastabilized Faujasite Zeolite

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Nature of Enhanced Brønsted Acidity Induced by Extraframework Aluminum in an Ultrastabilized Faujasite Zeolite: An In Situ NMR Study

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ABSTRACT: The enhancing effect of extraframework Al (EFAI) species on the acidity of bridging hydroxyl groups in a steam-calcined faujasite zeolite (ultrastabilized Y, USY) was investigated by in situ monitoring the H/D exchange reaction between benzene and deuterated zeolites by 1H MAS NMR spectroscopy. This exchange reaction involves Brønsted acid sites (BAS) located in sodalite cages and supercages. In a reference faujasite zeolite free from EFAI, both populations of BAS are equally and relatively slowly reactive toward C6H6. In USY, in stark contrast, the H/D exchange of sodalite hydroxyl groups is significantly faster than that of hydroxyl groups located in the faujasite supercages, even though benzene has only access to the supercages. This evidences selective enhancement of BAS near Lewis acidic EFAI species, which according to the NMR findings are located in the faujasite sodalite cages.

INTRODUCTION

Faujasite zeolite (framework code FAU, zeolite Y, Figure 1) is widely used as an acid catalyst for (hydro)cracking operations in the oil refining industry. In its as-synthesized form, the zeolite has a high density of framework aluminum (FAI) and exhibits only weak intrinsic acidity and limited hydrothermal stability. The Brønsted acidity and stability of such a Y zeolite can be strongly enhanced by removing Al from the framework (dealumination). Dealumination leads to ultrastabilized zeolite Y (USY), which is typically achieved by calcination of as-prepared Y zeolite in the presence of steam at temperatures in the range of 550−800 °C. The higher intrinsic Bronsted acidity of dealuminated zeolite relates to the increased concentration of isolated FAI sites (i.e., no framework Al in the second coordination shell). A substantial part of Al atoms extracted from the framework are relocated to positions outside the framework (extraframework Al, EFAI). While typically a part of these EFAI species are removed by further chemical treatment, it is known that residual EFAI species influence the acidity and reactivity of steam-calcined zeolites. This can for instance be
appreciated from the higher intrinsic acidity and acid activity of a USY zeolite in comparison with an EFAl-free zeolite Y reference with a comparable framework Al content, obtained by selective dealumination by ammonium hexafluorosilicate, (NH₄)₄SiF₆.⁶⁻⁷ Although the promoting effect of EFAl species on the acidity of the BAS in USY zeolites has been investigated before,⁶⁻¹⁵ important aspects such as the nature of the EFAl species, their location inside the faujasite micropores, and the way they enhance the intrinsic acidity of bridging hydroxyl groups are not understood yet.

Recently, Van Bokhoven et al. demonstrated that EFAl formed during steam calcination of an NH₄Y zeolite predominantly occupies the SI′ cages (Figure 1a).¹⁷ The structural details of such EFAl species are still unknown. Although most of the previous studies considered cationic mononuclear Al-oxo complexes as EFAl species,¹⁸,¹⁹ recent findings indicate that the coordinative unsaturation of such Al centers and the high basicity of the terminal oxygen ligands will cause such complexes to rearrange into multinuclear Al-oxo/hydroxo clusters inside sodalite cages.²⁰ A recent density functional theory (DFT) study by Liu et al.²¹ confirmed that such multinuclear complexes are preferentially located in sodalite cages (Figure S2, Supporting Information). Oxygenated and hydroxylated Al³⁺ cations condense within sodalite cages to form clustered O- and OH-bridged species, bearing a higher formal positive charge compensated through the direct interaction with lattice oxygen anions. In a subsequent work, it was shown that such EFAl species in faujasite strongly affect the acidity of the BAS, leading to a higher activity toward alkane activation.²²

Solid-state NMR spectroscopy is a powerful technique for studying acid sites in zeolites.²³⁻²⁵,²⁷ Al NMR spectroscopy can distinguish the different types of Al in zeolites. Recently, White et al. used one- and two-dimensional ¹H NMR spectroscopy to directly detect different types of acid sites in HZSM-5 and to reveal direct proton exchange between them.²⁶ Another possibility lies in the study of probe molecules that interact with the acid sites, e.g., acetonitrile (¹⁴C NMR).²⁷⁻²⁹ deuterated pyridine (¹H NMR),²⁵ and trimethylphosphine (¹⁹P NMR).³⁰,³¹ For example, the adsorption of 2-¹³C-acetone was used as a molecular probe in an NMR study to demonstrate the influence of EFAl on zeolite acidity.²⁵ In these works, the strong interplay between BAS and EFAl species was emphasized.

Herein, we employ in situ NMR spectroscopy to determine the acidity of a Y zeolite by following the H/D exchange of BAS with benzene. The suitability of this method for acidity characterization was first demonstrated by the group of Haw using NMR spectroscopy,³⁵ while our group later extended this approach using IR spectroscopy.³⁶ The sensitivity of IR spectroscopy allows quantification of strong BAS in zeolites, clays, and even amorphous silica–aluminas, which contain very few of such acid sites.³⁵,³⁶ For a range of EFAl-free Y zeolites, Almutairi et al. showed a strong correlation between acidity measured by CO IR spectroscopy and the H/D exchange rate with deuterated benzene as determined by IR spectroscopy.³⁵ Selective substitution of AlF with Si atoms can be achieved by treating a parent NH₄Y zeolite with ammonium hexafluorosilicate (NH₄)₄SiF₆ (AHFS).³ Thus, the H/D exchange rate can directly indicate the acidity of such an EFAl-free Y zeolite. The much higher H/D exchange rate of Y zeolites promoted by EFAl sites confirmed their enhancing effect on the BAS. Nevertheless, there was no clear correlation between the amount of EFAl sites and the Bronsted acidity. These H/D exchange IR spectroscopy studies showed that protons in sodalite cages exchange at similar rates as those in the more accessible supercages. In the present work, we turn back to ¹H NMR spectroscopy to follow the H/D exchange under mild conditions for two Y zeolites, one which was dealuminated by treatment with ammonium hexafluorosilicate such that it is free from EFAl and another one which is a commercial steam-calcined USY zeolite containing EFAl. The nature and location of EFAl species in USY were also investigated by NMR spectroscopy. The peculiar result of our current efforts is that, in the presence of EFAl sites, the sodalite hydroxyl groups exchange substantially faster than the hydroxyl groups located in the faujasite supercages even though benzene has only access to the supercages. The role of EFAl-oxo species stabilized in sodalite cages as acidity-enhancing species will be discussed.

**MATERIALS AND METHODS**

**Sample Preparation.** Steam-calcined zeolite USY (Si/Al 4.05) was received from Zeolyst. Dealuminated Y zeolite AHFSY (Si/Al 4.15) was prepared according to a literature procedure involving the isomorphous substitution of Al by Si using ammonium hexafluorosilicate (AHFS).³

**H/D Exchange.** The parent zeolite was dehydrated at 500 °C (heating rate 2 °C/min) for 12 h in a dynamic vacuum (p < 10⁻⁵ mbar). The dehydrated sample was deuterated by exposure to 10 mbar of D₂O gas at 150 °C for 30 min, followed by evacuation. This procedure was repeated two times. The sample was then evacuated at 450 °C for another 12 h. The two deuterated samples are denoted as D-USY and D-AHFSY. H/D exchange was carried out in a 4 mm zirconium NMR rotor. The dehydrated deuterated zeolite was loaded in the NMR rotor in a glovebox under inert (N₂) atmosphere. The rotor was then placed in a glass tube, connected to a manifold setup, and evacuated for 2 h. Thereafter, the tube containing the sample rotor was cooled to −40 °C, and the sample was brought in contact with a benzene reservoir (partial pressure of 4 mbar) for 1 min. The rotor was then tightly closed with a boron nitride cap and transferred to the NMR probe-head kept at −30 °C.

**Solid-State NMR Spectroscopy.** NMR measurements were performed on a Bruker DMX500 spectrometer operating at 500, 99, and 137 MHz for ¹H, ²⁹Si, and ²⁷Al, respectively. The NMR measurements were carried out using a 4 mm MAS probe-head with a sample rotation rate of 12.5 kHz. ¹H NMR spectra were obtained by a Hahn-echo pulse sequence of τ₁−τ₂−τ₁−τ₂−aq with a 90° pulse τ₁ = 5 μs and a 180° τ₂ = 10 μs. The interscan delay was chosen to be 120 s in order to obtain quantitative spectra. The same pulse sequence was used for T(CH)filter(¹H) filtered spectra by varying the τ₁ time. T(CH)filter(¹H) filtered spectra were recorded by introducing a lock pulse in the Hahn-echo pulse sequence (τ₁−tlock pulse−τ₁−τ₂−τ₁−aq) with τ₁ = 2.5 ms and a variable tlock pulse duration. Two-dimensional ¹H MAS NMR exchange experiments were performed using the 90°−τ−90°−tmax−90°−τ pulse sequence with evolution time τ₁ and signal detection time τ₂. A mixing time tmax of 0.3 and 1 s was used. ²⁷Al NMR spectra were recorded with a single-pulse sequence with a 180° pulse duration of 1 μs and an interscan delay of 1 s. MQMAS spectra were recorded by a three-pulse sequence p₁−τ₁−p₂−τ−p₁−τ₂ for triple-quantum generation and zero-quantum filtering (strong pulses p₁ = 3.4 μs and p₂ = 1.4 μs at a nutation
frequency \( \nu_1 = 100 \text{ kHz} \), a soft pulse \( p_1 = 11 \mu s \) at \( \nu_1 = 8 \text{ kHz} \), a filter time \( \tau = 20 \mu s \), and an interscan delay 0.2 s. \( ^{27}\text{Al}--^{1}\text{H} \) TRATransfer of Population in DOuble Resonance (TRAPDOR) \(^3\) spectra were recorded with the irradiation on and off on the \( ^{27}\text{Al} \) nuclei of 795 \( \mu s \), prior to the echo pulse, and an interscan delay of 10 s. Quantitative \( ^{29}\text{Si} \) NMR spectra were recorded using a high-power proton decoupling direct excitation (DE) pulse sequence with a 90° pulse duration of 3 \( \mu s \) and an interscan delay of 360 s. The \( ^{1}\text{H} \) and \( ^{29}\text{Si} \) pulse powers were adjusted to obtain a 90° pulse length equal to 5 \( \mu s \) in tetramethylsilane (TMS). An \( \text{Al(NO}_3\text{)}_3 \) solution was used to adjust the \( ^{27}\text{Al} \) pulse power. The temperature of the sample was controlled by a BVT300 variable temperature control unit and nitrogen gas. For low temperature, the nitrogen gas flow was cooled through a heat exchanger inserted in liquid nitrogen. The appropriate temperature was adjusted by using a heating element in the NMR probe-head. The true temperature inside the probe was calibrated using ethylene glycol and methanol for high and low temperatures, respectively.

**X-ray Diffraction (XRD).** XRD patterns of zeolites were recorded on a Bruker D4 Endeavor Diffractometer using Cu K\( \alpha \) radiation with a wavelength of 1.54056 \( \text{Å} \). 2\( \theta \) angles from 5 to 60° were measured with a step size of 0.077° and a time per step of 1 s. The catalysts were ground and pressed in sample holders for measurements. Crystallinity of the zeolite samples was calculated from the XRD patterns using the Topas software.

**Elemental Analysis.** The Al content in zeolite catalysts was determined by elemental analysis, which was carried out by ICP-OES analysis on a Spectro Ciros CCD ICP optical emission spectrometer with axial plasma viewing. For the ICP measurements, the samples were dissolved in a 1.5 mL solution of an HF/HNO\(_3\)/H\(_2\)O (1:1:1) mixture.

### RESULTS

**Basic Characterization.** The XRD patterns shown in Figure 2a indicate that USY and AHFSY are highly crystalline and exhibit the expected cubic crystal structure with nearly similar lattice constants (Table 1). The correlation between the FAI content in zeolite and the lattice constant can be used to determine the FAI content in zeolite \( \text{Y} \). \(^{10,38} \) This method is based on the FAI contents of the two zeolites found to be comparable, i.e., 3.0 mmol/g for USY and 3.3 mmol/g for AHFSY.

The \( ^{27}\text{Al} \) NMR spectrum of the AHFSY zeolite shows one symmetric peak at \( \sim 62 \text{ ppm} \) (Figure 3, right top), which can be assigned to FAI. In comparison, the \( ^{27}\text{Al} \) NMR spectrum of USY contains two additional peaks, i.e., an octahedral Al signal at \( \sim 0 \text{ ppm} \) (Figure 3, left top) belonging to EFAI and a broad peak around 40 ppm. The nature of these species was investigated by \( ^{27}\text{Al} \) MQMAS spectroscopy, which removes the second-order quadrupolar line broadening, thereby enhancing resolution and distinguishing between chemical-shift heterogeneity and quadrupolar broadening. The resulting \( ^{27}\text{Al} \) MQMAS NMR spectra (Figure 3, left) confirm that USY has both FAI with tetrahedral (T) and octahedral (O) oxygen coordination. The signal at 40 ppm in the 1D spectrum appears as a quadrupolar broadened tetrahedral signal (T in Figure 3) in the MQMAS spectrum. This distortion of some tetrahedral FAI is probably caused by the presence of EFAI in USY in the vicinity of FAI as will be confirmed below in \( ^{1}\text{H} \) 2D correlation NMR experiments.

The FAI content can also be estimated from the intensity of the \( ^{27}\text{Al} \) NMR signal at the tetrahedral position in the 1D spectrum. The calculated FAI content was 1.4 mmol/g for USY and 3.2 mmol/g for AHFSY. However, \( ^{27}\text{Al} \) NMR spectroscopy is not always accurate in determining the Al population due to the possible NMR invisibility of some Al nuclei, especially in steam-calcinated zeolites like USY. To verify these FAI values, we used \( ^{29}\text{Si} \) MAS NMR spectroscopy as a third method. \(^{39–41} \) The similar FAI contents of the two zeolite
samples are confirmed by the relative occurrences of Si atoms \( Q \) with different coordinations \( \text{Si}(	ext{OSi})_n(	ext{OAl})_m \) in the zeolite lattice. The respective Si/FAI ratios calculated from the \( ^{29}\text{Si} \) MAS NMR intensities (Figure 2b) are 5.4 and 4.6, corresponding to 30.1 and 34.1 FAl atoms per unit cell \( (\text{Si}_{192}\text{O}_{384}, \ T = \text{Si or Al}) \). The framework Al (FAI) contents of \( \text{Si} \) corresponding to 30.1 and 34.1 FAl atoms per unit cell MAS NMR intensities (Figure 2b) are 5.4 and 4.6, on continuous irradiation of the \( ^{27}\text{Al} \) spins during a rotor-

dipolar coupling between a quadrupolar nucleus, such as \( ^{27}\text{Al} \), and a nucleus with spin \( 1/2 \) such as \( ^{1}\text{H} \). The technique relies on 

coupling between the two nuclei is, and thus, the closer the two nuclei are. As can be seen in Figure 5, the signals at 2.8

\[ \text{Si/Al} = \sum \frac{n}{\sum n} \quad \text{for random Al distribution in lattice} \]

Before studying the H/D exchange between these samples and benzene, we investigate their proton and deuterium forms by \( ^{1}\text{H} \) NMR spectroscopy (Figure 4). The resonance at 1.9 ppm belongs to silanol moieties, while the signals at 3.9 and 4.6 ppm can be assigned to BAS in the sodalite cages and supercages, respectively. USY shows another signal at 2.8 ppm attributable to EFAI hydroxyl groups.

The framework Al content, Varying Numbers of Al Neighbors in the Zeolite Lattice and the Framework Al Content, \( \text{V} \) with different coordinations \( \text{Si}(	ext{OSi})_n(	ext{OAl})_m \) in the zeolite lattice. The respective Si/FAI ratios calculated from the \( ^{29}\text{Si} \) MAS NMR intensities (Figure 2b) are 5.4 and 4.6, corresponding to 30.1 and 34.1 FAl atoms per unit cell \( (\text{Si}_{192}\text{O}_{384}, \ T = \text{Si or Al}) \). The framework Al (FAI) contents of \( \text{Si} \) corresponding to 30.1 and 34.1 FAl atoms per unit cell MAS NMR intensities (Figure 2b) are 5.4 and 4.6, on continuous irradiation of the \( ^{27}\text{Al} \) spins during a rotor-

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\[
\begin{array}{|c|c|c|c|}
\hline
& \delta_{\text{Si}} & \text{USY} & \text{AHFSY} \\
\hline
\text{BAS}_{\text{sodalite}} & 4.6 & 0.57 \pm 0.01 & 1.85 \pm 0.01 \\
\text{BAS}_{\text{super}} & 3.9 & 0.39 \pm 0.01 & 1.40 \pm 0.01 \\
\text{Si}--\text{OH} & 1.8 & 0.13 \pm 0.03 & 0.07 \pm 0.01 \\
\text{Al}--\text{OH} & 2.6 & 0.40 \pm 0.01 & 0.06 \pm 0.01 \\
\hline
\end{array}
\]

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H/D exchange between the deuterated zeolites and benzene was initially investigated on D-USY at different temperatures. Figure 6 shows a stack plot of the $^1$H MAS NMR spectra recorded at different temperatures between $-30$ and $100 \, ^\circ C$. The spectra were obtained after a specific time at the indicated temperature. Between $-30$ and $35 \, ^\circ C$, the spectra were obtained after 2 h. The $55 \, ^\circ C$ spectrum was obtained after 14 h of H/D exchange, and the $100 \, ^\circ C$ spectrum was obtained after 1 h. For comparison, the spectrum of the dehydrated sample is added (red line).

Figure 6. In situ $^1$H NMR of H/D exchange between D-USY and benzene, recorded at different temperatures starting from $-30 \, ^\circ C$. The spectra were obtained after a specific time at the indicated temperature. Between $-30$ and $35 \, ^\circ C$, the spectra were obtained after 2 h. The $55 \, ^\circ C$ spectrum was obtained after 14 h of H/D exchange, and the $100 \, ^\circ C$ spectrum was obtained after 1 h. For comparison, the spectrum of the dehydrated sample is added (red line).

The reaction starts at $25 \, ^\circ C$ with the H/D exchange at the sodalite position followed by H/D exchange of the supercage position. At a temperature of $100 \, ^\circ C$, the proton signals of the BAS show an advanced exchange and a peak shape comparable to the fully protonated sample before deuteration and benzene exposure. At this stage, the silanol and EFAI hydroxyl groups are only slightly affected by exposure to benzene, which is expected due to the low acidity of these moieties. The chemical shift of the supercage BAS protons is slightly larger than that of the supercage protons in the zeolites without benzene. In fact, the selective change of this signal confirms its assignment to the supercage BAS protons, because benzene cannot access the sodalite cages and, therefore, mainly interacts with the supercage BAS protons.

The H/D exchange behavior in USY and AHFSY zeolites was then monitored at a constant temperature of $55 \, ^\circ C$ during 14 h, by recording quantitative $^1$H NMR spectra each 0.5 h. A series of spectra for USY and AHFSY at different times is given in Figure 7. As can be seen, the total signal intensity of the BAS signal at 4.0 and 4.5 ppm in both zeolites significantly increased during these experiments. A key difference noted is that whereas the sodalite sites in the USY zeolite exchange faster than the supercage sites, these two populations exchange at the same rate in the AHFSY zeolite.

As the sodalite and supercage proton signals overlap, line shape deconvolution was required to obtain quantitative information on the distinct exchange behavior (Figure S3). Deconvolution was done by use of the dmfit2008 program. A Gaussian line shape was used where the positions and the widths of the sodalite and supercage resonances were kept fixed within the series of spectra. Figure 8 shows the relative increase in the proton signals of BAS of USY and of AHFSY as a function of the exchange time. Confirming the qualitative difference above, the deconvolution confirms that the sodalite and supercage deuterexyl (OD) sites in AHFSY exchange in the same manner, while for USY, the sodalite OD sites exchange much faster than the supercage OD sites.

Figure 7. In situ $^1$H NMR of H/D exchange between D-USY and benzene as a function time at $55 \, ^\circ C$. Spectra were recorded every 0.5 h up to 14 h in total.

Figure 8. Relative protonation of OD sites in USY and AHFSY based on deconvolution of the in situ $^1$H NMR spectra recorded at $55 \, ^\circ C$ during H/D exchange of D-USY with $C_6H_6$ (cf., Figure 7).
The faster H/D exchange of sodalite sites is unexpected, because it is well-known that benzene cannot enter the sodalite cages. The exclusive location of benzene in the supercage is confirmed by a selective chemical-shift change of the supercage BAS signal from 3.9 to 4.1 ppm due to benzene, whereas the shift of the sodalite-cage BAS stays unaltered (Figure 9).

Furthermore, after benzene absorption, the transversal $^1$H NMR relaxation is only accelerated for the supercage BAS (Figure 9). The selective relaxation enhancement by a factor of 2 is caused by the dipole interactions between the supercage BAS protons and the relatively high concentration of benzene protons in the supercage. The absence of any benzene-induced relaxation effect on the BAS signal at 4.6 ppm also contradicts any tentative explanation that benzene has accidentally shifted part of the supercage BAS signals underneath the sodalite BAS signal in the $^1$H NMR spectrum.

2D spin-exchange spectroscopy (2D EXSY) provides information about the proximity of chemically different protons. For a sufficiently long mixing time, the protons that are close in space will show cross-peaks in the 2D NMR spectrum. As can be seen in the 2D EXSY spectrum of USY measured at a mixing time of 1 s (Figure 10), the sodalite, supercage, and EF proton spins show such cross-peaks. The relative intensities of these cross-peaks follow the total relative intensities in the sample as can be appreciated from the horizontal section spectra. This means that the proton magnetization at the three sites is mixed within an exchange time of 1 s. USY with adsorbed benzene shows, in addition to the previous exchange picture, cross-peaks with benzene protons. In contrast, the signal due to the silanol does not show cross-peaks with other hydroxyl groups in the zeolite. These findings point to the spatial separation of BAS and EF protons from the silanol groups at the external surface of the zeolite crystallites. Interestingly, in the presence of benzene molecules, the spin-exchange behavior of the EFAl proton spins with the supercage spins differs from the exchange without benzene. The amount of the exchanged supercage proton intensity with the EF hydroxyl groups is lower in the presence of benzene, while the intensity of sodalite BAS signal remains the same (i.e., by comparison of the horizontal section in Figure 10). This proves that benzene interacts selectively with BAS in the supercages.

**DISCUSSION**

For the investigation of the influence of EFAl on the acidity situation in a Y zeolite, an EFAl-containing zeolite USY prepared by steaming was compared to an EFAl-free and chemically dealuminated AHFSY zeolite with comparable Si/Al ratios. The two samples have similar XRD patterns, reflecting their high crystallinity. The FAI content in AHFSY (Table 1), determined from the XRD lattice constant and $^{27}$Al MAS NMR (Table S1) and $^{29}$Si MAS NMR (Table 2) spectra are similar and comparable to the total Al content in the sample determined by elemental analysis. This proves that the AHFSY zeolite is free from EFAl. As follows from the $^{27}$Al MQMAS NMR spectrum in Figure 3, the steamed USY sample contains octahedrally coordinated EFAl at ~0 ppm, a horizontally broadened peak at ~40 ppm, and a peak at ~56 ppm. The peak at ~40 ppm can be assigned to distorted FAI species. The signal at ~56 ppm lies on the diagonal, which therefore can be attributed to tetrahedrally coordinated FAI or FAI species compensated in charge by cationic EFAl instead of protons. The FAI content in USY zeolite determined by $^{27}$Al NMR spectra is lower than the value derived from the unit
cell volume, which can be attributed to the NMR invisibility of part of Al caused by strong quadrupolar interactions. The number of BAS in USY is 3 times lower than in AHFSY, as can be concluded from a comparison of the peak areas in $^1$H NMR spectra (Table 3). The distribution of the BAS over the sodalite cages and the supercages is nearly the same in both zeolites. The observed low BAS concentration in USY can be explained by their replacement by cationic EFAl. The high AlOH content as follows from the $^1$H NMR spectrum of USY is an indication that the cationic EFAl partially appears as Al(OH)$_x$ where $x$ equals 1 or 2. The silanol density in USY is twice that in AHFSY but 3 times lower than the number of AlOH groups. This low silanol density in USY is probably because, parallel to hydrolysis reactions occurring during steaming, a healing reaction between the SiOH groups takes place, leading to siliceous regions. The FAl content in USY and AHFSY, as extracted from XRD lattice constant values, is approximately similar. This forms a good basis for the investigation of the effect of EFAl species on the reactivity of the steamed zeolite. Differences in acidity and reactivity between the two zeolites, which could arise from the effect of framework Si/Al ratio, can therefore be neglected and instead correlated to the effect of EFAl species.

Before discussing the H/D exchange results in detail, some aspects concerning the diffusion and adsorption of benzene molecules in zeolite Y should be clarified. The benzene molecule has a kinetic diameter of ~6 Å, which is larger than the 6-membered ring (2.3 Å) of the sodalite cages and smaller than the 12-membered ring (7.4 Å) windows of the supercages. Therefore, benzene can freely diffuse in zeolite Y and will exclusively sit in the supercages and the pore windows interconnecting them. This is in line with the observed selective shift change and the decrease in the transversal relaxation $T_2(1H)$ of the supercage protons due to the presence of benzene. In contrast, the sodalite proton shift and $T_2(1H)$ relaxation do not change (Figures 6 and 9), implying that benzene cannot enter the sodalite cages. The downfield shift of the supercage signal originates from the effect of the induced magnetic field by the circulating electrons in the benzene aromatic ring. The effective field felt by the supercage protons depends on the orientation of the benzene molecule. When the benzene is facially coordinated to the supercage BAS, the proton will be more shielded, and hence, the peak position will shift upfield. The opposite will happen when the benzene ring and the proton are nearly in the same plane (Figure 11).

This could mean that the peripheral edge of benzene is more oriented in the direction of the supercage BAS such that the protons spend some time in the deshielding region. This configuration could be stabilized by weak or transient complexation of the benzene hydrogen atoms with zeolite oxygen atoms. An alternative explanation could be that the observed small downfield shift is the sum of two effects, namely (i) the upfield shift due to the planar coordination of benzene to the supercage BAS and (ii) a weak hydrogen bond along the molecular C$_6$ axis.

$^1$H NMR spectroscopy during H/D exchange is a frequently used method to measure the acidity and reactivity of the hydroxyl groups in a faujasite zeolite by monitoring the proton transfer between the BAS and reactants or model molecules, such as benzene. In all studies we found, however, the researchers focused on the total exchange of the BAS with adsorbed molecules. In the current study, we addressed the site-selective H/D exchange of sodalite and supercage hydroxyl groups. We started from almost completely deuterated zeolites and low benzene loading. Following the H/D exchange at low temperature in this manner provides a good contrast in the H/D exchange reactivity and selectivity of the different hydroxyl sites in the two investigated zeolites.

The USY zeolite showed a higher H/D exchange reactivity with benzene than AHFSY. This behavior agrees with our earlier H/D exchange IR study, which was attributed to the presence of EFAl. Interesting is the exchange of the sodalite BAS with benzene. Although benzene cannot enter the small cages, the sodalite BAS can exchange with molecules that are exclusively sitting in the supercage cavities. This can be explained by perturbation of the local zeolitic structure. These will lead to a flip of the SiO(3)Al and SiO(4)Al bonds in the direction of the supercage, when a guest molecule approaches the inner zeolite wall. The similarity in reactivity between sodalite and supercage BAS in AHFSY (Figure 8 bottom) indicates that all sites possess the same acidity. The faster H/D exchange of the sodalite BAS compared to supercage BAS in USY (Figure 8, top) implies that the reaction of the sodalite BAS is influenced by EFAl species in a different manner than the reaction with the supercage BAS. A possible cause may be the localization of EFAl species in USY zeolite. Van Bokhoven and co-workers showed in their in situ XRD and XAS investigation of the dealumination of NH$_4$Y by steaming that the formed EFAl species occupy the SI’ site, which is at the external base of the hexagonal prism just inside the sodalite cage. Mota et al. mentioned in their work that occupation of the SI’ site in the sodalite cage in the steamed Y zeolite by Al$^{3+}$ close to O(3) oxygen atoms and at the center of the cage (U site) by Al(OH)$_2$ leads to an increase in the acid strength of sodalite protons (O(3)H) and a decrease in the supercage (O(1)H) acid strength. They also mentioned that the role of the EFAl is to stabilize the conjugate base, formed upon deprotonation. Florian et al. demonstrated in their work on La in a Y zeolite that La cations are predominantly stabilized within sodalite cages.

To gain more insight in this, more detailed experimental information about the location of EFAl in the zeolite and the interaction between hydroxyl groups and benzene molecules is needed. For this purpose, we applied $^1$H NMR relaxometry and 2D $^1$H NMR in this study. Spin–spin or transversal relaxation originates from the dipolar interaction of a spin with local magnetic fields generated by other neighboring $^1$H spins. This dipolar interaction falls off rapidly as $\sim 1/r^3$ with the

![Downfield shifted $^1$H signal](image)

**Figure 11.** $^1$H NMR shift dependence on the relative benzene molecule orientation.
distance $r$ between two spins and, hence, is only effective over short distances ($\leq 0.5 \text{ nm}$). The similarity in $T_2$ relaxation behavior between supercage and sodalite-cage protons in AHFSY (Figure 9) indicates that the environments of the protons at the two types of sites are similar. This is in line with the picture outlined above about the similar acidity of the two types of BAS in AHFSY. The high proton density in benzene causes neighboring $^1\text{H}$ spins in the supercage to relax faster than without benzene. This reveals valuable information about the relative location of the different hydroxyl groups in the zeolite. With benzene present in the zeolites, the transversal relaxation of the protons in the sodalite cages remains unchanged, whereas the relaxation of the supercage protons becomes roughly twice as fast in both zeolites. This is because benzene can freely pass through the 12-membered ring window, which affects the $T_2(1\text{H})$ time of the supercage BAS. As a result of the inaccessibility of the sodalite cage for benzene, the $T_2(1\text{H})$ time of the sodalite BAS remains unaffected. The slight decrease in $T_2(1\text{H})$ relaxation time of the EFAI OH in USY suggests that the EFAI is positioned further away from the high proton density of benzene in comparison to the supercage BAS. In USY, benzene shows, in addition to the bulk chemical shift around 7.3 ppm, a downfield shift at $\sim 8.0$ ppm. An explanation for this shift could be that some of the benzene molecules are highly deshielded as result of a stronger H–benzene bond with negative framework oxygen atoms. The appearance of cross-peaks in 2D EXSY $^1\text{H}$ NMR spectra between bridged and EFAI hydroxyl groups suggests that the EFAI species are in close proximity to the BAS. The silanol protons show no cross-peaks with the other hydroxyl groups and are therefore exclusively at the external surface of the zeolite crystals. This is in good agreement with the unaltered $T_2$ of the silanol protons upon benzene adsorption and with the results reported by Mildner and Freude.42

In the presence of benzene, the situation outlined above is changed. The cross-peak signal arising from the interaction of the supercage and the EF protons is slightly attenuated (Figure 10). The attenuation of the cross-peak by benzene indicates that a fraction of the EF proton intensity is transferred to benzene. This could be explained by considering EF proton spins exchanging indirectly, via supercage protons, with the benzene. This is again an indication for the selective exchange of benzene with the supercage BAS protons. $T_{1ρ}(1\text{H})$ relaxometry, which is sensitive to short-range proximity (Figure S1), suggests also that cationic EFAI species are located in close proximity of the sodalite BAS. The $\text{H/D}$ exchange behavior between the BAS in USY and benzene as well as the obtained experimental information from $T_2(1\text{H})$, $T_{1ρ}(1\text{H})$ relaxometry, and 2D EXSY NMR spectroscopy indicate that the cationic EFAI is located in the sodalite cage.

In Figure 12, the $\text{H/D}$ exchange reaction between the BAS and benzene in the presence of EFAI is proposed. Upon deprotonation, the negatively charged zeolite surface is stabilized by a cationic EFAI complex. Consequently, the sodalite BAS reactivity is increased by the presence of EFAI species.

**CONCLUSION**

We carried out an in situ $^1\text{H}$ MAS NMR study of the $\text{H/D}$ exchange reaction between benzene and BAS in EFAI-free dealuminated AHFSY and steam-calcined USY zeolites with a main focus on unraveling the nature of the promoting effect of EFAI on zeolitic BAS. The NMR approach here differs from our earlier in situ IR spectroscopy approach by starting from the deuterated zeolite instead of the proton form and involving continuous exposure to low benzene concentrations instead of transient pulses at high benzene densities. Benzene selectively changes the $^1\text{H}$ NMR chemical shift of the supercage BAS yet does not influence the shift of the sodalite-cage BAS. This is consistent with the accepted picture that $\text{C}_6\text{H}_6$ exclusively adsorbs in the supercages, because the sodalite cages are inaccessible for benzene. Nevertheless, in the case of the EFAI-free AHFSY zeolite, our in situ NMR study shows that the sodalite and the supercage BAS undergo equally fast $\text{H/D}$ exchange. On the contrary, in USY, the $\text{H/D}$ exchange of the sodalite-cage BAS is strongly and, more importantly, selectively enhanced compared to that in AHFSY. Already at $25\,^\circ\text{C}$, the sodalite-cage BAS become significantly protonated within a day, and at $55\,^\circ\text{C}$, the $\text{H/D}$ exchange under the specific loading conditions (initial $\text{H}_2\text{benzene}/\text{D}_2\text{BAS}$ ratio $\approx 2$) approaches the equilibrium protonation within several hours.

Given the predominant interactions of benzene with the supercage BAS, the most stable supposedly axial binding configuration of $\text{C}_6\text{H}_6$ to this BAS type, through weak hydrogen bonding along the benzene $\text{C}_6$ axis, is not of direct importance for the $\text{H/D}$ exchange reaction. $\text{H/D}$ exchange is most likely controlled by a less stable peripheral binding state with the hydrogen bonding in the benzene plane. In such a configuration, the approachability of sodalite and supercage BAS for benzene located in the supercage may be more comparable. In addition, the local zeolite framework seems sufficiently flexible to allow for temporary flips of the Al–OH–Si bridges, such that the sodalite BAS may transiently point into the supercages. Such lattice flips alone, however, would at most explain roughly equal $\text{H/D}$ exchange rates of the two BAS types, as indeed observed for AHFSY. The strong selective enhancement of reactivity of the sodalite-cage BAS in USY thus appears to be caused by the EFAI species in the sodalite cages of this zeolite.

As indicated by the spatial proximity derived from the equal proton spin-diffusion driven $T_{1ρ}(1\text{H})$ relaxation behavior of protons in the EFAI species and the sodalite-cage BAS, the sodalite-cage BAS closely interacts with the EFAI. This is in
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Notes

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ABBREVIATIONS

BAS: Brønsted acid site(s); FAl: framework aluminum; EFAI: extraframework aluminum; H/D exchange: hydrogen/deuterium exchange; IR: infrared; ICP-OES: inductively coupled plasma optical emission spectroscopy; NMR: nuclear magnetic resonance (spectroscopy); EXSY: spin-exchange spectroscopy; MAS: magic angle spinning; MQMAS: multiple quantum magic angle spinning; TRAPDOR: TRAnsfer of Population in Double Resonance; DFT: density functional theory; XRD: X-ray diffraction; AHFSY: zeolite Y dealuminated by use of amoniumhexafluorosilicate; USY: ultrastabilized zeolite Y; u.c.: unit cell

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