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Reversible Tetrahedral−Octahedral Framework Aluminum Transformation in Zeolite Y

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Abstract: The hydration of a mildly calcined zeolite Y sample leads to the local destruction of the zeolite lattice. This way, besides the dealumination of the framework, a partial hydrolysis of framework Al−O bonds occurs generating framework connected Al−OH species. This hydrolysis is evidenced by a peak at 3.1 ppm in the ^{1}H MAS NMR spectrum, which can only be resolved by applying the ^{1}H spin−echo MAS NMR technique with different echo delay times. These framework Al−OH sites can host water molecules giving rise to octahedrally coordinated Al species seen in the ^{27}Al MAS NMR spectrum at 0 ppm. The subsequent adsorption of ammonia on this sample after hydration converts this octahedral coordinated Al back to tetrahedral Al sites. In the ^{27}Al MAS NMR spectrum these species are now seen by the increased line width of the 60 ppm line.

1. Introduction

The origin of the acidity of zeolites used as catalysts in the cracking and isomerization of alkanes has been a major topic of scientific and industrial research. The elucidation of the relationship between the acidity and the aluminum speciation generated during the activation process remains an intriguing question.

In activated zeolite catalysts two types of acidic sites have been demonstrated, Brönsted and Lewis acidity. Brönsted acid sites are formed by protons that compensate the excess of negative charges generated by the incorporation of Al atoms in the zeolite framework. The hydroxyl formed in this way is called the “bridging hydroxyl”. These acid sites are believed to be the primary catalytic centers for the cracking and isomerization reactions in the zeolite catalyst.[1,2] The second source of acidity, Lewis acidity, is related to the electron accepting capacity of the sites. Generally, it is accepted that the new aluminum species created during the activation process are the source of this Lewis acidity. The location of these sites, framework versus nonframework, is still a matter of debate.[3−5]

In the ^{27}Al MAS NMR spectra of activated zeolite samples, several peaks are observed. Besides the line at 60 ppm, referenced to $Al(H_2O)_6^{3+}$, which is assigned to tetrahedral framework aluminum species, bands at 0 and 30 ppm can be detected. Normally the peak at 0 ppm is ascribed to extraframework octahedral Al species[6] that are formed during the calcination process. When the severity of the calcination is increased, 30 ppm lines appear in the spectrum.

Bourgeat-Lami et al.[7] were the first to mention the existence of octahedral framework aluminum sites in zeolite β. They demonstrated that octahedral aluminum can be converted into tetrahedral aluminum by adsorption at 373 K of gaseous ammonia on the sample. Also ion exchanging the acid protons by sodium or potassium leads to the transformation of the octahedral coordination to a 4-fold coordinated aluminum site. Therefore it was believed that acid protons contribute to the appearance of these octahedrally coordinated aluminum species connected to the framework. ^{1}H{^{27}Al} spin−echo double resonance MAS NMR pointed out the complex nature of the Brönsted acid sites.[8] At room temperature, two distinct resonances at 4.1 and 5.5 ppm related to the bridging hydroxyl groups are observed. Proton signals associated with extraframework aluminum species were absent after calcination. It was suggested that the behavior toward hydration is a unique feature of the zeolite β.[7] The octahedral sites are thought to be composed of the four oxygen atoms from the zeolite lattice and the oxygens of the hydroxonium ion and one water molecule, or can result from the hydrolysis of the Al−O bond.

This specific framework octahedral Al has also been confirmed by temperature-induced dehydration of methanol over the acid zeolite β, forming dimethyl ether and water. The methanol-adsorbed sample reveals only a tetrahedral site in the ^{27}Al MAS NMR spectrum.[9]

Jia et al.[10] investigated the influence of the calcination procedure on the zeolite β. A zeolite β sample was calcined at 823 K in deep and shallow bed conditions. In the IR spectrum the 3659 cm^{-1} band, related to framework Al−OH,[11] was only present after deep bed calcination whereas for both the calcination procedures the ^{27}Al MAS NMR spectrum revealed an octahedral site. Therefore, it was concluded that shallow bed calcination generates framework Al species of which only one bond is ruptured. These species are restored into bridging hydroxyl groups when hydration takes place, and so the Al−

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OH species vibrating at 3659 cm^{-1} in the IR are not formed. On the contrary, deep bed calcined samples have Al species connected to the framework by only one or two bonds. Hydration cannot repair these bonds, which explains the appearance of the Al−OH band in the IR spectrum.

The existence of octahedral framework Al was also demonstrated for ZSM-5.[4] Temperature-programmed desorption of ammonia revealed the presence of both Brönsted and Lewis acid sites. After ammonia adsorption the ^{27}Al MAS NMR spectrum evidenced mainly tetrahedral Al sites. Hydrolysis of Al−O bonds occurred during the calcination and is at the origin of framework Lewis sites. These Lewis sites were described as tricoordinated Al species. In contrast to Bourgeat-Lami et al.[7] findings, the species causing the octahedral Al signal in the ^{27}Al MAS NMR spectrum were tentatively assigned to Al(OSi)$_3$(H$_2$O)$_3$, as a result of coordinating three water molecules to the Lewis site.

When studying the interaction of water with the aluminum sites, we have to be aware of the fact that ZSM-5 and zeolite β are hardly sensitive to framework dealumination due to hydration. On the other hand, it is well-known that the H−Y zeolite, which we examined, is unstable in the presence of water at room temperature.[12] This hydration will lead to the dealumination of the zeolite lattice. According to Barthomeuf two properties of the zeolite Y govern this behavior toward hydration: first the high framework aluminum content which makes the zeolite Y more hydrophilic and therefore facilitates the water interaction, and second the different topological arrangement of the tetrahedral atoms.[13] A high density of framework bonds decreases the tendency toward breaking these framework bonds. Compared to ZSM-5, zeolite Y is an open structure with a lower density of bonds and as a consequence it is less stable.

In this paper we report on the existence of an octahedral framework Al site in the acidic form of zeolite Y and show that this type of aluminum is related to the degradation of the zeolite lattice during the hydration. This local lattice destruction is observed by a proton peak in the ^{1}H MAS NMR that can be resolved from the normal Brönsted acid sites by applying the ^{1}H spin−echo MAS NMR technique.[14]

2. Experimental Section

2.1. Sample Preparation. A sodium Y zeolite (Zeocat Si/Al = 2.65) was ion exchanged three times in an 1 M solution of NH$_4$Cl (Acros) under reflux. The residual Na content was determined to be less than 0.5% of the initial concentration. Subsequently the sample was washed with deionized water until it was chloride free. This sample was then calcined at 673 K under deep bed conditions (diameter/height of the zeolite bed = 0.125) in an oxygen flow of 80 $cm^3\ min^{-1}$. The calcination temperature was raised at a rate of 5 deg K min^{-1}.

While the sample was still at 673 K, the calcination tube was closed, transferred directly into a glovebox containing dry N$_2$, and cooled to room temperature. Then a 4 mm zirconia MAS rotor was filled for the proton MAS NMR measurement.

The rest of the calcined sample was divided into two parts. The first part was partially loaded with water by storing the sample for 2 min in a N$_2$ atmosphere that contains 3 ppm of water. To remove the physisorbed water, the sample was evacuated in a vacuum of 10^{-3} Pa while raising the temperature first to 383 K. At this temperature, the sample was kept for 4 h. A second level at 673 K was maintained overnight. The rate of raising the temperature in both cases was 0.5 deg K min^{-1}. Also this sample was transferred into the glovebox filled with dry N$_2$ to prepare the sample for the proton MAS NMR measurement.

After the proton measurement, this sample was equilibrated at room temperature in a desiccator at a relative humidity of 79% generated by a saturated solution of NH$_4$Cl to measure both the ^{27}Al and ^{29}Si MAS NMR spectra of this calcined and hydrated sample. It was verified that no extra dealumination occurred during this hydration process.

Finally, gaseous ammonia (l' Air Liquide) was adsorbed on this calcined and hydrated sample following the procedure described by Coster et al.,[15] i.e., adsorption at 388 K for 1 h. Prior to the ^{27}Al and ^{29}Si MAS NMR the sample was equilibrated again in a desiccator at room temperature.

The second part of the calcined sample was directly used to adsorb ammonia, as described above, before equilibrating the sample at room temperature in a relative humidity of 79%.

The nature of the acid sites of the calcined sample, as well as the sample which was partially hydrated followed by an evacuation step, was determined by using trimethylphosphine, (CH$_3$)$_3$P, as a probe molecule. The adsorption was performed following the procedure described by Lunsford et al.[16] To remove the excess of physisorbed trimethylphosphine, the samples were evacuated at 353 K.

In the following, the samples are labeled according to the treatment, C for calcination, H representing the hydration, and A for ammonia adsorption followed by hydration. Thus Y CHA is a sample that is calcined at 673 K and hydrated and finally ammonia was adsorbed.

2.2. NMR Spectroscopy. ^{1}H, ^{31}P, and ^{29}Si MAS NMR spectra were obtained on a BRUKER AMX300 spectrometer with a magnetic field strength of 7 T. The ^{29}Si MAS NMR measurements were recorded with $\pi/4$ pulses and a recycle delay of 20 s. ^{1}H spin−echo MAS NMR experiments were performed by using a Hahn echo sequence ($\pi/2$, τ-delay, π, τ-delay)[14] with appropriate phase cycling. The τ-delay was adjusted to a multiple of the MAS rotor period. The acquisition was initiated at 2τ. The $\pi/2$ and π proton pulses were 2.5 and 5 μs, respectively. ^{1}H{^{27}Al} spin−echo double resonance MAS NMR experiments were performed according to the technique of Beck et al.[17] For both proton measurements the recycle time was set to 10 s. To reduce the spin−lattice relaxation times T_1, the samples were loaded with oxygen. It has been shown that this procedure does not alter the ^{1}H MAS NMR spectrum.[18] The quantification of the proton intensity of the ^{1}H MAS NMR spectra was done by means of a calibration curve constructed from the intensity of the ammonium peak in the proton NMR spectrum of several highly crystalline ammonium zeolite samples with known framework Al content. This way the intensity observed in the proton spectrum can be correlated to the number of ammonium ions present in the sample which is in a one to one relationship with the Al content. To achieve this, the sodium form of zeolite samples was ion exchanged according to the procedure explained above. The residual Na content in all cases was less then 1% of the initial amount. These samples were then evacuated at 448 K under high vacuum (10^{-3} Pa). This way the water is removed from the sample, while no decomposition of ammonium ions was observed. Dealumination of the framework did not occur during these treatments. Chemical shifts were referenced to tetramethylsilane (TMS) for both the ^{1}H and ^{29}Si NMR spectra. The ^{31}P spectra were measured with $\pi/4$ pulses and a recycle time of 10 s. Phosphoric acid (85% solution) is used as the external shift reference. For all the above-mentioned measurements the MAS rotors were spun at 10 kHz.

A BRUKER MSL400 spectrometer (9.4 T) was used to record the ^{27}Al MAS NMR spectra. The pulse length was 0.6 μs, which corresponds to $\pi/18$ pulses for nonselective excitation. The repetition time was set to 0.1 s and 3000 scans were accumulated. {^{1}H}−^{27}Al cross-polarization (CP) MAS NMR measurements were done on both the BRUKER MSL400 and the AMX300 spectrometers. Cross-polarization conditions were set by using pseudobeuhmite. An aqueous

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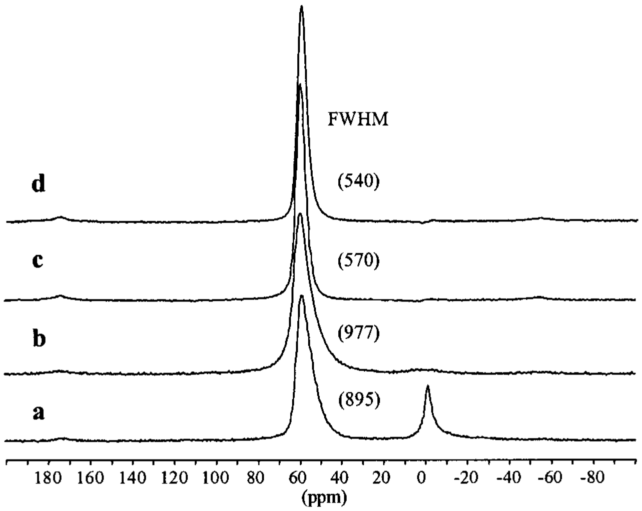

Figure 1. ^{27}Al MAS NMR spectra of (a) Y CH, (b) Y CHA, (c) Y CA, and (d) the parent ammonium Y. The spectra are displayed in the absolute intensity mode. The values between brackets represent the line width of the tetrahedral peak, measured at half-height and expressed in Hz.

Table 1. Composition of the Unit Cell Determined by ^{27}Al and ^{29}Si MAS NMR

	^{27}Al NMR			
sample	T site (Al/u.c.)[a]	O site (Al/u.c.)[b]	Si/Al	^{29}Si NMR Si/Al
NH_4Y	52.6	0	2.65	2.65
Y CH	40	12.6	3.81	2.94
Y CHA	48.9	3.7	2.92	2.95
Y CA	52.1	0	2.68	2.66

[a] Calculated from the intensity of the 60 ppm line in the ^{27}Al MAS NMR spectum relative to NH_4Y. [b] Calculated from the intensity of the 0 ppm line in the ^{27}Al MAS NMR spectum relative to NH_4Y.

solution of $Al(NO_3)_3$ is used as shift reference. The MAS frequency for all the aluminum measurements was 12 kHz.

3. Results

3.1. ^{27}Al and ^{29}Si MAS NMR. In Figure 1 the ^{27}Al MAS NMR spectra of the calcined and hydrated (Y CH) and subsequently ammonia adsorbed (Y CHA) sample are shown, as well as the spectrum of the sample on which ammonia is adsorbed before it was hydrated (Y CA). We observe two bands in the calcined and hydrated sample (Y CH): a peak at 60 ppm, which can be assigned to framework Al, and a peak at 0 ppm. On the basis of the 60 ppm line intensity, assuming a 100% cristalline structure, and taking the Al NMR intensity of the parent sample, which corresponds to 52.6 Al/u.c., as a reference, a Si/Al ratio of 3.81 was calculated (Table 1). The ^{29}Si MAS NMR spectrum of the same sample Y CH (Figure 2a) indicates a lower degree of dealumination, reflected by a Si/Al ratio of 2.94 that is calculated by using the formula V.6 of ref 19a.

Ammonia adsorption on this sample (Y CHA) converts part of the octahedral line in the ^{27}Al MAS NMR spectrum into tetrahedral sites (Figure 1b). This accounts for a decrease of the Si/Al ratio, obtained from the ^{27}Al MAS NMR spectrum, to 2.92. Except for the small downfield shifts of the resonance lines, the ^{29}Si MAS NMR spectrum is unchanged when adsorbing ammonia (Figure 2b). These small shifts are also observed when exchanging the sample with different cations.[19b]

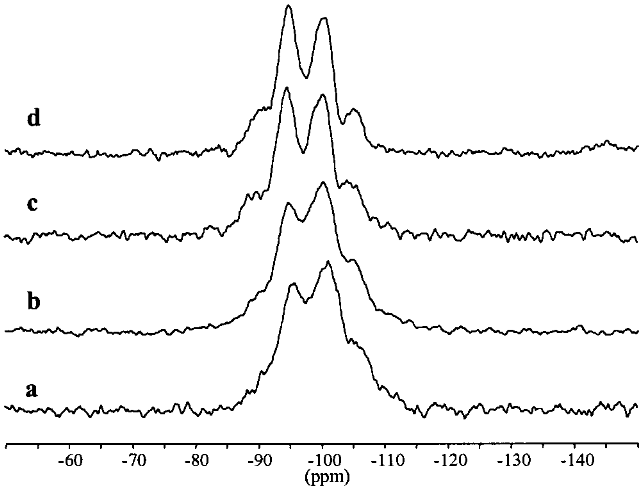

Figure 2. ^{29}Si MAS NMR spectra of (a) Y CH, (b) Y CHA, (c) Y CA, and (d) the parent ammonium Y sample.

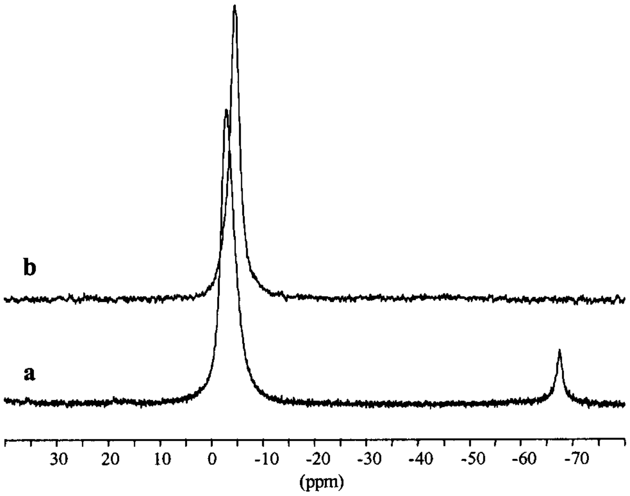

Figure 3. ^{31}P DEC MAS NMR spectra of trimethylphosphine adsorbed on (a) Y C and (b) Y CH.

The line width of the 60 ppm peak in the ^{27}Al MAS NMR spectrum of sample Y CHA (Figure 1b) is increased compared to that of the parent ammonium Y zeolite (Figure 1d).

When gaseous ammonia is adsorbed on the calcined sample prior to hydration (Y CA), both the ^{27}Al and ^{29}Si MAS NMR spectra (Figures 1c and 2c) reveal hardly any spectral changes when a comparison is made with the parent ammonium Y sample. This clearly shows that during the calcination step the Al is still in its original state, i.e., in the framework.

3.2. ^{31}P MAS NMR of Adsorbed Trimethylphosphine. We used the ^{31}P chemical shift of the adsorbed $(CH_3)_3P$ to evaluate the nature of the acid sites in the zeolite samples.[16] The adsorption was done on the sample after calcination (Y C) and after the hydration followed by outgassing (Y CH). The results obtained with high power broad band decoupling (DEC) are shown in Figure 3. The spectrum of Y C (Figure 3a) contains a first line at -2.5 ppm, which is related to the adsorption of the trimethylphosphine on the Brönsted acid sites with the formation of $[(CH_3)_3P{-}H]^+$. In the MAS spectrum obtained without DEC (not shown), we measured a J-coupling ($J \approx 525$ Hz) for the peak at -2.5 ppm. This is consistent with the result of Lunsford et al.[16] and clearly proves the presence of Brönsted acid sites. The second peak at -67 ppm is due to physisorbed $(CH_3)_3P$. No peaks in the -15 to -50 ppm range are visible in the spectrum. Therefore no Lewis

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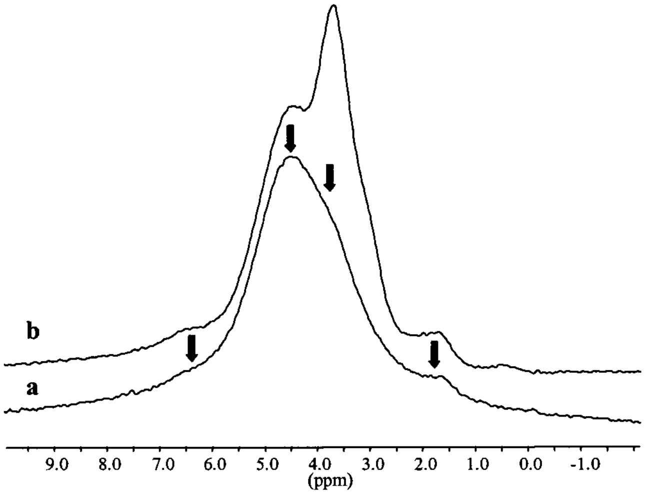

Figure 4. ^{1}H MAS NMR spectra of (a) Y C and (b) Y CH after outgassing.

Table 2. The Proton Amount Determined by ^{1}H (Spin−Echo) MAS NMR of the Sample Y CH after Outgassing

technique	NH$_4^+$	Sod	Sup	AlOH[b]	AlOH[c]	SiOH
^{1}H sim[a]	1.2	24.9	23.6[d]		0.9	2.3
^{1}H echo	1.3	26.1	13.1	8.4	1.1	3.2

[a] Amount determined by simulation of the 1D proton spectrum of Figure 4b. [b] Framework Al−OH species. [c] Extra-framework Al−OH species. [d] By simulation of the 3 to 4 ppm region of Figure 4b.

sites are present on which (CH$_3$)$_3$P is adsorbed. In the spectrum of Y CH that we evacuated (Figure 3b), the peak of [(CH$_3$)$_3$P−H]$^+$ is shifted to −4.5 ppm. This shift from −2.5 to −4.5 was also present in the measurements of Lunsford et al.[16] when the amount of physisorbed phosphine (−67 ppm line) decreased.

3.3. ^{1}H MAS NMR. The ^{1}H MAS NMR spectra of the calcined (Y C) and subsequently hydrated (Y CH) sample are given in Figure 4. After calcination (Figure 4a), the broad lines at 4.6 and 3.8 ppm are assigned to Brönsted acid protons in the sodalite cage (SOD) and supercage (SUP), respectively.[20] Due to the low calcination temperature, some residual ammonium ions are present at 6.5 ppm. Finally, the silanol band at 1.8 ppm is clearly resolved.

When the calcined sample was partially hydrated at room temperature and next outgassed (Figure 4b), the spectrum gained resolution. Especially the 3.8 ppm line becomes better resolved. The total intensity of the proton spectrum in the region of 3 to 5 ppm (SOD + SUP) corresponds to 48.5 acid protons per unit cell (Table 2).

3.4. ^{1}H Spin−Echo MAS NMR and ^{1}H {^{27}Al} Spin−Echo Double Resonance MAS NMR. By applying a Hahn echo sequence, the resolution of the proton spectrum of the calcined and hydrated sample (Y CH) was further increased (Figure 5) when the echo delay time τ was incremented. Now, a line at 3.1 ppm is clearly separated from the other peaks. The spectra were simulated by using three Gaussian lines centered at respectively 4.6, 3.7, and 3.1 ppm in the region 3−5 ppm. When we assume that magic angle spinning does not change the nature of the relaxation process, a first-order decay of the intensity can be expected. This is expressed by the equation $I = I_0 \exp(\tau/T_{2H})$, which can be derived from the expression for spin−echo measurements in liquids when the diffusion related factor is omitted.[21] In this equation T_{2H} stands for the proton spin−spin relaxation time and I_0 for the intensity without an echo delay. Figure 6 displays the logarithm of the intensities of these lines as a function of the echo delay time τ. The data points decay linearly, which is consistent with the first-order decay. By extrapolation to an echo delay of 0 ms, the absolute quantities of the various proton signals are calculated (Table 2). These data show a ratio of 2:1 for the Brönsted acidic protons in the sodalite cage (SOD) to the supercage (SUP). Small amounts (≈1 per u.c.) of ammonium ions and extraframework Al−OH species were calculated for this sample. Wolf et al.[22] indicated that the proton spin−spin relaxation behavior is better described by a superposition of two exponentials. This seems also the case for our data. However, from the comparison of the amount of the different proton signals obtained from the simulation of the spectrum represented in Figure 4b and the amounts calculated from the echo experiment (Table 2), it is seen that the relative proton intensities do not change much when we assume one exponential decay to describe the proton spin−spin relaxation behavior. The main advantage of the echo technique lies in the separation of the peaks at 3.7 and 3.1 ppm in the ^{1}H MAS NMR spectrum. Simulation of Figure 4b, for obvious reasons, cannot yield the exact intensity ratio of both sites.

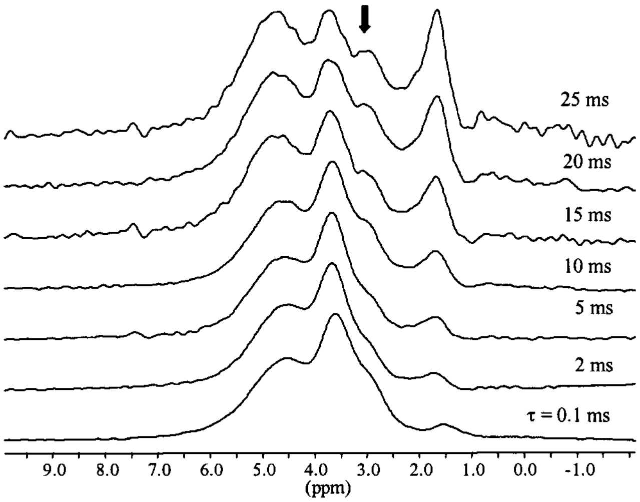

Figure 5. ^{1}H spin−echo MAS NMR spectra of Y CH as a function of the echo delay time τ.

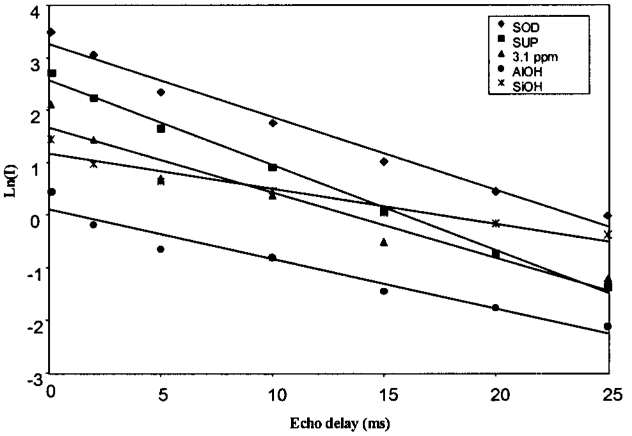

Figure 6. Logarithm of the intensity of the different lines in the Y CH sample as a function of the echo delay time τ.

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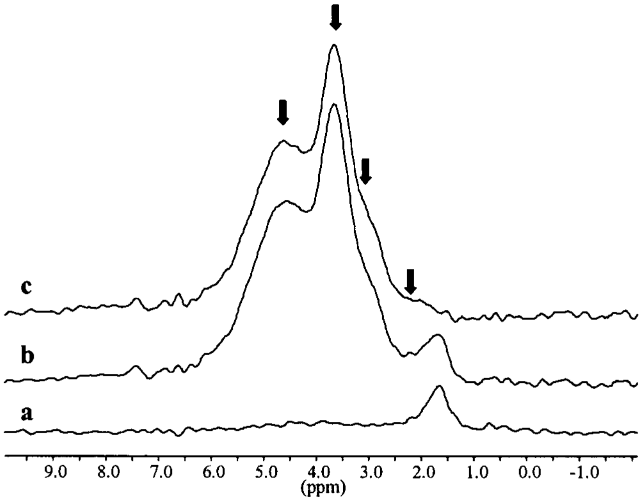

Figure 7. ^{1}H {^{27}Al} spin−echo double resonance MAS NMR of Y CH outgassed with the echo delay time of 2 ms: (a) with Al irradiation (rf$_{\mathrm{Al}}$ = 45 kHz), (b) without Al irradiation and (c) the difference spectrum.

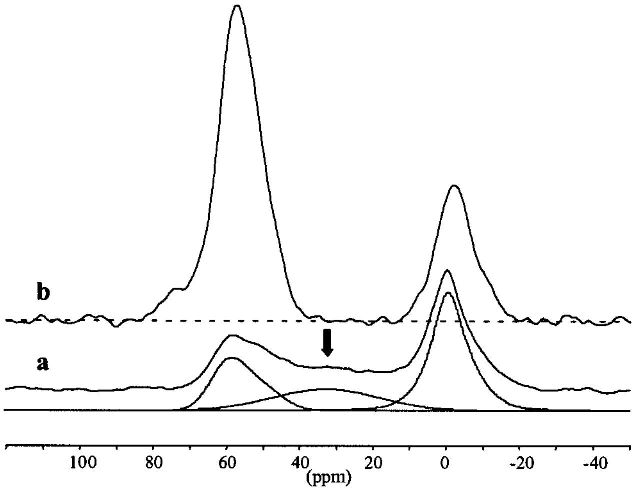

Figure 8. {^{1}H}−^{27}Al CP MAS NMR spectra at 9.4 T of (a) partial hydrated Y CH (5 min) and (b) Y CH equilibrated at 79% relative humidity.

By application of ^{1}H{^{27}Al} spin−echo double resonance MAS NMR it was verified whether this new proton line at 3.1 ppm is connected to Al (Figure 7). The aluminum-connected protons can be seen in the difference spectrum (Figure 7c). From this it is evident that four lines are present: the lines at 4.6 and 3.7 ppm, which correspond to the Brönsted acid sites, a small peak at 2.4 ppm related to the extraframework Al, and the line at 3.1 ppm.

3.5. {^{1}H}−^{27}Al Cross-Polarization MAS NMR. {^{1}H}−^{27}Al CP MAS NMR measurements were recorded as a function of the hydration state of the evacuated sample Y CH. These spectra are displayed in Figure 8. After 5 min of hydration in air, the {^{1}H}−^{27}Al CP MAS NMR spectrum exhibits a broad peak at 34 ppm, besides the normal lines in the calcined and hydrated sample. The second-order quadrupole shift for this peak is small as was verified by recording the sample at different magnetic field strengths B_0 of 7 and 9.4 T, respectively.

4. Discussion

The results summarized in Table 1 indicate that when ^{27}Al MAS NMR is used to quantify the framework Al content of the calcined zeolite Y sample (Y CH), a much higher framework Si/Al ratio is obtained compared to the value calculated from the ^{29}Si MAS NMR spectrum. The calculation based on the ^{27}Al MAS NMR spectrum yields a ratio of 3.81 for this sample, which is in contrast to the 2.94 obtained from the ^{29}Si MAS NMR data. This inconsistency can be explained when a lot of silanol species are present in the sample. These species mainly give rise to a band at −100 ppm in the ^{29}Si MAS NMR spectrum, therefore this band coincides with the Si(1Al) line that is also found at −100 ppm. As a result, the calculation of the framework Si/Al ratio, which is based on the different intensities of the Si(*n*Al) species, will be erroneous. However, from the ^{1}H MAS NMR spectrum (Figure 4b) we know that only a small amount of silanol species are present in the our sample. So, the contribution of the Si−OH line to the peak at −100 ppm is too small to account for the different Si/Al ratio we obtained from our ^{27}Al MAS NMR measurement. The {^{1}H}−^{29}Si CP MAS NMR spectrum of this sample (not displayed) revealed almost no enhancement of the −100 ppm line compared to the ^{29}Si MAS NMR spectrum. This further proves the low Si−OH concentration. Therefore, the Si/Al ratio of Y CH obtained from the ^{29}Si MAS NMR spectrum can be regarded as an accurate value, which means that the degree of dealumination of this Y CH sample is overestimated when calculating the framework Al content from the 60 ppm line in the ^{27}Al MAS NMR spectrum.

Upon the adsorption of ammonia on this calcined and hydrated sample (Y CHA), part of the octahedral Al is converted into a tetrahedral coordination (Figure 1). When an estimation of the framework Al content is made based on the intensity of the 60 ppm band in the ^{27}Al MAS NMR spectrum of this ammonia adsorbed sample, a good correlation is achieved with the aluminum content determined from the ^{29}Si MAS NMR spectrum. The weak dealumination evidenced by a decreased Si(2Al) peak intensity in the ^{29}Si MAS NMR spectrum of this Y CHA sample, relative to the parent material, is also observed in the ^{27}Al MAS NMR spectrum by some residual octahedral Al at 0 ppm after ammonia adsorption.

As a consequence, since the data from the ^{29}Si MAS NMR measurement give us the framework Al content or the framework Si/Al ratio, we have to assume that some framework Al species exist in the Y CH sample which coordinate octahedrally, giving a line at 0 ppm in the ^{27}Al MAS NMR spectrum but which can be transformed to a tetrahedral state by the adsorption of ammonia.

This observation is in agreement with the results of Bourgeat-Lami et al.[7] for zeolite β. Besides the adsorption of a strong base, as ammonia or pyridine, on their calcined zeolite β sample, the acid protons were also ion exchanged with sodium and potassium. In both cases they encountered a reduction of the octahedral ^{27}Al MAS NMR line while the tetrahedral line gained intensity. The octahedral framework Al was believed to be a unique feature of the zeolite β. It was suggested that sites which allow major local distortion are the host for two water molecules from which one is the hydroxonium ion.

Our results on zeolite Y and the work of Woolery et al.[4] prove that the reversible Al coordination seems to be a general property of zeolites. In a recent study of the mesoporous molecular sieve Al-MCM-41, the authors also indicate the change in coordination number of lattice-connected Al species.[23] The origin of the reversibility of the coordination of the framework Al sites in zeolite Y is then the predominant question.

Timken et al.[24] demonstrated that Lewis acid sites are formed during the calcination process of zeolite β. Hydration of these

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[23] Hitz, S.; Prins, R. *J. Catal.* **1997**, *168*, 194.

sites generates partially hydrolyzed framework Al. The same result was obtained for ZSM-5.[4] The adsorption of one water molecule on a framework Lewis site, giving an Al−OH_2 species, was thought to be the band at 3680 cm^{-1} they observed in the IR spectrum. This site can, upon full hydration, form the octahedral coordination that is observed in the ^{27}Al MAS NMR spectrum. Otherwise, an Al−OH that is connected to the framework by only one or two chemical bonds[10,11] was attributed to the 3665 cm^{-1} band in the IR spectrum. Jia et al.[10] linked this band up to the reversible Al in the ^{27}Al MAS NMR.

After calcination of our parent ammonium Y sample, we did not observe any Lewis acid sites as can been seen from the ^{31}P spectrum of trimethylphosphine adsorbed on the calcined sample (Figure 3a). As was indicated, bands corresponding to the adsorption of the phosphine on Lewis sites are situated in the −15 to −50 ppm region,[16] and are totally absent here. Since the ^{29}Si MAS NMR spectrum of the sample on which ammonia is adsorbed after calcination but before it was hydrated (Y CA) (Figure 2c) exactly resembles that of the parent zeolite Y sample, it is clear that no destruction of the zeolite lattice had occurred during the activation process. Also the line width of the tetrahedral line in the ^{27}Al MAS NMR spectrum (Figure 1c) remains unchanged after this treatment, indicating the same result. These observations rule out the possibility of the formation of framework Lewis sites during the mild calcination of zeolite Y as was suggested before in the case of ZSM-5[4] and zeolite β.[24]

Nor can the reversible Al coordination in our zeolite Y result from special tetrahedral Al sites which allow local distortion, as was suggested by Bourgeat-Lami.[7] This would mean that the ^{27}Al MAS NMR spectrum of the parent ammonium sample and the Y CHA sample should be alike, since adsorbing ammonia on the acid sample converts the bridging hydroxyls again into ammonium ions. When comparing spectra a and d in Figure 1, which come from sample Y CHA and the parent ammonium Y, it is obvious that the line width of the tetrahedral peak at 60 ppm has increased for Y CHA.

For zeolite Y another explanation has to be found. In Figure 4a the ^{1}H MAS NMR spectrum of Y C is displayed. In contrast to the spectra normally presented, we observe a low resolved spectrum for this calcined Y sample. Spin−echo measurement on this sample indicate the presence of two Brönsted acid sites with different relaxation times T_{2H} in the region of 3 to 5 ppm (not displayed).

After hydration and subsequent outgassing (Y CH), the proton spectrum resembles the results published in the literature. This observation is consistent with the results of Shertukde et al.;[5] however, due to the low spinning rate of their MAS rotor[25] they were only able to resolve two sites in the ^{1}H MAS NMR spectrum, namely the silanol and the total pool of Brönsted acid sites.

^{1}H spin−echo MAS NMR measurements of the calcined and hydrated sample (Y CH) reveal a third peak at 3.1 ppm (Figure 5). The amount of the different proton signals was calculated on the assumption of one exponential decay (Figure 6). The 3.1 ppm peak accounts for 17.6% of the total intensity in the 3 to 5 ppm region. This is 8.4 protons per unit cell. Double resonance measurements indicate that this 3.1 ppm peak is connected to Al sites. From the adsorption of trimethylphosphine on this sample (Figure 3b), it can be deduced that only Brönsted acid sites are present in the sample. The proton signal at 3.1 ppm disappeared after adsorption of bases such as $(CH_3)_3P$ and ammonia; therefore this 3.1 ppm peak has Brönsted acid properties.

It is generally known that the protonic form of zeolite Y is unstable in the presence of water.[12] For our sample (Y CH), as was stated before, this is observed by the decreased intensity of the Si(2Al) line in the ^{29}Si MAS NMR spectrum (Figure 2a) which indicates that dealumination has taken place. The origin of this 3.1 ppm peak in the proton spectrum has to be related to this hydration process since in the calcined sample only two lines were present. Al−OH-like species, which also have Brönsted acid properties, are reported in the range of 2.6 to 3.6 ppm.[20] From the adsorption of ammonia on the calcined and next hydrated sample (Y CH), it was concluded before that the aluminum species which coordinate tetrahedrally after this treatment must be related to the framework. The increased line width of the tetrahedral signal in the ^{27}Al MAS NMR spectrum after ammonia adsorption (Figure 1) clearly proves that this 3.1 ppm line cannot be due to the regeneration of the original Brönsted acid site, as has been suggested for zeolite β calcined under shallow bed conditions,[10] since in that case we would expect the same line width as for the parent sample. A partial hydrolysis of the Al−O bonds with the formation of a framework Al−OH species seems to be the logical result.

From Tables 1 and 2, it can be seen that the amount of Al species having the reversible octahedral coordination, calculated from the difference of the octahedral line intensity of sample Y CHA and Y CH, and the amount of acid sites giving the 3.1 ppm line in the proton NMR spectrum are, within experimental error, identical. When variations of the Si/Al ratio or of the treatment were investigated, we always encountered this relationship between the proton content and the amount of reversible Al. Therefore it can be suggested that in case of zeolite Y the formation of Al−OH, which results from the disruption of the zeolite lattice by hydration, is the host for water molecules to form reversible octahedral framework Al in the hydrated zeolite Y sample.

The Al speciation caused by the gradual hydration of the outgassed sample (Y CH) has been followed by $\{^{1}H\}-^{27}Al$ CP MAS NMR. After a short hydration time (5 min) we can observe a line at 34 ppm, whereas the completely hydrated sample only contains a tetrahedral and an octahedral line in the ^{27}Al MAS NMR spectrum (Figure 8). It was stated before that this 34 ppm line in the ^{27}Al MAS NMR spectrum does not possess a large quadrupole coupling constant, which indicates that the line is subjected to a small quadrupolar shift. Therefore it is reasonable to attribute this line to pentacoordinated Al species, for which indeed a chemical shift of 34 ppm can be expected in the ^{27}Al MAS NMR spectrum.[26] From these observations it can be concluded that the hydration is a consecutive process and that part of the octahedral Al species are formed as hydrated Al complexes instead of polymeric aluminum species. Several cationic species have been postulated to be present in a calcined zeolite sample.[27,28] From our ^{27}Al CP MAS NMR measurement these cannot be excluded. However, cationic species are a source of Lewis acidity. This kind of acidity is not observed by the phosphine adsorption experiment. Therefore we can rule out the presence of such species.

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Our experiment shows that the mechanism, suggested by Barthomeuf,[13] of consecutive interaction of bases with the zeolite framework can to a large extent explain the interaction of water in zeolite Y. Some modifications, however, should be taken into account. For HY it was stated that the interaction of water results in the complete removal of Al from the lattice. Intermediate situations can be encountered where only partial hydrolysis of the framework Al takes place, while this site can host some coordinatively bonded water molecules.

The above presented results also show that one has to be cautious when interpreting the ^{1}H MAS NMR spectrum of a calcined zeolite Y, since the normally presented spectrum of the acid sites is the result of some hydration causing the destruction of the zeolite lattice (Figure 4).

5. Conclusion

When a zeolite Y sample is calcined under mild deep bed conditions, only Brönsted acid sites are present in the sample and the framework remains intact. Not only does the hydration of this acid Y sample lead to the lattice dealumination, which is normally evidenced by the octahedral line in the ^{27}Al MAS NMR spectrum, also framework Al−OH species are formed as a result of the partial hydrolysis of the framework Al−O bonds. In the proton spectrum these Al−OH are observed at 3.1 ppm when the spin−echo editing technique is applied.

In the ^{27}Al MAS NMR spectrum of the hydrated Y sample, species are detected from which the coordination can be changed from a 6-fold state to tetrahedrally coordinated species by means of the adsorption of ammonia. These Al sites are believed to originate from the interaction of water with the framework Al−OH sites.

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