Characterization of water-free aluminum-containing catalysts by ^{27}Al solid-state NMR

Spectroscopic background: ^{27}Al nuclei have a spin of I = 5/2 and a quadrupole moment of Q = 14.66 x 10^{-30} m^2. Therefore, ^{27}Al NMR signals of aluminum atoms in dehydrated solids with high local electric field gradients are affected by strong quadrupolar interactions. The ^{27}Al isotope has a natural abundance of 100 % and a sensitivity of 0.21 in comparison with ^{1}H nuclei (1.0), making this isotope a very suitable candidate for NMR studies of solids. For basic principles of solid-state NMR, see lectures "Solid-State NMR Spectroscopy" for Bachelor students or PhD seminars, accessible via the link "Lectures for Students".

While ^{27}Al nuclei of Al(4Si) units in hydrated aluminosilicates are involved in weak quadrupolar interactions only, corresponding to quadrupole coupling constants of C_Q = 1 to 2 MHz, this spectroscopic parameter reaches values of up to C_Q = 16 MHz in the water-free, i.e. the non-hydrated or dehydrated state (if they were initially hydrated) of these materials. On the other hand, **hydration of aluminosilicates can modify the chemical state of catalytically important framework and extra-framework aluminum species** acting e.g. as Lewis sites. In some cases, also intact framework Al(4Si) units can be attacked by water molecules and, subsequently, change their local structure. Therefore, ^{27}Al solid-state NMR studies of water-free aluminosilicates are interesting for understanding the state of aluminum atoms in these materials, e.g. upon an anhydrous modification or catalytic application.

^{27}Al solid-state NMR spectroscopy of non-hydrated and, in the same manner, of dehydrated aluminosilicates may require specific experimental techniques [1-5]. Possible approaches are static (without MAS) spin-echo NMR experiments using a phase-cycled selective echo sequence [6]. In this case and at a ^{27}Al resonance frequency of ν_0 = 130.3 MHz, the width of the signals varies from 24 kHz for dehydrated zeolite Na-ZSM-5 to 100 kHz for dehydrated zeolite H-ZSM-5. The static ^{27}Al spin-echo NMR spectra of dehydrated aluminosilicate-type zeolites often consist of two signals, a **broad "quadrupole pattern", QP,** corresponding to coupling constants of **C_Q = 12.7 MHz for 92H-Y** to **C_Q = 16.0 MHz for H-ZSM-5**, and a **narrow "quadrupole line", QL,** corresponding to **C_Q = 5.5 MHz for NH$_4$- and Na-Y** and **C_Q = 4.7 MHz for NH$_4$- and Na-ZSM-5**. Signal **QP** is due to framework **Al^{IV}** species in the local structure of a **bridging OH group (Al^{IV}/H$^+$)**, while the framework **Al^{IV}** species causing signal **QL** have **neighboured extra-framework cations (Al^{IV}/Na^+, Al^{IV}/NH_4^+).** As a demonstration, **Fig. 1** shows the ^{27}Al spin-echo NMR spectra of dehydrated zeolites NH_4-ZSM-5 (left) and H-ZSM-5 (right) [4, 5].

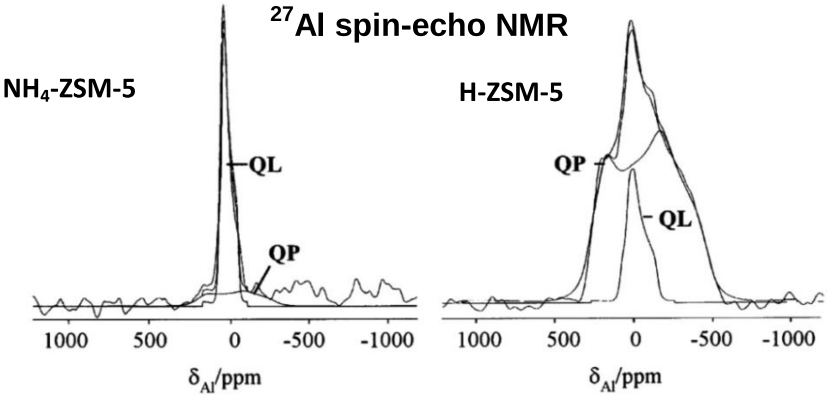


Fig. 1

In **Table 1**, the ^{27}Al NMR parameters of framework aluminum atoms in NH_4- and H-form zeolites Y (n_{Si}/n_{Al} = 2.6), dealuminated zeolites deH,Na-Y (n_{Si}/n_{Al} = 8.0), mordenite (n_{Si}/n_{Al} = 8.0), and zeolites ZSM-5 (n_{Si}/n_{Al} = 22.0), recorded upon dehydration at T = 723 K, are summarized. These data were determined via static ^{27}Al spin-echo NMR experiments und subsequent quantitative evaluation of the spectra by NMR simulation software [5]. The parameter η_Q is the asymmetry parameter of the observed quadrupole pattern. See above-mentioned lecture texts or Refs. [7] and [8] for an explanation of the NMR spectroscopic parameters of quadrupolar interactions.

Zeolites	**Signals**	**C_Q / MHz**	η_Q	I_{rel} / %
NH_4-Y	QL	5.0	0.7	89
	QP	*ca.* 9.0	*ca.* 0.8	11
H-Y	QL	6.0	0.7	17
	QP	13.5	0.4	83
deNH_4-Y	QL	6.0	0.7	41
	QP	*ca.* 9.0	*ca.* 0.8	59
deH,Na-Y	QL	7.0	0.7	16
	QP	13.7	0.5	84
NH_4-MOR	QL	5.0	0.7	100
H-MOR	QL	6.8	0.7	14
	QP	15.0	0.35	86
NH_4-ZSM-5	QL	7.0	0.7	81
	QP	*ca.* 9.0	*ca.* 0.8	19
H-ZSM-5	QL	7.3	0.7	21
	QP	15.5	0.5	79

Table 1

The data in **Table 1** indicate that static ^{27}Al spin-echo NMR spectra of dehydrated NH_4-form zeolites consist of a strong QL signal caused by non-protonated framework AlO_4 species and a very weak QP signal due to few protonated AlO_4 units or extra-framework aluminum species. After deammoniation, the ^{27}Al spin-echo NMR spectra of these samples are dominated by strong patterns QP caused by the AlO_4 units of the protonated H-form zeolites. Hence, the framework protonation results in a significant increase in the ^{27}Al quadrupole coupling constant, C_Q, of the involved framework aluminum atoms. This finding hints at a strong decrease of the local symmetry of these framework AlO_4 units due to a significant increase of the Al-O bond length to those oxygen atoms, which are bound to hydroxyl protons.

Because of the overlap of the various signals in the ^{27}Al solid-state NMR spectra of non-hydrated or dehydrated zeolites, these studies require recording of spectra under different conditions, such as in different magnetic B_0 fields, without (static combined with spin-echo) and with MAS, and, if possible, utilizing the MAS NMR and two-dimensional (2D) MQMAS techniques. If the simulation of all obtained spectra with identical parameters is possible, correct spectral parameters were found (**Fig. 2**).

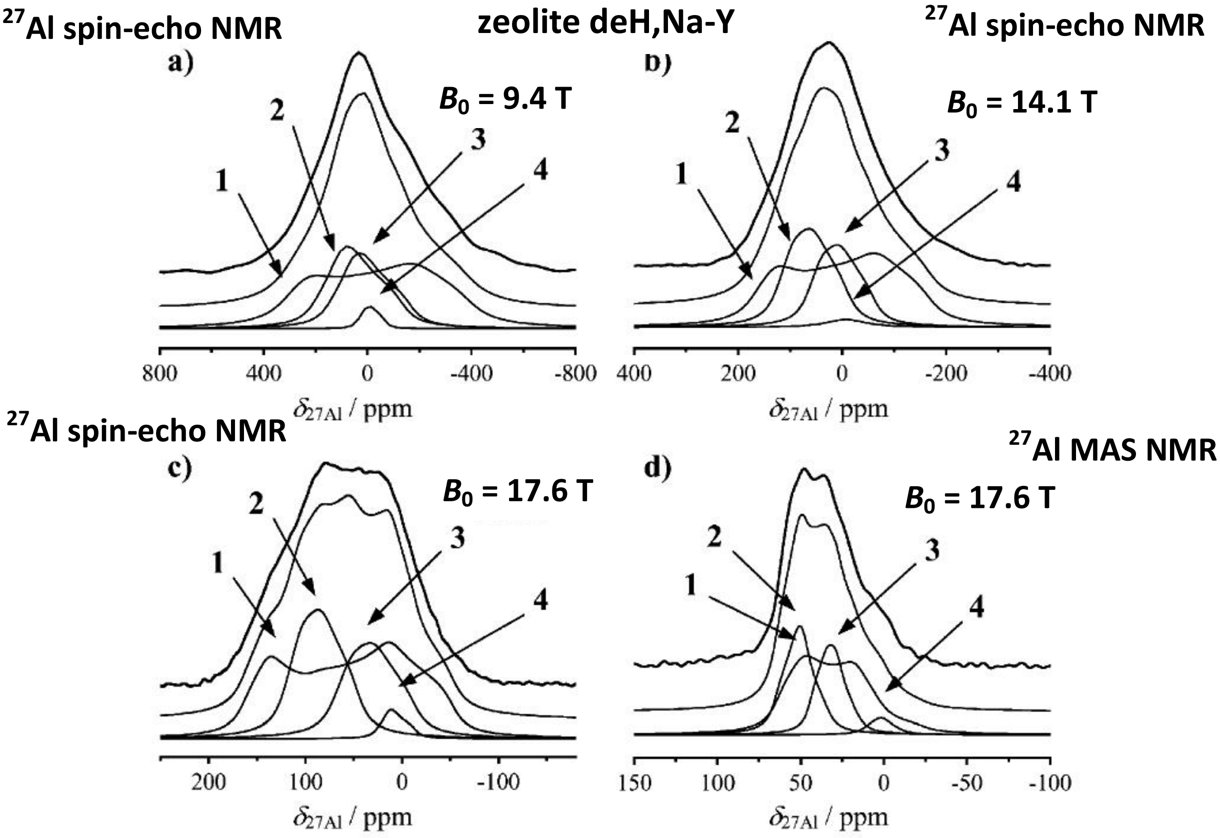


Fig. 2

As a demonstration, **Fig. 2** shows ^{27}Al solid-state NMR spectra of a dealuminated zeolite deH,Na-Y, which was not rehydrated after the steaming process (non-hydrated state). The static ^{27}Al spin-echo NMR spectra were recorded in magnetic fields of B_0 = 9.4 (a), 14.1 (b), and 17.6 T (c), and the corresponding ^{27}Al MAS NMR spectrum (ν_{rot} = 30 kHz) was recorded at B_0 = 17.6 T (d) [9]. The 2D ^{27}Al MQMAS NMR spectrum of the non-hydrated zeolite deH,Na-Y, recorded at B_0 = 17.6 T with ν_{rot} = 30 kHz and utilizing a split-t_1 echo pulse sequence [10, 11], is shown in **Fig. 3** [9].

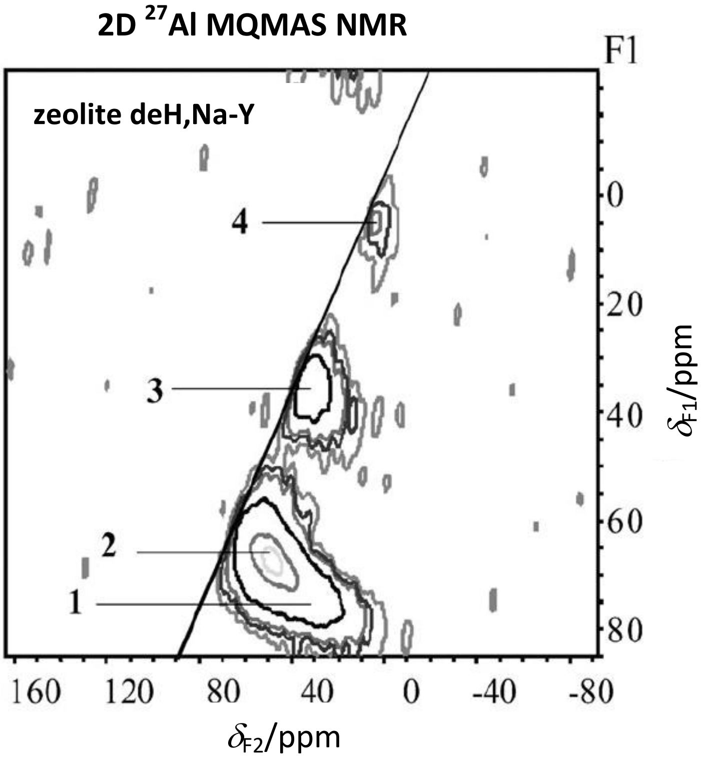
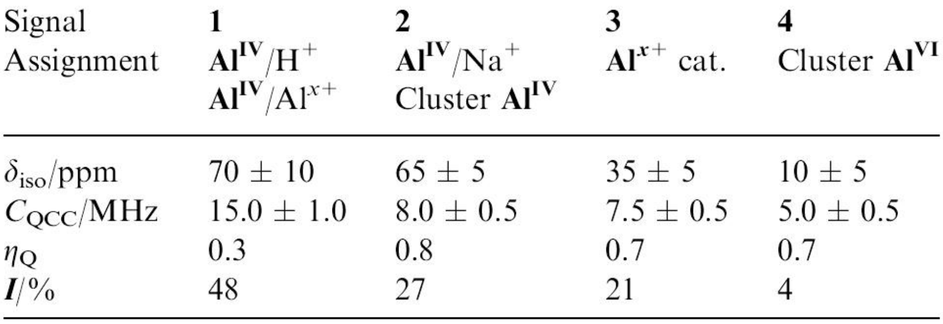


Fig. 3

An adequate simulation of all these ^{27}Al solid-state NMR spectra by NMR software required the assumption of at least four signals 1 to 4. The obtained isotropic chemical shifts $\delta_{27\mathrm{Al,iso}}$, quadrupole coupling constants C_Q (corresponds to C_{QCC}), asymmetry parameters η_Q, and relative intensities I are summarized in **Table 2** [9].

For the assignment of signals 1 to 4 in the ^{27}Al solid-state NMR spectra of non-hydrated zeolite deH,Na-Y, the spectroscopic parameters of the signals obtained for dehydrated γ-Al_2O_3 and dehydrated zeolites Al,Na-Y and H,Na-Y were utilized as reference [9]. Considering the large C_Q value and the isotropic chemical shift $\delta_{27\mathrm{Al,iso}}$ of signal 1, this signal was attributed to framework aluminum atoms in the vicinity of



Signal Assignment	**1** $\mathbf{Al^{IV}}/H^+$ $\mathbf{Al^{IV}}/Al^{x+}$	**2** $\mathbf{Al^{IV}}/Na^+$ Cluster $\mathbf{Al^{IV}}$	**3** $\mathbf{Al}^{x+}$ cat.	**4** Cluster $\mathbf{Al^{VI}}$
δ_{iso}/ppm	70 ± 10	65 ± 5	35 ± 5	10 ± 5
C_{QCC}/MHz	15.0 ± 1.0	8.0 ± 0.5	7.5 ± 0.5	5.0 ± 0.5
η_Q	0.3	0.8	0.7	0.7
$\boldsymbol{I}$/%	48	27	21	4

Table 2

bridging hydroxyl protons (Al^{IV}/H^+) as well as framework aluminum atoms, which are compensated in their negative electric charge by extra-framework aluminum cations (Al^{IV}/Al^{x+}). Signal 2 was assigned to framework aluminum atoms compensated by extra-framework sodium cations (Al^{IV}/Na^+) as well as tetrahedrally coordinated aluminum atoms in neutral extra-framework aluminum oxide clusters (cluster Al^{IV}). Finally, signals 3 and 4 were attributed to extra-framework aluminum cations (Al^{x+} cat.) and octahedrally coordinated aluminum atoms in neutral extra-framework aluminum oxide clusters (cluster Al^{VI}), respectively. In the last line of **Table 2**, the relative intensities of signals 1 to 4 are summarized. Utilizing the total number of aluminum atoms, determined by chemical analysis, the absolute numbers of aluminum species corresponding to the assignments of signals 1 to 4 can be calculated (see Ref. [9]). For a survey on ^{27}Al NMR parameters of aluminum atoms in dehydrated powder materials, see Refs. [7] and [8].

The significant decrease of the **quadrupole coupling constant, C_Q, of framework aluminum atoms** in H-form zeolites upon hydration from ca. 16 MHz to ca. 2 MHz demonstrates the **high sensitivity of this NMR spectroscopic parameter for an interaction of bridging OH groups (Si(OH)Al) with water molecules**. This effect is caused by changes of the electric field gradient in the local structure of the framework aluminum atoms. As demonstrated by quantum-chemical investigations [12], also the adsorption of adsorbate molecules and reactants at Si(OH)Al groups of water-free H-form zeolites influence the local electric field gradients of the involved framework aluminum atoms. Depending on the base strength of the adsorbed molecules, described by the proton affinity, *PA*, the formation of hydrogen bonds or a proton transfer from the Si(OH)Al group to the adsorbate molecules occurs.

Solid-state NMR studies delivered the experimental proof that the type of the interaction between adsorbate molecules and Si(OH)Al groups in water-free H-form zeolites is reflected by the ^{27}Al quadrupole coupling constant C_Q [4, 13]. As an example, **Fig. 4** shows the ^{1}H and ^{27}Al MAS NMR spectra of water-free zeolite H,Na-Y, recorded upon *in situ* adsorption of ammonia (see “method 27” via link “*In Situ*

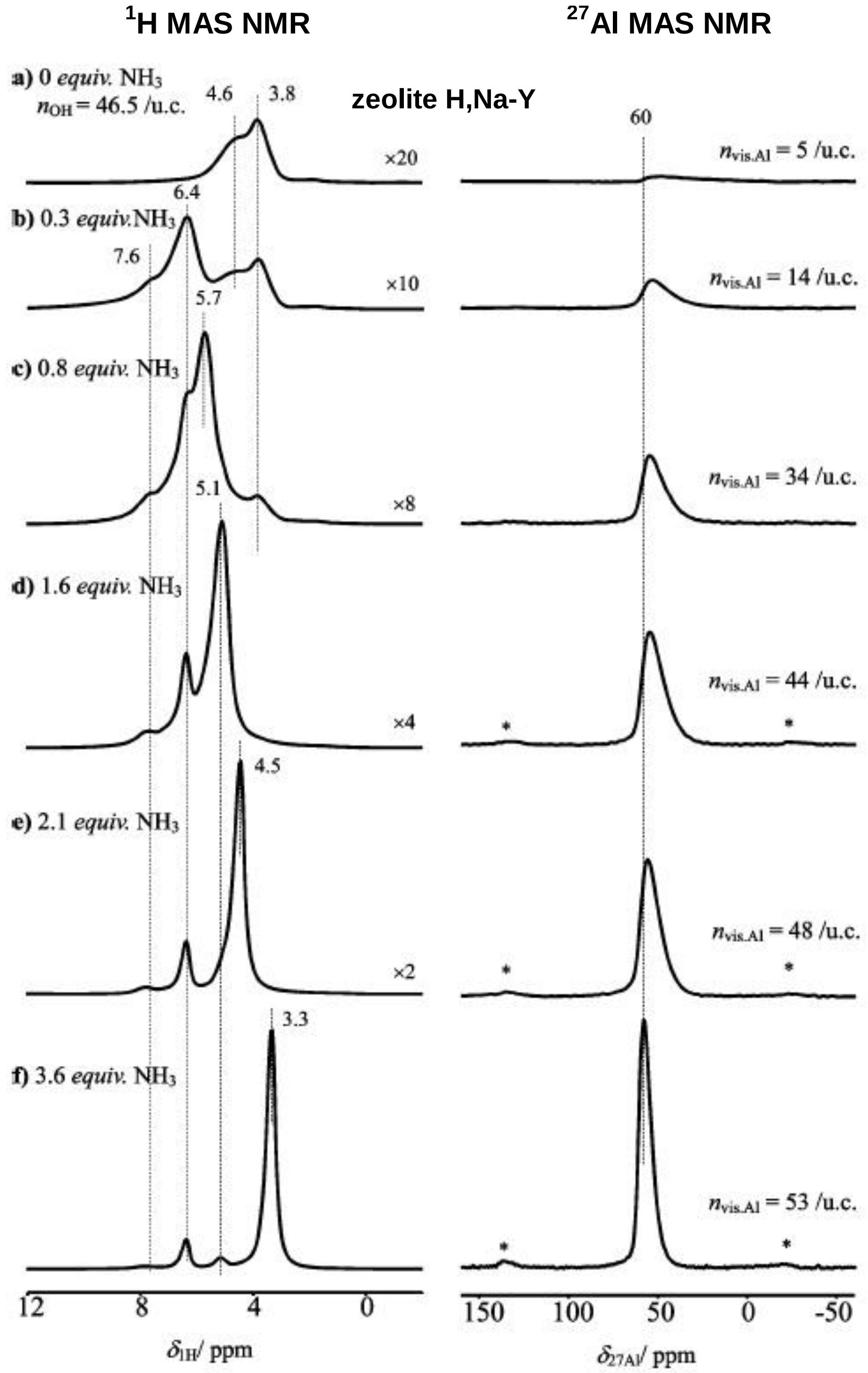


Fig. 4

NMR Methods for Heterogeneous Catalysis") [13]. In this Figure, the NH_3 loading is given by *equiv* = $n_{NH3}/n_{OH,}$ where n_{OH} corresponds to the number of Si(OH)Al groups. For a coverage of < 0.3 *equiv* of ammonia molecules, all molecules are protonated by Si(OH)Al groups (δ_{1H} = 3.8 and 4.6 ppm), resulting in ^{1}H MAS NMR signals at δ_{1H} =

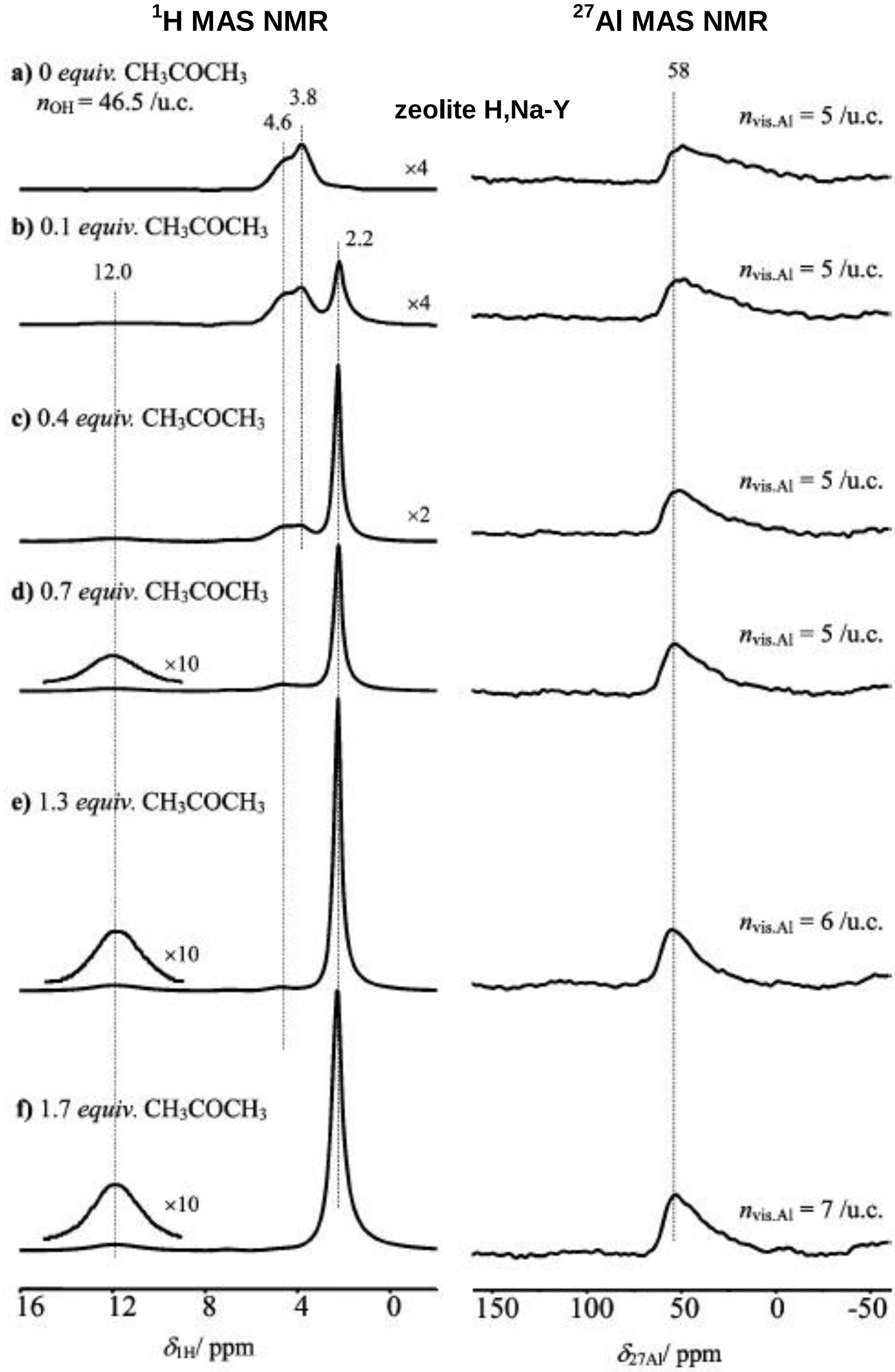


Fig. 5

7.6 and 6.4 ppm due to ammonium ions formed by a proton transfer from the Si(OH)Al groups of the water-free zeolite H,Na-Y to the adsorbate molecules (**Fig. 4, left**). For loadings of > 0.3 *equiv* of ammonia, different ^{1}H MAS NMR signals of ammonium ions in rapid exchange with non-protonated ammonia molecules ($\delta_{1\mathrm{H}}$ = 0.8 ppm) occurs [13].

Fig. 4, right-hand side, shows the ^{27}Al MAS NMR spectra of the water-free zeolite H,Na-Y loaded with ammonia molecules. Upon ammonia adsorption, a narrow ^{27}Al MAS NMR signal of tetrahedrally coordinated framework aluminum occurs at $\delta_{27\mathrm{Al}}$ = 60 ppm and is continuously increased (increasing n_{visAl} value). This finding is explained by the deprotonation of the framework AlO_4 tetrahedra, in result of the above-mentioned formation of ammonium ions, leading to an improved tetrahedral symmetry and decreased local electric field gradient of the involved aluminium atoms [13].

Adsorption of acetone on water-free zeolite H,Na-Y causes only a slight narrowing of the ^{27}Al MAS NMR signal of tetrahedrally coordinated framework aluminum at $\delta_{27\mathrm{Al}}$ = 58 ppm, as show on **Fig. 5, right-hand side**. Furthermore, the adsorbate-induced shift of the ^{1}H MAS NMR signal of Si(OH)Al groups from $\delta_{1\mathrm{H}}$ = 3.8 and 4.6 ppm to $\delta_{1\mathrm{H}}$ = 12.0 ppm (**Fig. 5, left-hand side**) indicates the formation of hydrogen bridges between the hydroxyl protons and the acetone molecules, i.e. no proton transfer occurs [13].

Via 2D ^{27}Al MQMAS NMR spectroscopy, the strength of the ^{27}Al quadrupolar coupling constant can be determined by the second-order quadrupolar effect parameter, *SOQE*. The relationship between the *SOQE* parameter and the quadrupole coupling constant C_Q is given by $SOQE = C_Q\ (1 + \eta_Q^{2/3})^{1/2}$, with the asymmetry parameter, η_Q, in the range of 0 to 1 [7, 8, 14]. Because $\eta_Q^{2/3}$ is often << 1 in the above-mentioned relationship, C_Q and *SOQE* are utilized in a similar manner for describing the local symmetry and electric field gradient in the vicinity of quadrupolar nuclei in solids.

In **Fig. 6 left,** and **right**, the 2D ^{27}Al MQMAS NMR spectra of water-free zeolite H,Na-Y recorded upon adsorption of 3 *equiv* of ammonia and 2 *equiv* of acetone, respectively, are shown. The evaluation of the spectra in **Fig. 6** led to *SOQE* parameters of 3.5±0.5 MHz and 12.0±1.0 MHz for the tetrahedrally coordinated framework aluminum atoms of Si(OH)Al groups involved in the adsorption of ammonia (signal 1) and acetone (signals 3), respectively [13]. Similar 2D ^{27}Al MQMAS NMR spectra were obtained upon adsorption of pyridine and acetonitrile on water-free zeolite H,Na-Y (see Ref. [13]).

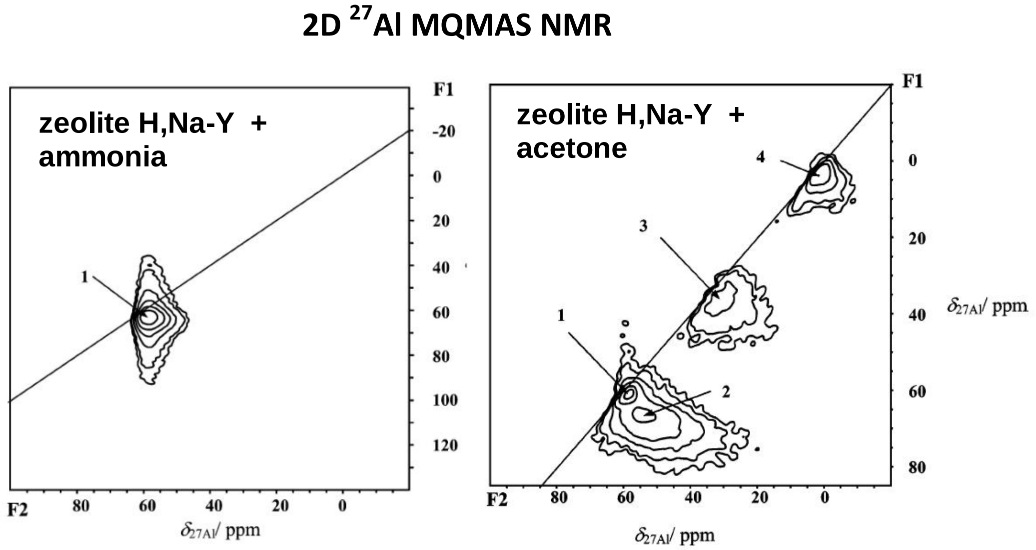

2D ^{27}Al MQMAS NMR

Fig. 6

In **Fig. 7**, an overview on the effect of adsorbate molecules on the experimentally determined *SOQE* parameters of framework aluminum atoms in water-free zeolite H,Na-Y is given [13]. For adsorption of dry nitrogen (*PA* = 494 kJ/mol [15]), the ***SOQE* parameter has a value of 16.0 MHz**. It is well-accepted that only very weak van der Waals interactions between nitrogen and the zeolite framework exist in this case. Therefore, no influence of nitrogen on the *SOQE* parameter occurs (**Fig. 7,**

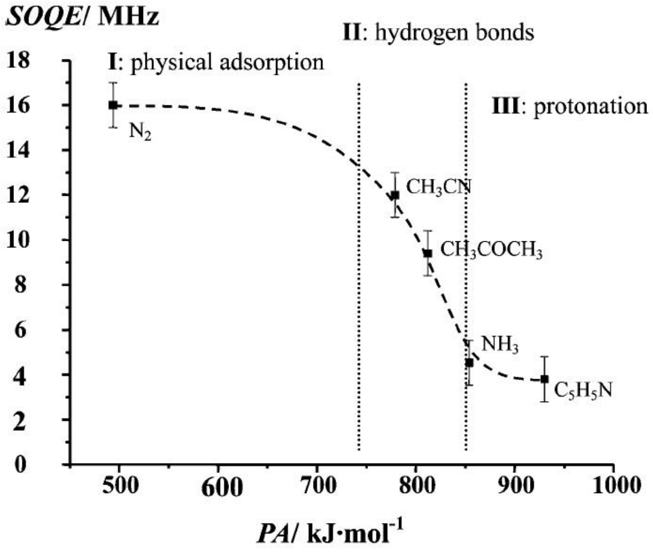


Fig. 7

region I: physical adsorption). With increasing base strength of adsorbate molecules, such as for adsorption of acetonitrile (CH_3CN) and acetone (CH_3COCH_3) with *PA* = 779 kJ/mol [15] and *PA* = 812 kJ/mol [15], respectively, hydrogen bonds are formed between the Brønsted acidic Si(OH)Al groups and the molecules, which leads to ***SOQE* parameters of 12.0±1.0 MHz** (**Fig. 7, region II: hydrogen bonds**). In the case of adsorption of molecules with further increased proton affinities, such as of ammonia (NH_3, *PA* = 854 kJ/mol [15]) and pyridine (C_5H_5N, *PA* = 930 kJ/mol [15]), also a further decrease of the ***SOQE* parameter to 3.5±0.5 MHz** occurs. This finding is explained by the formation of cationic adsorbates, which is accompanied by a deprotonation of the Brønsted acidic Si(OH)Al groups (**Fig. 7, region III: protonation**). Hence, if the proton affinity of adsorbate molecules reaches a value of higher than *PA* = 812 kJ/mol (*PA* value of acetone), the above-mentioned strong decrease of the *SOQE* parameter of framework aluminum atoms in water-free zeolite H,Na-Y indicates a deprotonation the zeolite framework accompanied by a significant decrease of the electric field gradient in the local structure of the framework AlO_4 tetrahedra. Hence, the experimentally accessible *SOQE* parameter and quadrupole coupling constant, C_Q, are sensitive for the interaction type of molecules adsorbed at the catalytically important Si(OH)Al groups in water-free H-form zeolites [13].

In the final example, the influence of **chemically bound surface complexes**, such as of **alkoxy species** formed at Si(OH)Al groups, on the electric field gradient in the local structure of the framework AlO_4 tetrahedra of water-free H-form zeolites is demonstrated. These surface methoxy groups are the result of the conversion of methanol at Brønsted acidic Si(OH)Al groups of calcined H-form zeolites [16]. Via ^{13}C

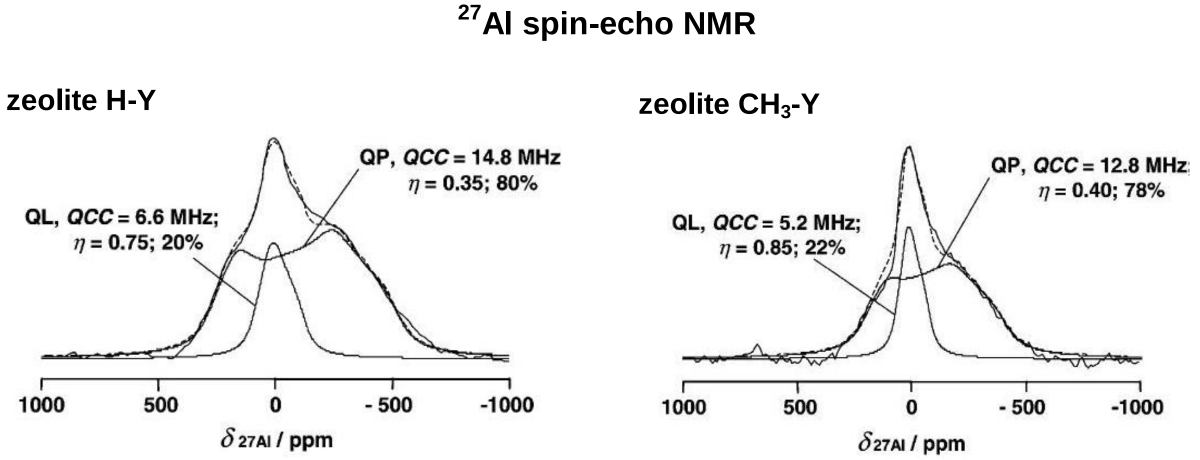


Fig. 8

MAS NMR spectroscopy, the presence of methoxy groups on methylated zeolites is evidenced by signals at δ_{13C} = 57±1 ppm. The effect of surface methoxy groups on zeolitic framework aluminum atoms was studied by ^{27}Al spin-echo NMR spectroscopy. For water-free and methylated zeolite Y, a decrease of the ^{27}Al quadrupole coupling constant of framework aluminum atoms from C_Q = 14.8 MHz (**Fig. 8, left-hand side**) for the parent H-Y zeolite (uncovered Si(OH)Al groups) to **C_Q = 12.8 MHz** (**Fig. 8, right-hand side**) upon formation of methoxy groups (Si(OCH_3)Al) was found [16].

Catalyst preparation: The assignment "non-hydrated" was used in literature, if catalyst materials had no contact with air, i.e. no contamination by humidity after a modification process or catalytic application. In these cases, no hydration of unstable aluminum species or Lewis sites can occur. For ^{27}Al solid-state NMR studies of catalysts, which had air contact for longer time and was hydrated, a standard dehydration ("dehydrated" materials) inside a „sample tube system 1" at „vacuum line 1" (accessible via the link "*In Situ* Solid-State NMR Techniques") was performed.

The dehydration starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to 393 K within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to 723 K within 3 hours and evacuated at this temperature for 12 hours. After this treatment, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1", after the line was ventilated with air. The transfer of the dehydrated sample into the MAS NMR rotor should be performed without air contact, e.g. in a mini glove box purged with dry nitrogen gas (see Section "mini glove box", accessible via the link "*In Situ* Solid-State NMR Techniques"). The samples obtained via this way are assigned "dehydrated" catalysts and were utilized, like the "non-hydrated" samples, for the ^{27}Al solid-state NMR studies described in the present section.

The dealuminated zeolite deH,Na-Y in Figs. 2 and 3 was prepared by steaming using the steaming set-up described in the Section "set-up", accessible via the link "*In Situ* Solid-State NMR Techniques". The zeolite deH,Na-Y was obtained using a zeolite H,Na-Y with n_{Si}/n_{Al} = 2.7 by steaming at T = 748 K for 2.5 h under a water vapour pressure of 81.5 kPa [9]. Upon a subsequent purging with dry nitrogen gas at T = 748

K for 1 h, the sample material was transferred into a gas-tight glass container without air contact inside a sample lock and, subsequently, into a MAS NMR rotor inside a mini glove box, both purged with dry nitrogen gas.

^{27}Al solid-state NMR studies: A p_1-τ_1-p_2-τ_1 spin-echo sequence with $p_1 = p_2 = 0.61$ µs, $\tau_1 = 10$ µs, $\tau_2 = 9$ µs and a repetition time of 2 s were applied. ^{27}Al MAS NMR experiments were performed using a 2.5 mm MAS NMR probe with a sample spinning frequency of $\nu_{\mathrm{rot}} = 30$ kHz, a single-pulse $\pi/12$ excitation and a repetition time of 2 s. 2D ^{27}Al MQMAS NMR spectra were obtained applying the split-t_1 echo pulse sequence with hard pulses of 3.3 µs and 13.7 µs, a soft pulse of 47 µs, and a repetition time of 2 s. Also in this case, a 2.5 mm MAS NMR probe with an rf field corresponding to $\nu_{\mathrm{rf}} = 120$ kHz and a sample spinning frequency of $\nu_{\mathrm{rot}} = 30$ kHz were utilized. The Bruker software WINNMR, WINFIT, and XWINNMR were applied for the deconvolution and simulation of 1D NMR spectra and the transformation and evaluation of the 2D MQMAS spectra. Referencing of the chemical shift is performed with 0.1 M aqueous $Al(NO_3)_3$ solution ($\delta_{27\mathrm{Al}} = 0$ ppm).

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