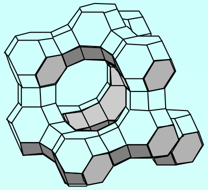


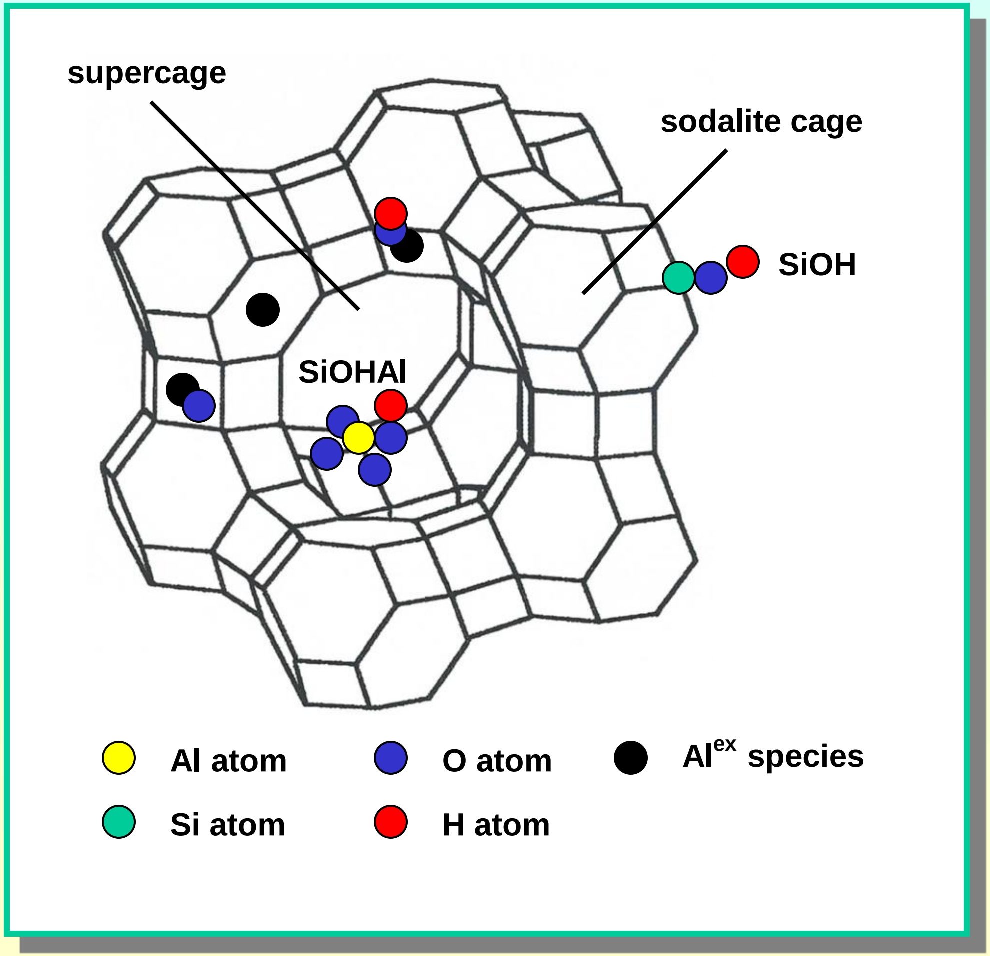
Aluminum distribution in non-hydrated zeolite catalysts studied by ex situ and in situ solid-state NMR spectroscopy

Michael Hunger

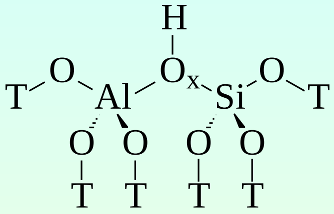
Institute of Chemical Technology
University of Stuttgart, Germany

Dealumination of Zeolites

- **dealuminated zeolite Y:**



- **Broensted acid sites:**

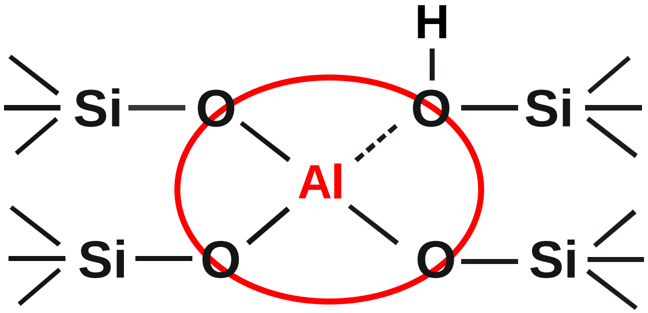


bridging OH group (SiOHAl)

- **results of steaming:**
  - **dehydroxylation of SiOHAl groups**
  - **dealumination of the framework**
  - **formation of extra-framework species**
  - **formation of defect sites (e.g. SiOH)**

Quadrupolar Interaction of Aluminum Atoms in Non-hydrated Zeolites

^{27}Al: spin $I = 5/2$



- electric field gradient:

$$V_{zz} = eq$$

- quadrupole coupling constant:

$$QCC = \frac{e^2qQ}{h}$$

samples	*QCC* values*
hydrated H-Y and H-ZSM-5	2 MHz
non-hydrated Na-Y	5 MHz
non-hydrated H-Y	16 MHz
Al^{ex} in non-hydrated H-ZSM-5	ca. 9 MHz
pyridine-loaded H-Y	5 MHz
ammonia-loaded H-Y	5 MHz

*) D. Freude et al., Solid State Nucl. Magn. Reson. 3 (1994) 271; M. Hunger et al., Stud. Surf. Sci. Catal. 94 (1995) 756; C.D. Grey, A.J. Vega, J. Am. Chem. Soc. 117 (1995) 8232; M. Hunger, Catal. Rev.-Sci. Eng. 39 (1997) 345; K.U. Gore et al. J. Phys. Chem. B 106 (2002) 6115; W. Wang et al., Chem. Phys. Lett. 370 (2003) 88.

Aims of Recent Studies

NMR studies of non-hydrated zeolite catalysts:

- **possibilities and limitations of NMR spectroscopy for the study of non-hydrated zeolites**
- **number and coordination of framework aluminum atoms in steamed zeolite catalysts**
- **number and nature of extra-framework aluminum species in steamed zeolite catalysts**

Preparation of Samples

commercial
zeolite Na-Y
(n_{Si}/n_{Al} = 2.7)

$\xrightarrow[\text{exchange}]{\text{ammonium}}$

NH_4,Na-Y (exchange degree of 93 %)

calcination and steaming at 475°C
flowing nitrogen (100 ml/min)
water vapor pressures of 3.4 to 81.5 kPa

→

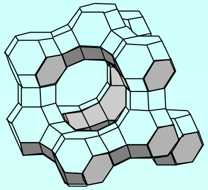
dealuminated zeolites Y
denoted as deH,Na-Y/p_{H2O}
p_{H2O}: water vapor pressure

→

transfer into gas-tight
glass tubes and
MAS NMR rotors

→

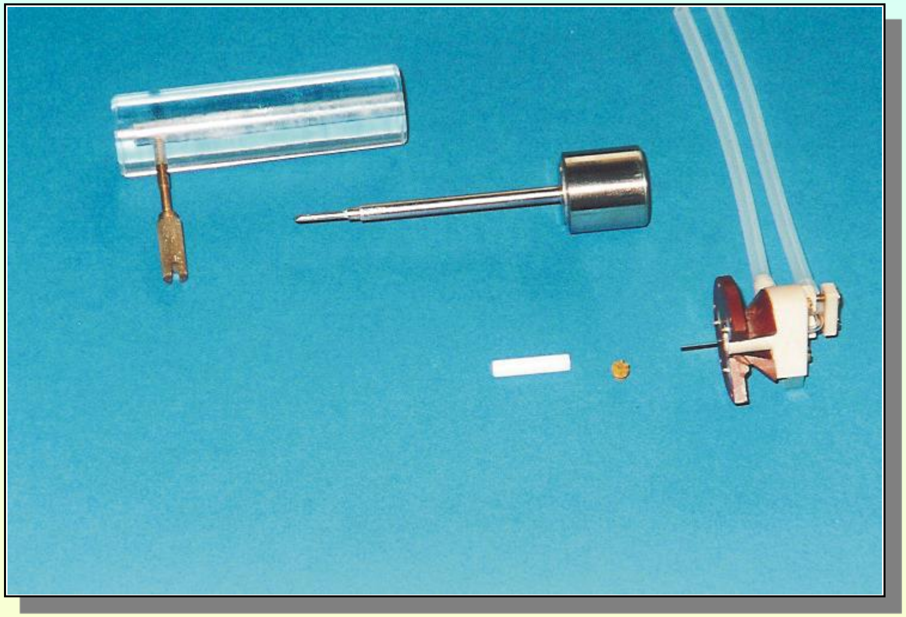
NMR characterization in the
non-hydrated state

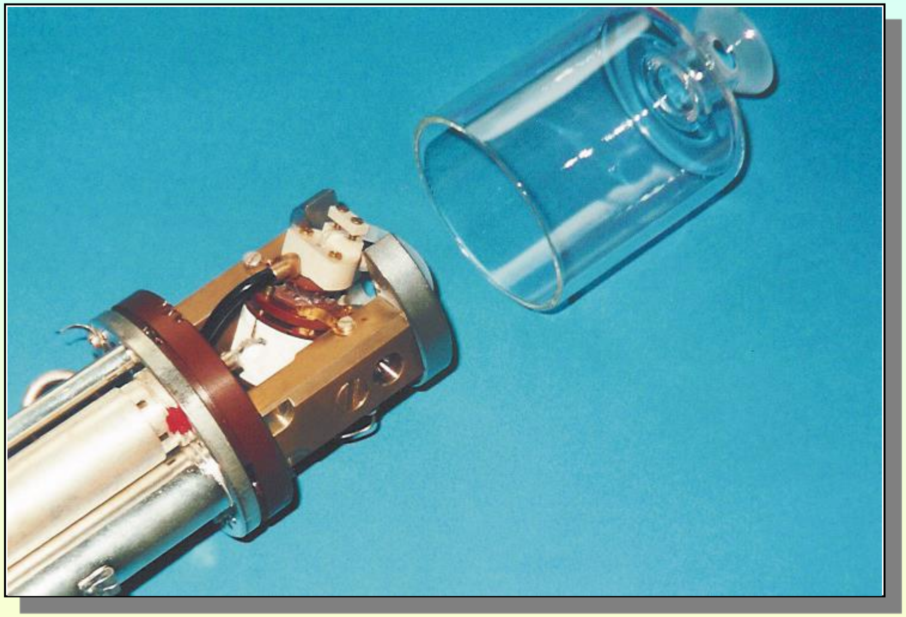


I. Solid-state NMR Investigation of the Framework Aluminum Content of Non-hydrated Zeolites

Continuous-flow (CF) MAS NMR Probe

- modified 4 mm Bruker VT MAS NMR probe, ν_{rot} = 9 kHz, sample ca. 50 mg

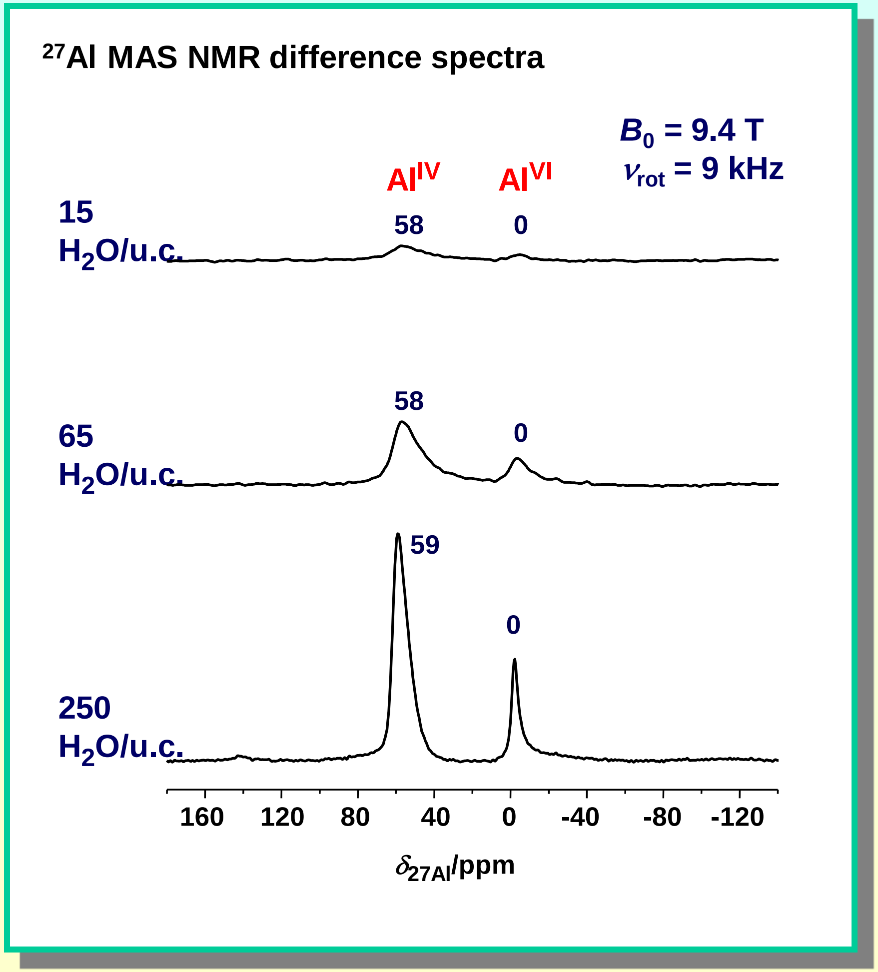


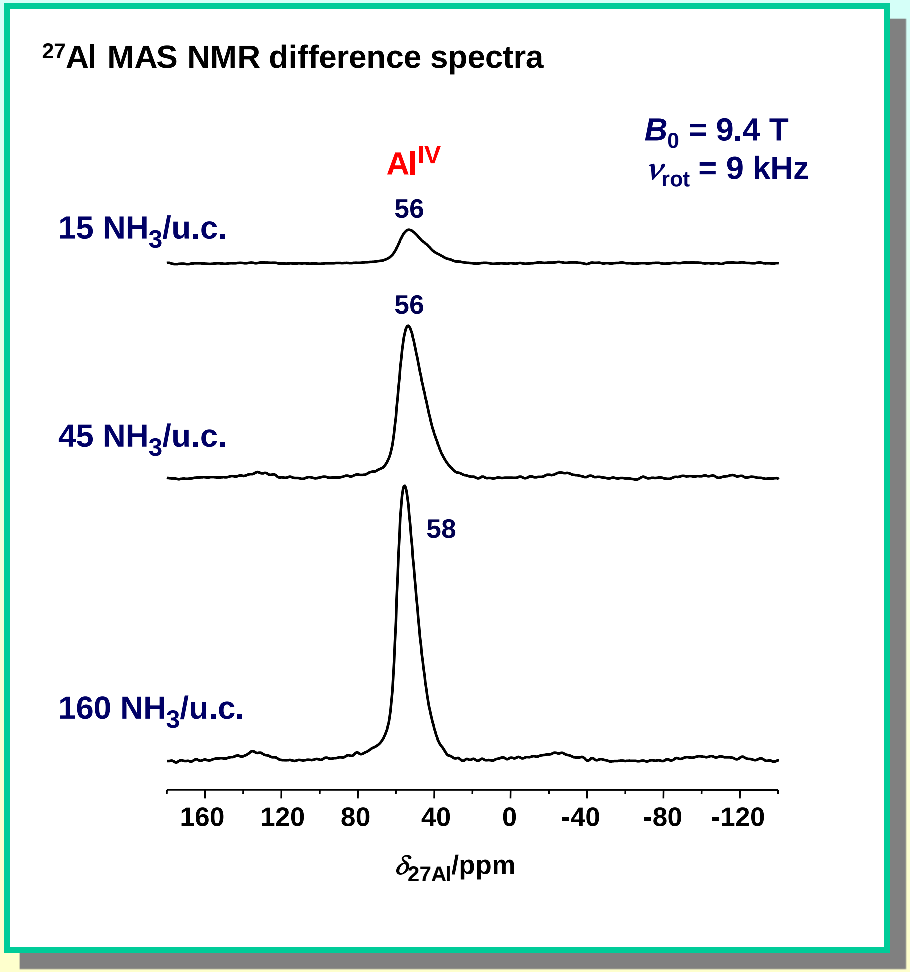


A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.

Effect of Adsorption Studied by ^{27}Al MAS NMR

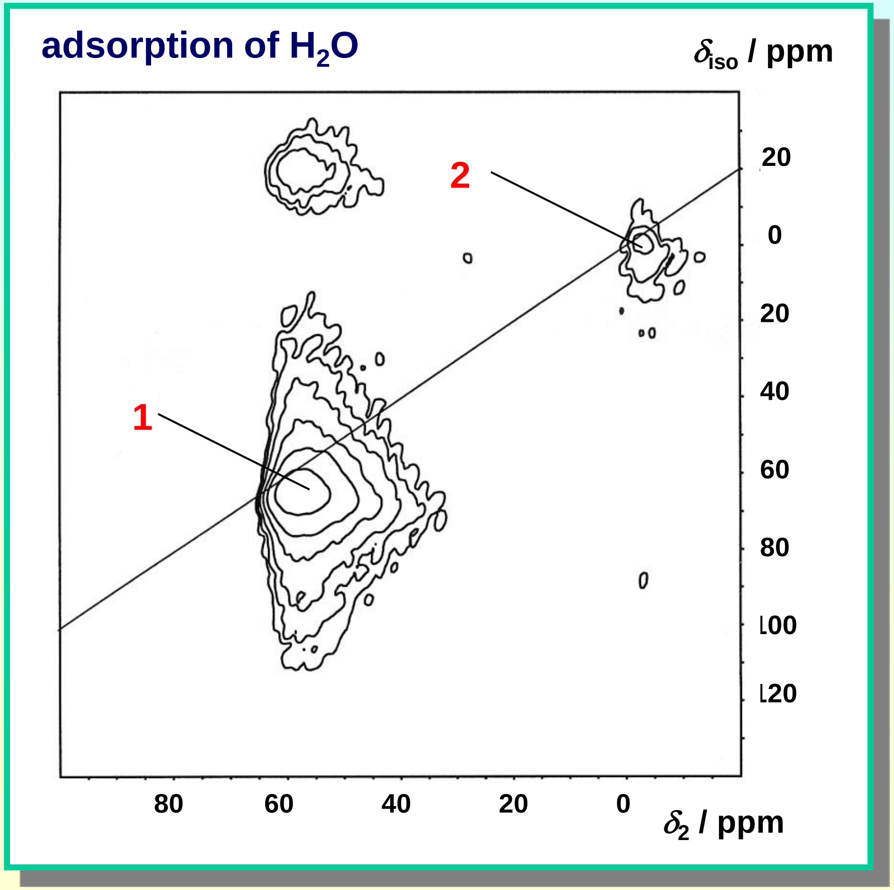
- effect of the adsorption of H_2O and NH_3 on non-hydrated H,Na-Y



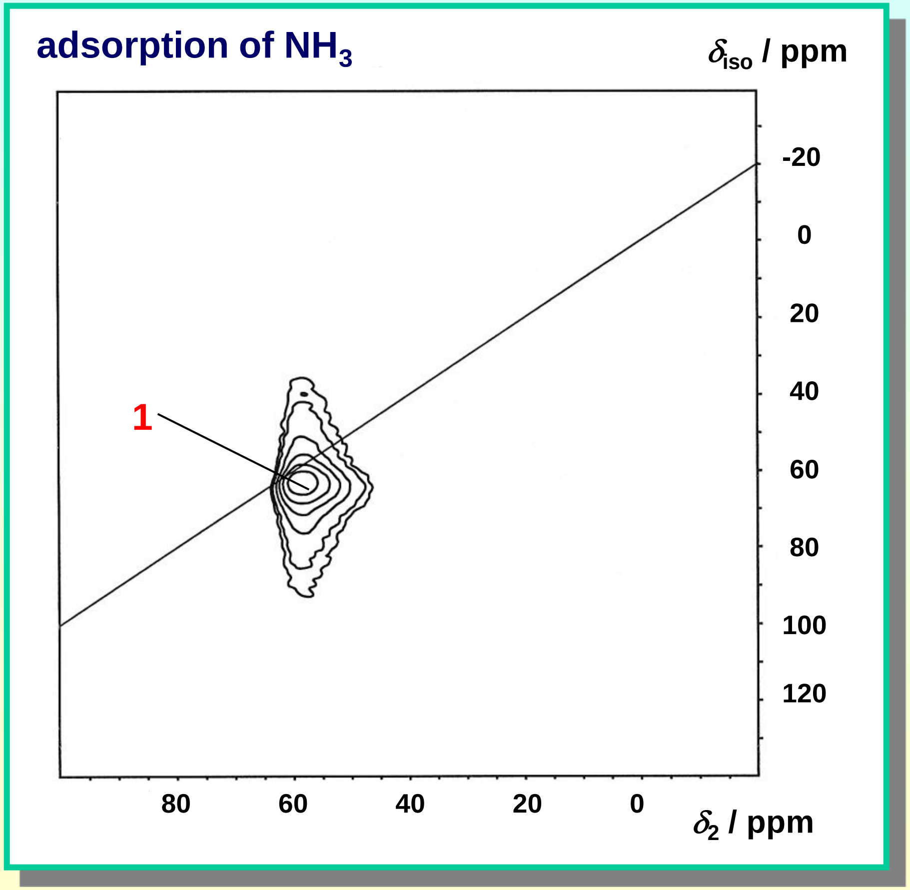


^{27}*Al MQMAS NMR of Zeolite H,Na-Y*

- **MQMAS experiments at B_0 = 9.4 T, ν_{rot} = 9 kHz**



adsorption of H_2O



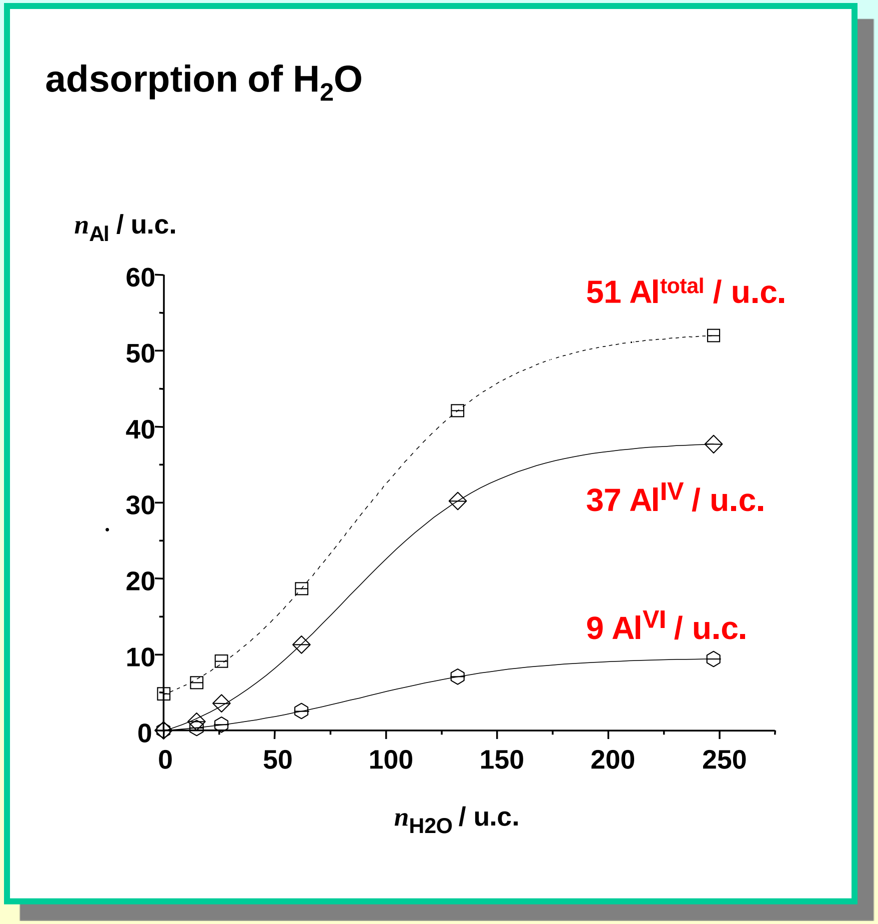
adsorption of NH_3

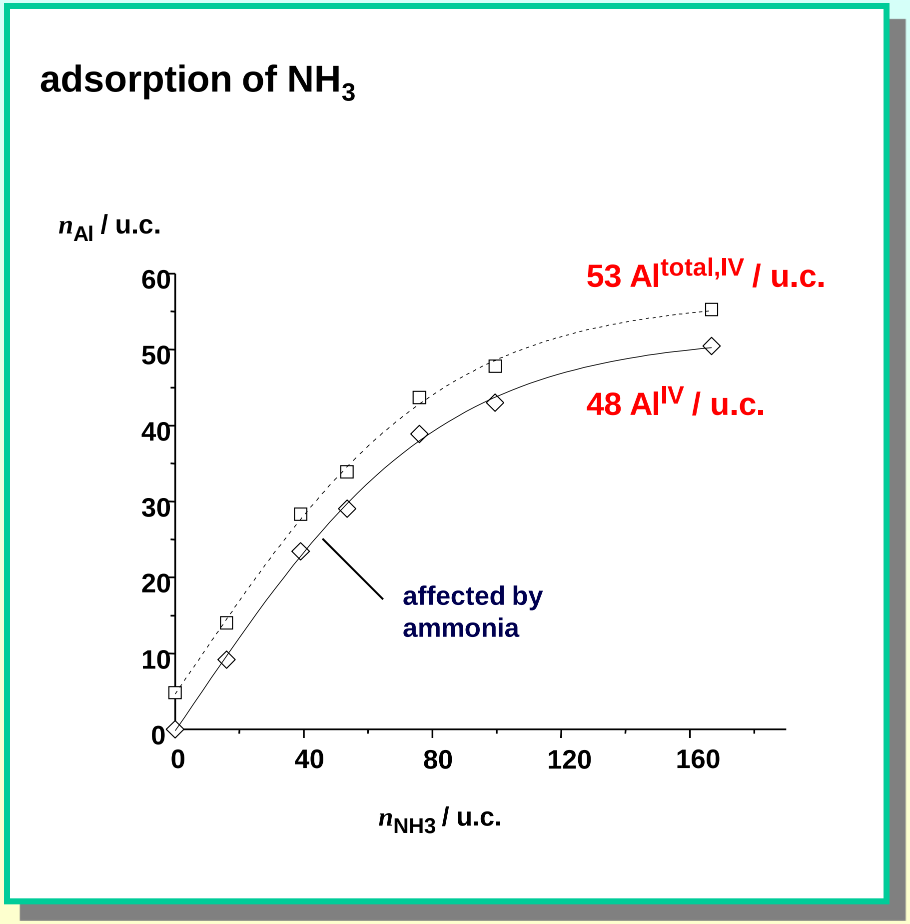
signal 1: δ_{iso} = 64 ppm, *SOQE* = 3.3 MHz
signal 2: δ_{iso} = 0 ppm, *SOQE* = 2.3 MHz

signal 1: δ_{iso} = 62 ppm, *SOQE* = 2.1 MHz

Effect of Adsorption Studied by ^{27}Al MAS NMR

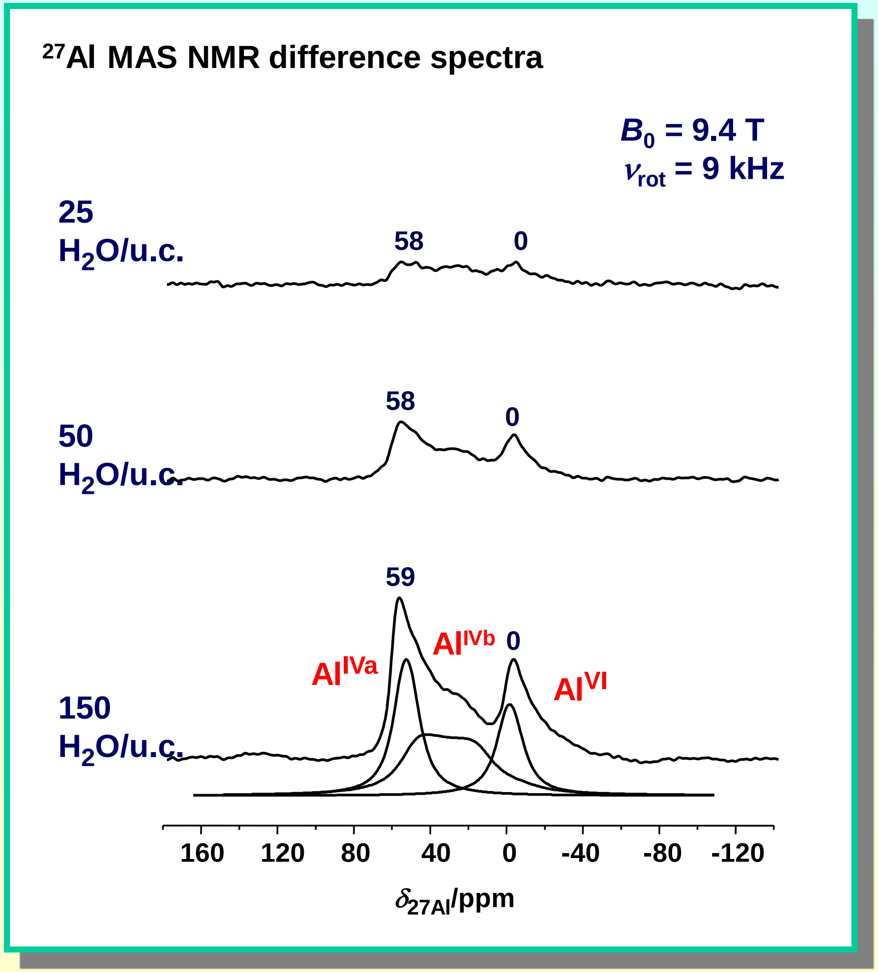
- **adsorption of H_2O and NH_3 on non-hydrated H,Na-Y**

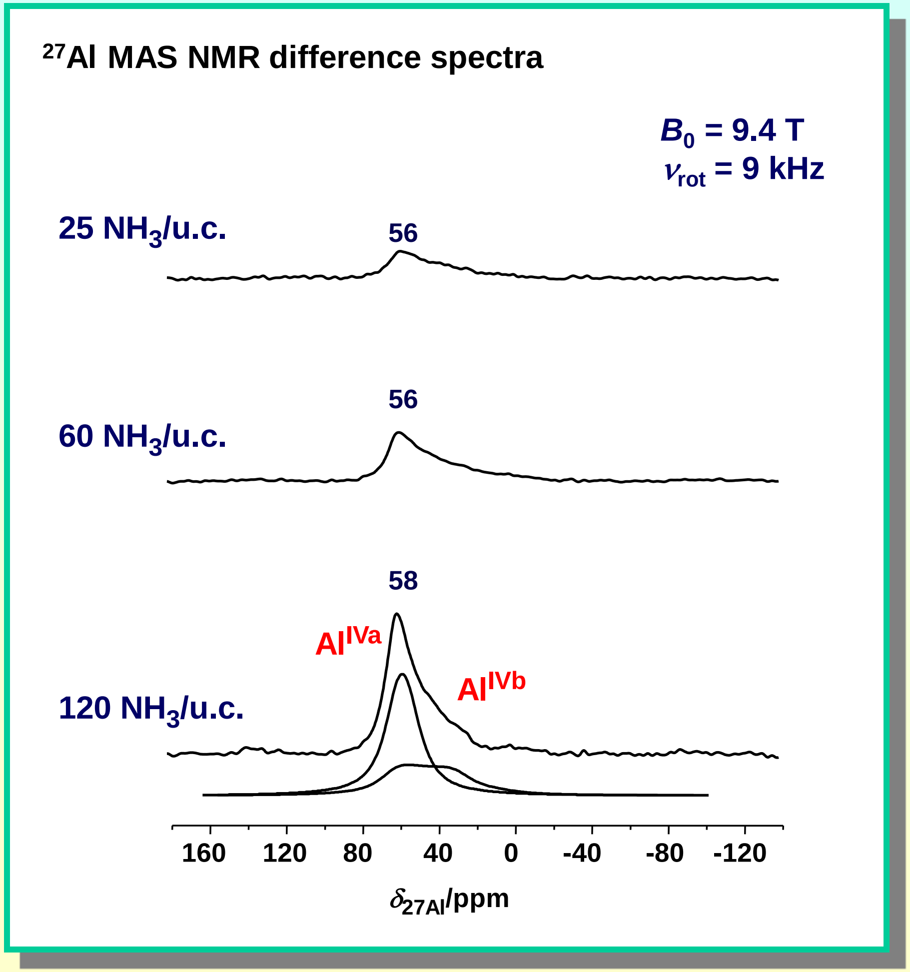




Effect of Adsorption Studied by ^{27}Al MAS NMR

- adsorption of H_2O and NH_3 on dehydrated zeolite deH,Na-Y/81.5

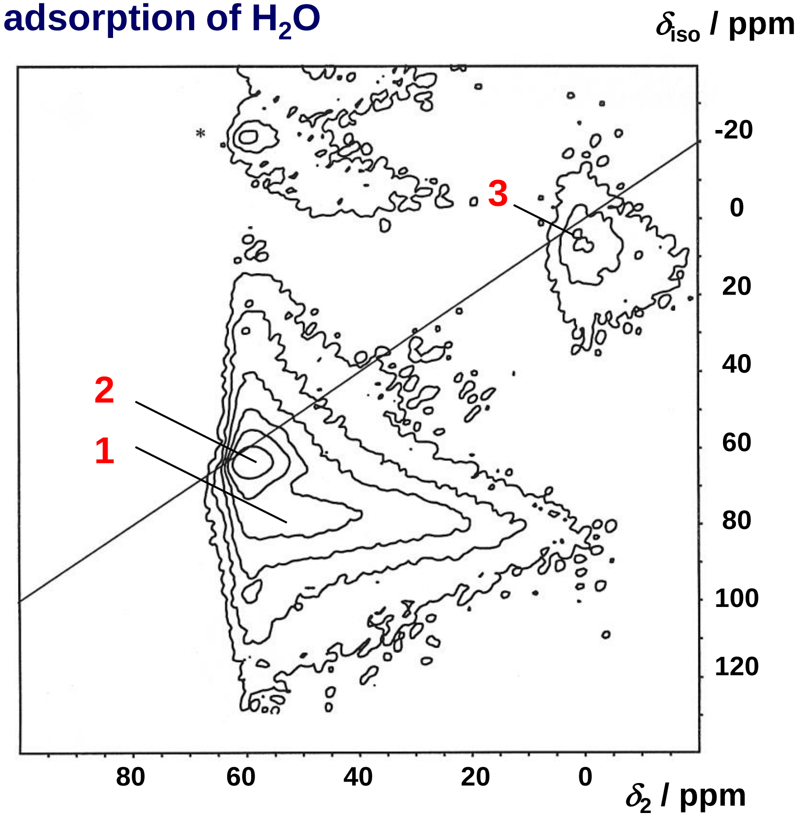




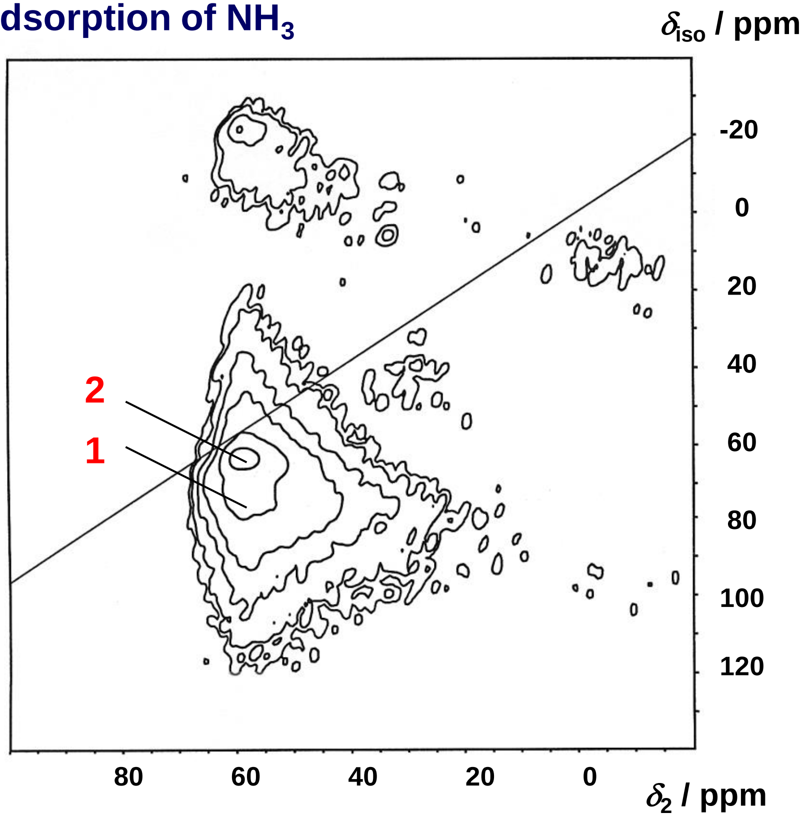
^{27}*Al MQMAS NMR of Zeolite deH,Na-Y*

- **MQMAS experiments at B_0 = 9.4 T, ν_{rot} = 9 kHz**

adsorption of H_2O



adsorption of NH_3



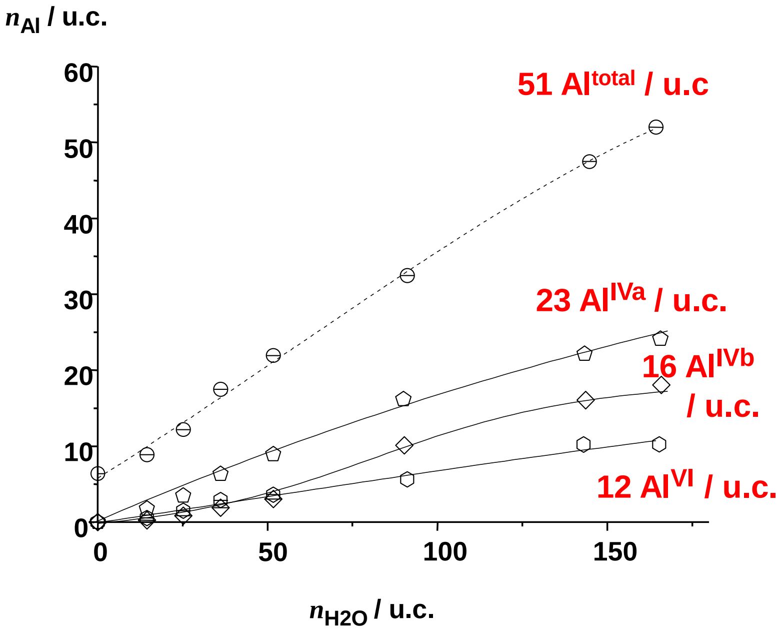
signal 1: δ_{iso} = 75 ppm, *SOQE* ca. 5.8 MHz
signal 2: δ_{iso} = 62 ppm, *SOQE* = 2.6 MHz
signal 3: δ_{iso} = 3 ppm, *SOQE* = 2.3 MHz

signal 1: δ_{iso} ca. 70 ppm, *SOQE* ca. 5.0 MHz
signal 2: δ_{iso} = 62 ppm, *SOQE* = 2.6 MHz

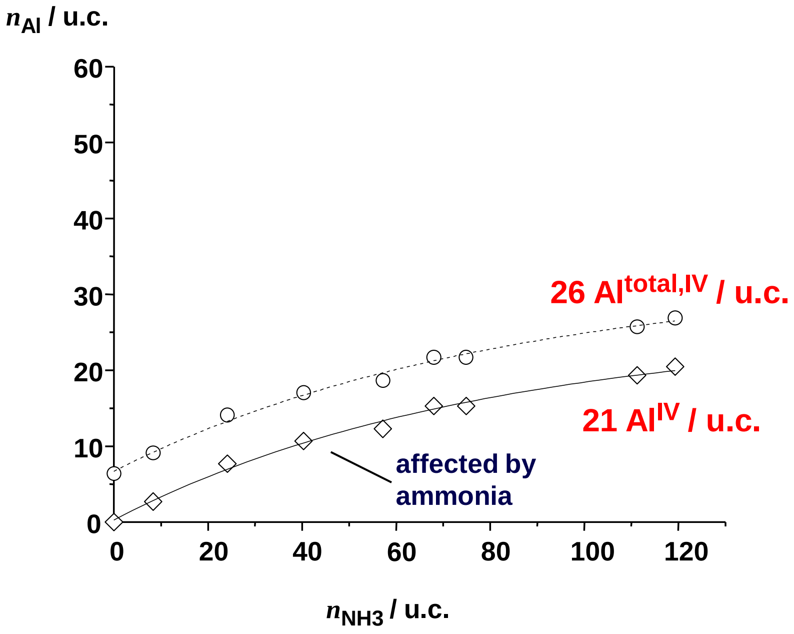
Effect of Adsorption Studied by ^{27}Al MAS NMR

- **adsorption of NH_3 and H_2O on non-hydrated deH,Na-Y/81.5**

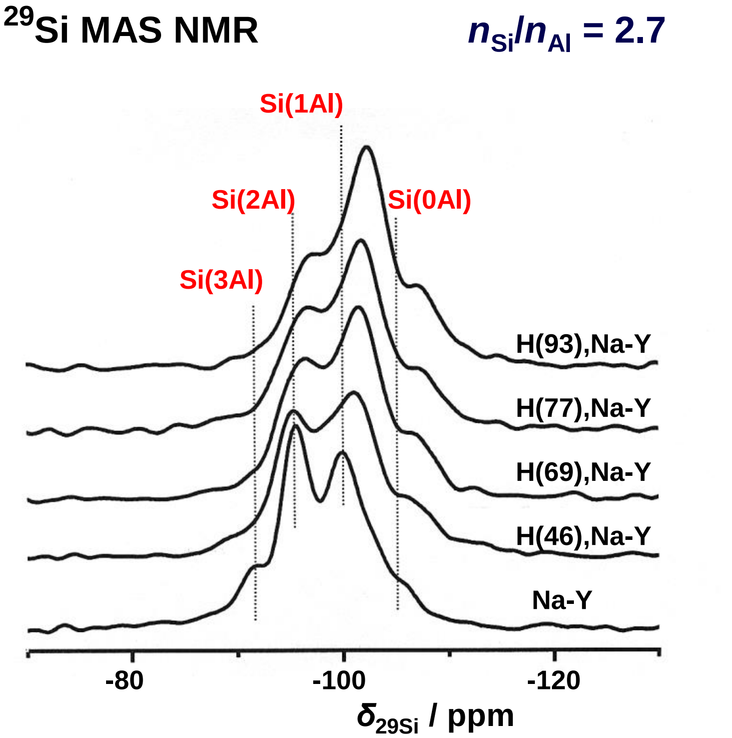
adsorption of H_2O



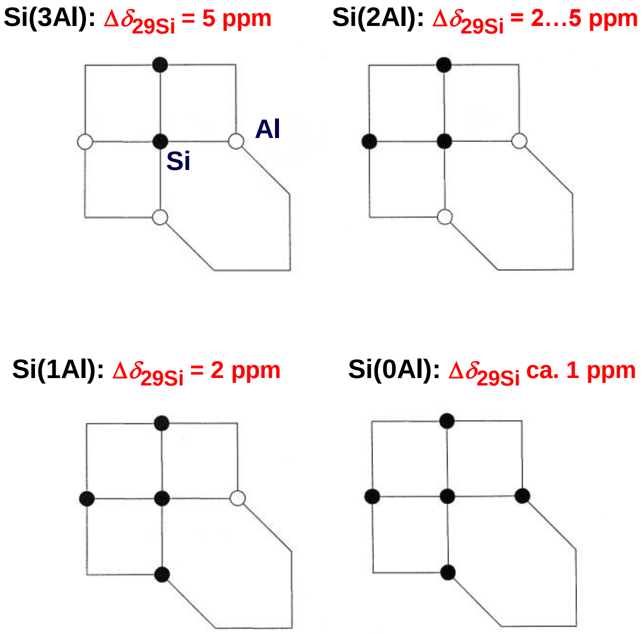
adsorption of NH_3



Strain of Si(nAl) Tetrahedra in Non-hydrated Zeolites

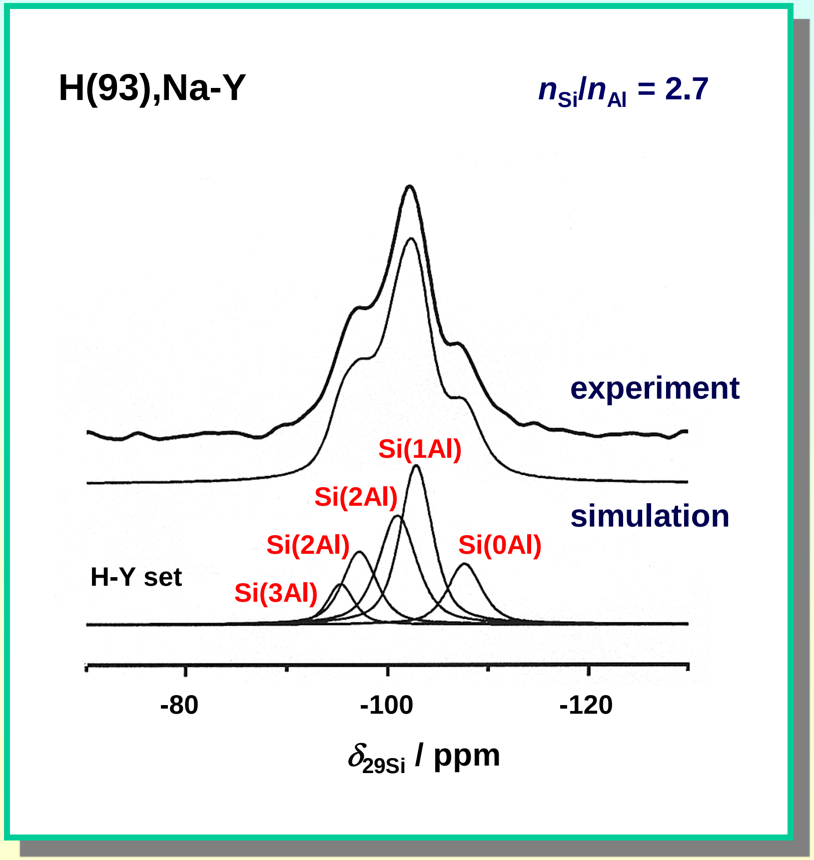


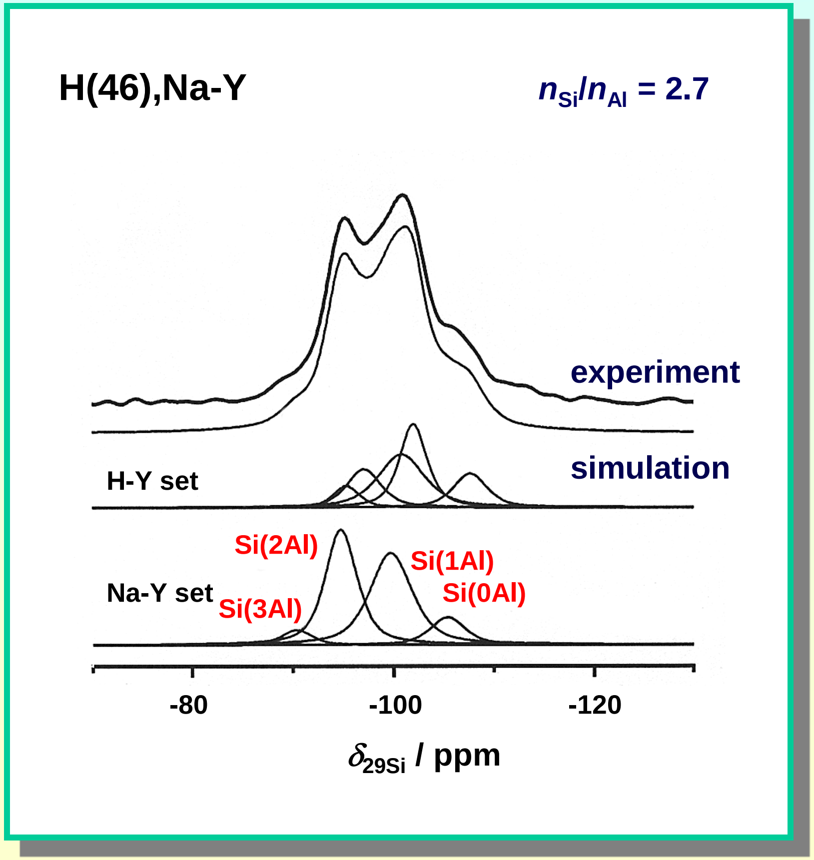
loop configuration of the FAU structure:



J. Jiao et al., Z. Anorg. Allg. Chem. 631 (2005) 484.

Simulation of ^{29}Si MAS NMR Spectra of Non-hydrated Zeolites

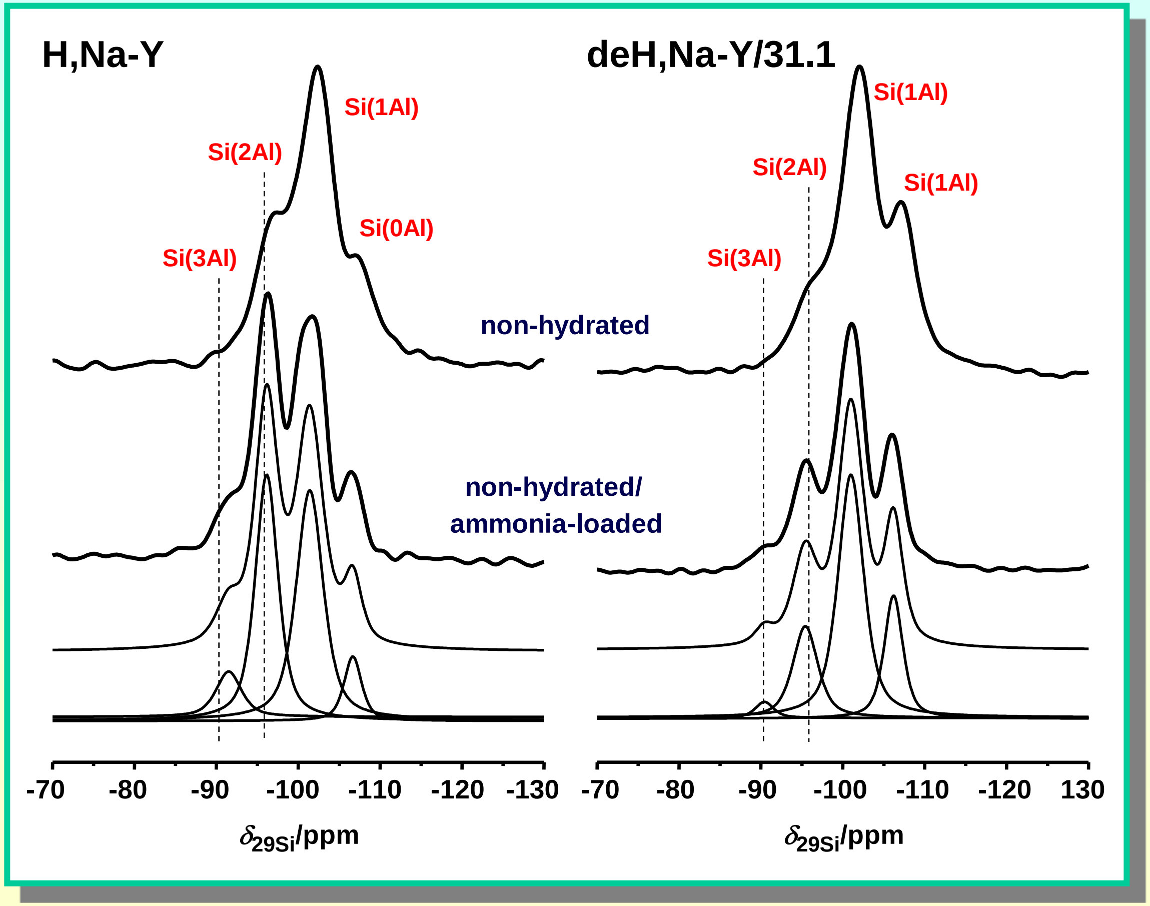




J. Jiao et al., Z. Anorg. Allg. Chem. 631 (2005) 484.

^{29}Si MAS NMR of Non-hydrated Zeolites upon Loading of Ammonia

- determination of the framework aluminum content after loading of ammonia



→ no high-field shift of the signals of Si(*n*Al) species upon loading of ammonia

→ relaxation of the local structure in the vicinity of SiO_4 tetrahedra upon loading of ammonia

J. Jiao et al., Microporous & Mesoporous Mater., accepted.

Comparison of ^{27}Al and ^{29}Si MAS NMR

- effect of the rehydration and ammonia-loading of non-hydrated zeolites Y

samples	framework n_{Si}/n_{Al} ratio, ^{27}Al MAS NMR	framework n_{Si}/n_{Al} ratio, ^{29}Si MAS NMR
H,Na-Y, rehydrated	3.6	2.8
H,Na-Y, non-hydrated/ ammonia-loaded	2.6	2.7
deH-Y/31.1, rehydrated	3.5	4.0
deH-Y/31.1, non-hydrated/ ammonia-loaded	3.8	3.8
deH-Y/81.5, rehydrated	3.8	5.9
deH-Y/81.5, non-hydrated/ ammonia-loaded	6.1	5.8

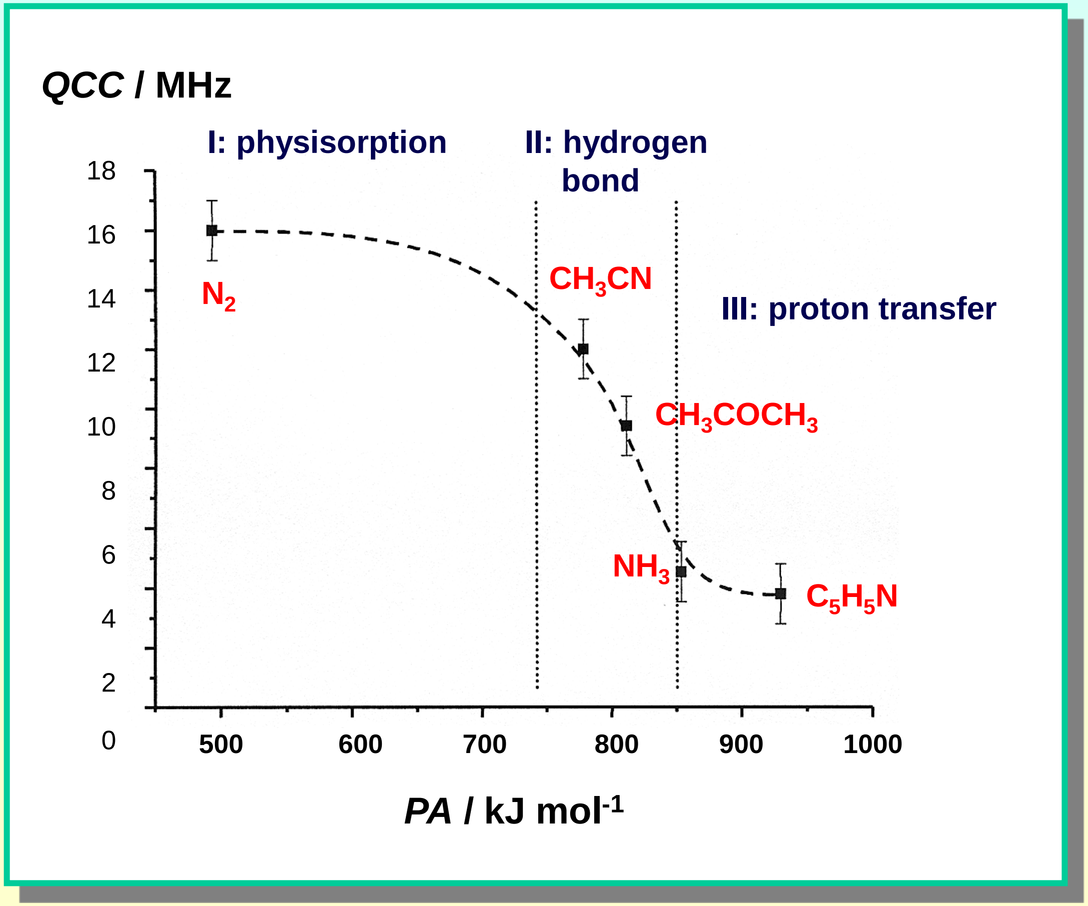
→ reasonable agreement of framework n_{Si}/n_{Al} ratios obtained for non-hydrated/ ammonia-loaded samples

→ slight hydrolysis of framework aluminum in rehydrated zeolites and overlap of signals

J. Jiao et al., Microporous & Mesoporous Mater., accepted.

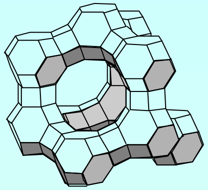
Effect of the base strength of adsorbates

- quadrupole coupling constant plotted as a function of the proton affinity *PA*



→ the *QCC* value of framework aluminum atoms in non-hydrated zeolite catalysts is sensitive to the adsorbate complexes formed at acid sites (SiOHAl)

→ proton transfer to adsorbate molecules occurs for proton affinities of *PA* $\geq$ 850 kJ/mol



II. Solid-state NMR Investigation of Extra-framework Aluminum Species in Non-hydrated Zeolites Y

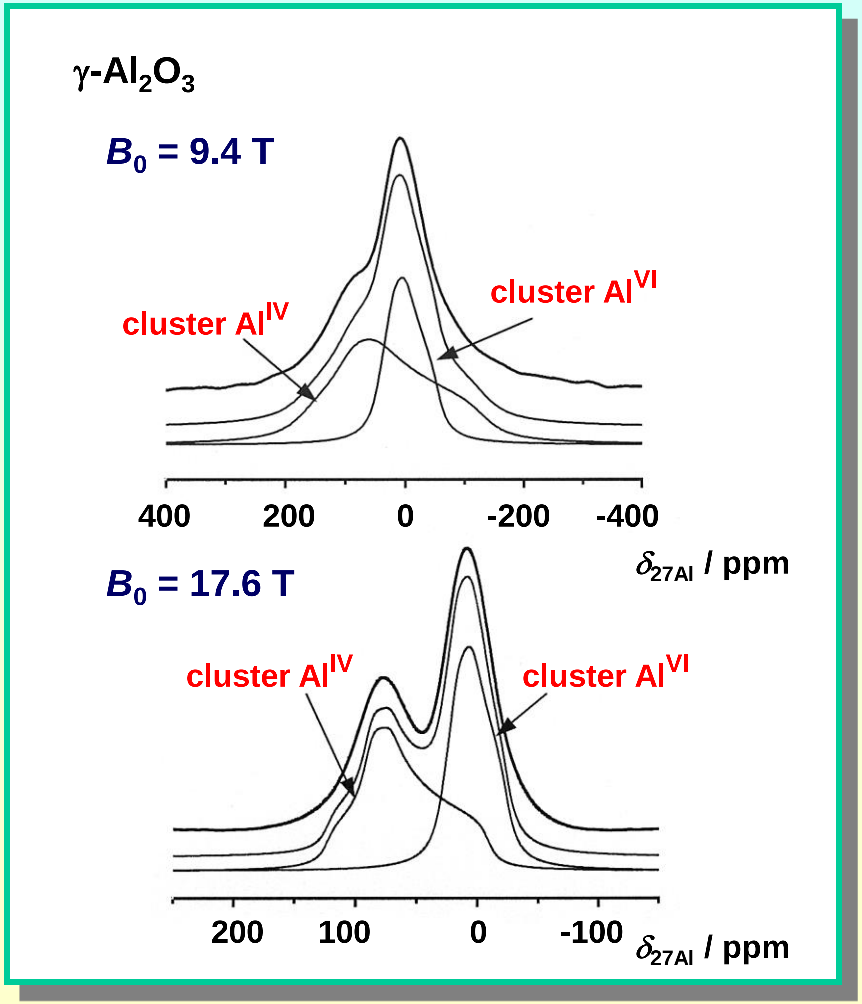
Characterization of the Aluminum Distribution in Zeolites Y

- **dealuminated zeolite (non-hydrated state):**
  - **zeolite H,Na-Y steamed at 475°C with a water vapor pressure of 81.5 kPa**
  - **framework n_{Si}/n_{Al} ratio of 5.8**

- **reference materials (dehydrated state):**
  - **parent zeolite H,Na-Y**
  - **zeolite Al,Na-Y with a cation exchange degree of 69 %**
  - **X-ray amorphous γ-Al_2O_3, specific surface area of 150 m^2/g**

- **spectroscopic methods:**
  - **^{27}Al spin-echo NMR at B_0 = 9.4, 14.1, and 17.6 T**
  - **^{27}Al high-speed MAS NMR at B_0 = 17.6 T with ν_{rot} = 30 kHz**
  - **^{27}Al MQMAS NMR at B_0 = 17.6 T, split-t_1 pulse sequence**

^{27}Al Spin-echo NMR Studies of Reference Materials

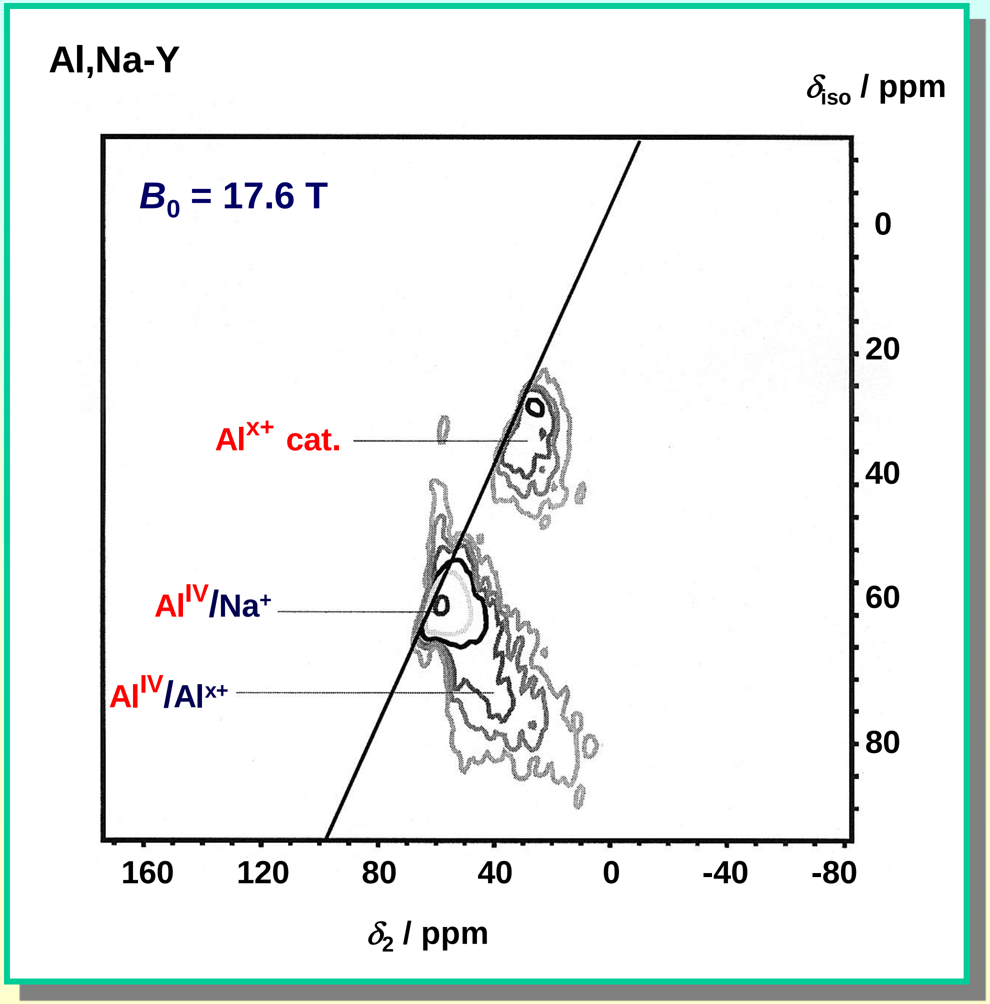


- **spectroscopic parameters of cluster Al^{IV}:**
  - **- *QCC* = 8.5 MHz, η = 0.8**
  - **- δ_{iso} = 68±5 ppm**
  - **- I_{rel} = 60 %**

- **spectroscopic parameters of cluster Al^{VI}:**
  - **- *QCC* = 5.5 MHz, η = 0.7**
  - **- δ_{iso} = 12±5 ppm**
  - **- I_{rel} = 40 %**

J. Jiao et al., Phys. Chem. Chem. Phys., accepted.

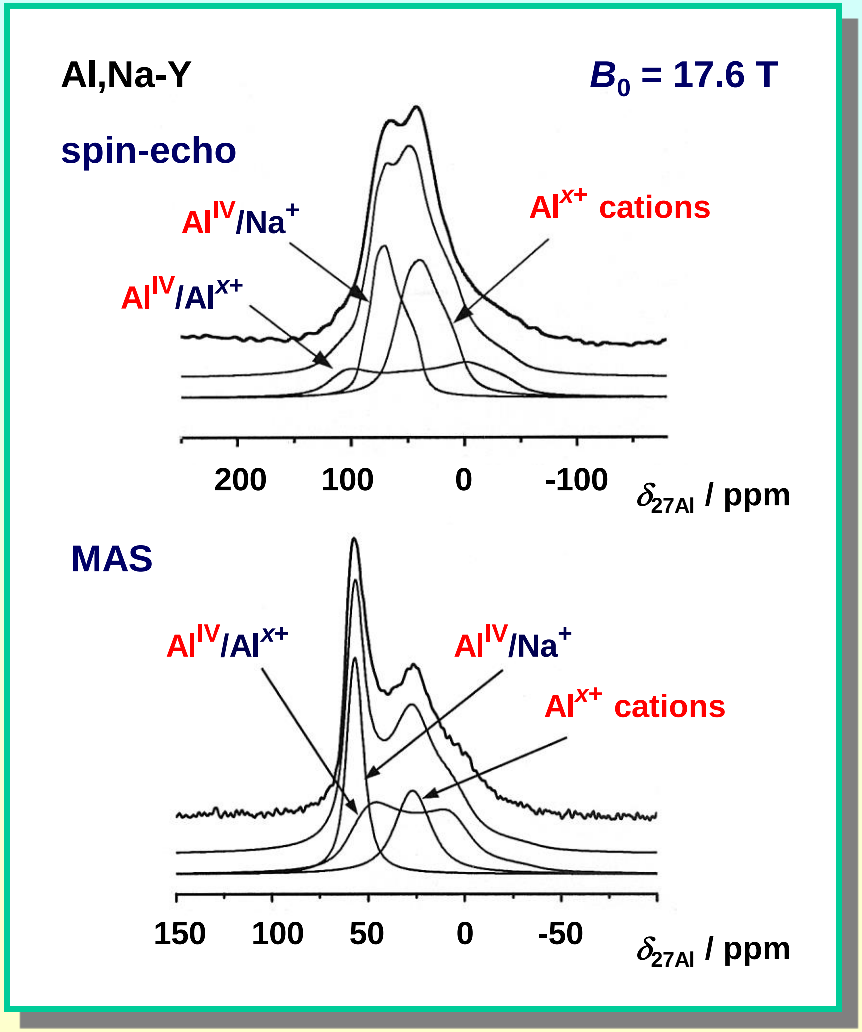
^{27}Al MQMAS NMR Studies of Reference Materials



- parameters of signal Al^{x+} cations:
  - *SOQE* = 6.0 MHz
  - δ_{iso} = 35±5 ppm
- parameters of signal Al^{IV}/Na^+:
  - *SOQE* = 5.5 MHz
  - δ_{iso} = 60±5 ppm
- parameters of signal Al^{IV}/Al^{x+}:
  - *SOQE* = 14.5 MHz
  - δ_{iso} = 70±5 ppm

J. Jiao et al., Phys. Chem. Chem. Phys., accepted.

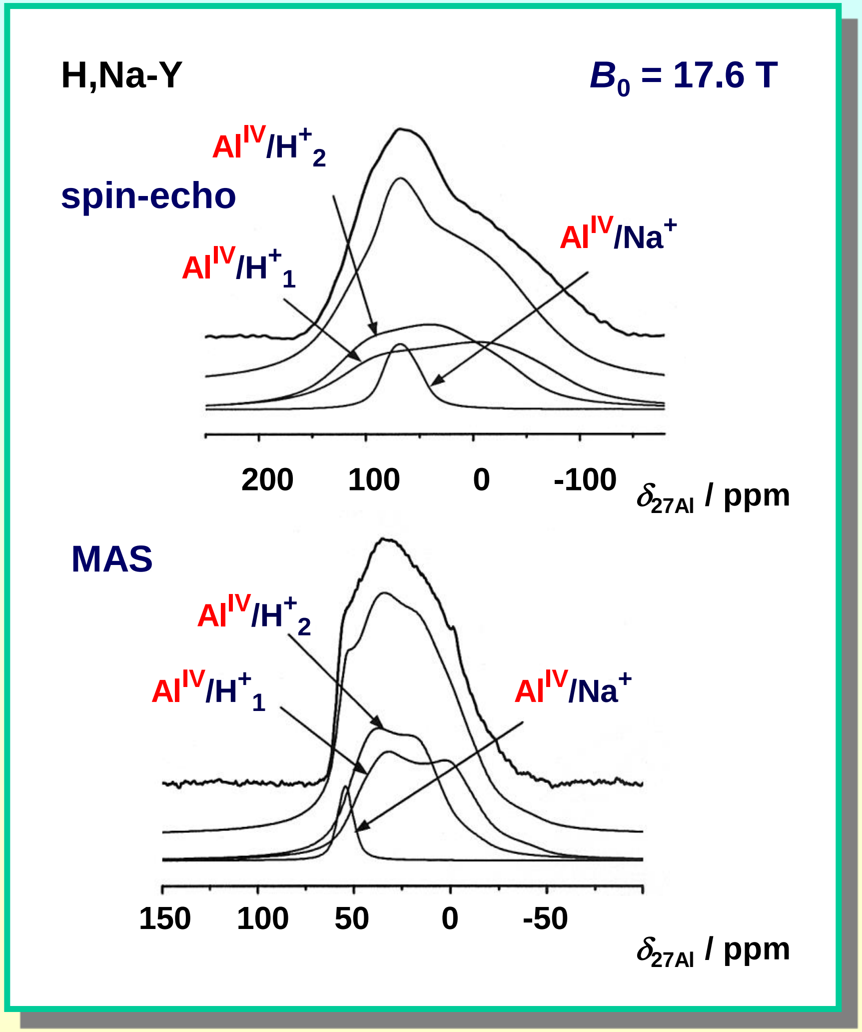
^{27}Al Solid-state NMR Studies of Reference Materials



- parameters of signal Al^{x+} cat.:
  - *QCC* = 6.0 MHz, η = 0.7
  - δ_{iso} = 35±5 ppm
  - I_{rel} = 24 %
- parameters of signal Al^{IV}/Na^+:
  - *QCC* = 5.5 MHz, η = 0.8
  - δ_{iso} = 60±5 ppm
  - I_{rel} = 28 %
- parameters of signal Al^{IV}/Al^{x+}:
  - *QCC* = 14.5 MHz, η = 0.3
  - δ_{iso} = 70±5 ppm
  - I_{rel} = 48 %

J. Jiao et al., Phys. Chem. Chem. Phys., accepted.

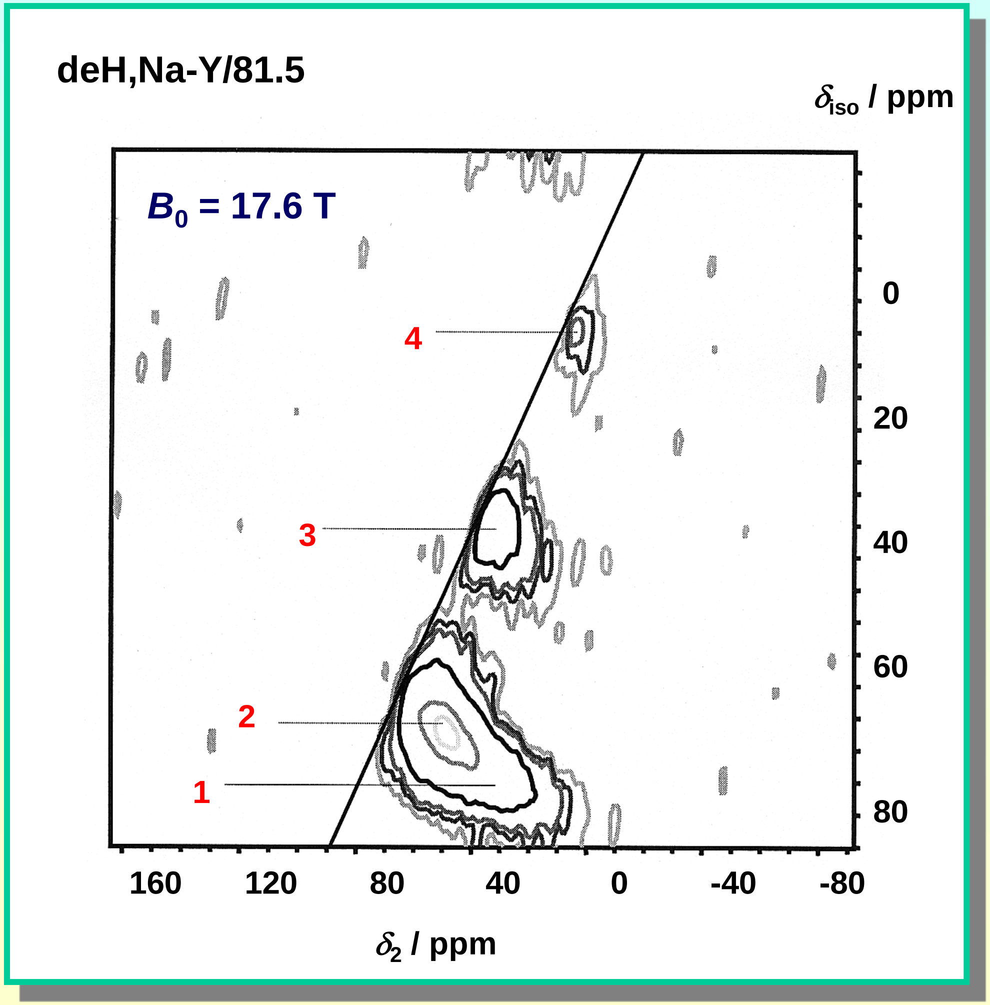
^{27}Al Solid-state NMR Studies of Reference Materials



- **parameters of signal Al^{IV}/Na^+:**
  - **- *QCC* = 5.5 MHz, η = 0.8**
  - **- δ_{iso} = 60±5 ppm**
  - **- I_{rel} = 6 %**
- **parameters of signal Al^{IV}/H^+_1:**
  - **- *QCC* = 16.0 MHz, η = 0.3**
  - **- δ_{iso} = 70±10 ppm**
  - **- I_{rel} = 47 %**
- **parameters of signal Al^{IV}/H^+_2:**
  - **- *QCC* = 14.0 MHz, η = 0.3**
  - **- δ_{iso} = 70±10 ppm**
  - **- I_{rel} = 47 %**

J. Jiao et al., Phys. Chem. Chem. Phys., accepted.

^{27}Al MQMAS NMR Studies of Dealuminated Zeolite Y



- parameters of signal 1:
  - $SOQE$ = 15.0±1.0 MHz
  - δ_{iso} = 70±10 ppm

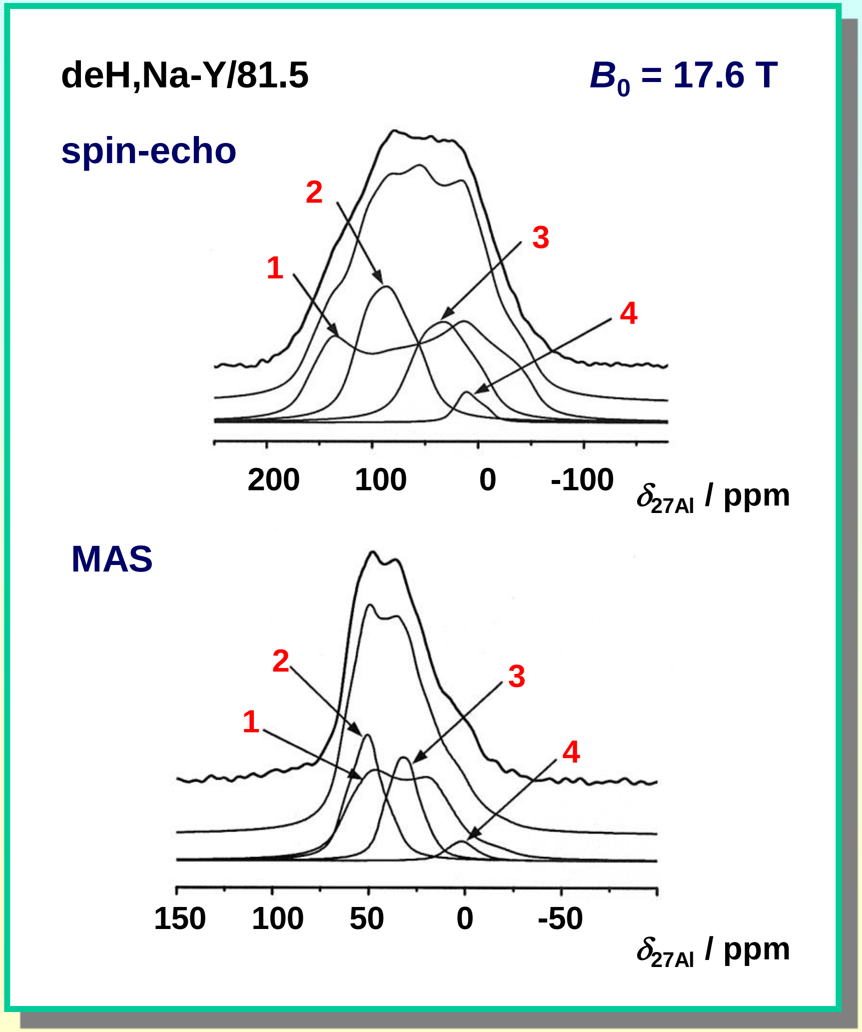
- parameters of signal 2:
  - $SOQE$ = 8.0±0.5 MHz
  - δ_{iso} = 65±5 ppm

- parameters of signal 3:
  - $SOQE$ = 7.5±0.5 MHz
  - δ_{iso} = 35±5 ppm

- parameters of signal 4:
  - $SOQE$ = 5.0±0.5 MHz
  - δ_{iso} = 10±5 ppm

J. Jiao et al., Phys. Chem. Chem. Phys., accepted.

^{27}Al Solid-state NMR Studies of Dealuminated Zeolite Y



- signal 1 (70 ppm, *QCC*: 15 MHz):
  - Al^{IV}/H^+: 17 SiOHAl/u.c.
  - Al^{IV}/Al^{x+}: 8 Al/u.c.
- signal 2 (65 ppm, *QCC*: 8 MHz):
  - Al^{IV}/Na^+: 4 Al/u.c.
  - cluster Al^{IV}: 10 Al/u.c.
- signal 3 (35 ppm, *QCC*: 7.5 MHz):
  - Al^{x+} cations: 11 Al/u.c.
- signal 4 (10 ppm, *QCC*: 5 MHz):
  - cluster Al^{VI}: 2 Al/u.c.

J. Jiao et al., Phys. Chem. Chem. Phys., accepted.

Summary

NMR characterization of steamed zeolites Y in the non-hydrated state:

- adorption of ammonia on non-hydrated zeolites leads to a selective narrowing of the ^{27}Al MAS NMR signals of framework aluminum atoms and well-resolved ^{29}Si MAS NMR spectra allowing the determination of the framework n_{Si}/n_{Al} ratio

- hydration of calcined and steamed zeolites with high aluminum contents is accompanied by a partial hydrolysis of framework aluminum atoms

- application of ^{27}Al spin-echo, high-speed MAS, and MQMAS NMR of steamed zeolite Y allow to separate up to four signals:
  - superposition of Al^{IV}/H^+ and Al^{IV}/Al^{x+} species (70 ppm, *QCC*: 15 MHz)
  - superposition of Al^{IV}/Na^+ and cluster Al^{IV} species (65 ppm, *QCC*: 8 MHz)
  - Al^{x+} cations (35 ppm, *QCC*: 7.5 MHz)
  - cluster Al^{VI} species (10 ppm, *QCC*: 5 MHz)

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