Solid-state NMR characterization of Broensted acid sites in solid catalysts

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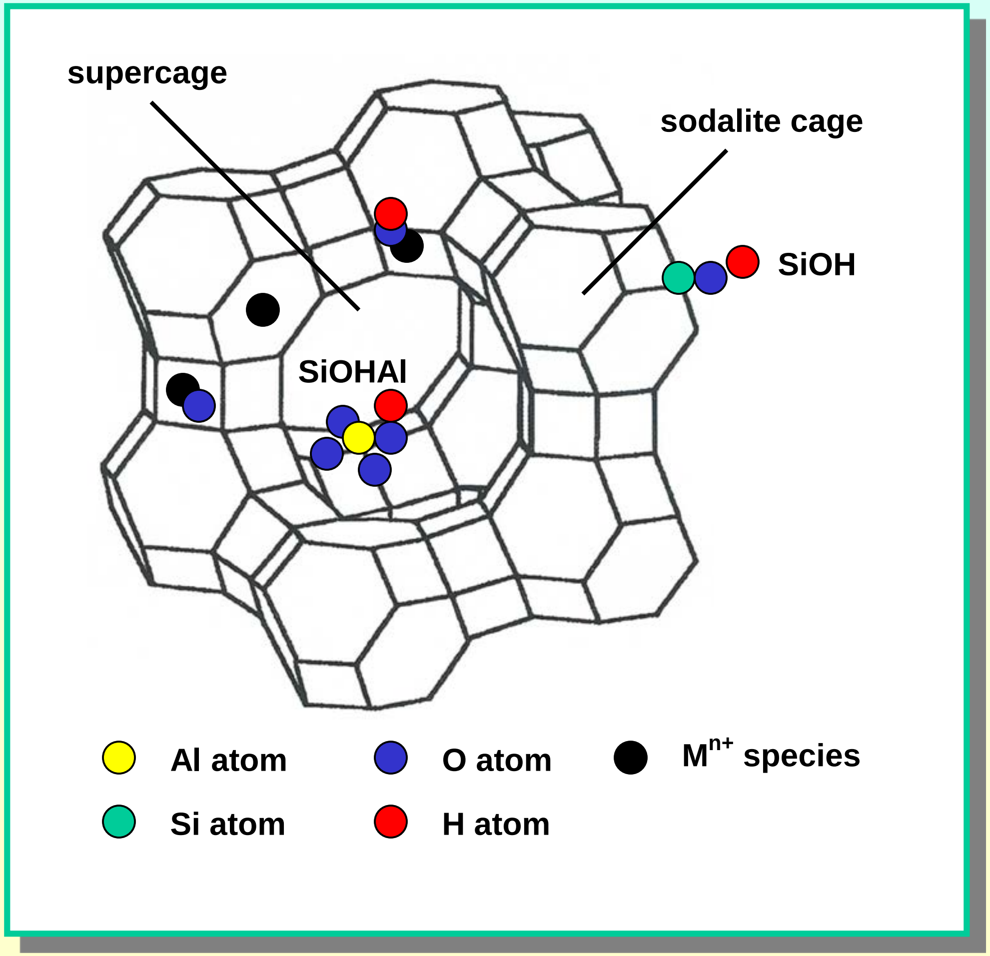
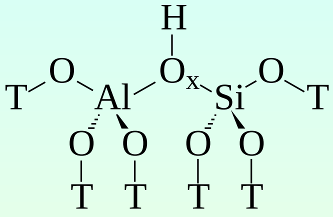
Different types of OH groups in zeolites

- **structure of zeolite Y (FAU: faujasite):**



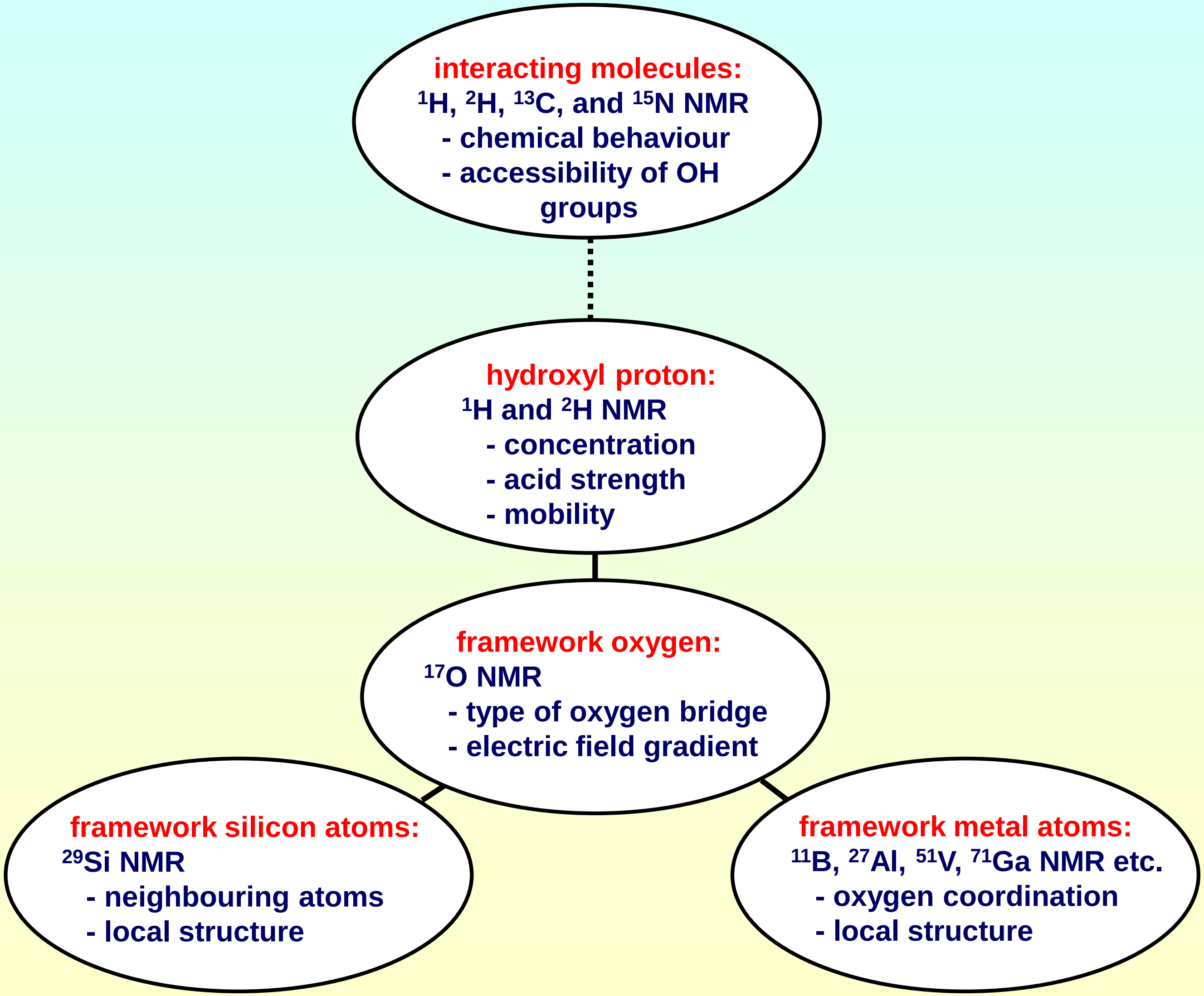
- **Broensted acid sites:**



bridging OH group, SiOHAl

- **results of modification:**
  - **- formation of OH groups at multivalent cations, $M^{n+}(OH)_x$**
  - **- dehydroxylation of SiOHAl groups**
  - **- formation of OH groups at extra-framework species**
  - **- formation of defect sites, SiOH**

Resonances available for NMR of Broensted acid sites



interacting molecules:
^{1}H, ^{2}H, ^{13}C, and ^{15}N NMR
- chemical behaviour
- accessibility of OH groups

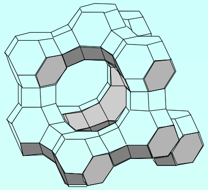
hydroxyl proton:
^{1}H and ^{2}H NMR
- concentration
- acid strength
- mobility

framework oxygen:
^{17}O NMR
- type of oxygen bridge
- electric field gradient

framework silicon atoms:
^{29}Si NMR
- neighbouring atoms
- local structure

framework metal atoms:
^{11}B, ^{27}Al, ^{51}V, ^{71}Ga NMR etc.
- oxygen coordination
- local structure

Contents



1. Experimental techniques of NMR on Broensted acid sites

Origin of line broadening in solid-state ^{1}H NMR

- **Hamiltonians of the magnetic interactions of spins $I = 1/2$:**

$$H_{\text{total}} = H_0 + H_{\text{DI}} + H_{\text{CS}} + H_{\text{J}}$$

H_0 : Zeeman interaction $\gamma \cdot h \cdot I_z \cdot B_0$ of nuclear spins I in the external magnetic field B_0 $\nu_0 \leq 10^9$ s^{-1}

H_{DI} : dipolar interaction with the magnetic dipole moments of nuclei in their vicinity $\nu_{\text{DI}} \leq 5 \times 10^4$ s^{-1}

$$H_{\text{hetero.DI}} = \gamma_i \gamma_k \hbar^2 \frac{\mu_0}{4\pi} \frac{1}{r_{ik}^3} \left(\frac{1 - 3\cos^2 \beta_{ik}}{2} \right) I_{\text{zi}} I_{\text{zk}}$$

- vector between interacting nuclei i and k: r_{ik}

- angle between B_0 and r_{IS}: β_{ik}

H_{CS} : shielding interaction caused by the electron shell around the resonating nuclei $\nu_{\text{CS}} \leq 5 \times 10^3$ s^{-1}

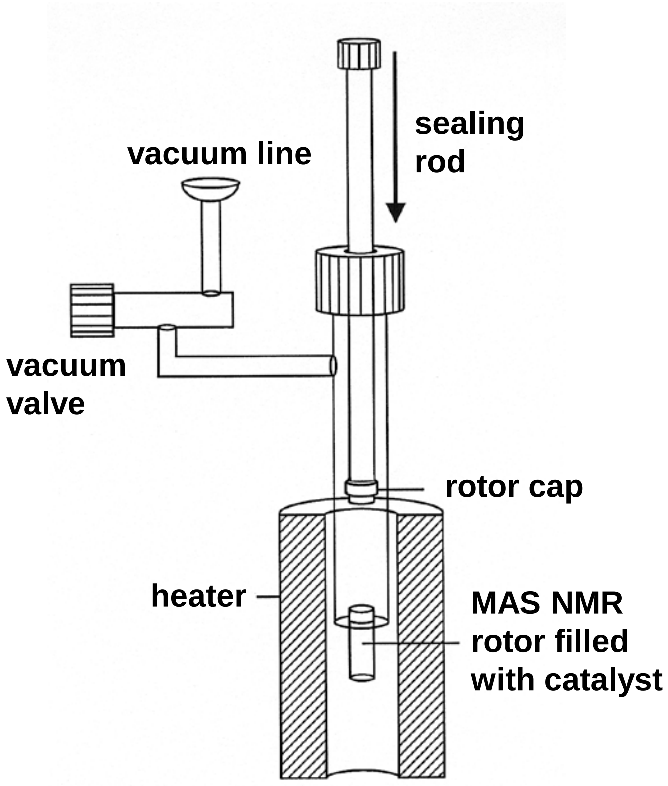
H_{J} : indirect or J-coupling of nuclei via their bond electrons

$\nu_{\text{J}} \leq 5 \times 10^2$ s^{-1}

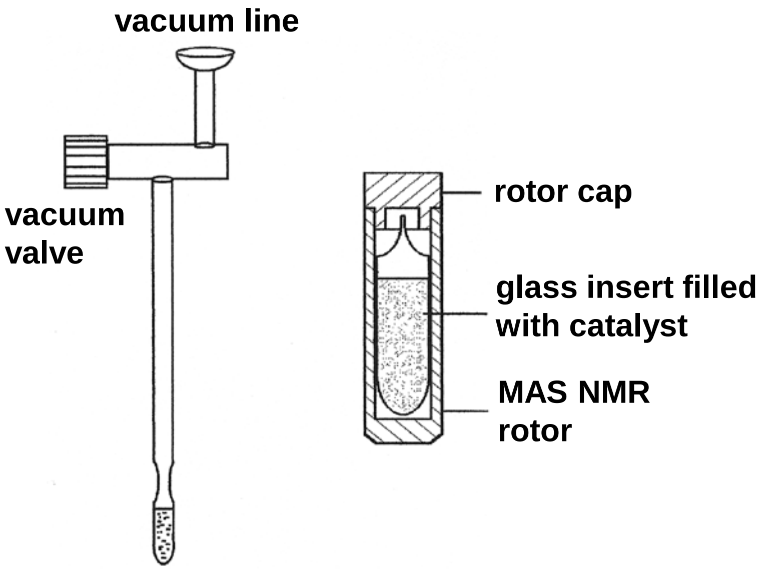
Handling of dehydrated catalysts in MAS NMR

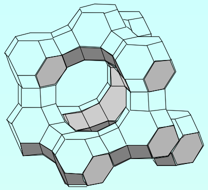
- **study of activated samples requires exclusion of rehydration**

equipment for *in situ* dehydration and sealing of samples inside the MAS NMR rotor



dehydration of catalysts inside of glass inserts (e.g. commercial Wilmad MAS NMR inserts for 4 mm and 7 mm rotors)

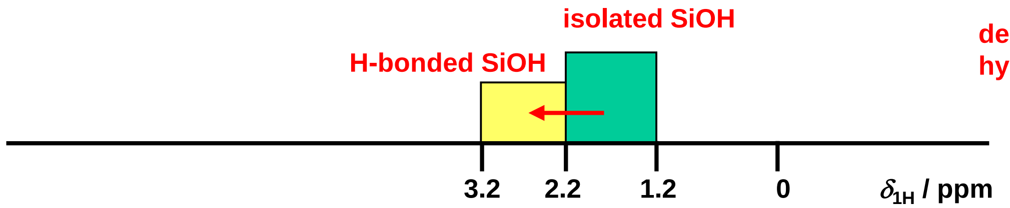




2. Assignment of surface OH groups

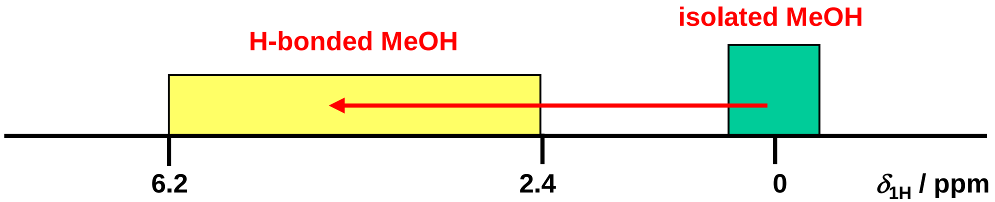
Shift ranges of ^{1}H MAS NMR signals of OH groups

- **silanol groups (SiOH) at lattice defects and on the outer surface**

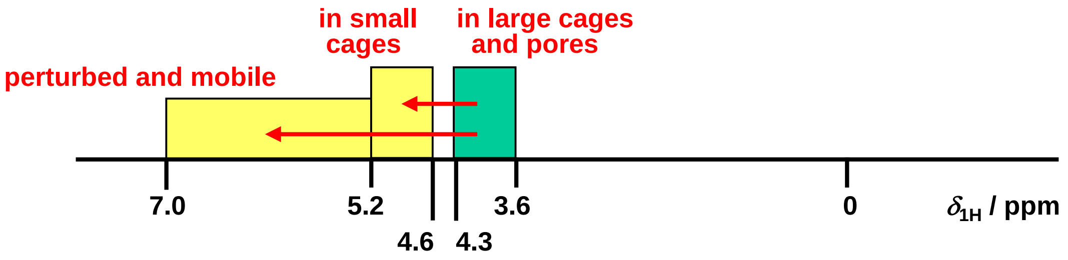


deshielding effect of hydrogen bonding

- **metal OH groups (MeOH), e.g. $MgOH^+$, $CaOH^+$, $AlOH^{2+}$, $LaOH^{2+}$, etc.**



- **bridging OH groups (SiOHAl)**



Correlation of OH-O distance and shift

- **dependence of the low-field shift $\Delta\delta_{1H}$ on the OH-O distance $d_{OH\text{-}O}$**

$$\Delta\delta_{1H} \,/\, \mathrm{ppm} = 79.05 - 0.255\, d_{OH\text{-}O} \,/\, \mathrm{pm}$$

J.P. Yesinowski, H. Eckert, J. Am. Chem. Soc. 109 (1987) 6274

CaOH groups in the sodalite cages of zeolite Ca,Na-Y:

- OH-O distance of $d_{OH\text{-}O}$ = 0.297 nm to the next nearest framework oxygen atom
- calculated low-field shift of $\Delta\delta_{1H}$ = 3.3 ppm agrees with the experimental value of 2.8 to 3.2 ppm

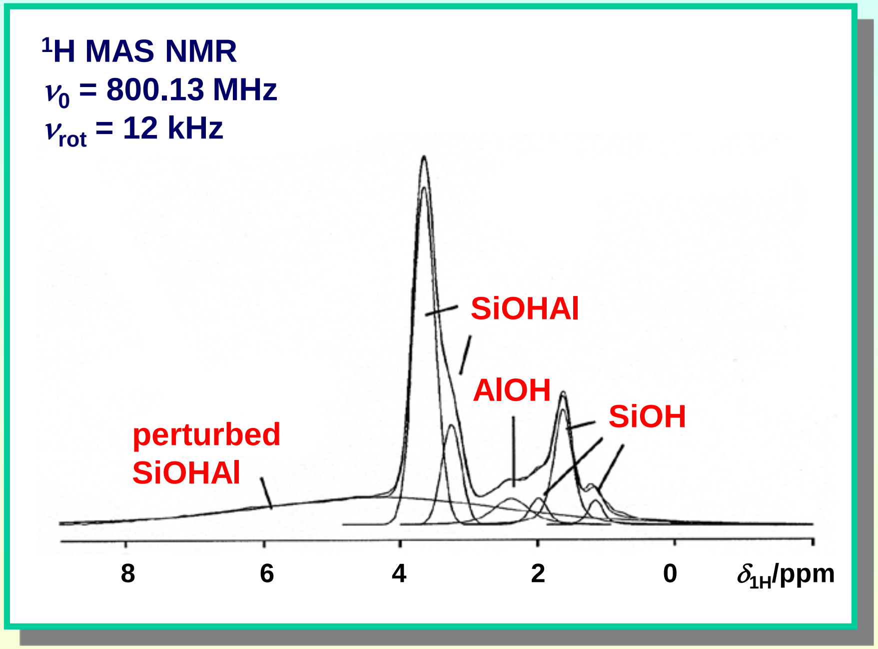
LaOH groups in the sodalite cages of zeolite La,Na-Y:

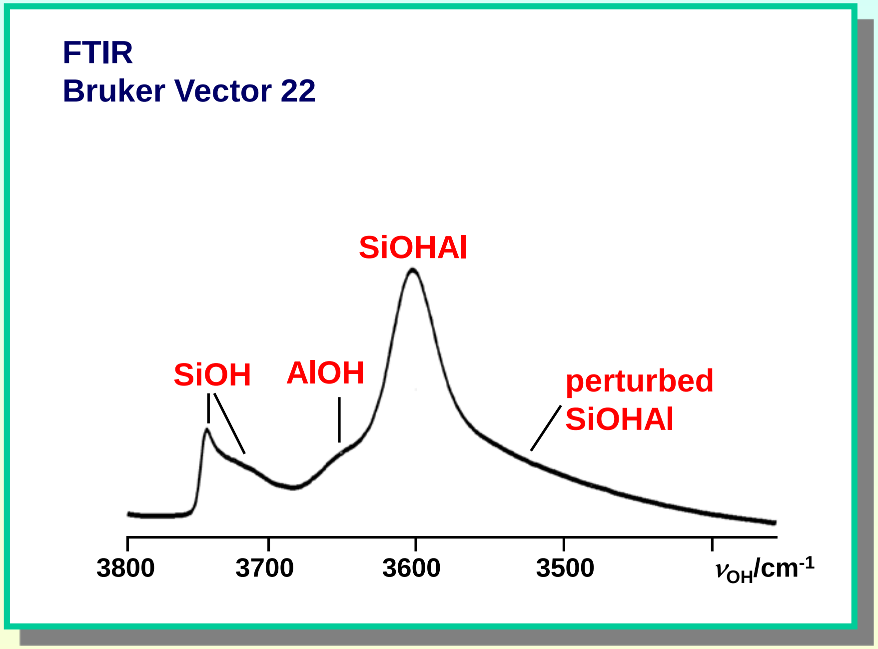
- experimental low-field shift of $\Delta\delta_{1H}$ = 5.6 ppm gives an OH-O distance of $d_{OH\text{-}O}$ = 0.288 nm

M. Hunger, Catal. Rev.-Sci. Eng. 39 (1997) 345.

Comparison of ^{1}H MAS NMR and FTIR spectroscopy

- **resolution of ^{1}H MAS NMR and FTIR spectra of dehydrated zeolite H-ZSM-5 (n_{Si}/n_{Al} = 20)**





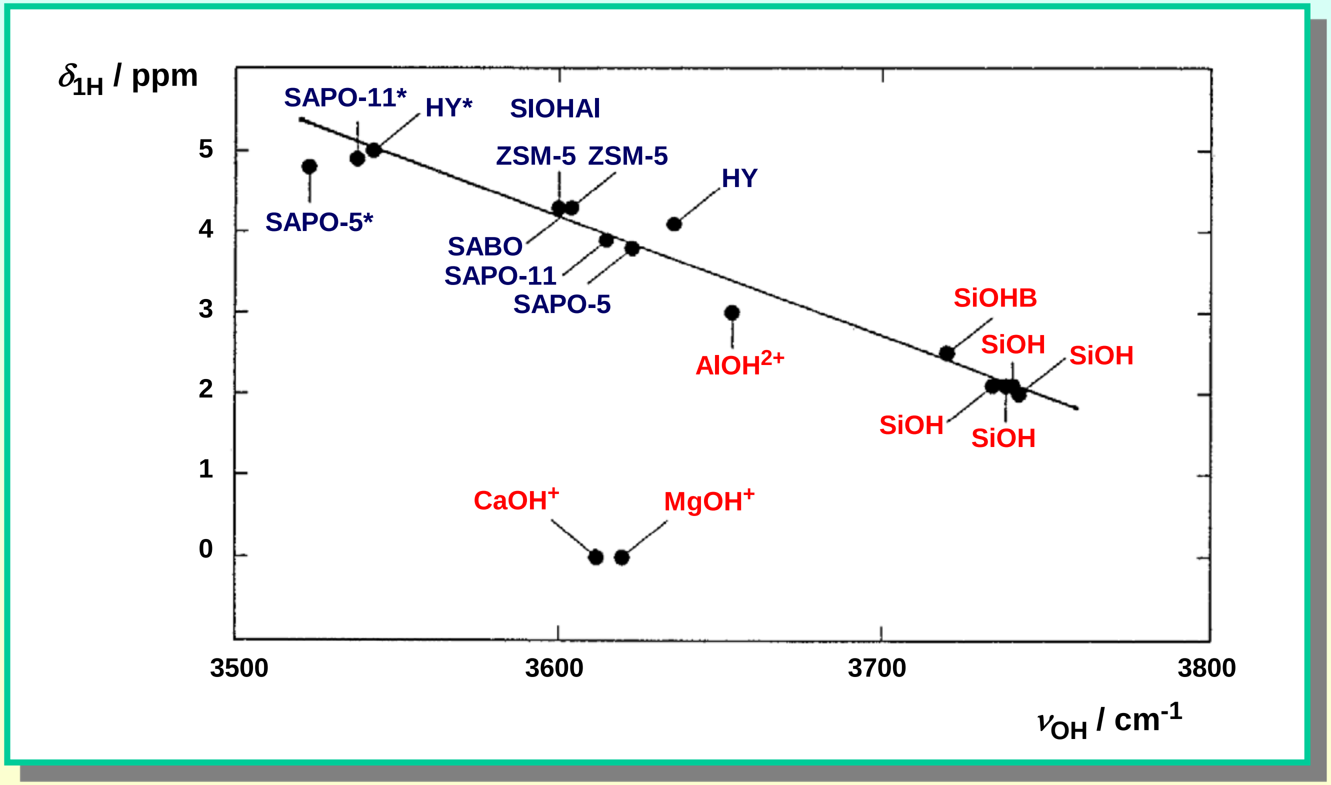
- **residual ^{1}H MAS NMR linewidths:**

SiOH $\Delta\nu_{1/2}$ = 200 - 400 Hz
AlOH $\Delta\nu_{1/2}$ = 500 - 600 Hz
SiOHAl $\Delta\nu_{1/2}$ = 200 - 450 Hz
SiOHAl^{pert} $\Delta\nu_{1/2}$ = 2500 - 3500 Hz

M. Hunger et al., Microporous Mater. 6 (1996) 349.

Comparison of ^{1}H MAS NMR and FTIR spectroscopy

- plot of shifts δ_{1H} and wavenumbers ν_{OH} of bridging and metal OH groups in zeolites



asterisks indicate small cages or pores

E. Brunner, H.G. Karge, H. Pfeifer, Z. Phys. Chem. 176 (1992) 173.

Correlation of ^{1}H MAS NMR and FTIR

- relationship between ^{1}H NMR shift δ_{1H} and stretching vibration mode ν_{OH} of isolated OH groups in zeolites

$$\delta_{1H} \,/\, \text{ppm} = 57.1 - 0.0147\ \nu_{OH} \,/\, \text{cm}^{-1}$$

and for hydrogen bonded OH groups*

$$\delta_{1H} \,/\, \text{ppm} = 37.9 - 0.0092\ \nu_{OH} \,/\, \text{cm}^{-1}$$

type of OH group	ν_{OH} / cm^{-1}	calc. δ_{1H} / ppm	exp. δ_{1H} / ppm
SiOH	3740	2.1	1.8
AlOH*	3654	4.2	3.0
SiOHB	3720	2.4	2.5
SiOHAl	3640	3.6	3.6

E. Brunner, H.G. Karge, H. Pfeifer, Z. Phys. Chem. 176 (1992) 173.

Comparison of FTIR and ^{1}H MAS NMR

- advantages of FTIR:

  - high sensitivity
  - lower costs
  - better separation of bands shifted due to hydrogen bonding

- advantages of ^{1}H MAS NMR:

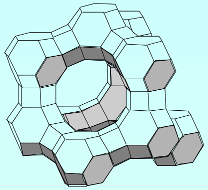
  - easy sample preparation
  - no problems with particel sizes
  - direct determination of OH concentration by intensities *)

*) determination of OH concentration by ^{1}H MAS NMR:

- measurement of the intensity of the material under study (I_{OH}) and of an external reference (I_{ref}) with identical parameters (number of scans, receiver gain etc.),
- determination of the weight of the dehydrated sample (m_{OH}) inside to MAS NMR rotor,
- calculation of the OH concentration according to:

$$(n_{OH} / \mathrm{g}) = (n_{ref} / \mathrm{g}) \times (m_{ref} / m_{OH}) \times (I_{OH} / I_{ref})$$

reference: e.g. dehydrated zeolite 35H,Na-Y with weight m_{ref} and n_{ref} hydroxyl groups per g

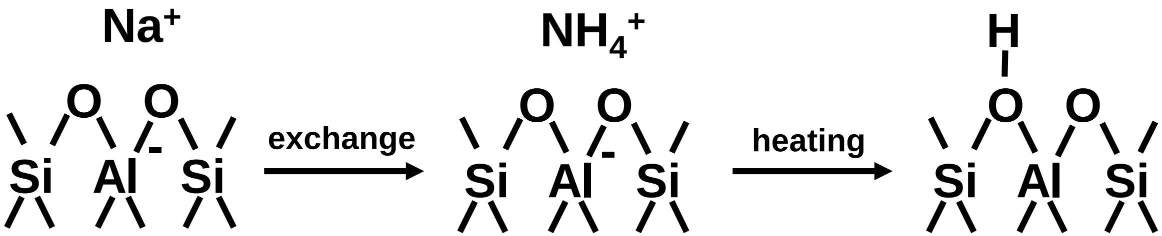


3. Formation of OH groups and their dehydroxylation

Preparation of OH groups via the NH_4-form

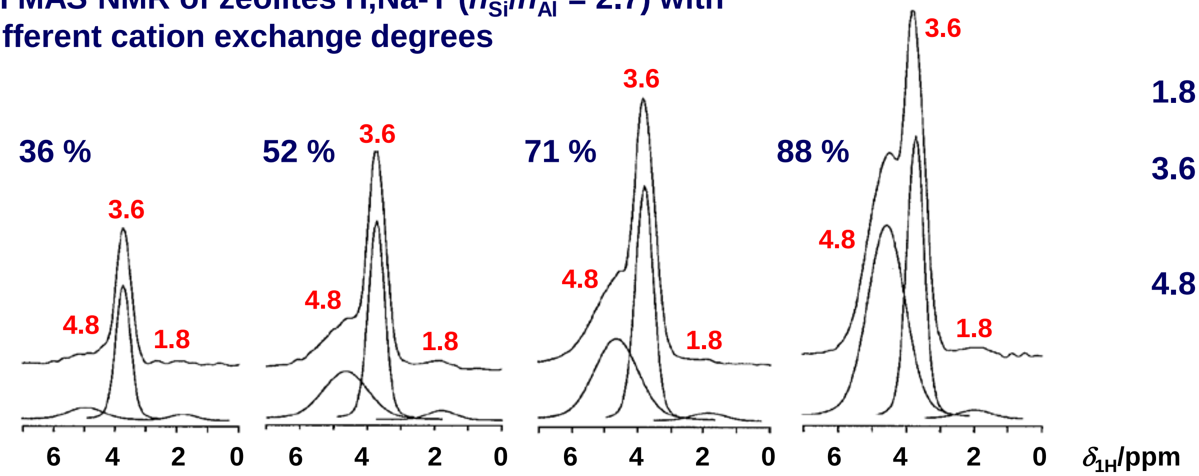
commercial zeolite Na-Y (n_{Si}/n_{Al} = 2.7) → **ammonium exchange e.g. 1.0 M NH_4NO_3** → **NH_4,Na-Y**

→ **calcination at ca. 400°C flowing nitrogen (100 ml/min) or vacuum $p < 10^{-2}$ Pa** → **zeolites H,Na-Y SiOHAl groups in different cages**



Preparation of OH groups via the NH_4-form

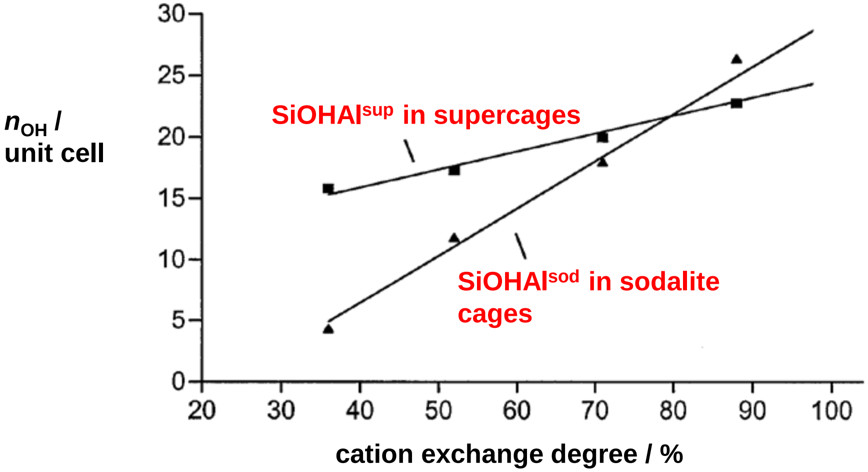
^1H MAS NMR of zeolites H,Na-Y (n_{Si}/n_{Al} = 2.7) with different cation exchange degrees



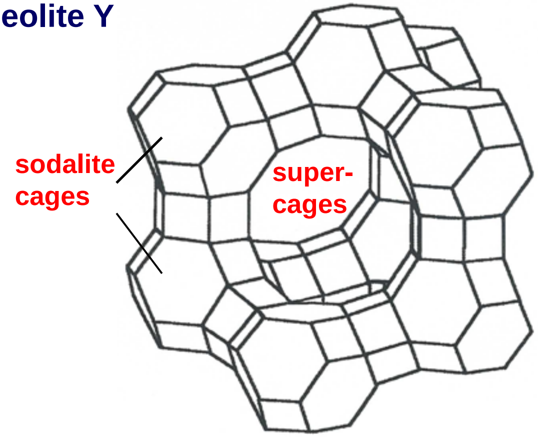
1.8 ppm: SiOH, outer surface

3.6 ppm: $SiOHAl^{sup}$ in supercages

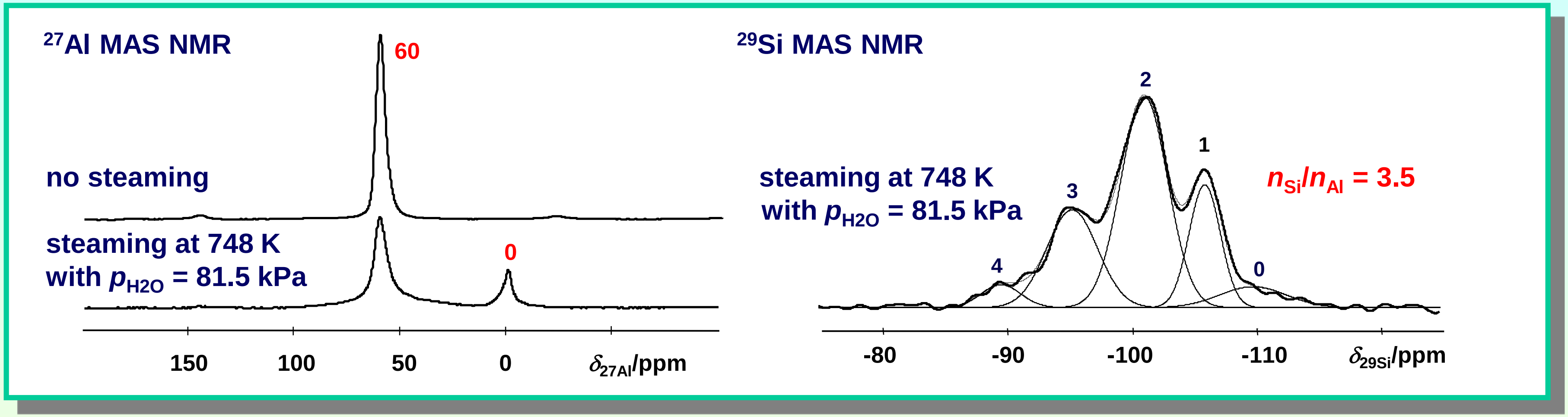
4.8 ppm: $SiOHAl^{sod}$ in sodalite cages

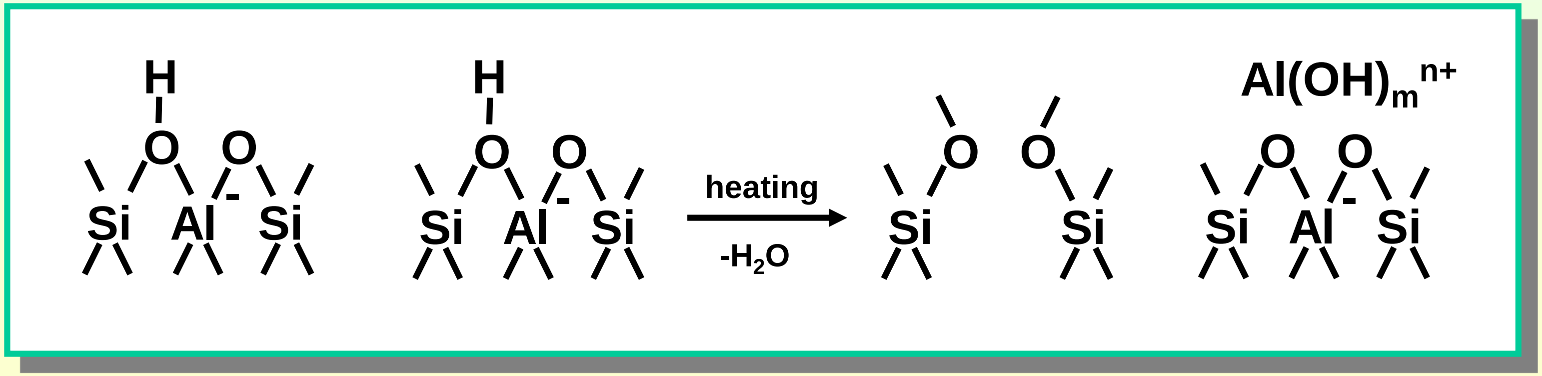


zeolite Y



Dealumination of zeolites H,Na-Y





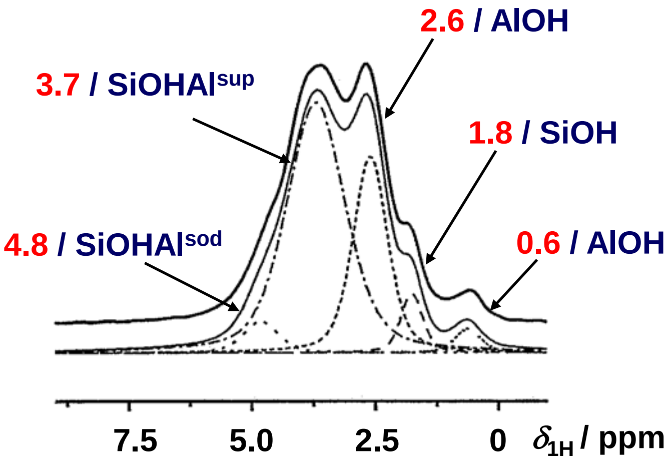
→ **dehydroxylation is accompanied by strong dealumination, strong modification of the acidity or damage of the framework**

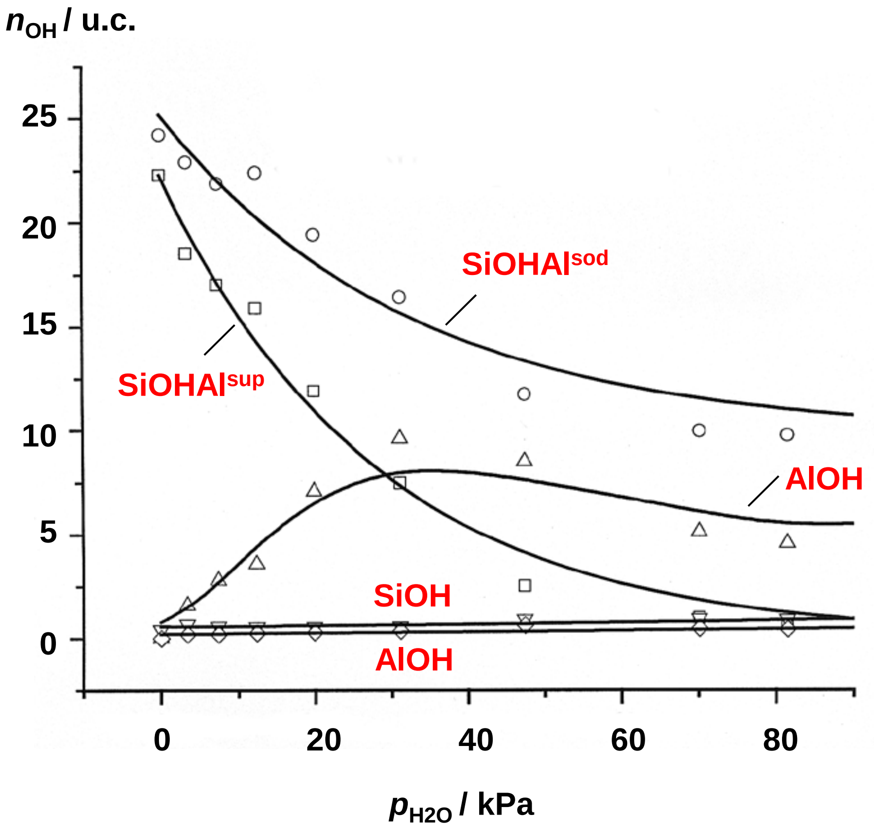
Dealumination of zeolites H,Na-Y

- ^{1}H MAS NMR study of zeolites H,Na-Y dehydroxylated by steaming

at 748 K with water vapor pressures of 3.4 to 81.5 kPa for 2 h

^{1}H MAS NMR of deH,Na-Y steamed with p_{H2O} = 81.5 kPa



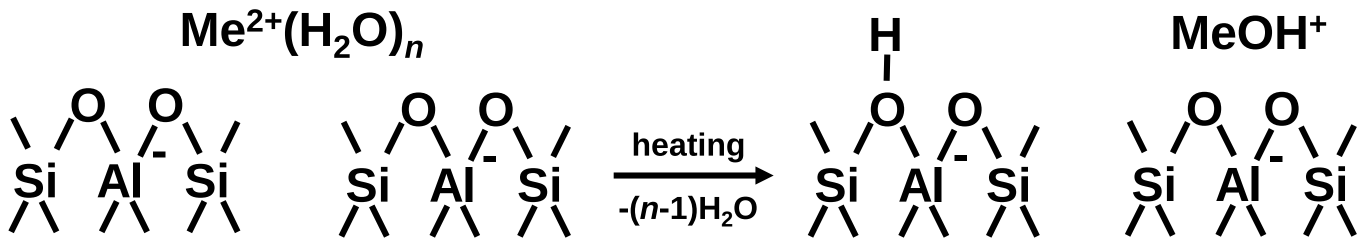


J. Jiao et al., J. Phys. Chem B. 108 (2004) 14305.

Preparation via the Hirschler-Plank mechanism

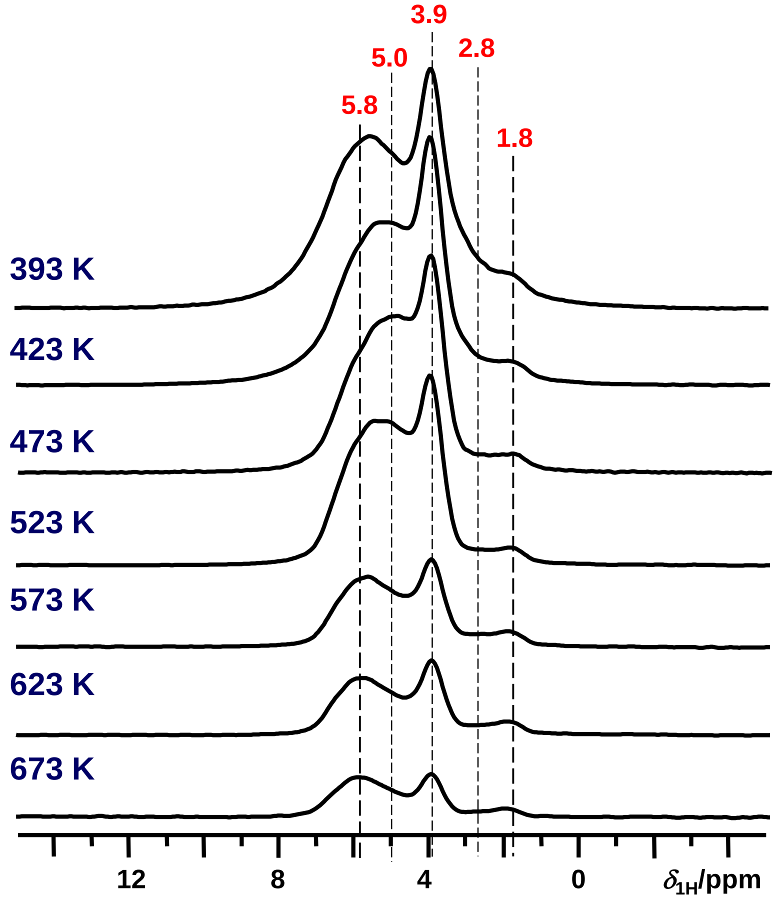
commercial zeolite Na-Y (n_{Si}/n_{Al} = 2.7) → **exchange with multi-valent cation Me^{n+}** → **Me,Na-Y**

→ **dehydration at 200-400°C**
flowing nitrogen (100 ml/min)
or vacuum $p < 10^{-2}$ Pa → **zeolites H,Me,Na-Y**
SiOHAl and MeOH groups
in different cages

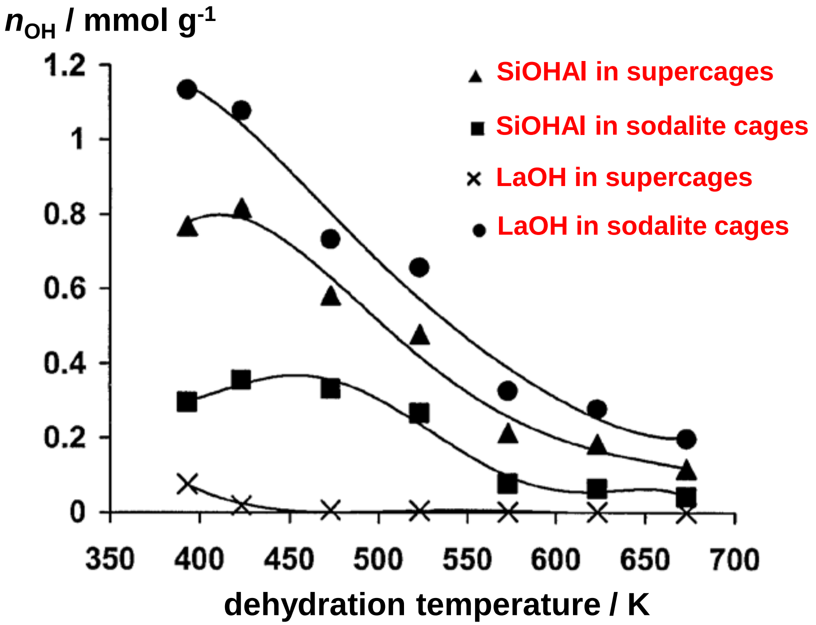


Preparation via the Hirschler-Plank mechanism

^{1}H MAS NMR of zeolite La,Na-Y/74 (n_{Si}/n_{Al} = 2.7) upon dehydration at 393 to 673 K



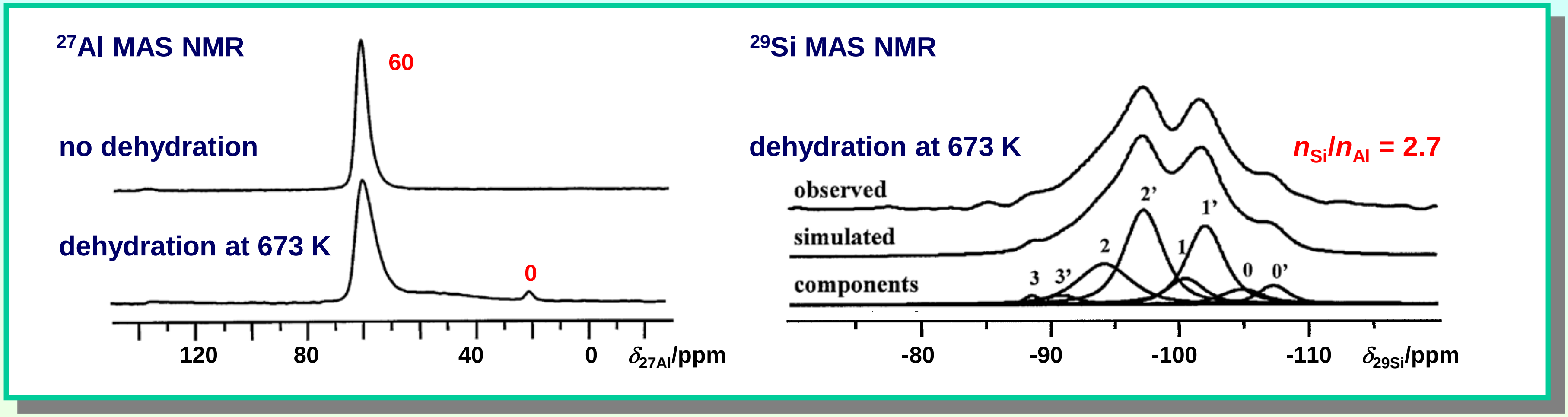
hydroxyl coverage of zeolite La,Na-Y/74 (n_{Si}/n_{Al} = 2.7) upon dehydration at 393 to 673 K

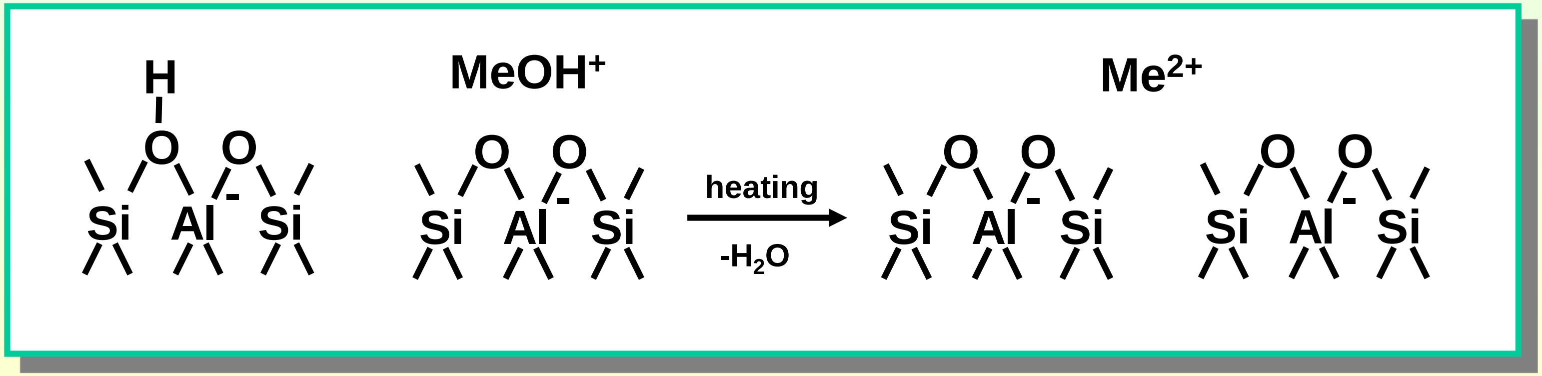


→ **recombination of hydroxyl groups to water**

J. Huang et al., Microporous Mesoporous Mater. 104 (2007) 129.

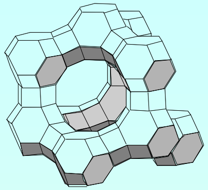
Dehydroxylation of zeolite La,Na-Y/74





→ **only a negligible dealumination occurs during dehydroxylation, the Hirschler-Plank mechanism is a reversible process**

J. Huang et al., Microporous Mesoporous Mater. 104 (2007) 129.

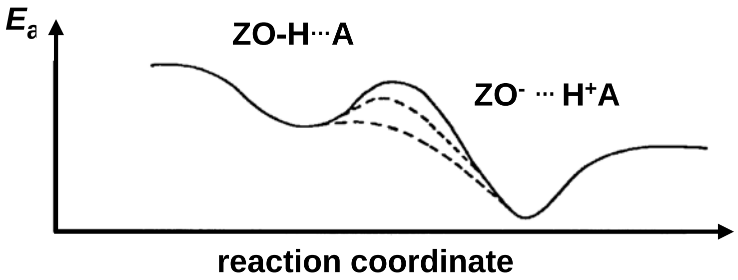


4. Characterization of the acid strength of surface OH groups

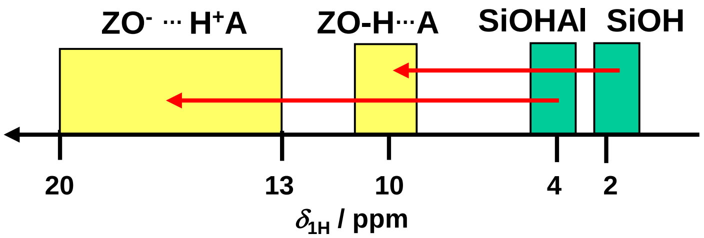
Acid strength of OH groups on solid catalysts

- characterization of acid strength *via* proton transfer or H-bond formation

energy profile of proton transfer reactions



^{1}H NMR shift of OH groups upon pyridine (A) adsorption



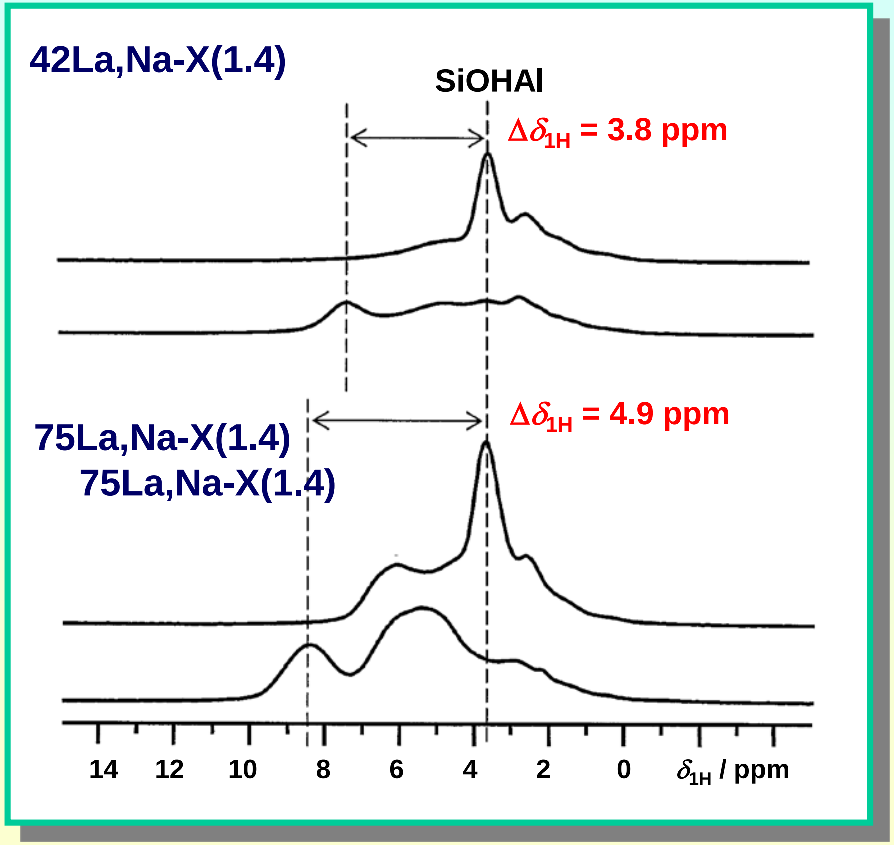
low-field shift $\Delta\delta_{1H}$ of the ^{1}H MAS NMR signal of SiOHAl groups upon adsorption of acetonitrile (CD_3CN):

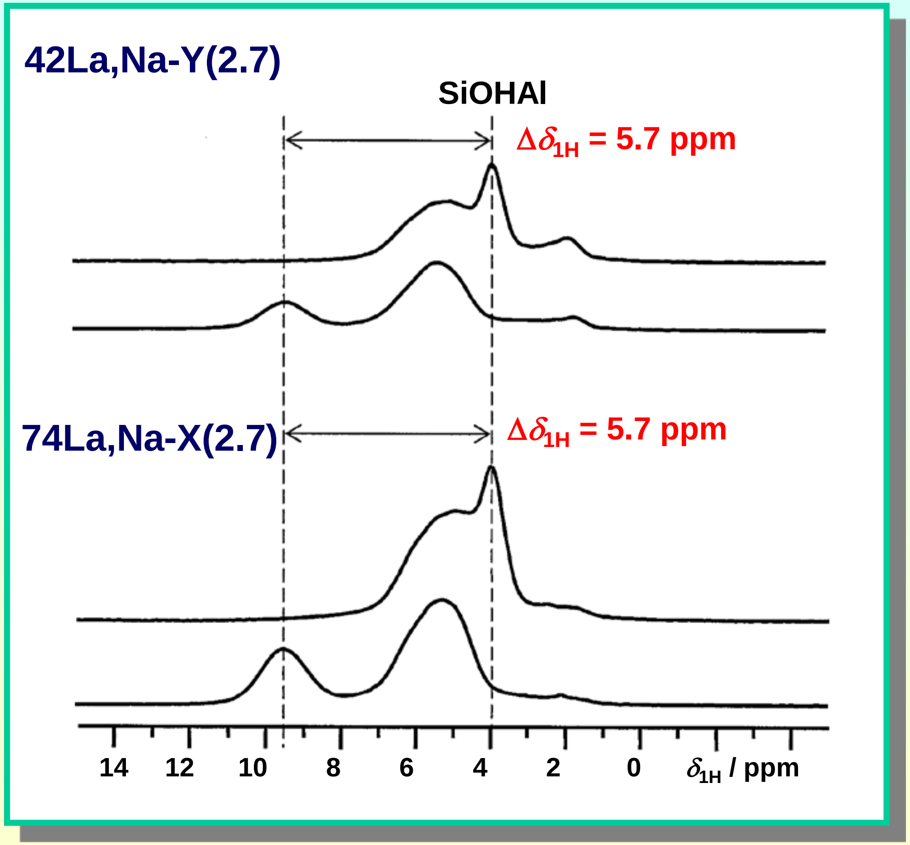
sample	$\Delta\delta_{1H}$ / ppm
H-ZSM-5 (52)	7.1
H-Y(18)	7.0
H-MOR (10)	6.7
H-MOR (6.7)	6.2
H-Y (5)	6.4

J. Jaenchen et al., Catal. Lett. 39 (1996) 147.

Adsorption of CD_3CN on zeolites La,Na-X and La,Na-Y

- **characterization of acid strength via H-bond-induced low-field shift $\Delta\delta_{1H}$**





→ **acid strength: 42La,Na-X(1.4) < 75La,Na-X(1.4) < 42La,Na-Y(2.7) = 75La,Na-Y(2.7)**

J. Huang et al., Microporous Mesoporous Mater., in press.

Correlation of the resonance position of non-interacting OH groups and low-field shift $\Delta\delta_{1H}$

- calculation of the deprotonation energy *via* the resonance position of isolated OH

$$\Delta E \;/\; \text{kJ mol}^{-1} = -84\,(\delta_{1H} - \delta_{1H}^{SiOH}) \quad \text{with} \quad \delta_{1H}^{SiOH} = 2.0 \text{ ppm}$$

and *via* low-field shift upon adsorption of C_2Cl_4 at low temperature (77 K)

$$\Delta E^{lfs} \;/\; \text{kJ mol}^{-1} = -442.48 \log\,(\delta_{1H} \;/\; \Delta\delta_{1H}^{SiOH}) \quad \text{with} \quad \Delta\delta_{1H}^{SiOH} = 0.75 \text{ ppm}$$

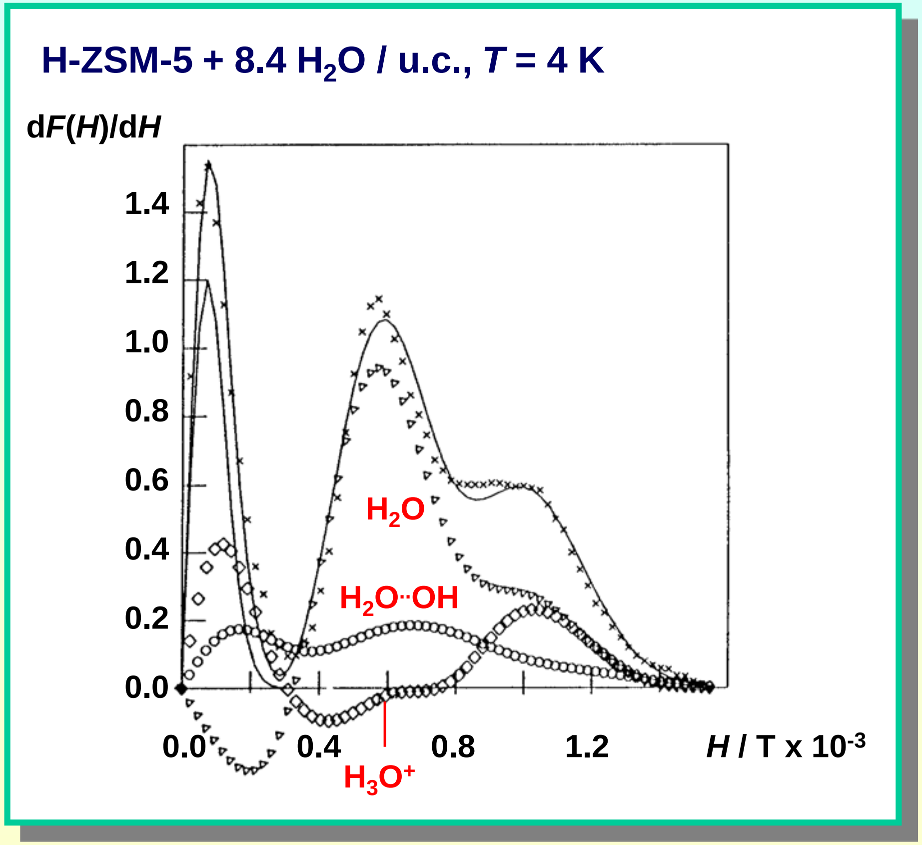
sample	OH type	δ_{1H} / ppm *)	ΔE / kJ mol^{-1}	$\Delta\delta_{1H}$ / ppm	ΔE^{lfs} / kJ mol^{-1}
30H,Na-Y	SiOHAl	3.9	160	1.6	146
H-ZSM-5	SiOHAl	4.2	185	1.9	179
deH-ZSM-5	SiOHAl	4.3	193	1.9	179

*) not affected by hydrogen bondings

H. Sachsenroeder et al., Microporous Mater. 6 (1996) 341.

Formation of H_3O^+ on acidic catalysts

- low-temperature ^1H broad-line NMR of partially hydrated acids



$ZOH{\cdots}H_2O \longleftrightarrow ZO^-{\cdots}H_3O^+$

ionization coefficient C_{ion} corresponds to the number of H_3O^+ per initial OH

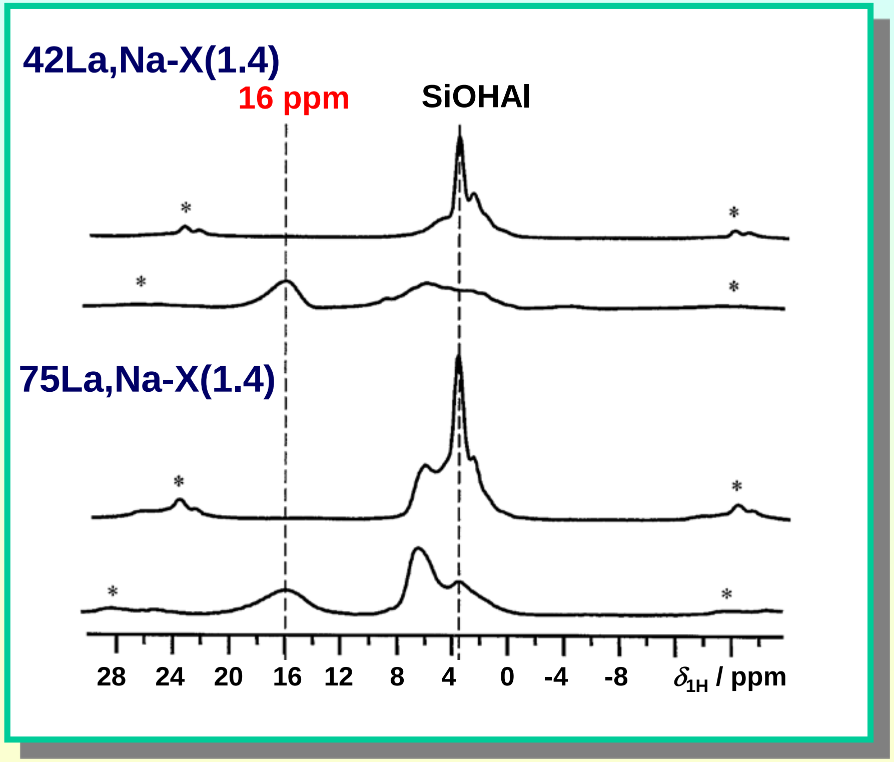
sample	C_{ion}
SiOH (H-Y)	0
SiOHAl (H-Y)	0.2
$H_2Sb_4O_{11}$ $2H_2O$	0.4
Nafion	1.0

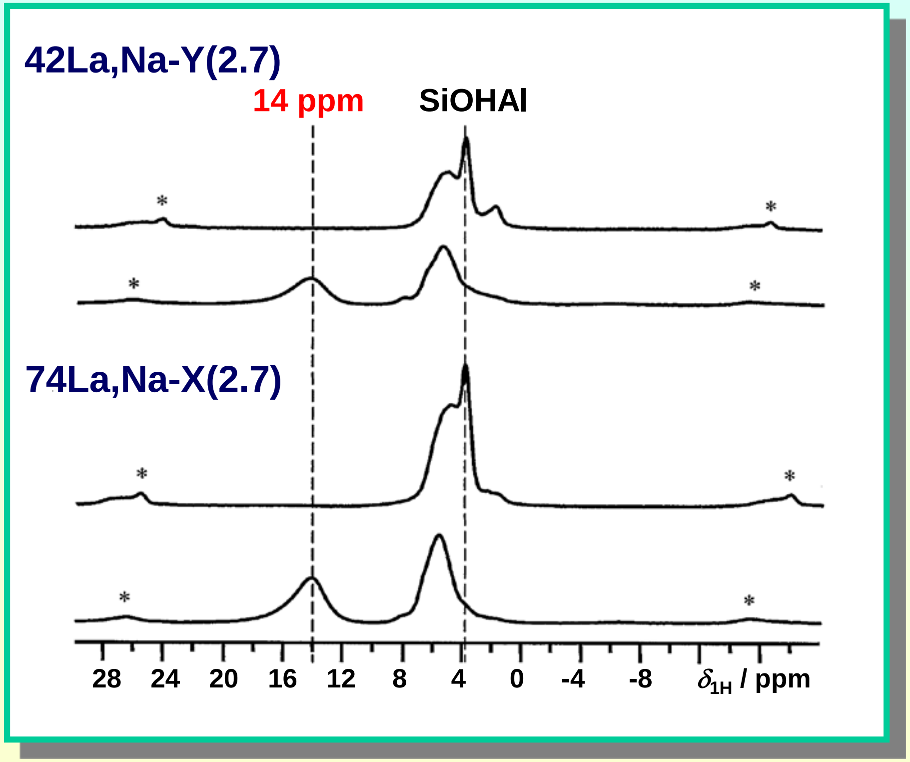
→ content of H_3O^+, i.e., the ionization coefficient C_{ion} is suggested as acidity scale

P. Batamack et al., J. Phys. Chem. 97 (1993) 9779.

Adsorption of C_6D_5N on zeolites La,Na-X and La,Na-Y

- **identification of strongly acidic OH groups via proton transfer**





→ **resonance position of pyridinium ions don‘t correlate with different acid strengths**

J. Huang et al., Microporous Mesoporous Mater., in press.

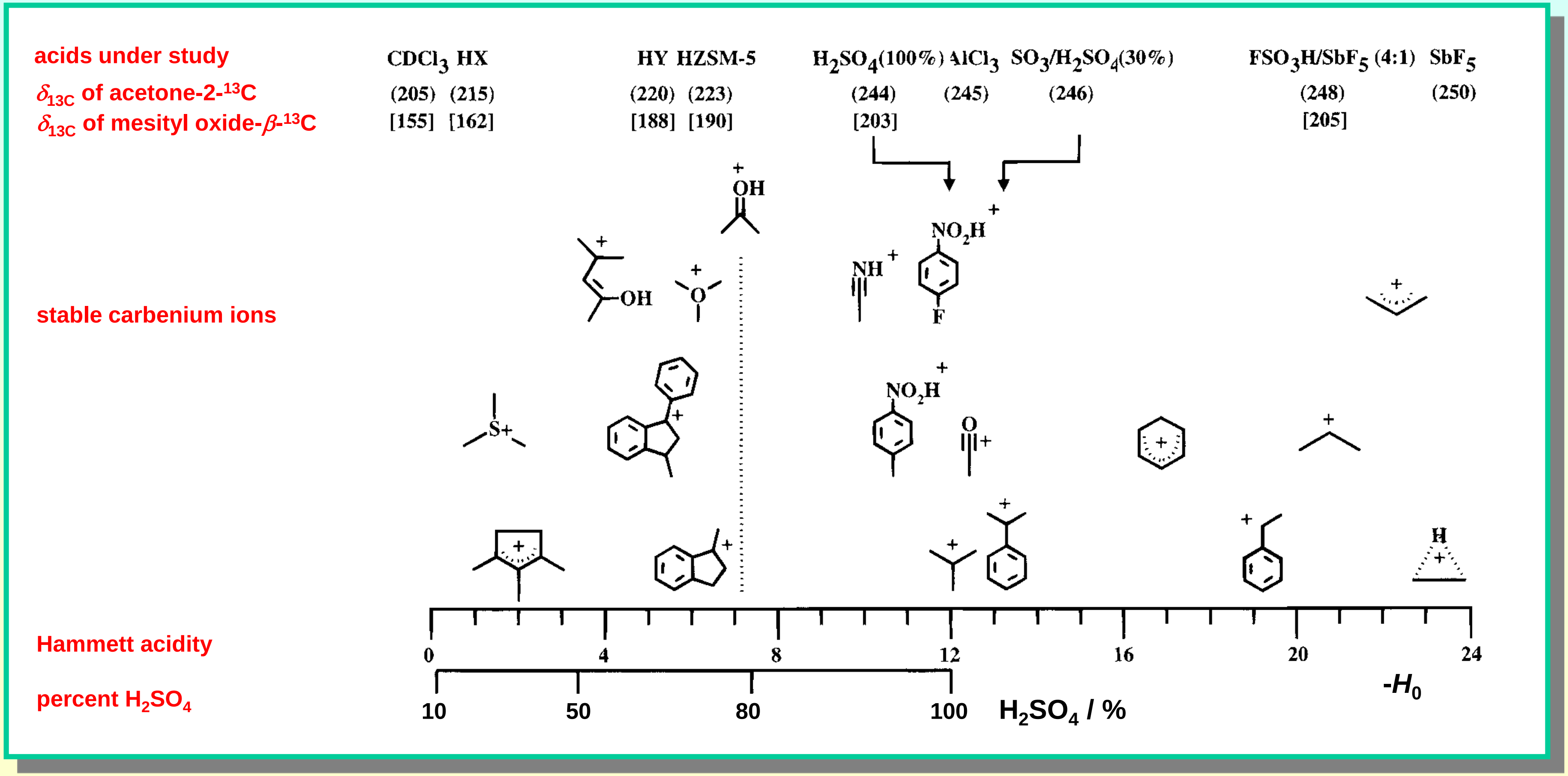
Survey on NMR probes for Broensted acid sites

Surface site	Probe molecule	Resonance / Effect
Brønsted acid sites:	pyridine-d_5	**^{1}H:** hydrogen-bonded pyridine at ca. δ_{1H} = 10 ppm (SiOH) and pyridinium ions at δ_{1H} = 12 to 20 ppm (SiOHAl)
	acetonitrile-d_3	**^{1}H:** adsorbate-induced low-field shift by $\Delta\delta_{1H}$ = 4.3 (H-Y) to 7.1 ppm (H-ZSM-5)
	trichloroacetonitrile	**^{1}H:** adsorbate-induced low-field shift by $\Delta\delta_{1H}$ = 3.0 (H-Y) to 4.9 ppm (H-ZSM-5)
	perchloroethylene	**^{1}H:** adsorbate-induced low-field shift by $\Delta\delta_{1H}$ = 0.75 (SiOH) to 1.9 ppm (SiOHAl)
	perfluorotributyl amine	**^{1}H:** adsorbate-induced low-field shift of accessible OH groups by $\Delta\delta_{1H}$ = 0.23 (SiOH) to 0.47 ppm (AlOH)
	deuterated alkanes and aromatics	**^{1}H:** H/D exchange, activation energy
	^{13}C-2-acetone	**^{13}C:** hydrogen-bonded acetone at δ_{13C} = 216.8 (H-SAPO-5) to 225.4 ppm (H-ZSM-22)
	^{15}N-pyridine	**^{15}N:** hydrogen-bonded pyridine at δ_{15N} = 295 ppm and pyridinium ions at 198 ppm

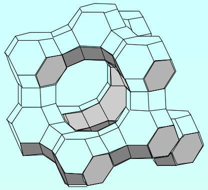
M. Hunger, J. Weitkamp, in: In-situ Spectroscopy of Catalysts, B.M. Weckhuysen (ed.), ASP, Stevenson R., 2004, p. 175.

Stable carbenium ions as acidity scale

- **comparison of different acidity scales**



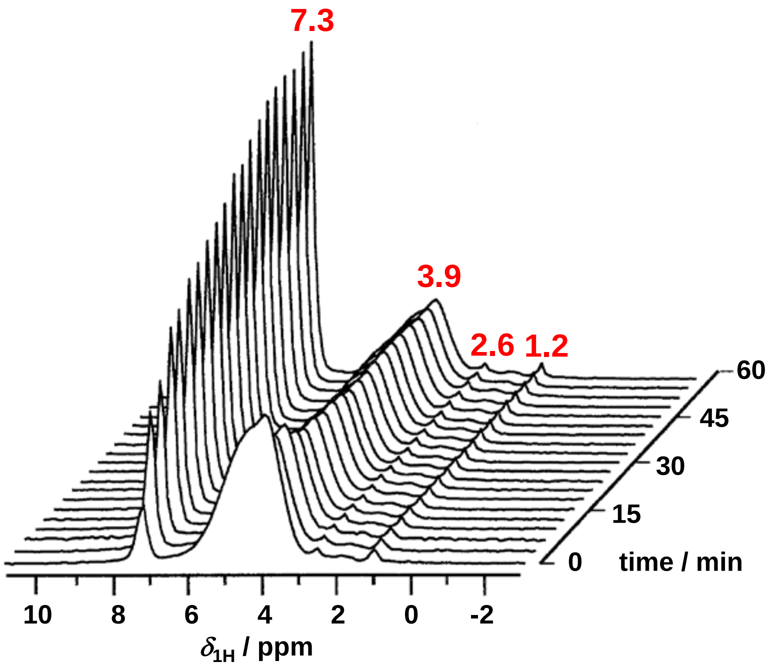
J.F. Haw et al., Acc. Chem. Res. 29 (1996) 259.



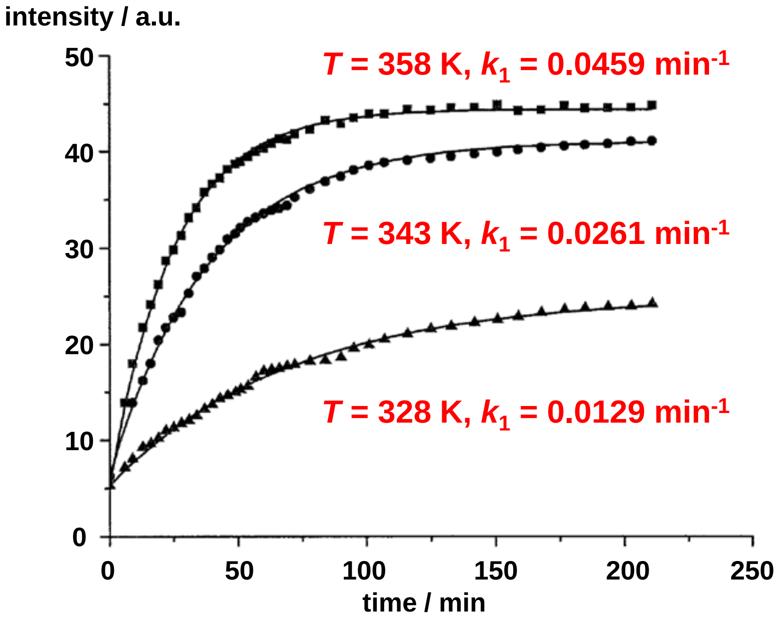
5. Reactivity of hydroxyl protons studied by H/D exchange

H/D exchange between deuterated reactants and protons of surface OH groups

- ^{1}H MAS NMR spectroscopy of zeolite H,Na-Y loaded with C_6D_6



stack plot of spectra recorded at *T* = 358 K

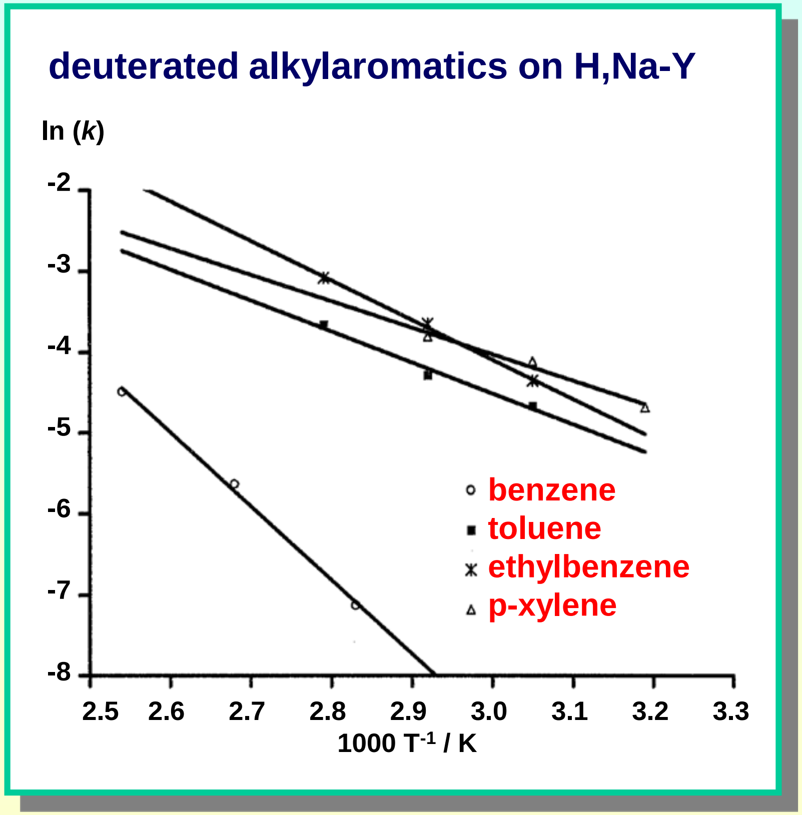


H/D exchange rates at *T* = 328 - 358 K

J. Huang et al., Microporous Mesoporous Mater. 99 (2007) 86.

H/D exchange between deuterated reactants and protons of surface OH groups

- **H/D exchange with deuterated alkylaromatics on zeolites H,Na-Y, La,Na-Y, and H-ZSM-5**



deuterated alkylaromatics on H,Na-Y

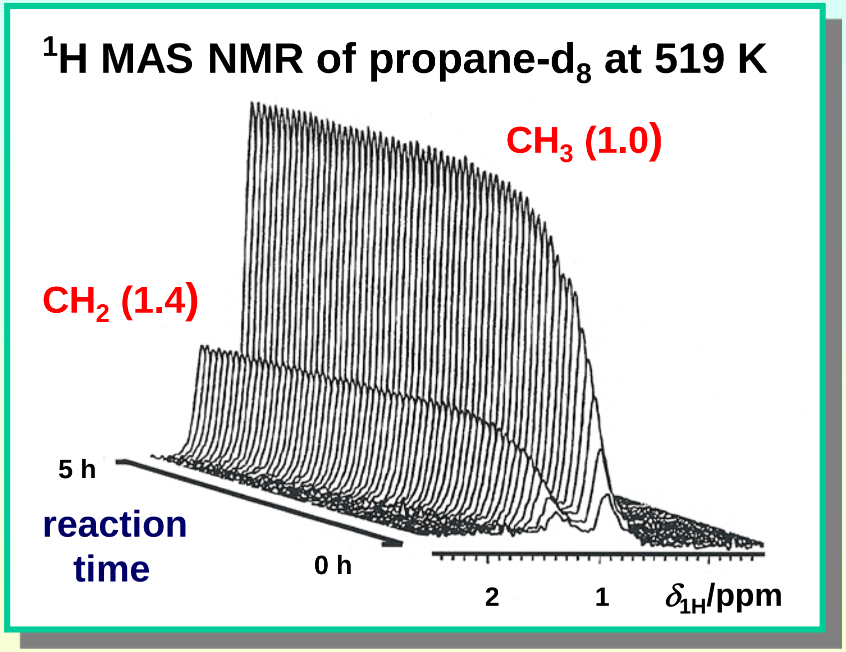
correlation of activation energies E_A of H/D exchange and low-field shifts $\Delta\delta_{1H}$ upon adsorption CD_3CN:

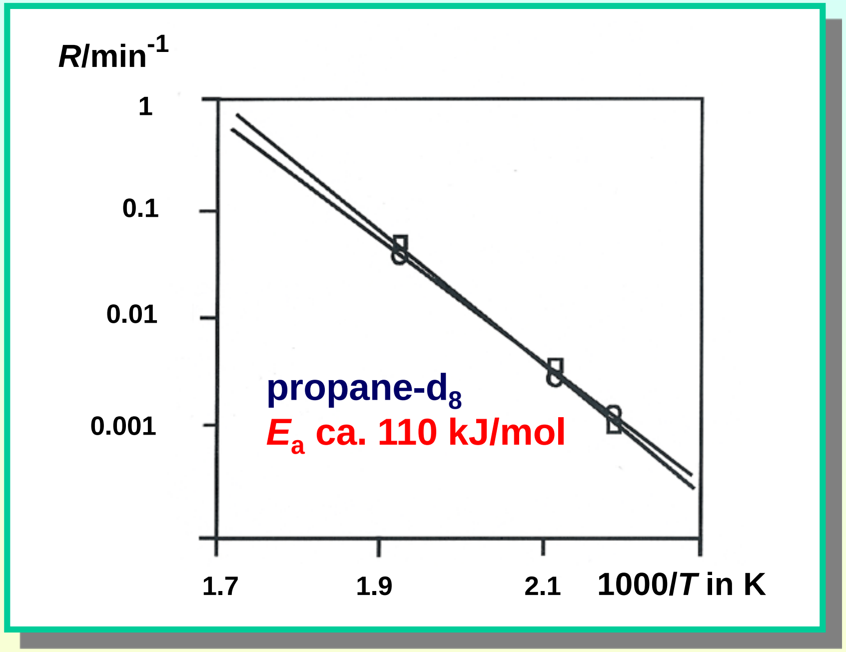
catalyst	molecule	E_A / kJ mol^{-1}	$\Delta\delta_{1H}$ / ppm
H,Na-Y	benzene	76	5.1
La,Na-Y	benzene	67	5.7
H-ZSM-5	benzene	46	7.9
H,Na-Y	benzene	76	
	ethylbenzene	41	
	toluene	32	
	p-xylene	27	

J. Huang et al., Microporous Mesoporous Mater. 99 (2007) 86.

Evaluation of reaction mechanisms by H/D exchange on acidic zeolites

- **H/D exchange of propane-d_8 (A) and isobutane-d_{10} (B) with SiOHAl groups on H-ZSM-5**


^{1}H MAS NMR of propane-d_8 at 519 K



A:

- **no regiospecific H/D exchange**
- **E_a of ca. 110 kJ/mol**

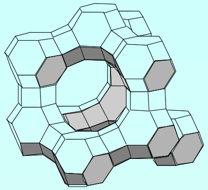
→ **no formation carbenium ions**

B:

- **regiospecific H/D exchange**
- **E_a of ca. 50 kJ/mol**

→ **formation carbenium ions**

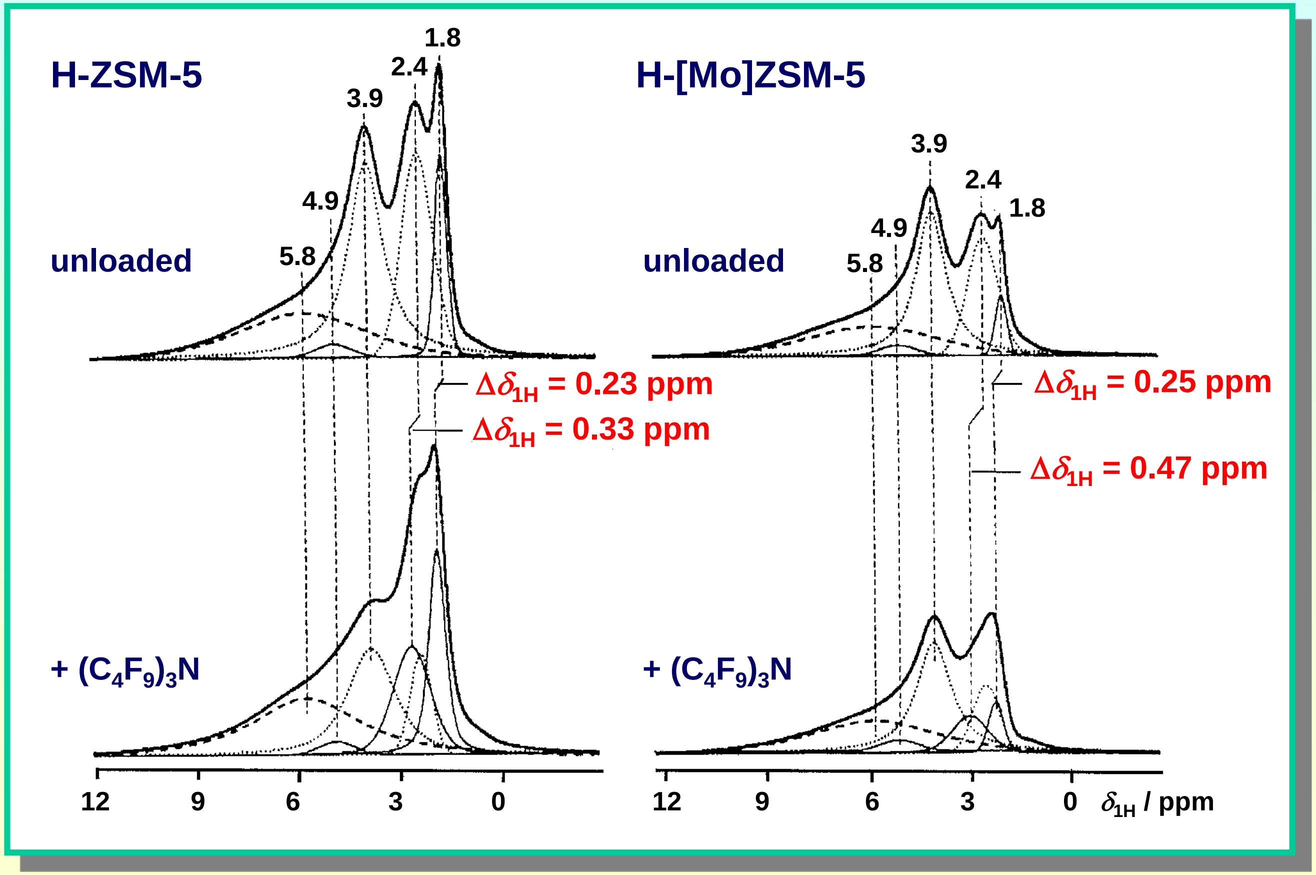
A.G. Stepanov et al., Catal. Lett. 54 (1998) 1; J. Sommer et al., J. Catal. 181 (1999) 265.



6. Study of the location of OH groups in porous catalysts

Distribution of OH on the outer and inner surface

- ^{1}H MAS NMR studies of zeolites loaded with perfluorotributylamine (Ø: 0.94 nm)

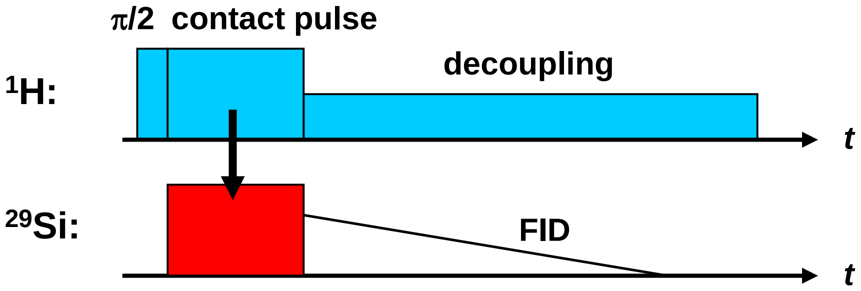


→ the outer surface is exclusively covered by SiOH (1.8 ppm) and AlOH (2.4 ppm) groups with sligthly increase acid strength upon Mo modification

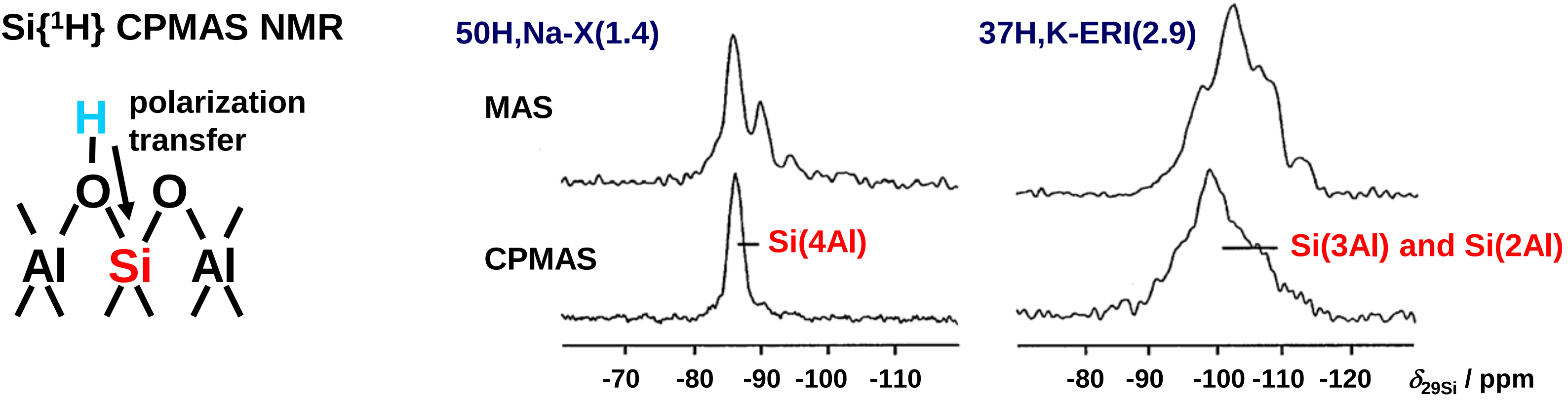
W. Zhang et al., Chem. Commun. (1999) 1091.

Distribution of SiOHAl groups in zeolites

- **pulse sequence of a cross polarization (CP) experiment:**



^{29}Si{^{1}H} CPMAS NMR

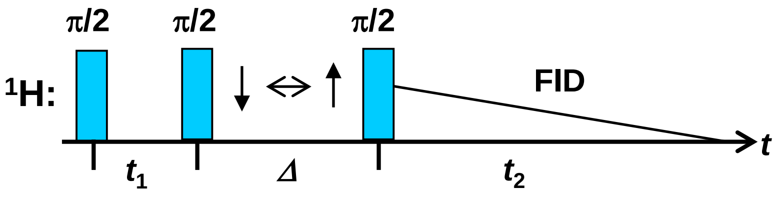


→ **SiOHAl groups are preferentially formed at Si-O-Al bridges with Si(*n*Al) atoms having a maximum number *n* of framework aluminum atoms in their vicinity**

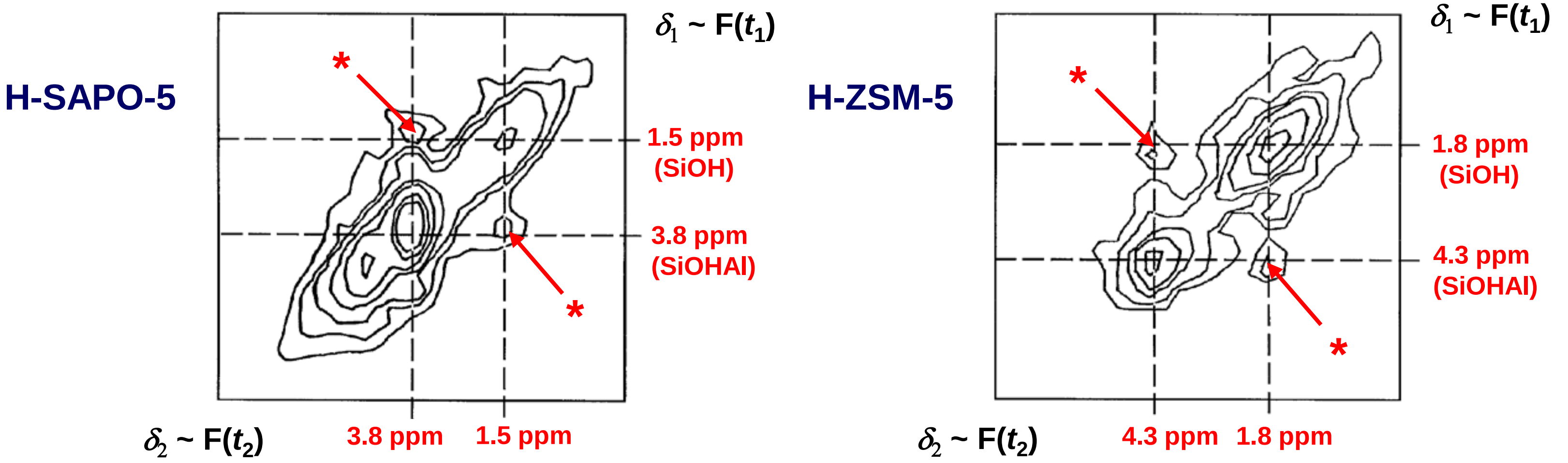
M. Hunger et al., Microporous Mater. 1 (1993) 17.

Distribution of SiOH groups in zeolites

- **pulse sequence of an 2D ^{1}H-^{1}H spin exchange experiments:**

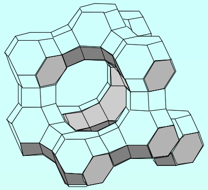


t_1: state before spin exchange
Δ: period of spin exchange (50 ms)
t_2: state after spin exchange



→ **cross peaks (*) indicate that some of the defect SiOH groups are located close to SiOHAl groups, i.e., inside the pores**

M. Hunger, Microporous Mater. 6 (1996) 1.



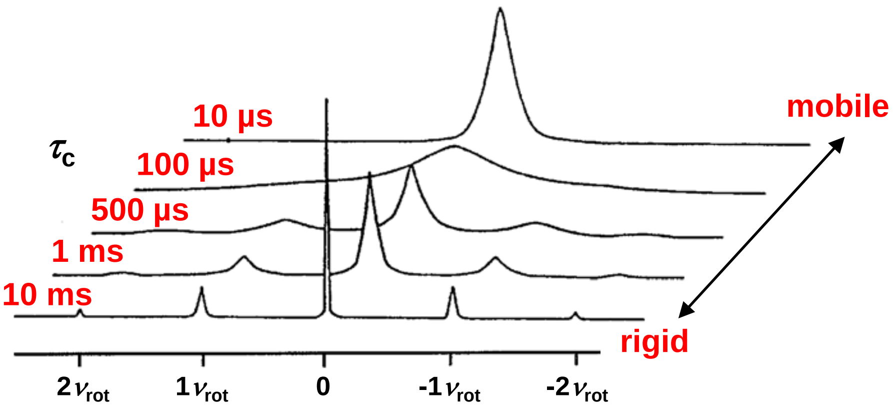
7. Mobility of hydroxyl protons at elevated temperatures

Effect of proton mobility on the ^{1}H MAS NMR spectrum

- **free induction decay *G*(*t*) of an ^{1}H MAS NMR experiment:**

$$G(t) = \exp\{-(M_2/3)\,[\,2J(\nu_{rot}, \tau_c, t) + J(2\nu_{rot}, \tau_c, t)\,]\}$$

calculated ^{1}H MAS NMR spectra of SiOHAl groups



M_2: second moment, strength of dipolar interaction, $4.5 \cdot 10^8$ s^{-2}

ν_{rot}: sample spinning rate, 3 kHz

τ_c: correlation time of thermal mobility, 10 µs to 10 ms

→ **thermal mobility leads to strong broadening of the MAS NMR spectra, simulation allows to determine the correlation time**

M. Hunger, Catal. Rev.-Sci. Eng. 39 (1997) 345.

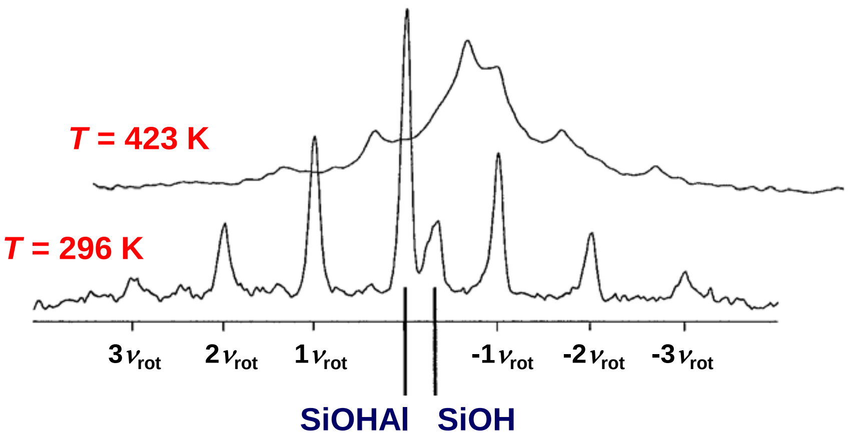
Study of the mobility of hydroxyl protons by the ^{1}H MAS NMR

- **experimental ^{1}H MAS NMR spectrum of H-ZSM-5:**

  ν_0 = 400 MHz
  ν_{rot} = 3 kHz

  simulation gives:

  τ_c = 250 µs at T = 423 K



M. Hunger, Solid State Nucl. Magn. Reson. 6 (1996) 1.

- **temperature dependence (T = 296 – 658 K) of the intensities of ^{1}H MAS NMR sidebands:**

sample	activation energy
H,Na-Y	61 kJ mol^{-1}
H-MOR	54 kJ mol^{-1}
H-ZSM-5	45 kJ mol^{-1}

→ **H-ZSM-5:**
τ_c = 251 µs at T = 423 K

P. Sarv et al., J. Phys. Chem. 99 (1995) 13763.

Summary

Solid-state NMR characterization of Broensted acid sites in solid catalysts:

- techniques for well-defined preparation and handling of activated solid catalysts
- resolution of ^{1}H MAS NMR comparable with FTIR; correlation of signals is possible
- direct quantitative evaluation of the signal intensities gives concentration of OH groups
- different routes of OH formation in zeolites lead to different thermal stabilities and dehydroxylation behaviors
- there are different scales of acid strength, such as low-field shift of the ^{1}H MAS NMR signal upon adsorption of probe molecules and the ionization coefficient upon water adsorption
- the activation energy of H/D exchange between deuterated reactants and surface OH groups correlates with above-mentioned scales of acid strength
- location of OH groups in porous catalysts can be studied by spin-transfer and -exchange experiments and probe molecules with well-defined size
- catalytically active hydroxyl protons are mobile under reaction conditions

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