University of Stuttgart

Institute of
Chemical Technology

Solid-state NMR Spectroscopy in Heterogeneous Catalysis

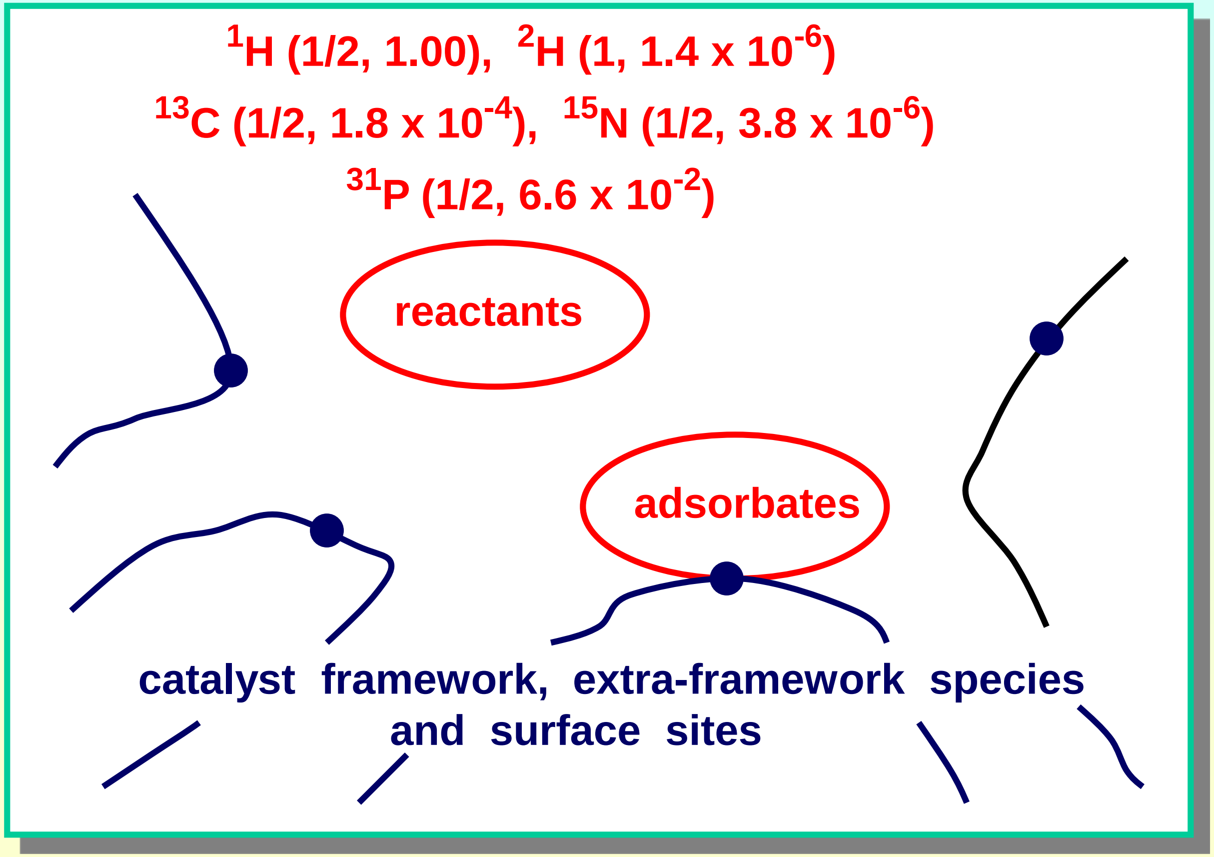
Michael Hunger

Institute of Chemical Technology
University of Stuttgart, Germany

Lecture Series Heterogeneous Catalysis
Fritz Haber Institute, Berlin, November 11, 2005

Examples of nuclei accessible for in situ NMR in heterogeneous catalysis

- **interesting isotopes (nuclear spin, relative sensitivity in comparison with ^{1}H)**



^{1}H (1/2, 1.00), ^{2}H (1, 1.4 x 10^{-6})

^{13}C (1/2, 1.8 x 10^{-4}), ^{15}N (1/2, 3.8 x 10^{-6})

^{31}P (1/2, 6.6 x 10^{-2})

reactants

adsorbates

catalyst framework, extra-framework species and surface sites

^{7}Li (3/2, 0.27)
^{11}B (3/2, 0.13)
^{17}O (5/2, 1.1 x 10^{-5})
^{23}Na (3/2, 9.2 x 10^{-2})
^{27}Al (5/2, 0.21)
^{29}Si (1/2, 3.7 x 10^{-4})
^{31}P (1/2, 6.6 x 10^{-2})
^{51}V (7/2, 0.38)
^{67}Zn (5/2, 1.2 x 10^{-2})
^{71}Ga (3/2, 5.6 x 10^{-2})
^{133}Cs (7/2, 4.7 x 10^{-2})

http://www.chem.tamu.edu/services/NMR/periodic/

Contents

- basics and specific problems of solid-state NMR spectroscopy
- experimental techniques of solid-state NMR spectroscopy
- applications of solid-state NMR spectroscopy:
  - characterization of surface sites on solid catalysts
  - investigation of the framework of solid catalysts
  - local structure of particels during the synthesis of solid catalysts
  - study of the mechanisms of reactions catalyzed by solid materials

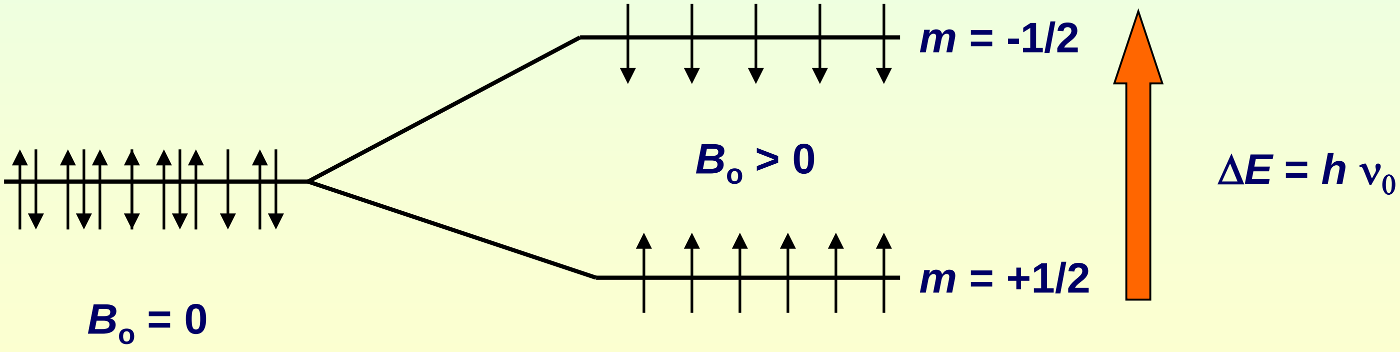
Basics and specific problems of solid-state NMR spectroscopy

Basics of NMR spectroscopy

- **Hamiltonians of the magnetic interactions of spins *I*:**

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

H_0 : **Zeeman interaction $\gamma\cdot\hbar\cdot I_z\cdot B_0$ of nuclear spins *I* in the external magnetic field B_0**



$m = -1/2$

$B_o > 0$

$\Delta E = h\,\nu_0$

$m = +1/2$

$B_o = 0$

$\nu_0 \leq 10^9\ \text{s}^{-1}$

Basics of NMR spectroscopy

H_{CS} : **shielding interaction caused by the electron shell around the resonating nuclei**

$\nu_{CS} \leq 5 \times 10^3\ s^{-1}$

$$H_{CS} = \gamma \cdot \hbar \cdot I_z \cdot B_0 [(1-\sigma_{iso}) + \Delta\sigma \left(\frac{3\cos^2\beta - 1}{2} + \frac{\eta}{2}\sin^2\beta\cos 2\alpha \right)]$$

- **isotropic shielding:** σ_{iso} **in ppm (parts per million)**
- **shielding anisotropy:** $\Delta\sigma$
- **asymmetry parameters:** η
- **Euler angles:** α **and** β

→ **characteristic resonance positions for different local structures:**

- **number and type of coordinated atoms (σ_{iso}, δ_{iso})**
- **bond angle and bond lengths (σ_{iso}, δ_{iso})**
- **symmetry of local structure (η)**

Basics of NMR spectroscopy

H_{DI} : **dipolar interaction with the magnetic dipole moments of nuclei in the local structure**

$\nu_{DI} \lesssim 5 \times 10^4\ s^{-1}$

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

- **vector between interacting nuclei *i* and *k*: r_{ik}**
- **angle between B_0 and r_{IS}: β_{ik}**

→ **strength of dipolar interaction (broadening):**

- **distance of interacting nuclei (r_{ik})**
- **number of interacting nuclei**
- **orientation of molecules and complexes in solids (β_{ik})**

Basics of NMR spectroscopy

H_Q : quadrupolar interaction of the electric quadrupole moment with the electric field gradient

$\nu_Q \leq 10^7\ s^{-1}$

$$H_Q \approx \frac{e^2 qQ}{4I(2I-1)}\ [3I_z^2 - I(I+1)]\ f\,\{P_2(\alpha, \beta); P_4(\alpha, \beta)\}$$

- electric quadrupole moment in the nuclei: eQ
- z-component of the electric field gradient: $V_{zz} = eq$
- quadrupole coupling constant: $QCC = e^2qQ/h$
- second- and fourth-order Legendre polynomials: $P_2(\alpha, \beta)$, $P_4(\alpha, \beta)$

→ charge distribution in the local structure of the resonating nuclei

H_J : indirect or J-coupling of nuclei via their bond electrons

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

Problems of NMR spectroscopy on working catalysts

magnetization:

$$M_0 = \frac{N \gamma^2 h^2 I (I + 1) B_0}{(2\pi)^2 \, 3 \, k_B \, T}$$

- **rapid chemical exchange of adsorbate complexes at elevated temperatures**
- **observation times of 10 ms (flow conditions) to hours (batch conditions)**
- **absolute number of spins of $N > 10^{19}$ per gram (^{1}H NMR)**
- **quenching of signals in the neighborhood of paramagnetic and ferromagnetic sites**
- **decrease of magnetization M_0 with increasing temperature T**
- **broadening of signals due to solid-state interactions**

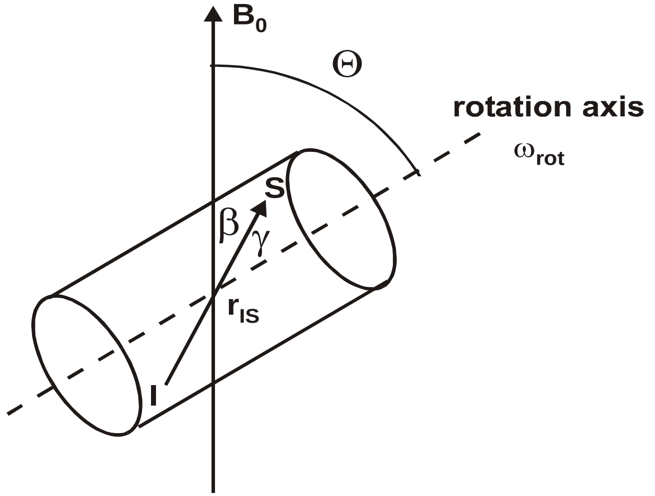
Experimental techniques of solid-state NMR spectroscopy

High-resolution solid-state NMR techniques

spin *I* = ½ :

- **magic angle spinning (MAS)**

$\nu_{CSA,DI,1QI} = f\,\{3\cos^2\Theta - 1\} \longrightarrow \Theta = 54.7^o$

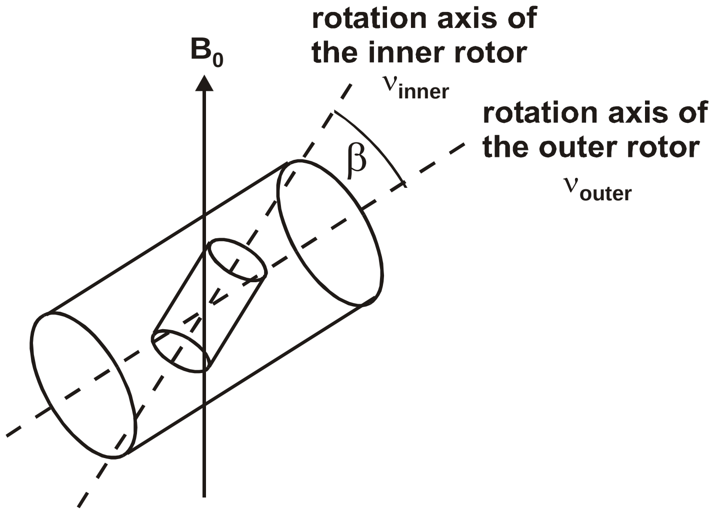


spin *I* > ½ :

- **double oriented rotation (DOR)**

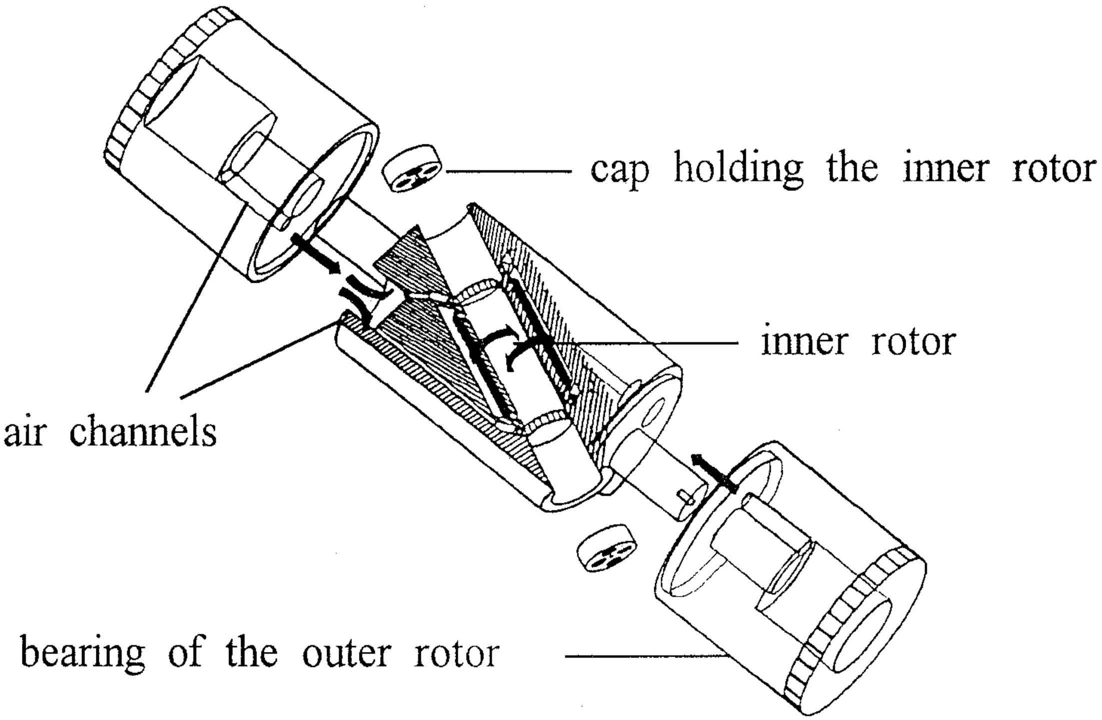
$\nu_{2QI} = f\,\{35\cos^4\beta - 30\cos^2\beta + 3\}$

$\longrightarrow \beta = 30.6^o\ ,\ \beta = 70.1^o$



High-resolution solid-state NMR techniques

- **technique of double oriented rotation (DOR)**



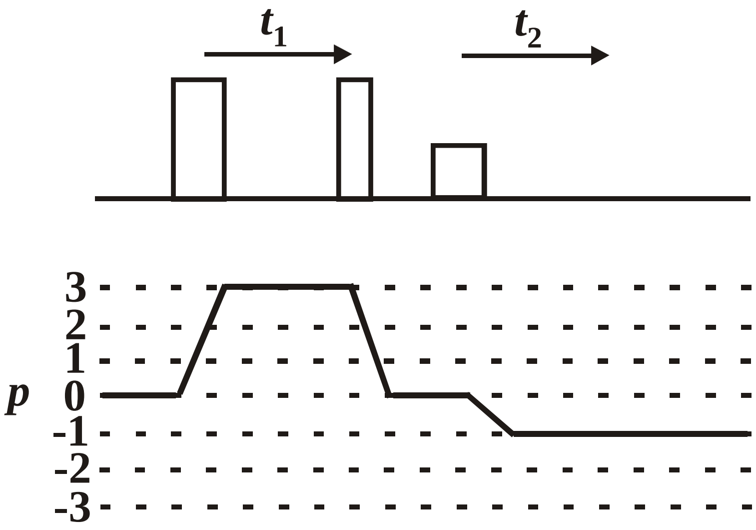
High-resolution solid-state NMR techniques

spin *I* > ½ :

- **multiple-quantum MAS NMR (MQMAS)**
  - **sampling of three- and five-quantum transitions**
  - **recording of spin-echoes free of anisotropic contributions in the case of**

$$t_2 = p \cdot \frac{36I(I+1) - 17p^2 - 10}{36I(I+1) - 27} \cdot t_1$$

- **MQMAS pulse sequence (z-filter)**



with ***p*: multiple-quantum level**

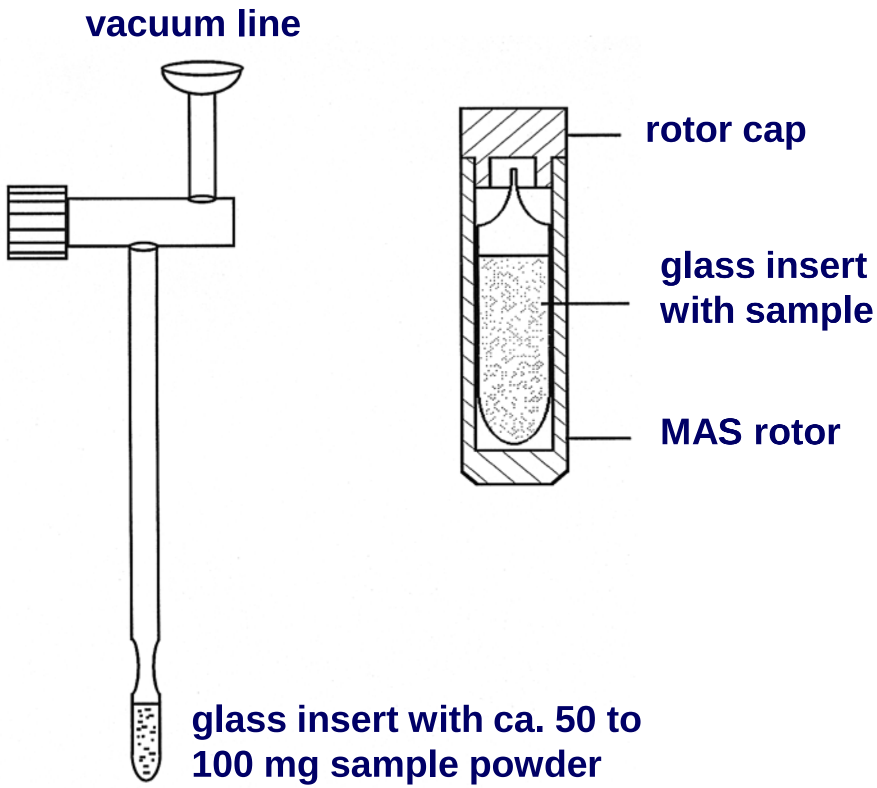
***t_1*: pulse delay**

***t_2*: echo delay**

J. Rocha et al., Topics in Current Chemistry 246 (2004) 141.

Preparation of samples under vacuum in glass inserts

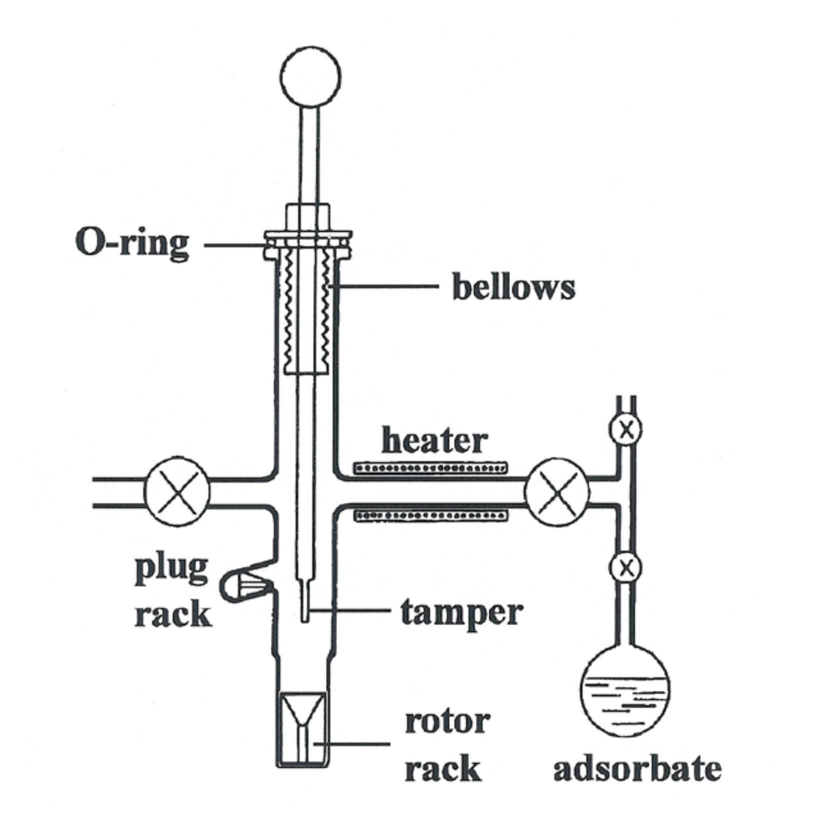
- **calcination and loading of the catalyst material inside a glass insert (Pyrex)**
- **fusing of the glass inserts during the sample in cooled with liquid nitrogen**
- **suitable for *ex situ* and *in situ* MAS NMR studies under batch conditions**



M. Hunger et al., in: B.M. Weckhuysen, In Situ Spectroscopy of Catalysts, ASP, 2004, p. 177.

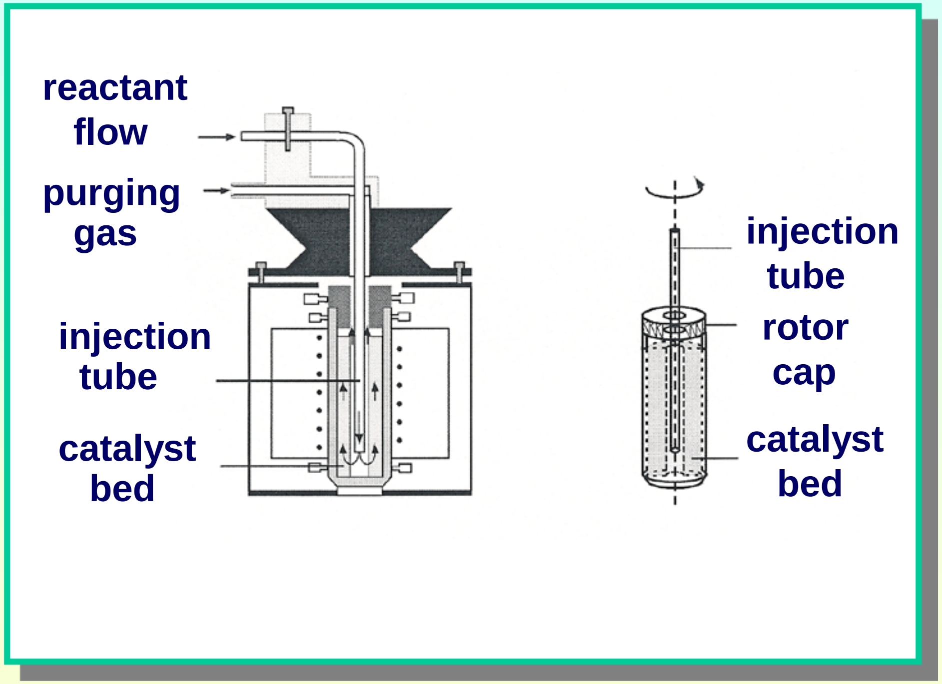
Approach for batch and continuous-flow experiments in an external reactor

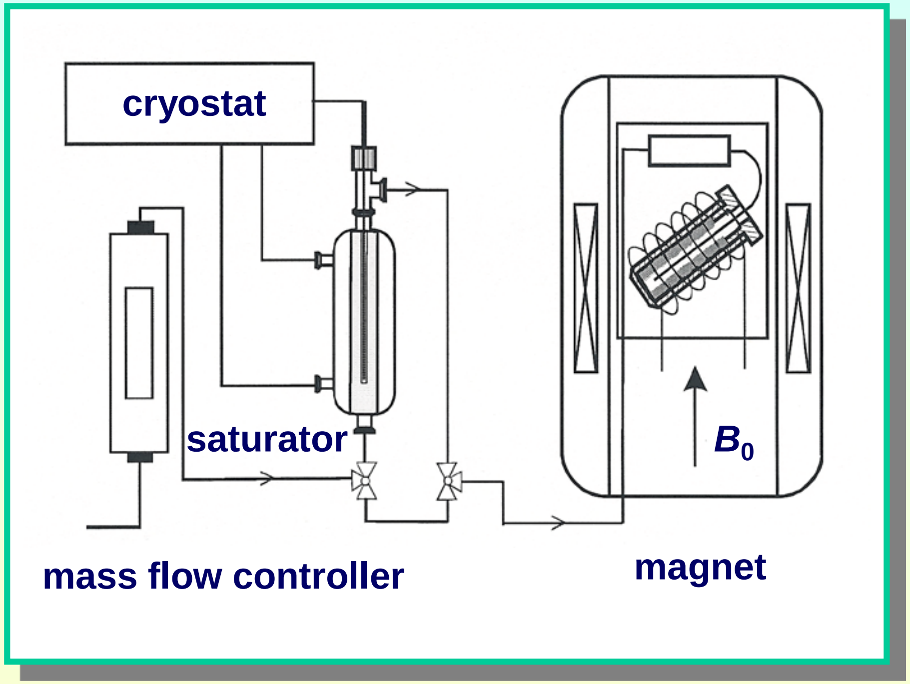
- **apparatus for evacuation, loading and catalysis on solid materials in an external reactor**
- **no contact to air during the transfer of the catalyst material into an MAS NMR rotor**
- **sealing of the MAS NMR rotor inside the apparatus**



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

Continuous-flow (CF) MAS NMR technique

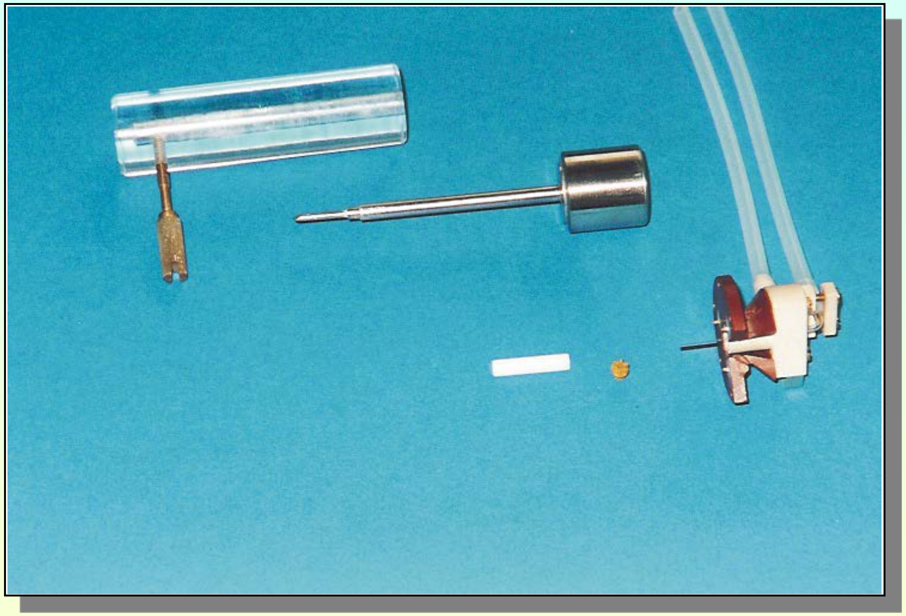


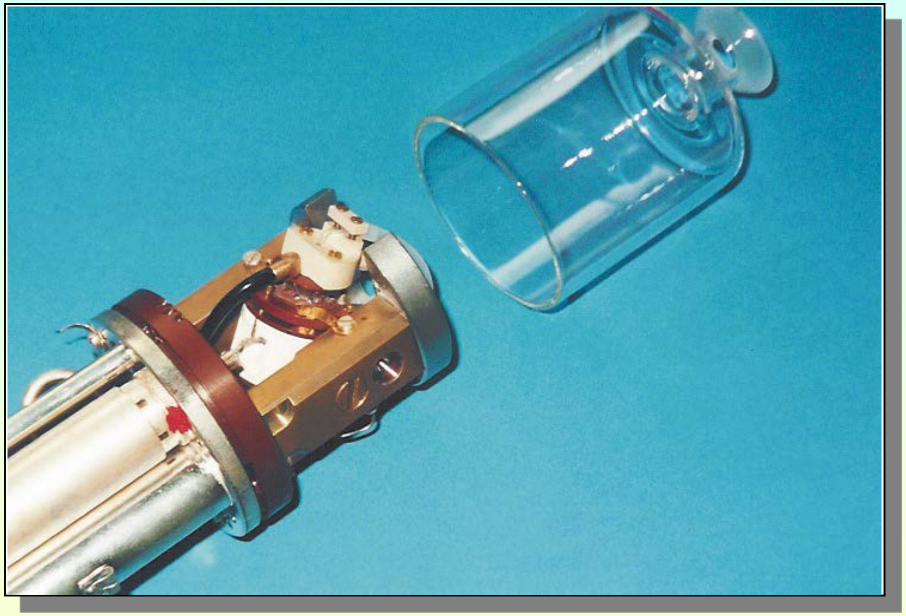


- **continuous injection of reactants into a spinning MAS NMR rotor reactor (T < 923 K)**

M. Hunger, T. Horvath, J. Chem. Soc., Chem. Commun. (1995) 1423.

Continuous-flow (CF) MAS NMR technique





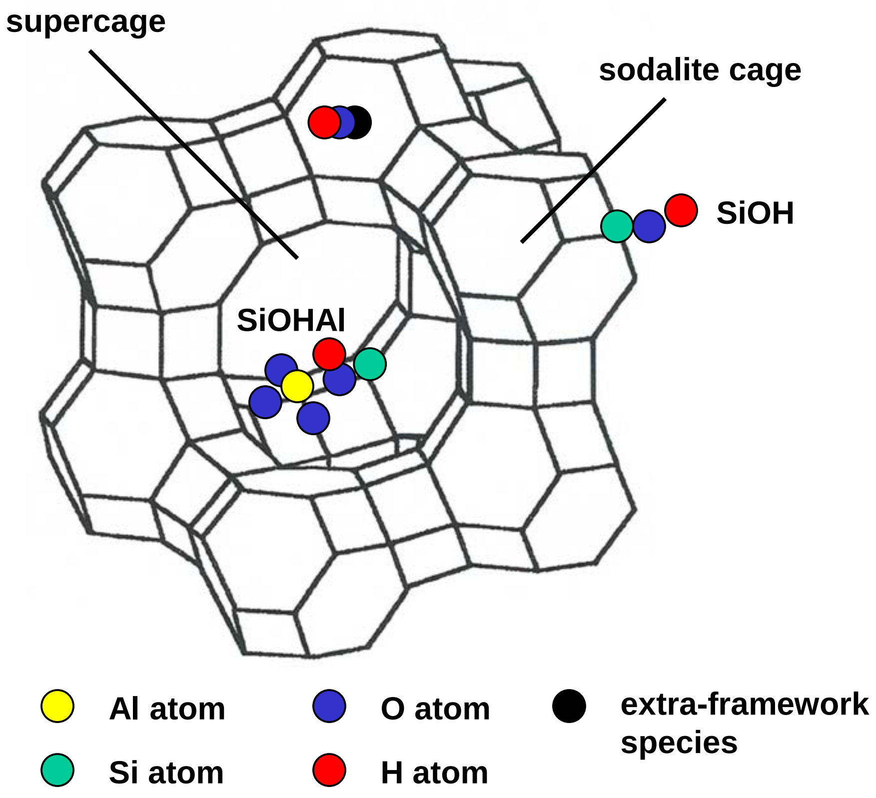
- **modified 4 mm Bruker MAS NMR probe equipped with an injection system**

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

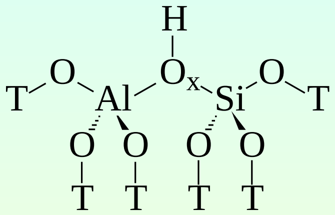
Characterization of surface sites on solid catalysts

Surface OH groups

- typical OH groups on solid catalysts (e.g. zeolite Y):



- Broensted acid sites, bridging OH group (SiOHAl):



- defect SiO OH groups

- metal OH groups at extra-framework species:
  - AlOH formed upon dealumination
  - cation OH groups (MgOH, CaOH, LaOH …) formed upon exchange with multivalent cations

^{1}H MAS NMR studies of the hydroxyl coverage

- **typical ^{1}H NMR shifts of OH groups:**

  undisturbed metal OH groups:
  -0.5 to 0.5 ppm

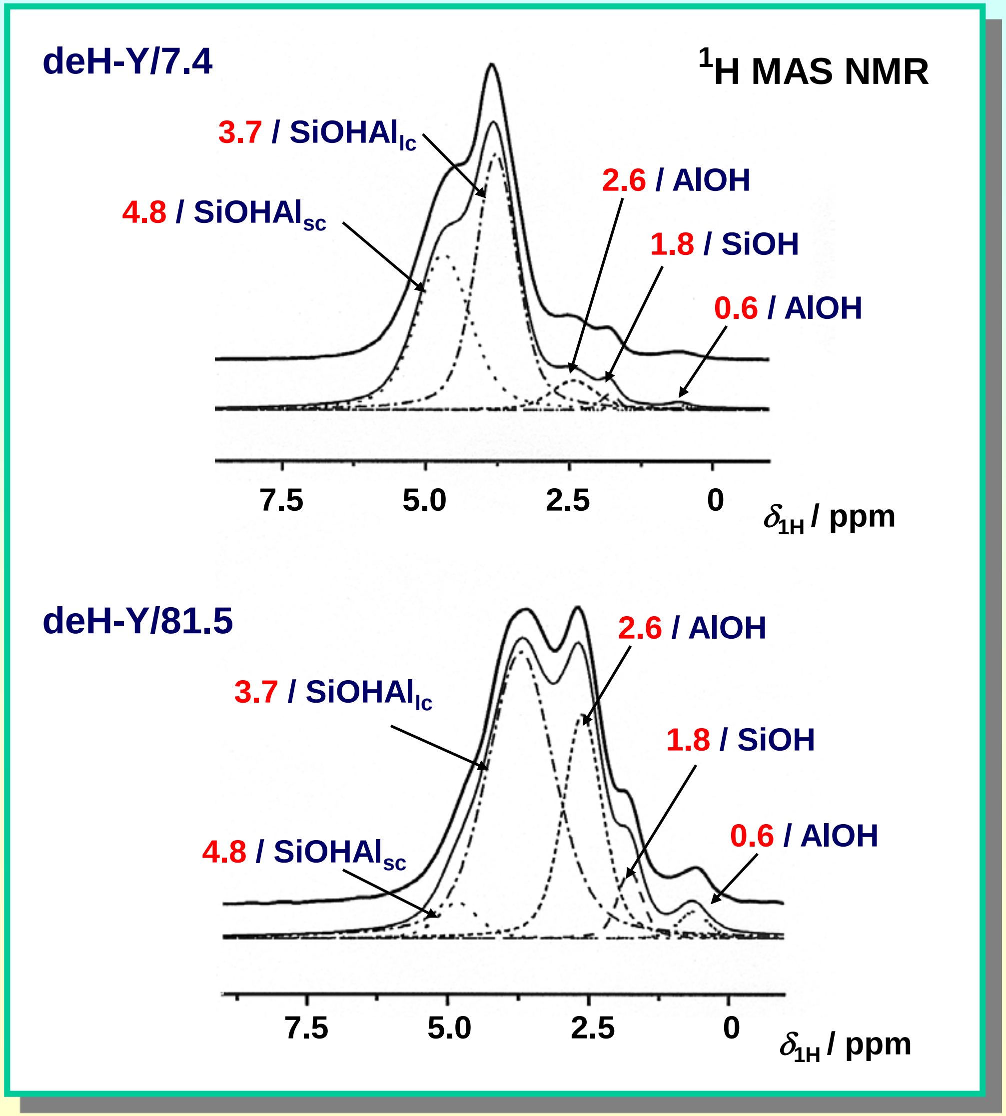
  defect SiOH groups:
  1.2 to 2.2 ppm

  OH groups at extra framework Al:
  2.8 to 3.6 ppm

  bridging OH groups in large cages and pores ($SiOHAl_{lc}$):
  3.6 to 4.3 ppm

  bridging OH groups in small cages and pores:
  4.6 to 5.2 ppm

  hydrogen bonded SiOH and SiOHAl groups:
  5.2 to 13 ppm



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

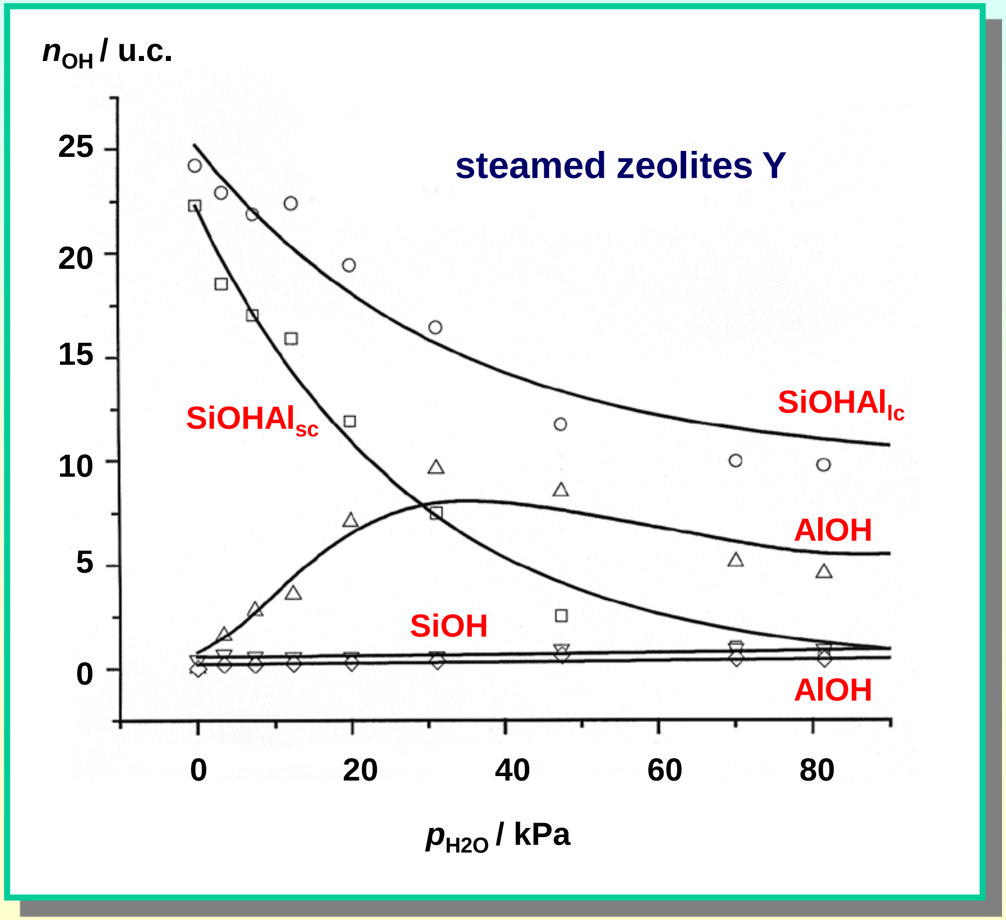
Quantitative studies of the hydroxyl coverage

- comparison of the ^{1}H MAS NMR intensities with that of a well defined standard:

total OH intensities:
give the total OH concentrations,
determination of the samples mass

relative OH intensities:
simulation and separation of the
^{1}H MAS NMR spectra,
distribution of the OH concentrations

absolute concentrations of different OH groups:
calculation using the above-mentioned
experimental values and the OH
concentration of the standard



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

Study of the accessibility and strength of surface sites

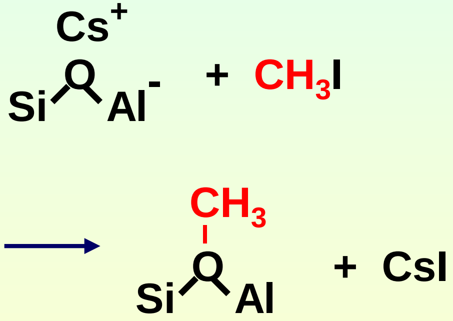
Surface site	Probe molecule	Resonance / Effect
Brønsted acid sites:	pyridine-d_5	**^{1}H:** hydrogen-bonded pyridine at ca. δ_{1H} = 10 ppm (SiOH) and pyridinium ions at δ_{1H} = 12 to 20 ppm (SiOHAl)
	acetonitrile-d_3	**^{1}H:** adsorbate-induced low-field shift by $\Delta\delta_{1H}$ = 4.3 (H-Y) to 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

Study of the accessibility and strength of surface sites

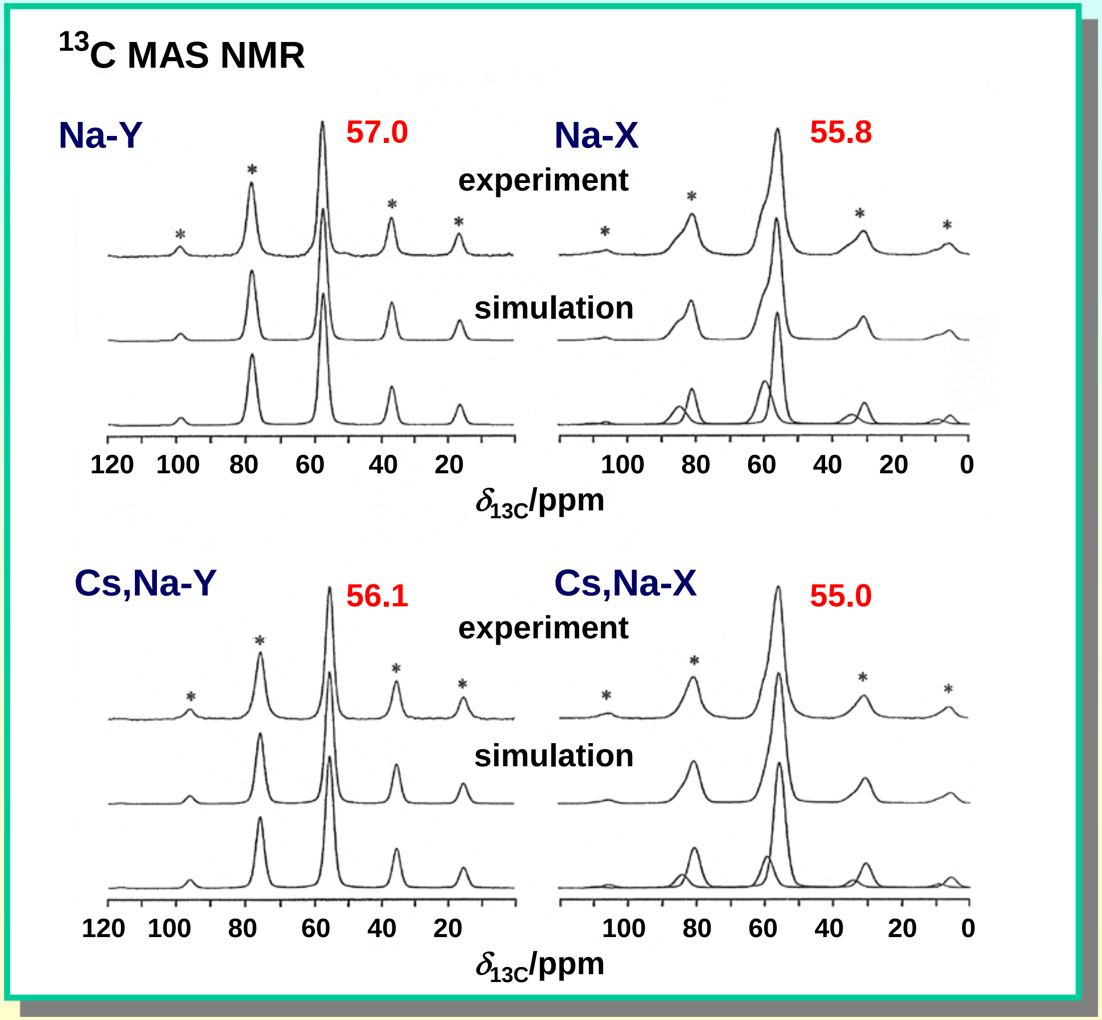
Lewis acid sites:	^{13}C-2-acetone	**^{13}C:** adsorbed acetone at δ_{13C} = 233 ppm
	^{15}N-pyridine$^{*)}$	**^{15}N:** adsorbed pyridine at δ_{15N} = 265 ppm
	trimethylphosphine oxide (TMPO)	**^{31}P:** adsorbed TMPO at δ_{31P} = 37 ppm
Base sites:	trichloromethane	**^{1}H:** hydrogen-bonded trichloromethane at δ_{1H} = 7.55 (Li-Y) to 8.23 ppm (Cs;Na-Y-90)
	pyrrole	**^{1}H:** hydrogen-bonded pyrrole at δ_{1H} = 8.4 (Li-Y) to 11.5 ppm (K-X)
	chloroform	**^{1}H:** hydrogen-bonded chloroform at δ_{1H} = 7.45 (H-Y) to 8.70 ppm (Na,Ge-X)
	^{13}C-chloroform	**^{13}C:** hydrogen-bonded ^{13}C-chloroform at δ_{13C} = 77.9 (H-Y) to 81.7 ppm (Na,Ge-Y)
	^{13}C-methyl iodide, ^{13}C-methanol	**^{13}C:** methoxy groups occurring at δ_{13C} = 58.5 (Na-ZSM-5) to 54.0 ppm (Cs,Na-X)

Characterization of basic sites on solid catalsts

- ^{13}C MAS NMR spectroscopy of surface methoxy groups formed on basic oxygen atoms
- conversion of CH_3I on basic zeolites:



→ signals at 54.3 to 59.2 ppm with a chemical shift anisotropy of ca. $\Delta\sigma$ = - 40 ppm



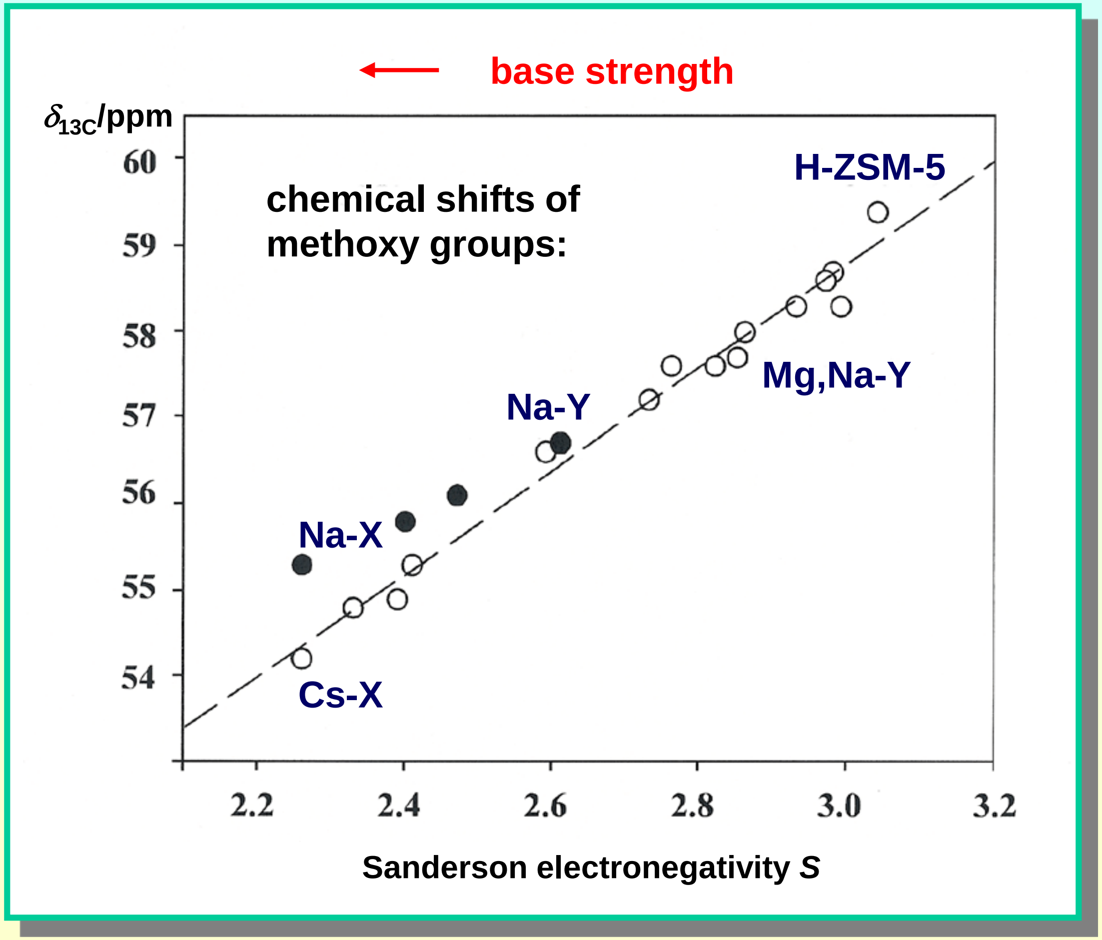
U. Schenk, PhD thesis, University of Stuttgart, 2001.

Base strengh of zeolite catalysts

- **mean Sanderson electronegativity:**

$$S = (S_{Al}{}^{k} S_{Si}{}^{l} S_{O}{}^{m} S_{Me}{}^{n})^{1/(k+l+m+n)}$$

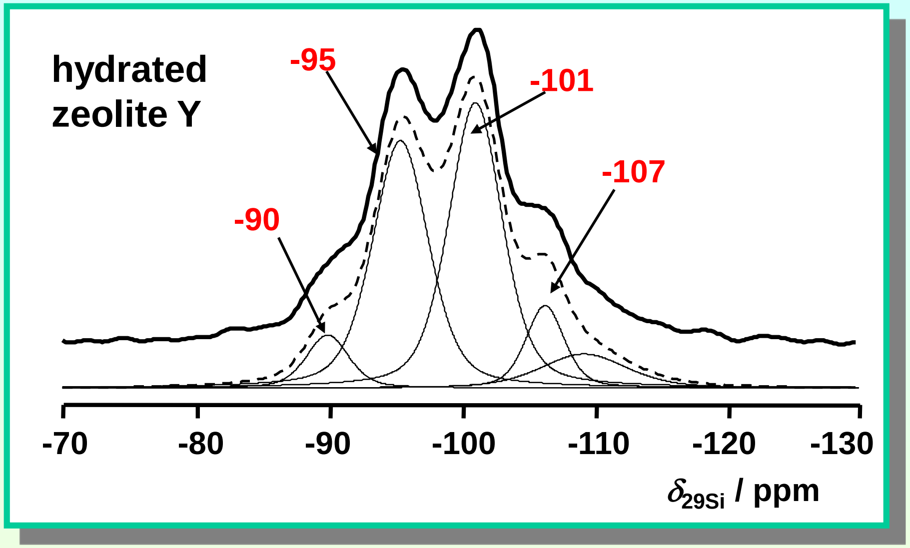
→ **decreasing ^{13}C NMR shift of surface methoxy groups with increasing base strength of the framework oxygen atoms**

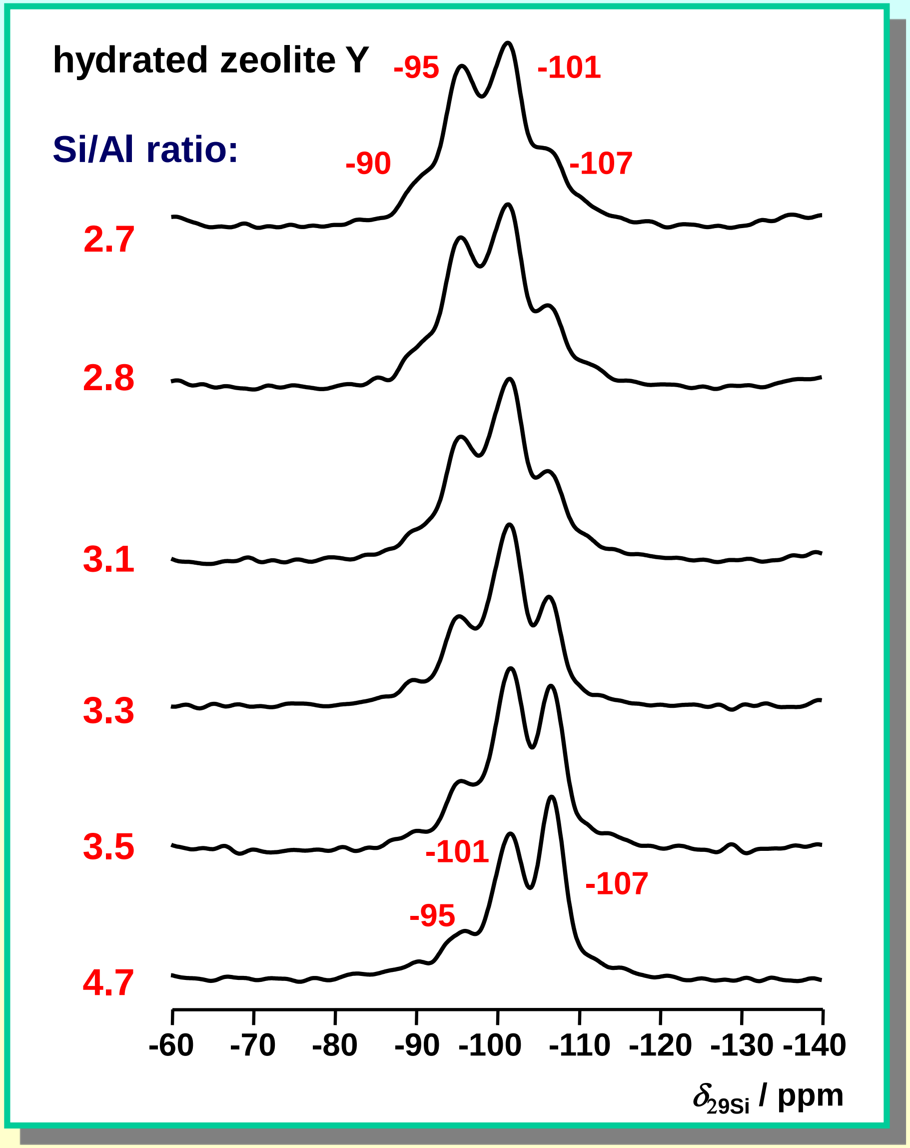


V. Bosacek et al., Z. Phys. Chem. 189 (1995) 241.

Investigation of the framework of solid catalysts

Determination of the framework aluminum content of zeolites by ^{29}Si MAS NMR





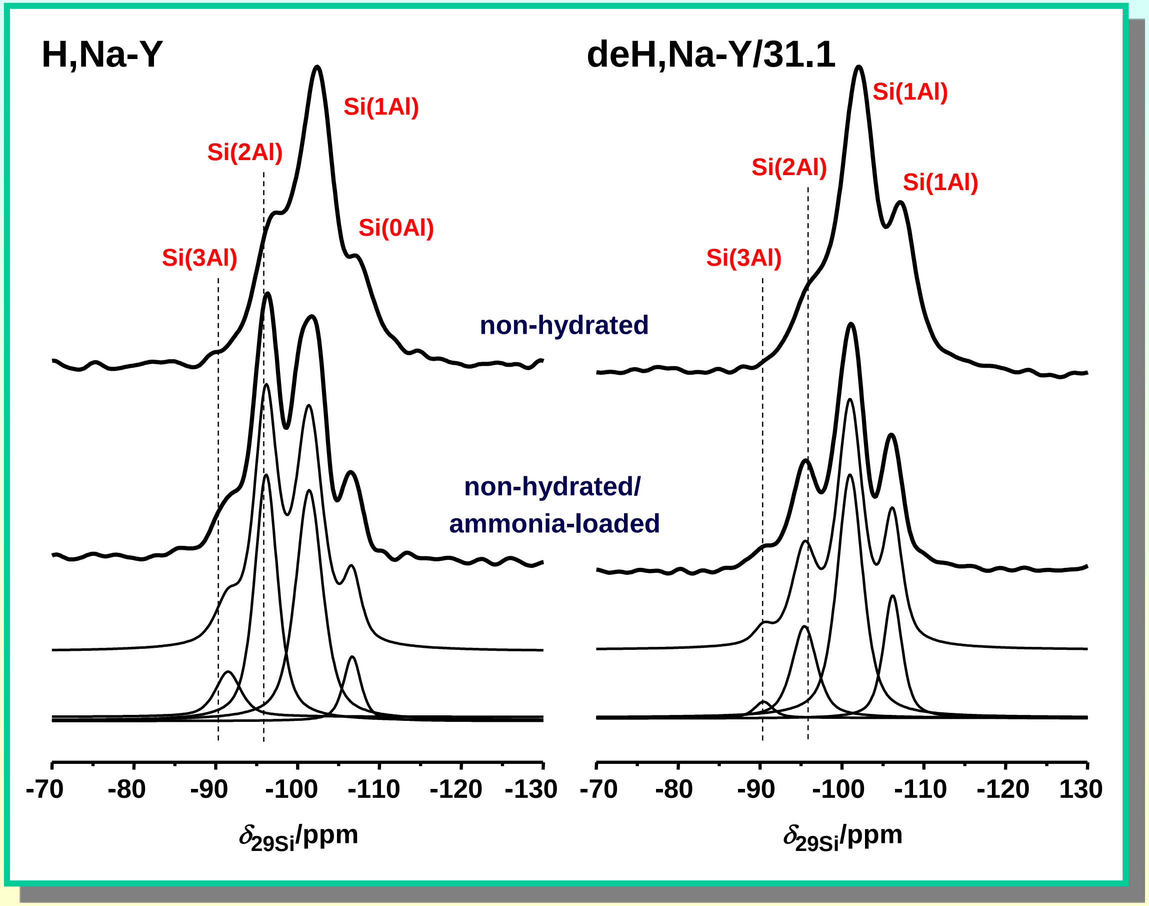
- **signals of Q^4 silicon atoms:**

-90 ppm	**Si(1Si,3Al)**
-95 ppm	**Si(2Si,2Al)**
-101 ppm	**Si(3Si,1Al)**
-107 ppm	**Si(4Si)**

$$n_{\mathrm{Si}} / n_{\mathrm{Al}} = \sum_{n=0}^{4} I_{\mathrm{Si}(n\mathrm{Al})} \Bigg/ \sum_{n=0}^{4} \frac{n}{4} \cdot I_{\mathrm{Si}(n\mathrm{Al})}$$

^{29}Si MAS NMR of non-hydrated zeolites

- **determination of the framework aluminum content after loading with ammonia**



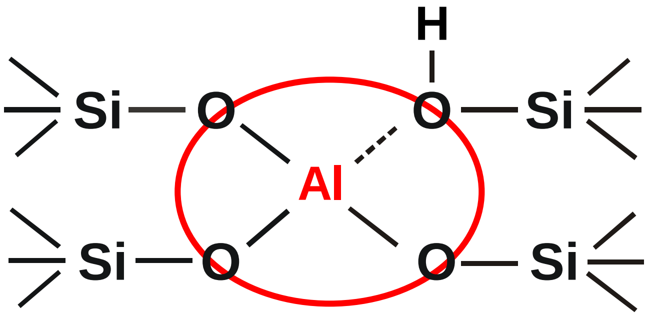
→ **high-field shift of the signals of Si(*n*Al) species upon dehydration**

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

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

Quadrupolar interaction of aluminum atoms in zeolite catalysts

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



- electric field gradient:

$$V_{zz} = eq$$

- quadrupole coupling constant:

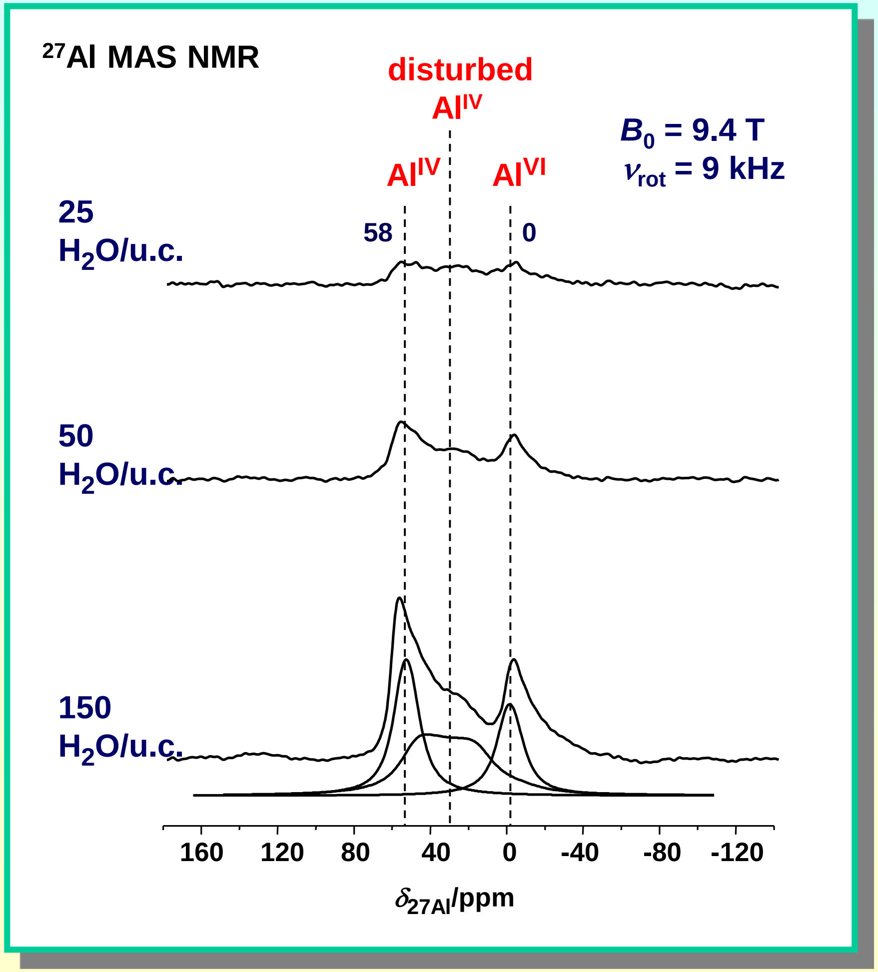
$$QCC = \frac{e^2qQ}{h}$$

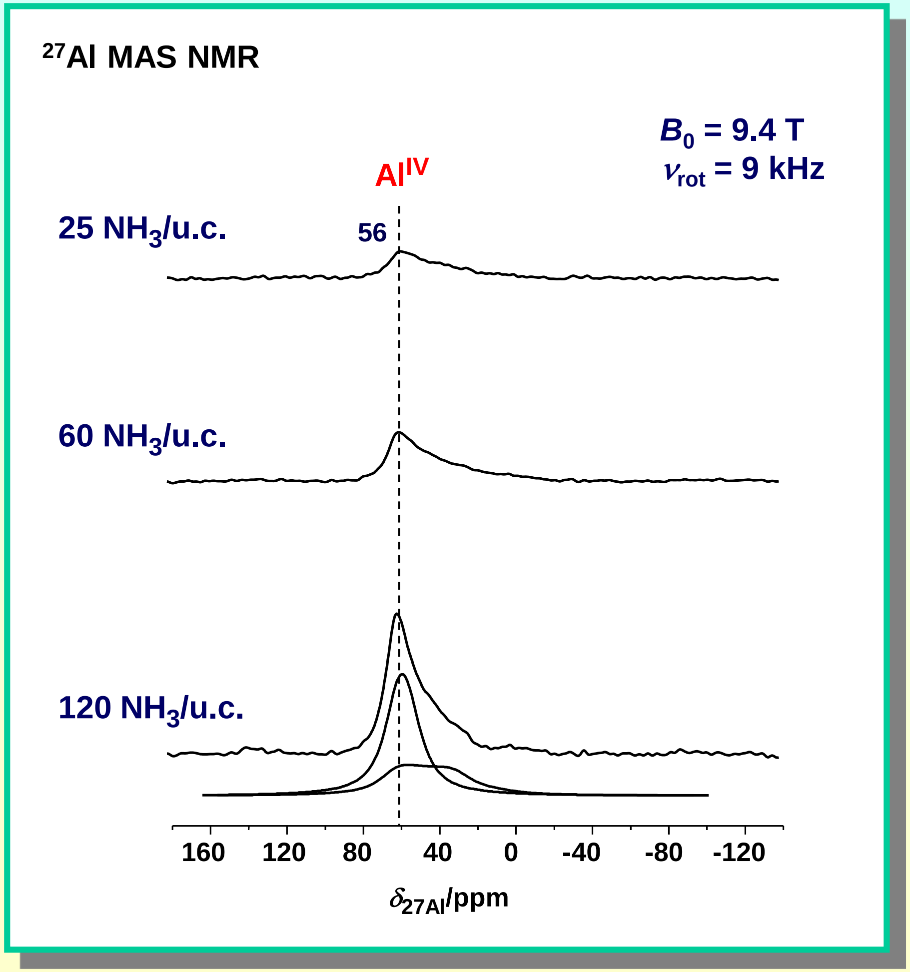
samples	*QCC* values*
hydrated H-Y and H-ZSM-5	2 MHz
non-hydrated Na-Y	5 MHz
non-hydrated H-Y	16 MHz
Al^{ex} in non-hydrated H-ZSM-5	ca. 9 MHz
pyridine-loaded H-Y	5 MHz
ammonia-loaded H-Y	5 MHz

*) 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.

Study of aluminum species by ^{27}Al MAS NMR

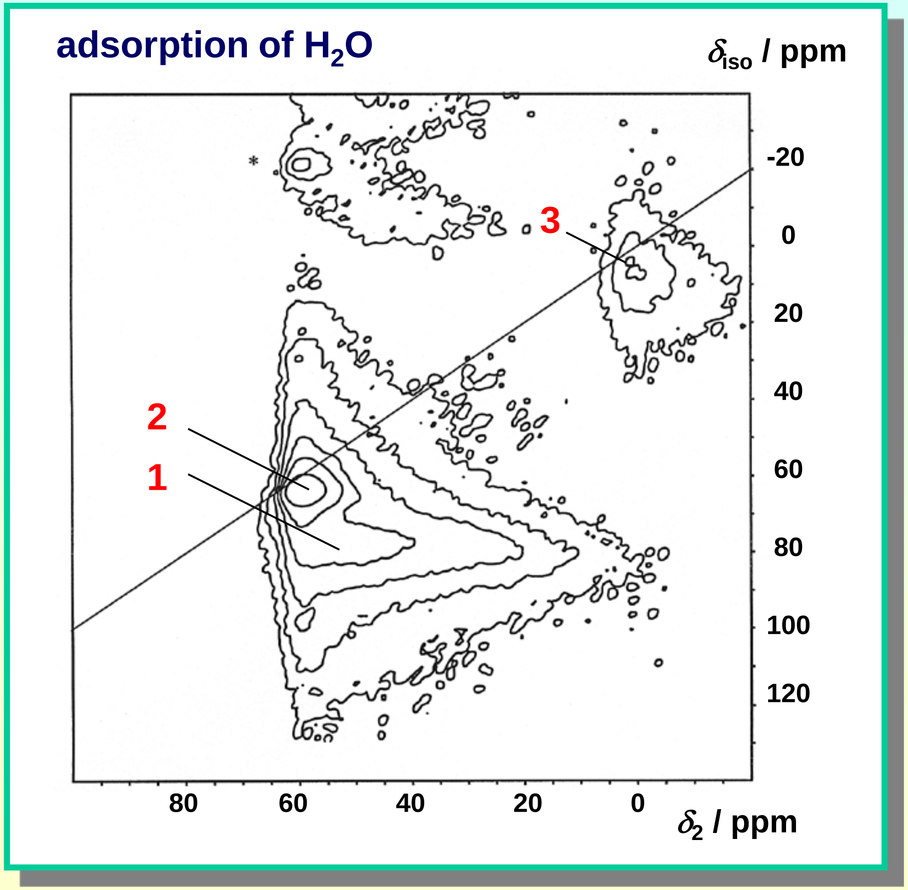
- **comparison of hydrated and ammonia-loaded zeolites Y**



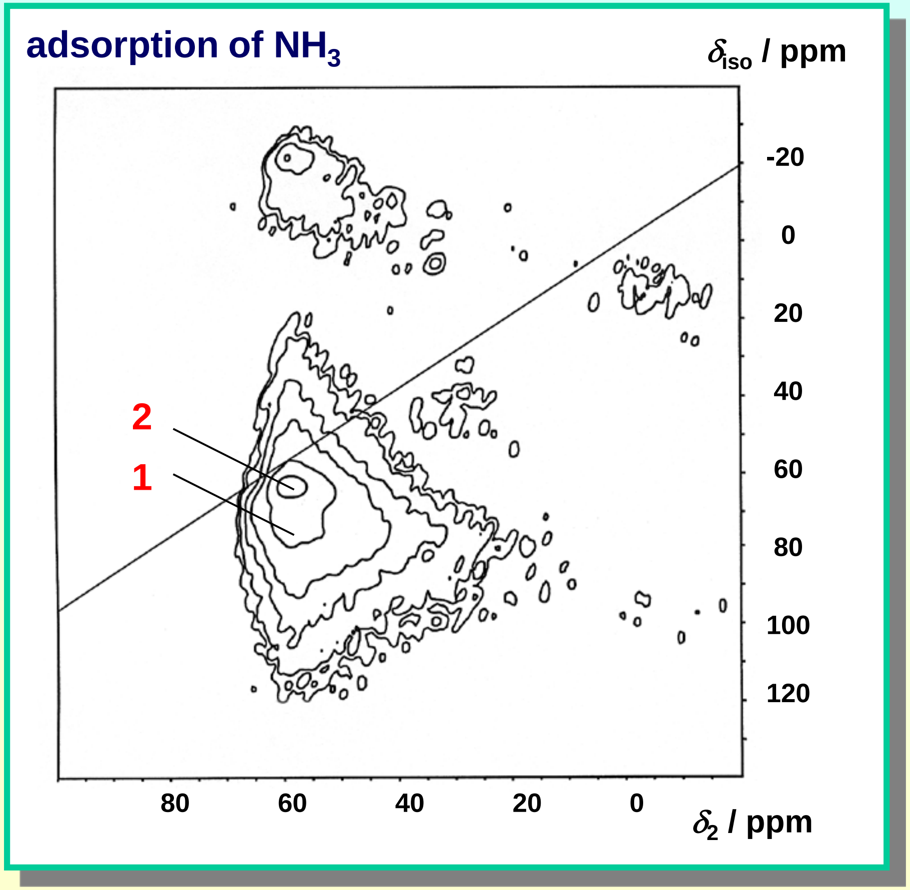


^{27}Al MQMAS NMR of zeolite deH,Na-Y

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



adsorption of H_2O



adsorption of NH_3

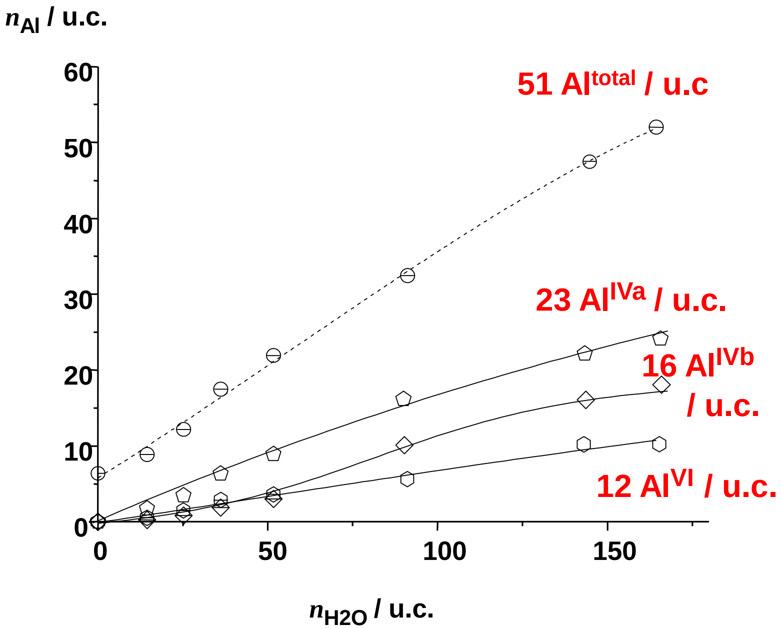
signal 1: δ_{iso} = 75 ppm, *SOQE* ca. 5.8 MHz
signal 2: δ_{iso} = 62 ppm, *SOQE* = 2.6 MHz
signal 3: δ_{iso} = 3 ppm, *SOQE* = 2.3 MHz

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

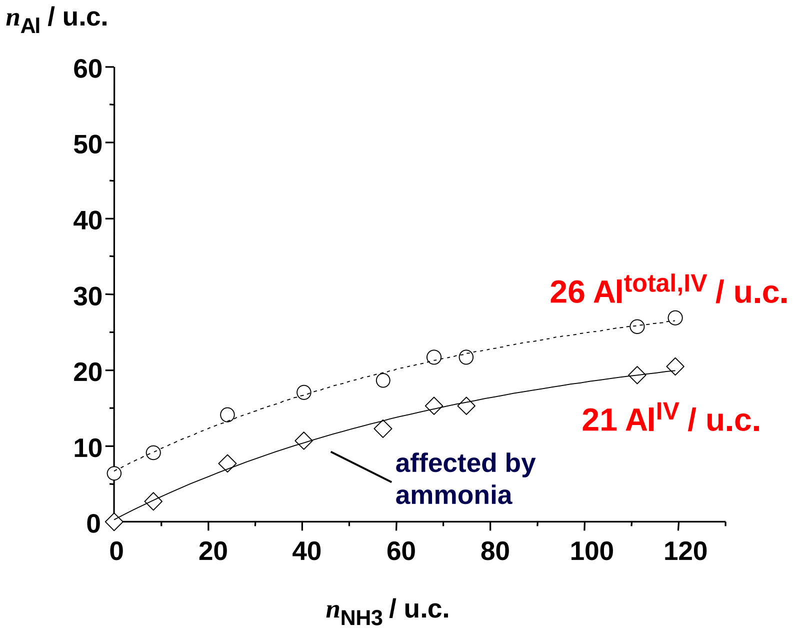
Effect of adsorption studied by ^{27}Al MAS NMR

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

adsorption of H_2O

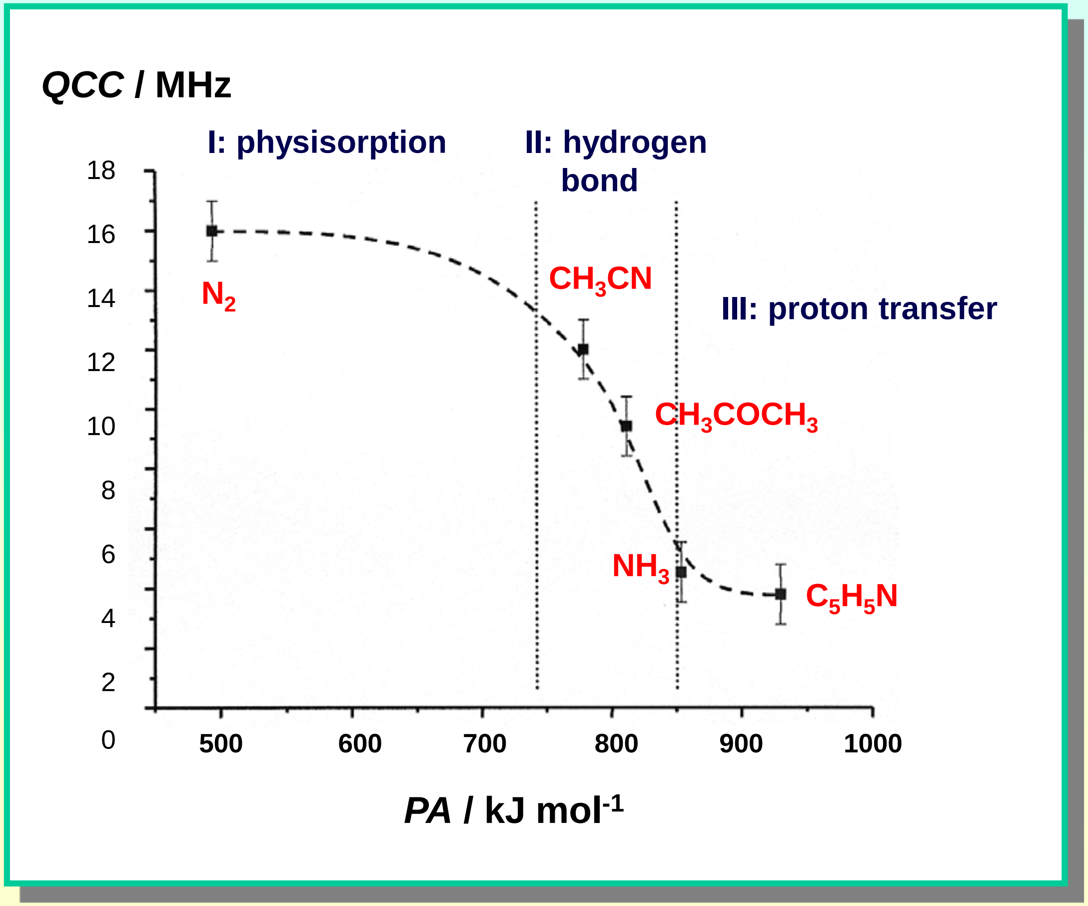


adsorption of NH_3



Effect of the base strength of the adsorbate molecules on ^{27}*Al nuclei*

- **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**

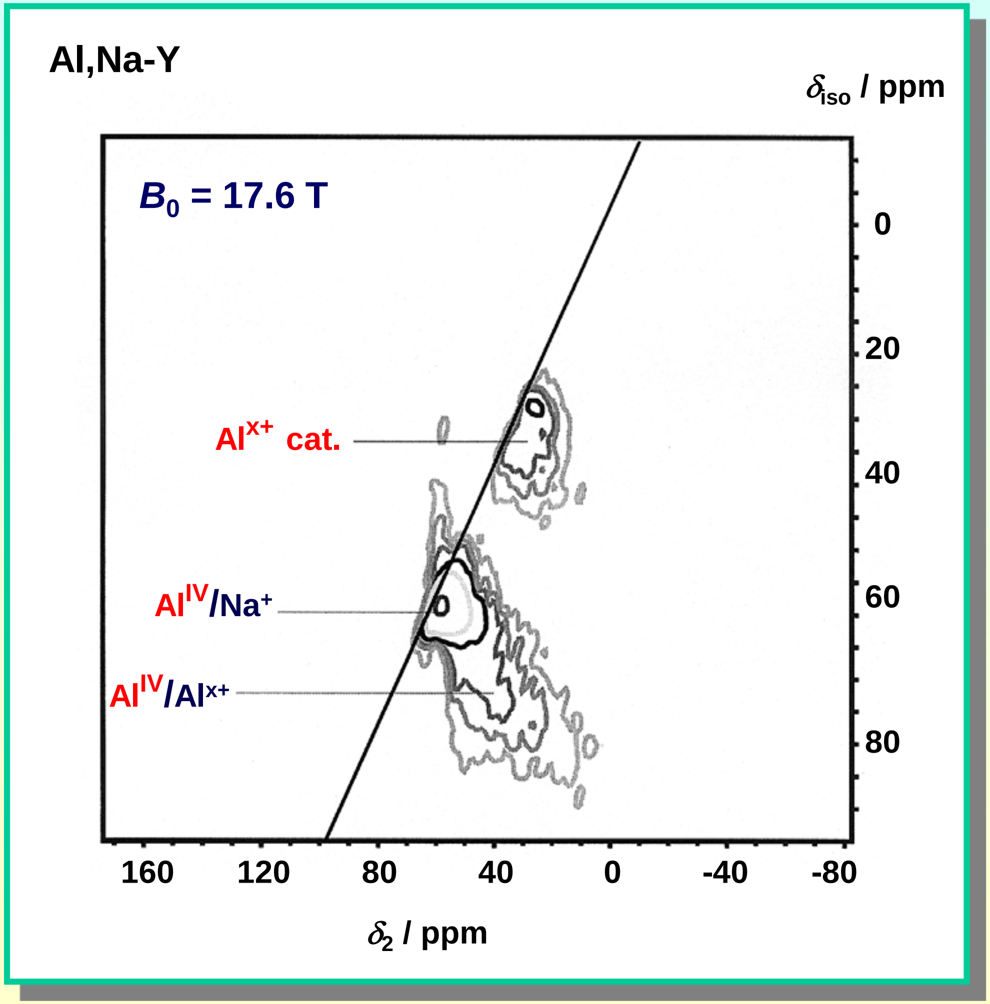
Characterization of the aluminum distribution in zeolites

- **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**

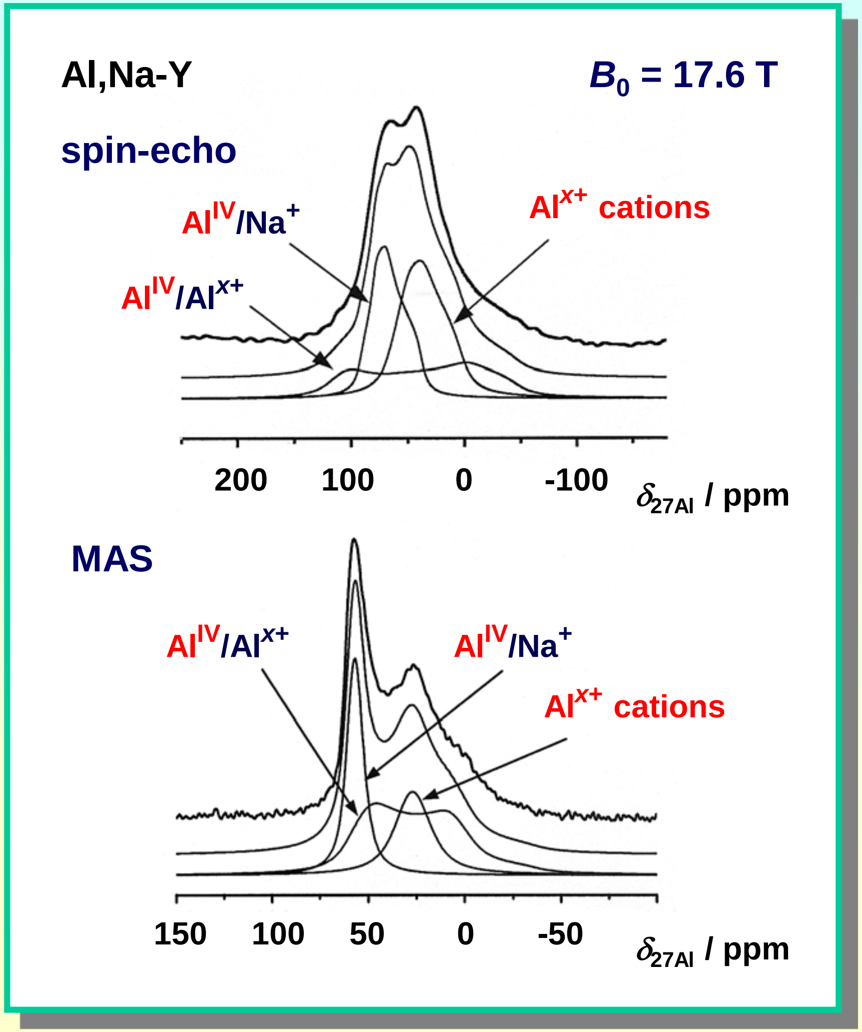
^{27}Al MQMAS NMR studies of reference materials



- 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. 7 (2005) 3221.

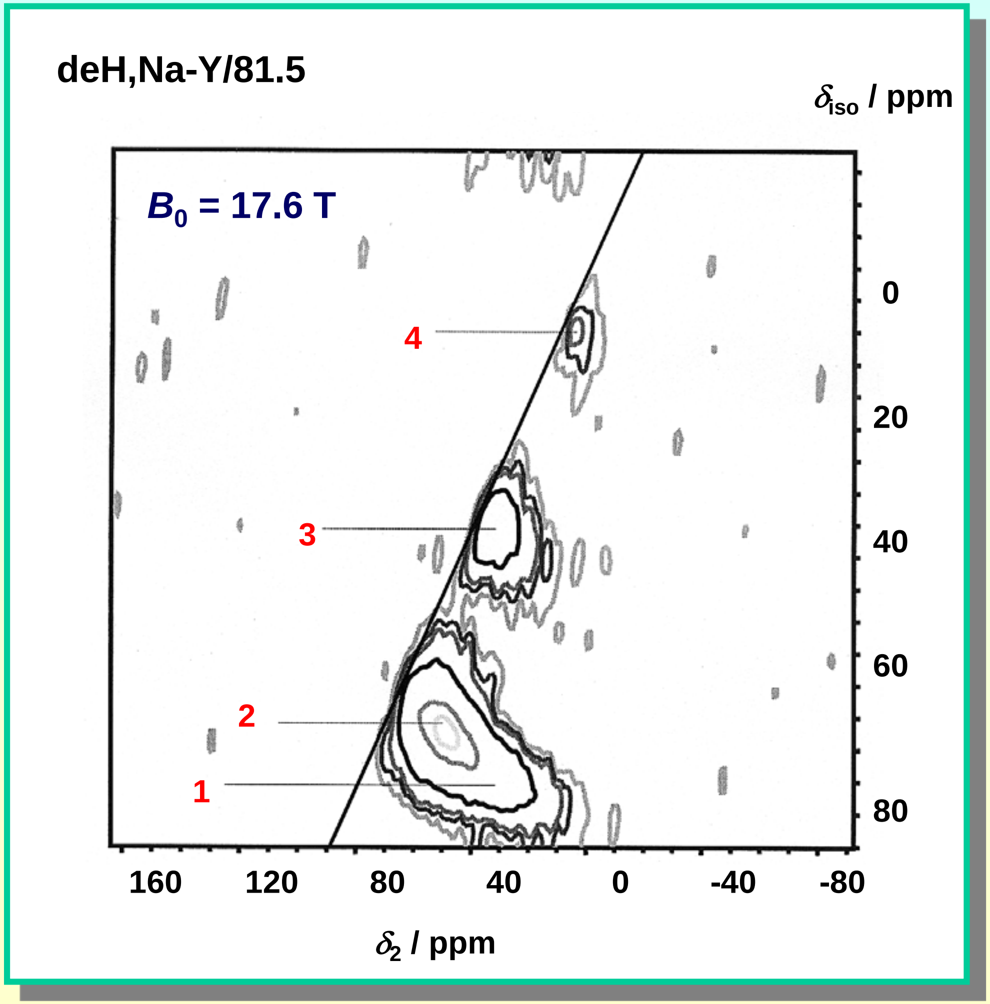
^{27}Al solid-state NMR studies of reference materials



- 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. 7 (2005) 3221.

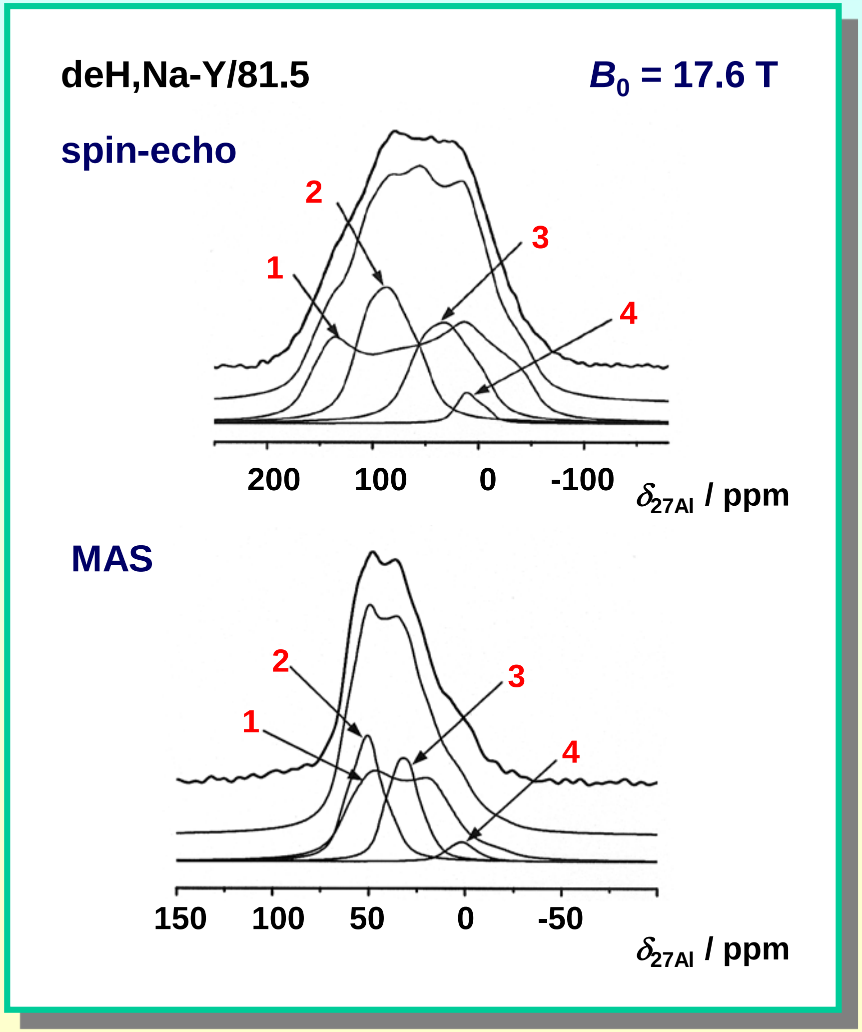
^{27}Al MQMAS NMR studies of dealuminated zeolite Y



- 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. 7 (2005) 3221.

^{27}Al solid-state NMR studies of dealuminated zeolite Y

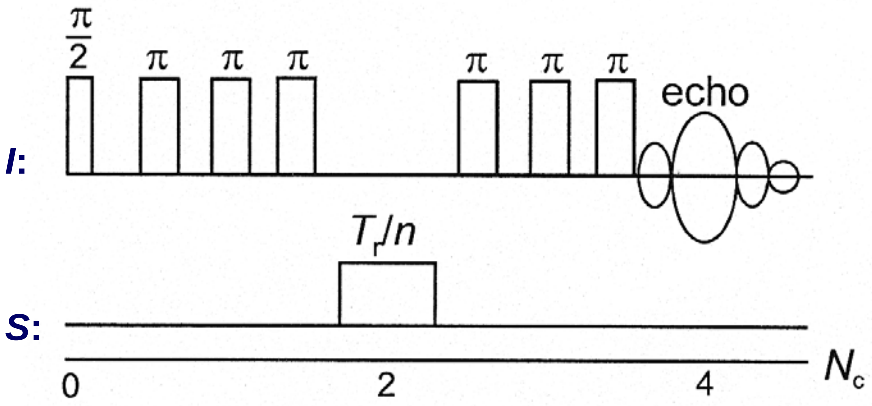


- signal 1 (70 ppm, *QCC*: 15 MHz):
  - Al^{IV}/H^+: 17 SiOHAl/u.c.
  - Al^{IV}/Al^{x+}: 8 Al/u.c.
- signal 2 (65 ppm, *QCC*: 8 MHz):
  - Al^{IV}/Na^+: 4 Al/u.c.
  - cluster Al^{IV}: 10 Al/u.c.
- signal 3 (35 ppm, *QCC*: 7.5 MHz):
  - Al^{x+} cations: 11 Al/u.c.
- signal 4 (10 ppm, *QCC*: 5 MHz):
  -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

J. Jiao et al., Phys. Chem. Chem. Phys. 7 (2005) 3221.

Determination of the distance between resonating nuclei

- **REAPDOR experiment (Rotational Echo Adiabatic Passage Double Resonance):**



T_r: rotation period

N_c: number of rotation cycles

- **echo decay is described by REAPDOR fraction:**

$$\frac{S_0 - S(N_c T_r)}{S_0} = \frac{1}{\pi^2 S(S+1)} (N_c T_r)^2 M_2^{\mathrm{IS}}$$

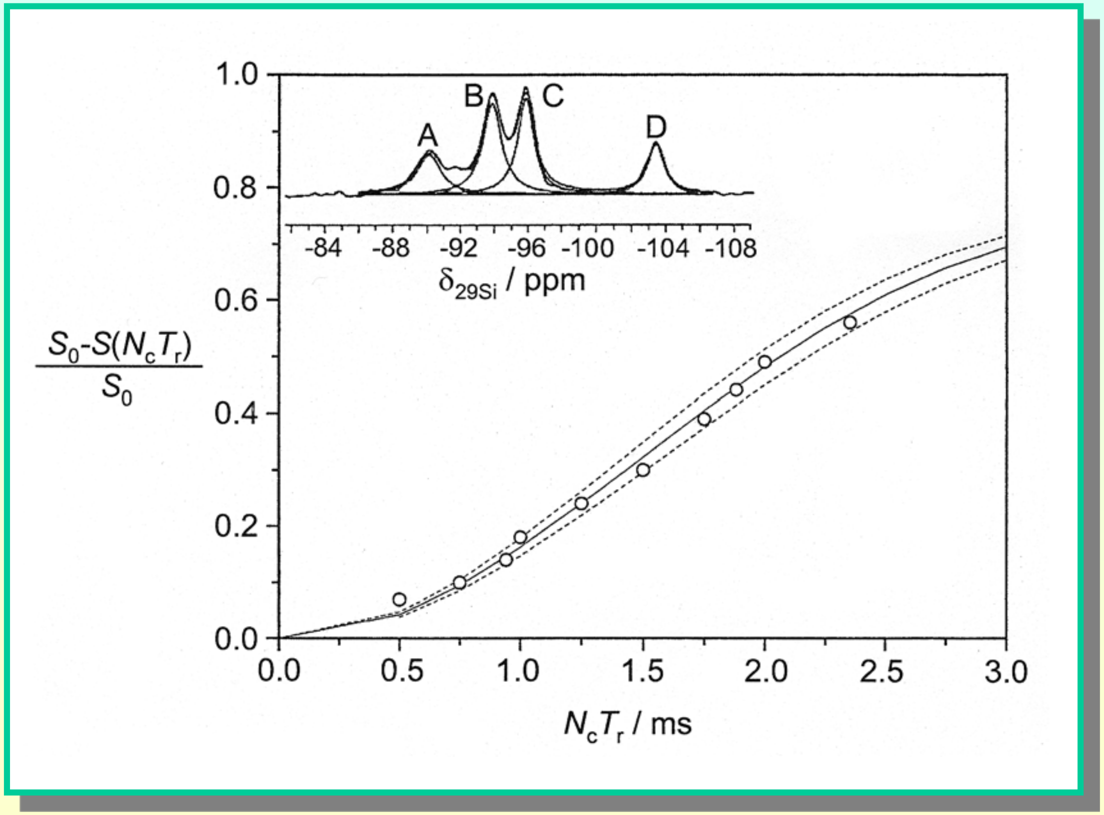
with

$$M_2^{\mathrm{IS}} = \frac{4}{15}\left(\frac{\mu_o}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{1}{N_I} \sum_{j=1}^{N_I} \sum_{k=1}^{N_S} r_{jk}^{-6}$$

T. Gullion, Chem. Phys. Lett. 246 (1995) 325.

Determination of the distance between Si and Al nuclei in ETAS-10

- **^{29}Si/^{27}Al REAPDOR NMR experiment on aluminotitanosilicate ETAS-10:**



→ **only signal A shows a REAPDOR response:**
Si(2Si, 1Ti, 1Al)

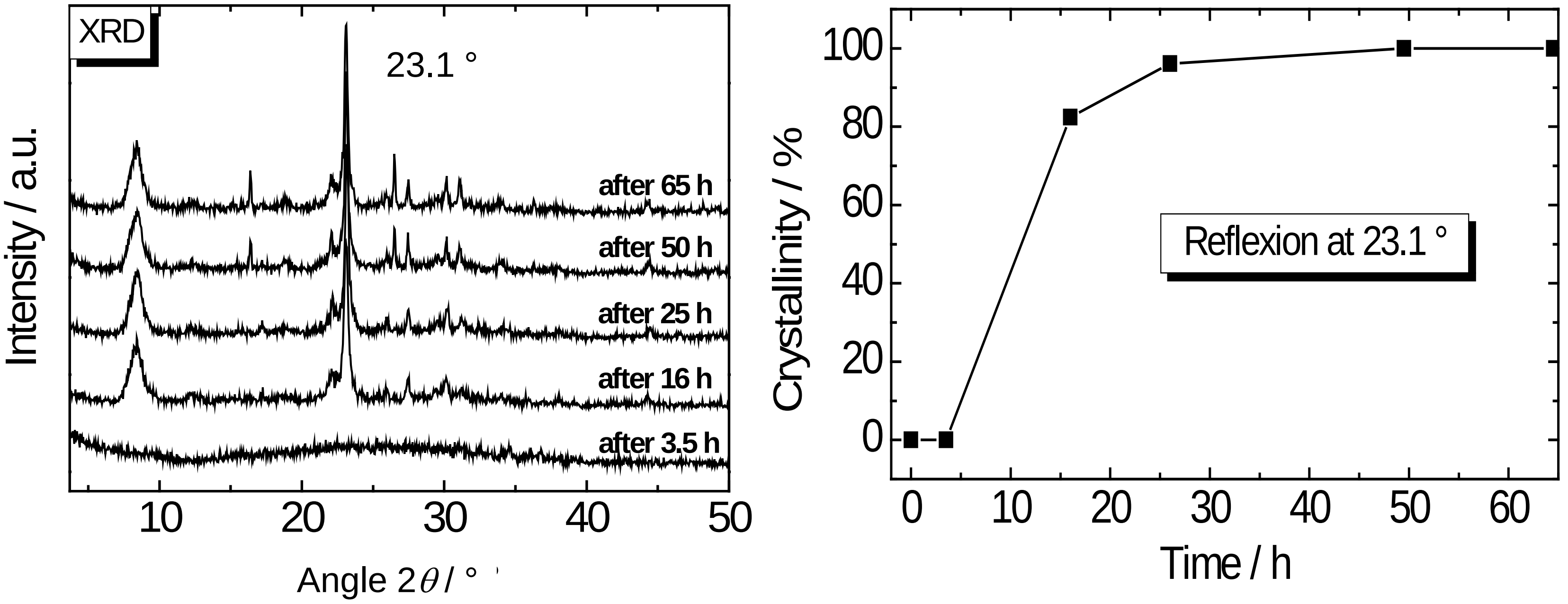
→ **REAPDOR fraction gives a Si-Al distance of:**
0.323 nm

S. Ganapathy et al., Chem. Phys. Lett. 390 (2004) 79.

Local structure of particels during the synthesis of solid catalysts

Crystallinity of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.2)

- **powder X-ray diffractograms and crystallinity as a function of the dry-gel conversion time**

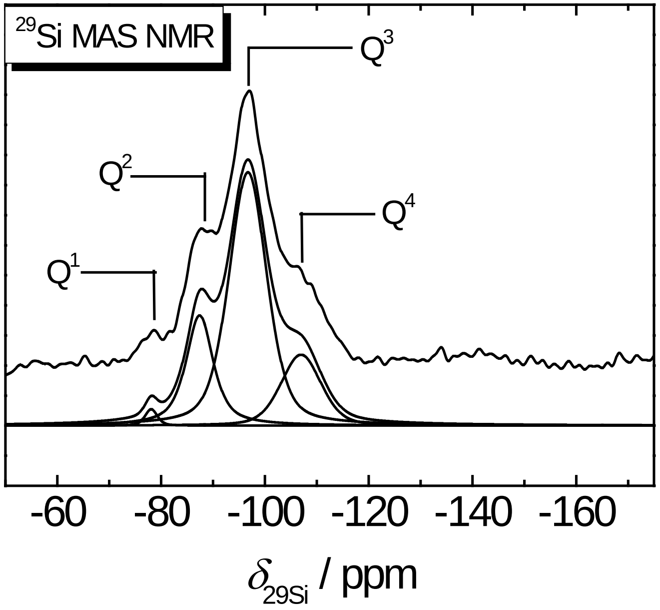


→ **formation of zeolite particles already within the first 16 h**

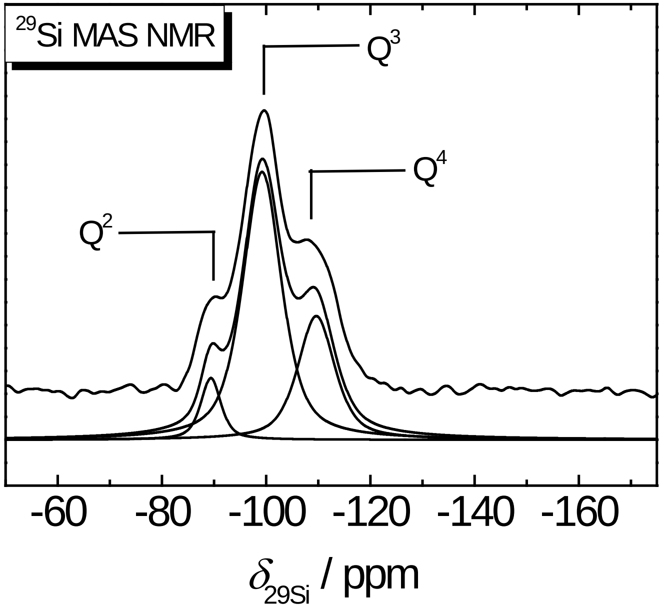
^{29}Si MAS NMR of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.2)

- **^{29}Si MAS NMR spectra recorded after different conversion times**

fresh dry-gel particles (0 h)



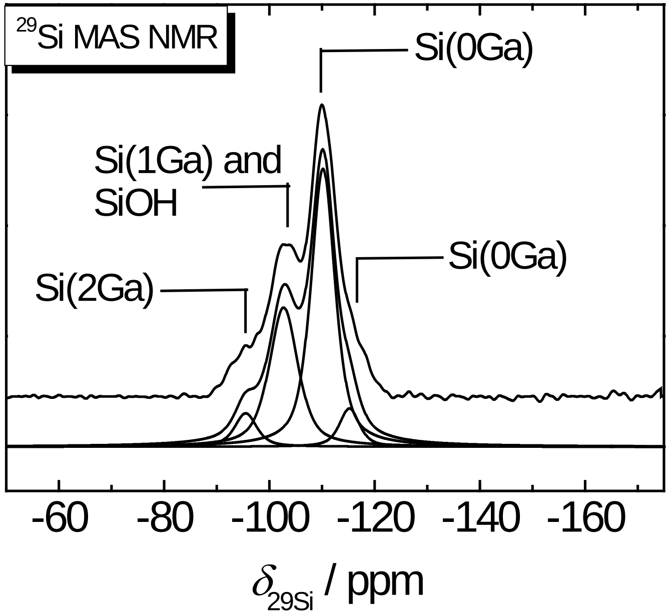
conversion time of 3.5 h



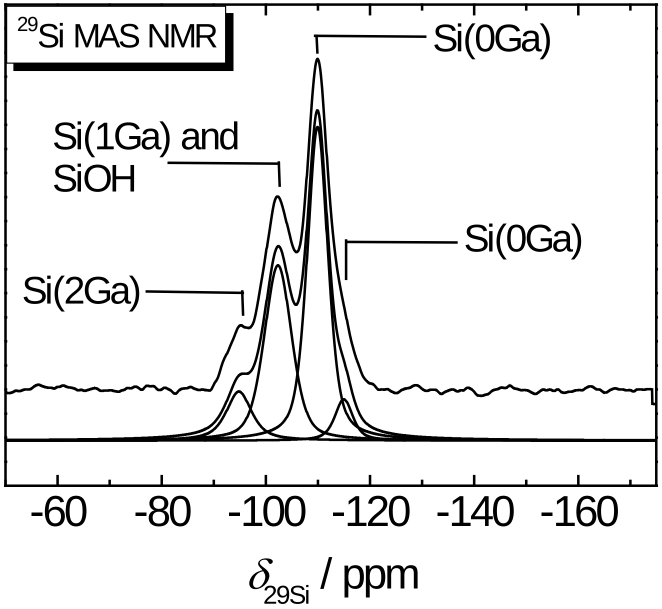
^{29}Si MAS NMR of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.2)

- **^{29}Si MAS NMR spectra recorded after different conversion times**

conversion time of 16 h

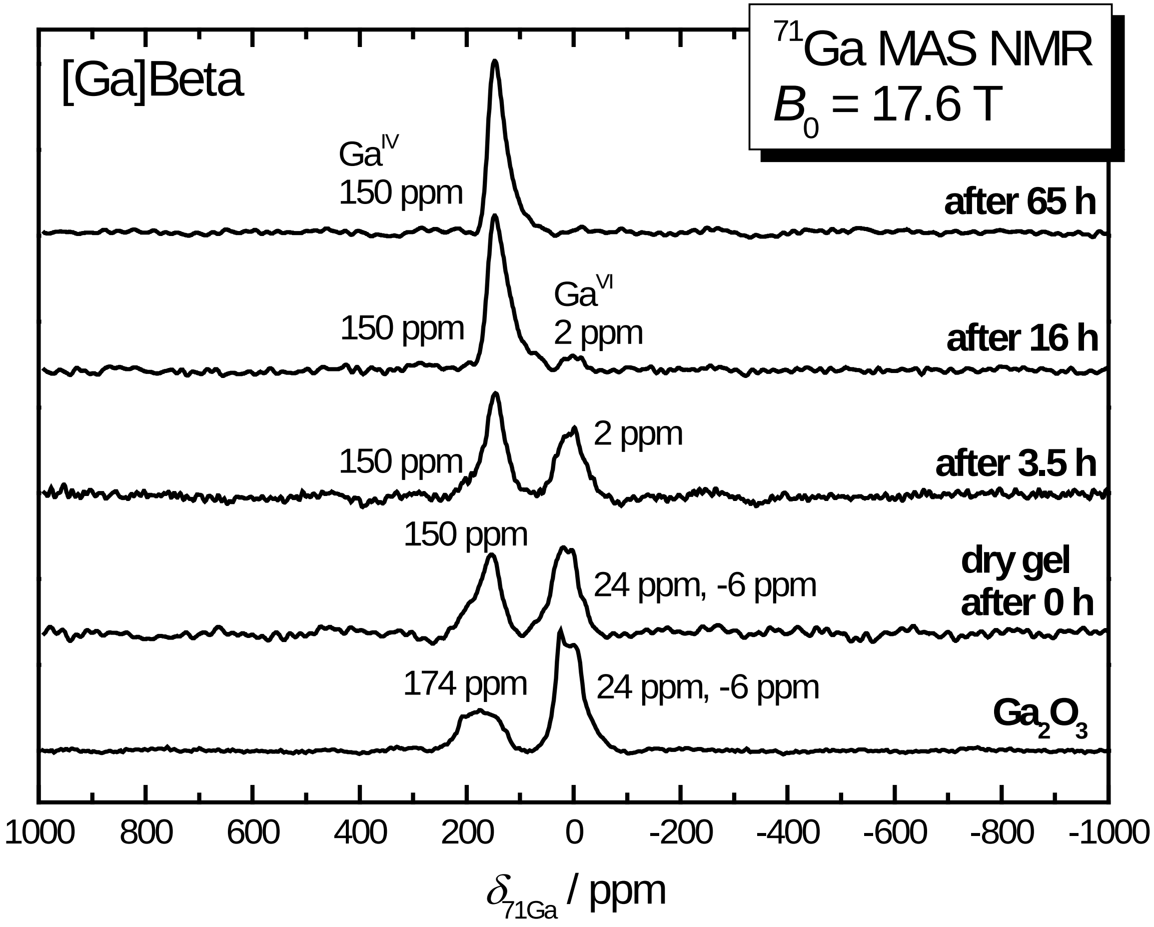


conversion time of 65 h



→ **incorporation of gallium into the zeolite framework**

^{71}Ga MAS NMR of zeolite [Ga]Beta (n_{Si}/n_{Ga} = 8.2)



Ga^{IV}	Ga^{VI}
100	0
93	7
58	42
45	55
34	66

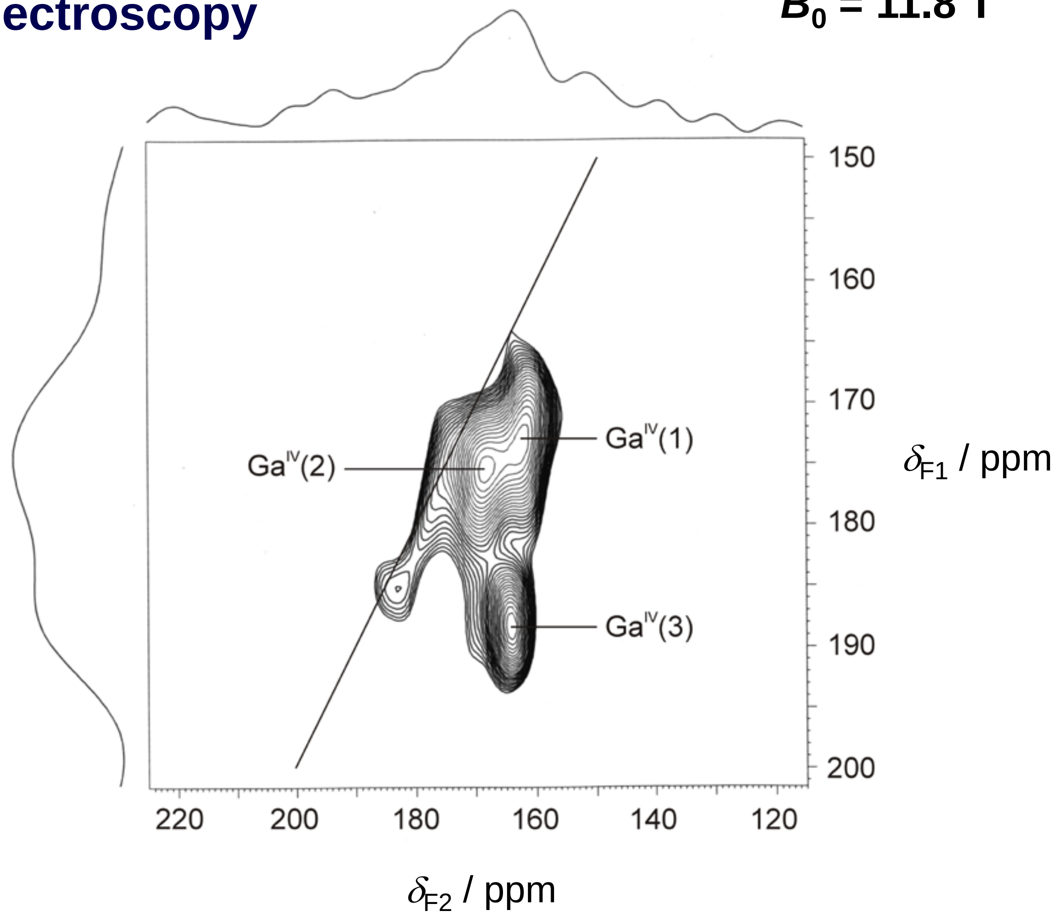
Two-dimensional ^{71}Ga MQMAS NMR spectroscopy of [Ga]Beta obtained after 65 h

- **different types of Ga^{IV} as evidenced by ^{71}Ga MQMAS NMR spectroscopy**

B_0 = 11.8 T

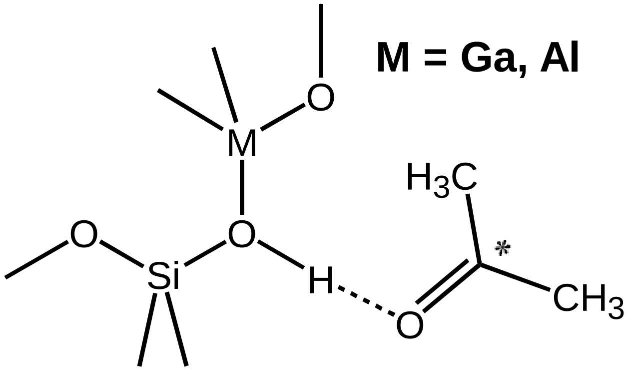
Ga^{IV}(1, 2):
framework gallium species

Ga^{IV}(3):
extra-framework gallium species at defect sites or in an amorphous phase



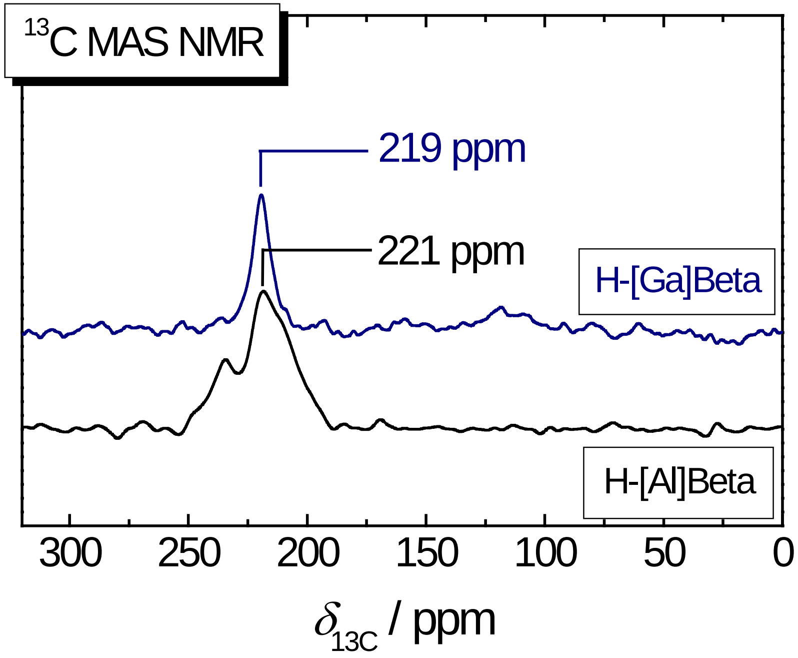
Acid strength of zeolites Beta and EU-1

- **adsorption of ^{13}C-2-acetone as probe molecule**



Zeolite	**δ_{13C} / ppm**
H-[Ga]EU-1	**214**
H-[Al]EU-1	**215**
H-[Ga]Beta	**219**
H-[Al]Beta	**221**
H-ZSM-5	**223**

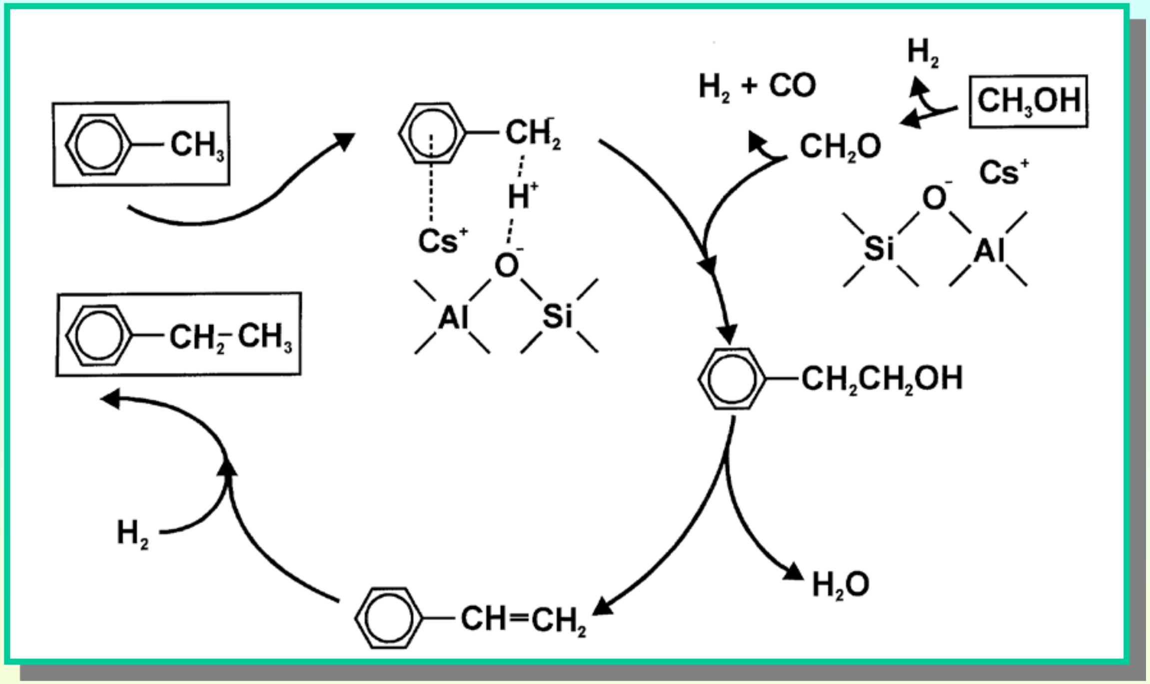
- **^{13}C MAS NMR shift as a measure of the acid strength**



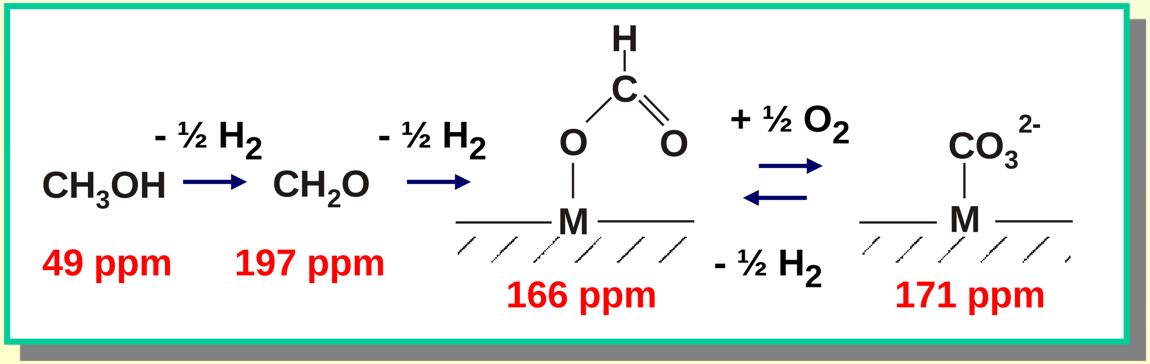
Study of the mechanism of reactions catalyzed by solid materials

Side-chain alkylation of toluene with methanol on basic zeolites

- **reaction scheme proposed by Yashima et al. , J. Catal. 26 (1972) 303:**
  - **activation of toluene by adsorption on the zeolite**
  - **conversion of methanol to formaldehyde catalyzed by base sites**

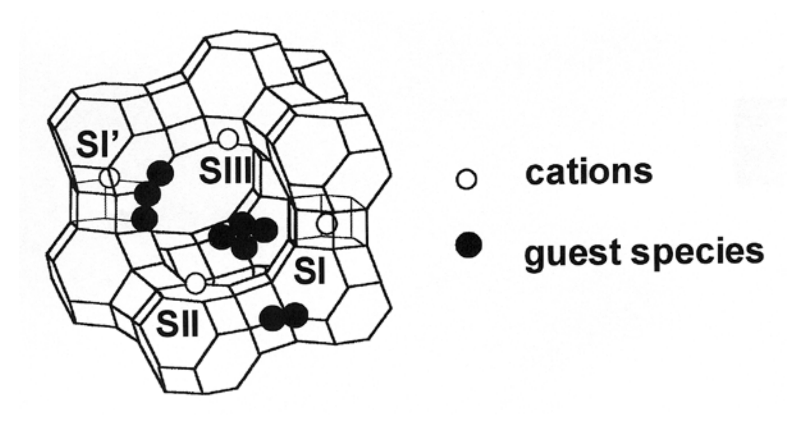


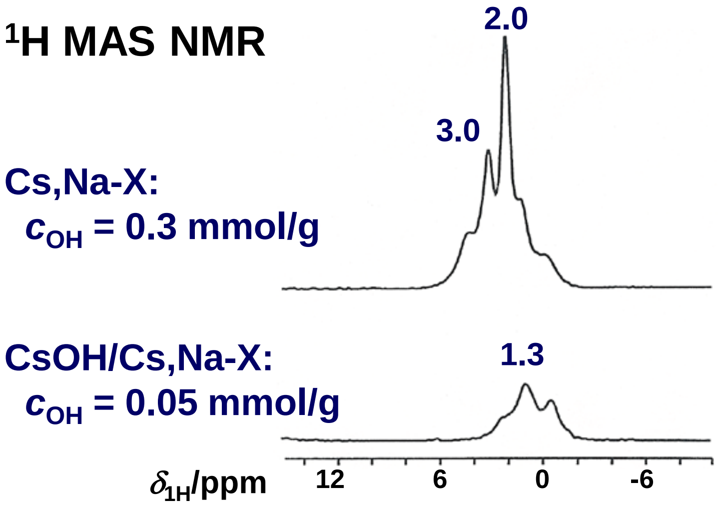
- **proposed surface species:**
  - **formate (δ_{13C} = 166 ppm)**
  - **carbonate (δ_{13C} = 171 ppm)**



NMR characterization of the calcined zeolite CsOH/Cs,Na-X

- **zeolite Na-X (n_{Si}/n_{Al} = 1.4) exchanged with cesium cations (55 %) and impregnated with cesium hydroxide (24 CsOH/u.c.)**

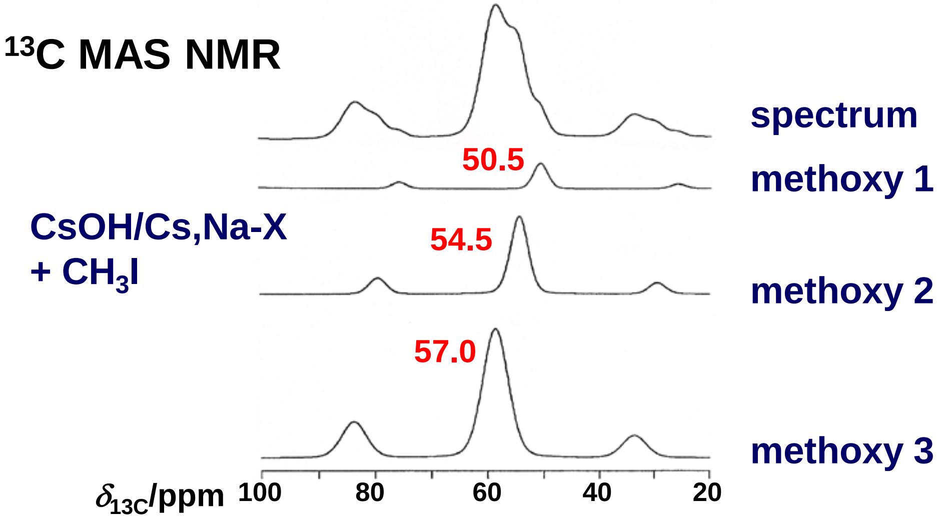




^{1}H MAS NMR

**Cs,Na-X:
c_{OH} = 0.3 mmol/g**

**CsOH/Cs,Na-X:
c_{OH} = 0.05 mmol/g**



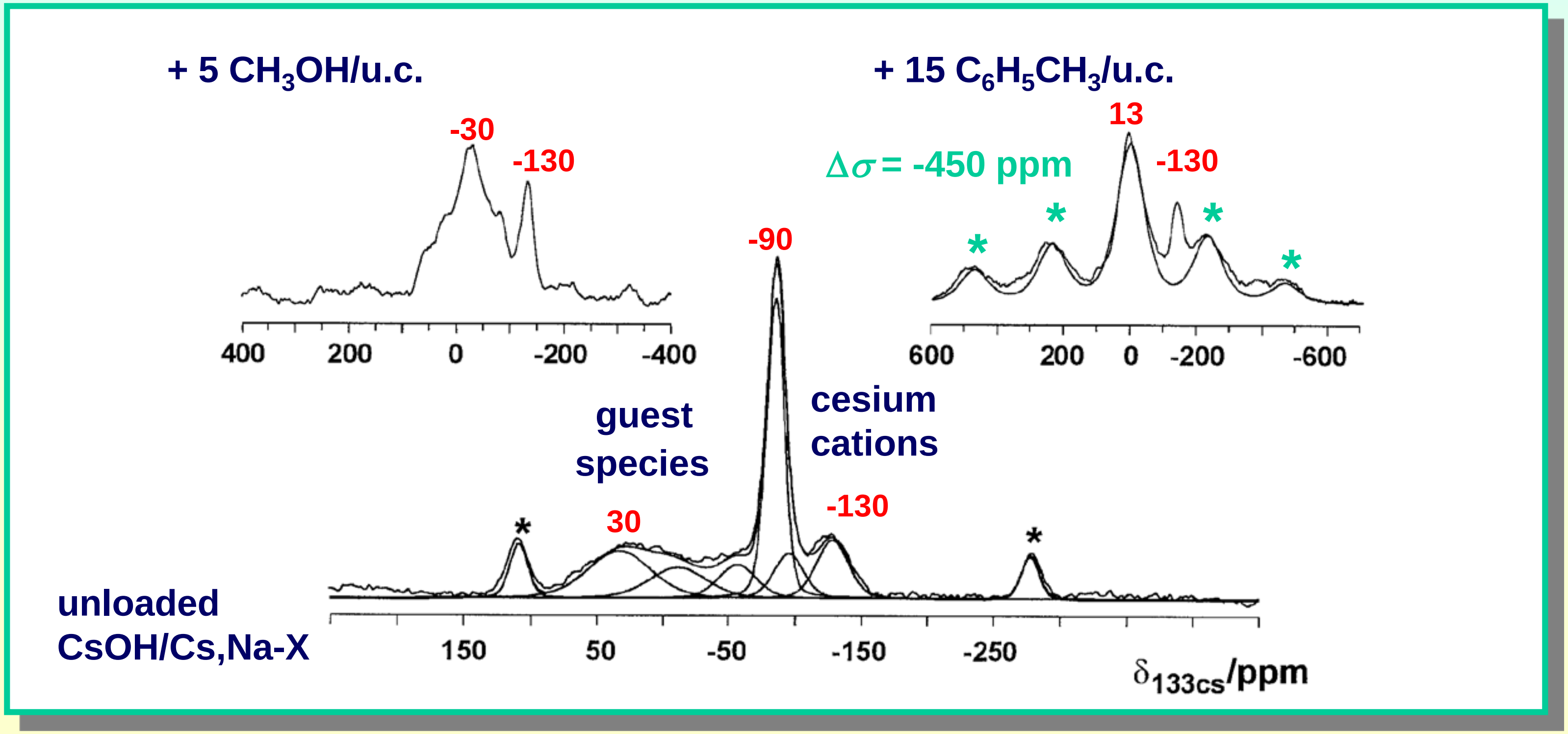
^{13}C MAS NMR

**CsOH/Cs,Na-X
+ CH_3I**

U. Schenk, PhD thesis, University of Stuttgart, 2001.

Adsorbate complexes formed by the reactants on zeolite CsOH/Cs,Na-X

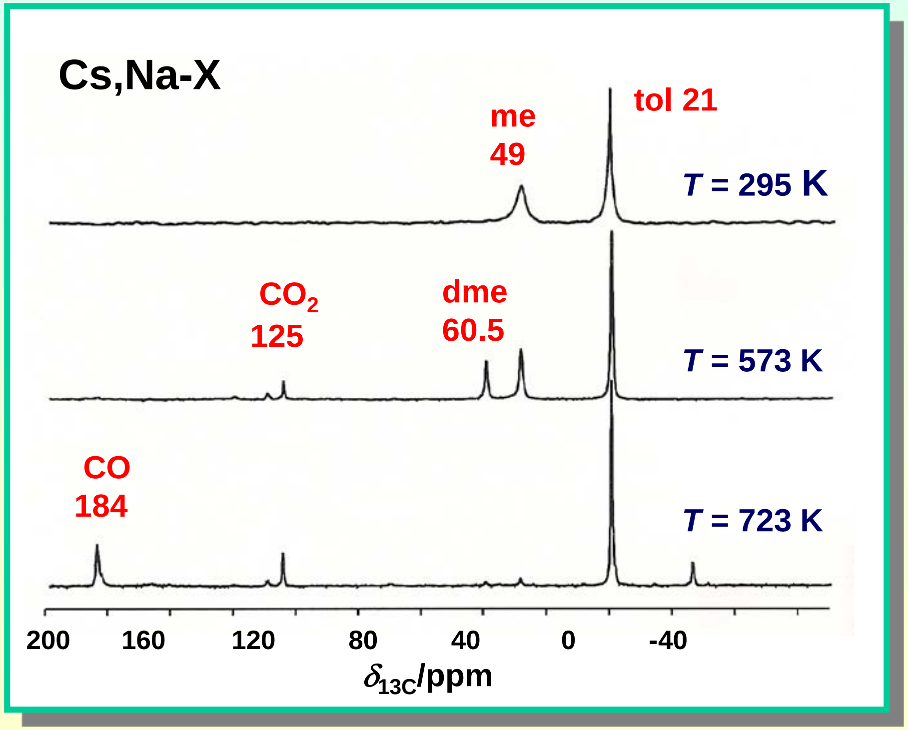
- ^{133}Cs MAS NMR spectroscopy performed before and after adsorption of methanol and toluene

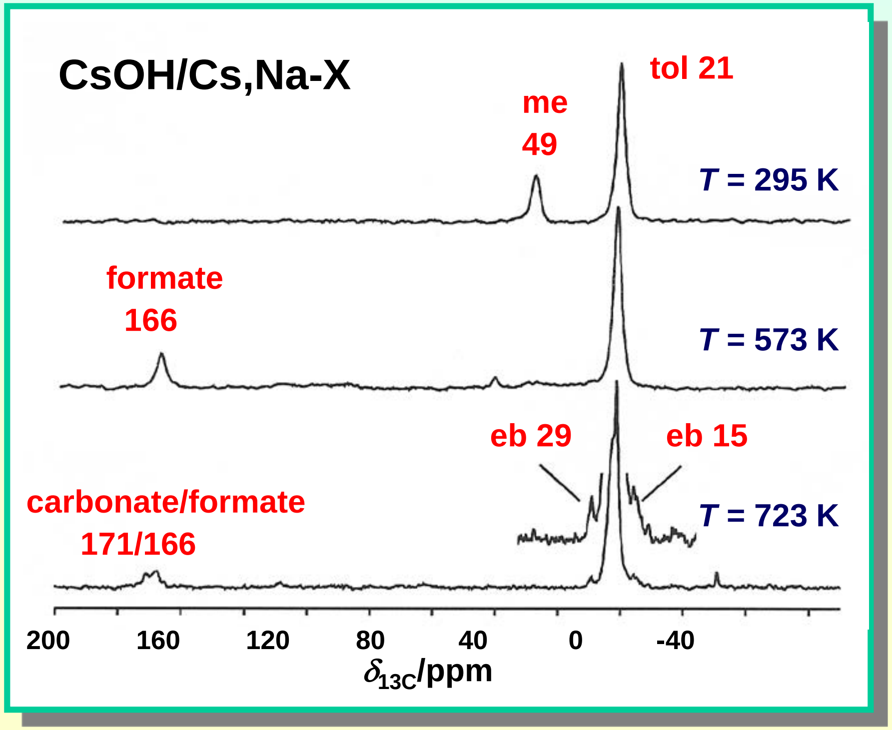


M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

Side-chain alkylation of toluene on basic zeolites X under batch conditions

^{13}C MAS NMR spectroscopy: $15\ C_6H_5{}^{13}CH_3$/u.c.
$5\ {}^{13}CH_3OH$/u.c.





M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

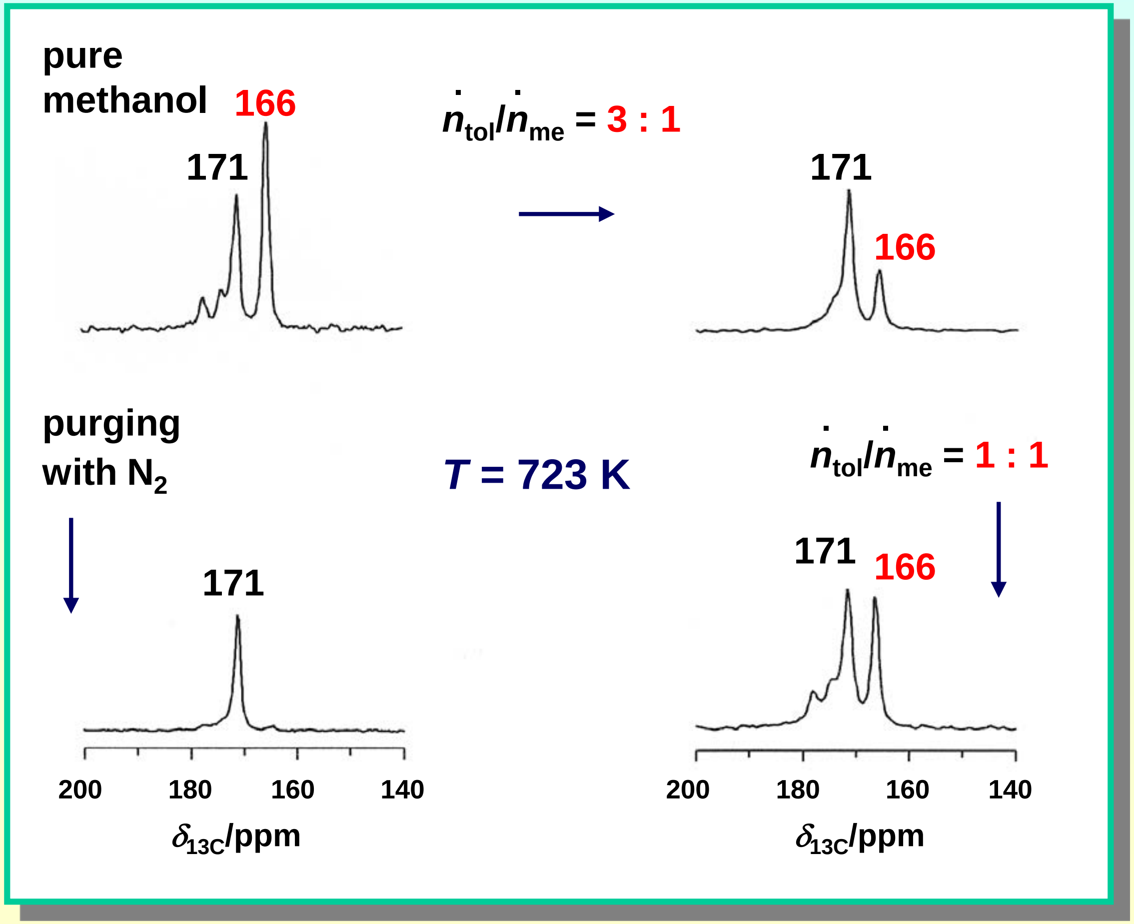
Reactivity of formate species on zeolite CsOH/Cs,Na-X under flow conditions

- ***in situ*** **^{13}C CF MAS NMR spectroscopy:**

W_{cat}/F_{me} = 60 gh/mol

→ **carbonate species are chemically stable**

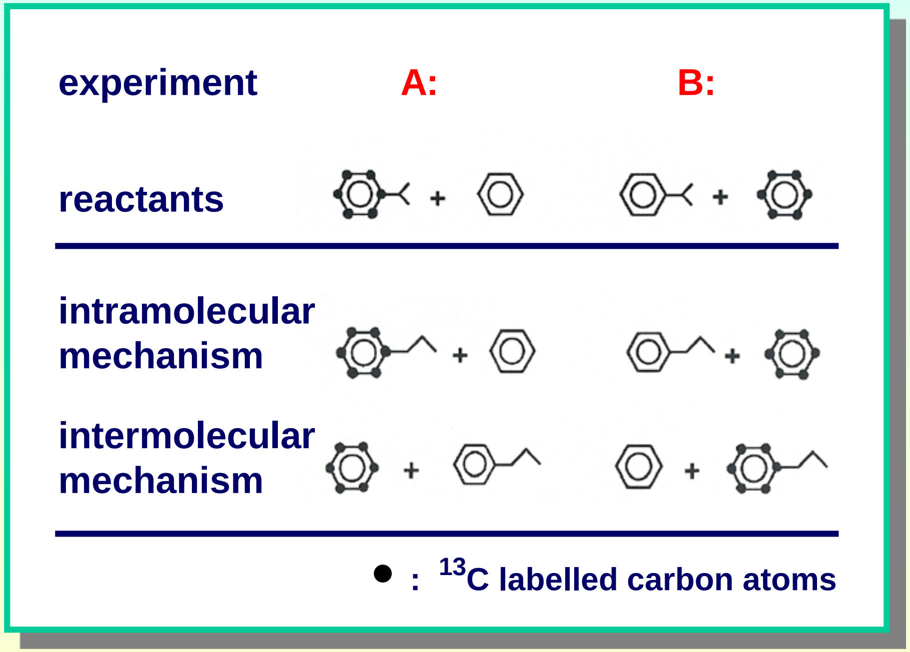
→ **formate species are consumed by toluene which indicates a high reactivity**

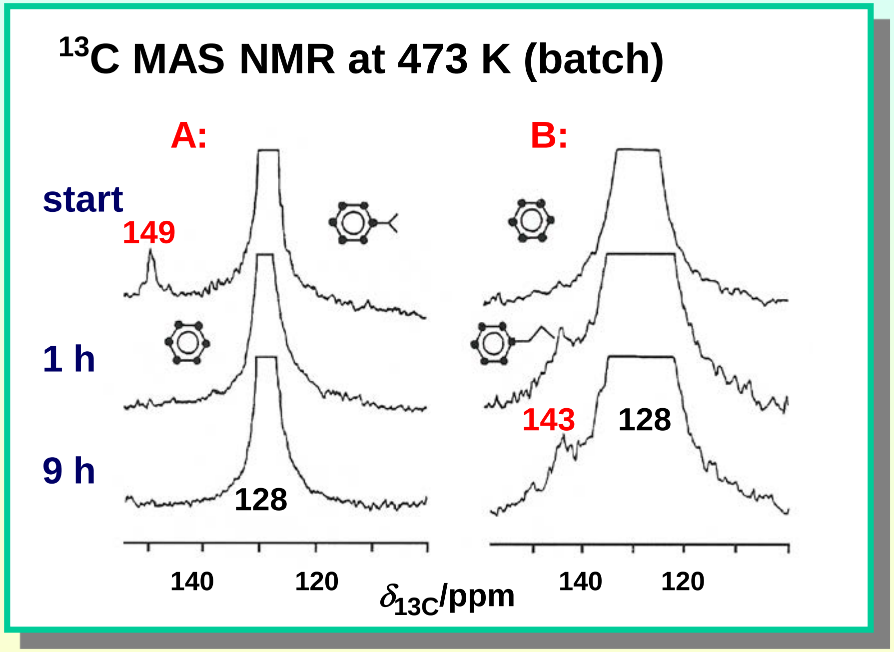


M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

Investigation of reaction pathways by selectively labelled reactants

- isomerization of cumene to n-propylbenzene on zeolite H-ZSM-11 in the presence of benzene




^{13}C MAS NMR at 473 K (batch)

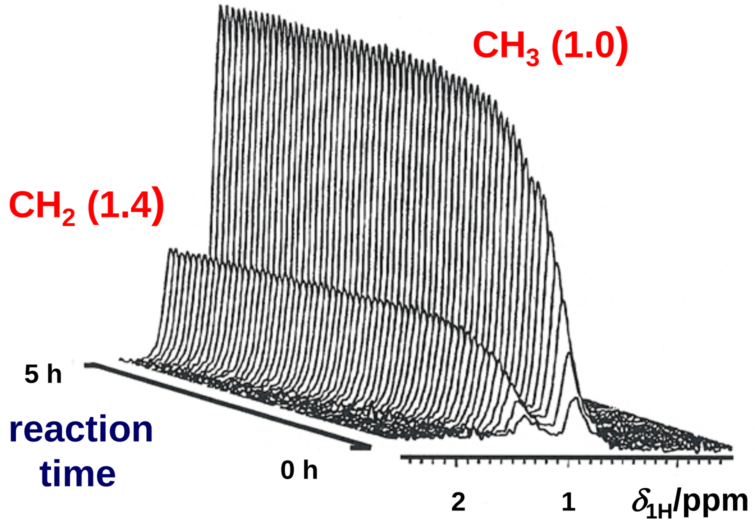
→ experiments A and B indicate an intermolecular reaction mechanism

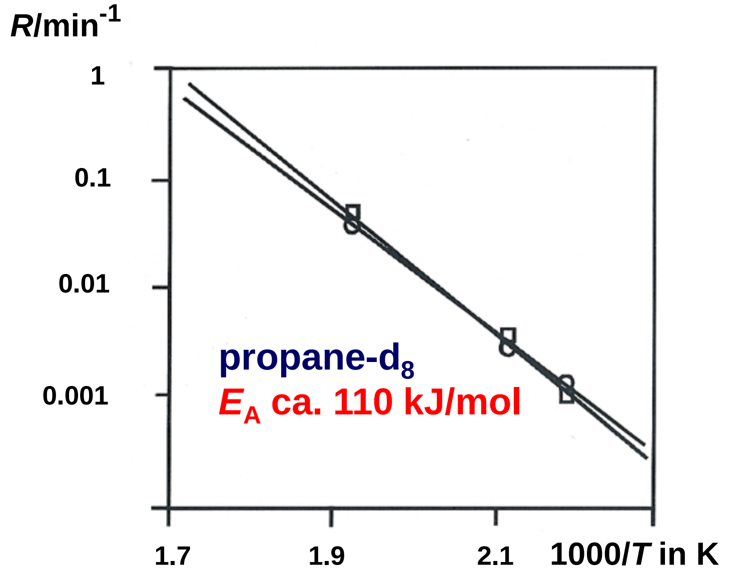
E. Derouane et al., Catal. Lett. 58 (1999) 1.

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

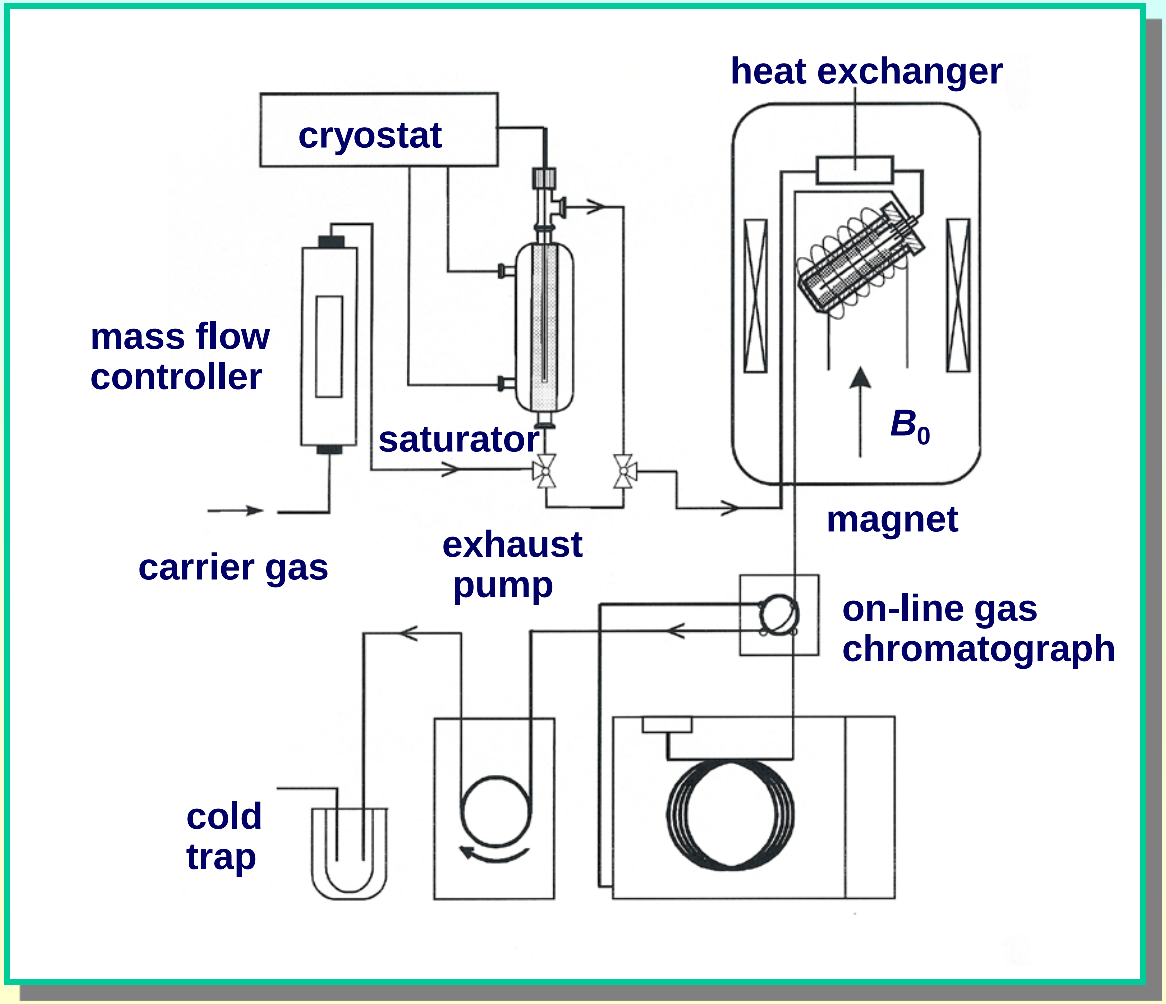
B:

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

→ formation carbenium ions

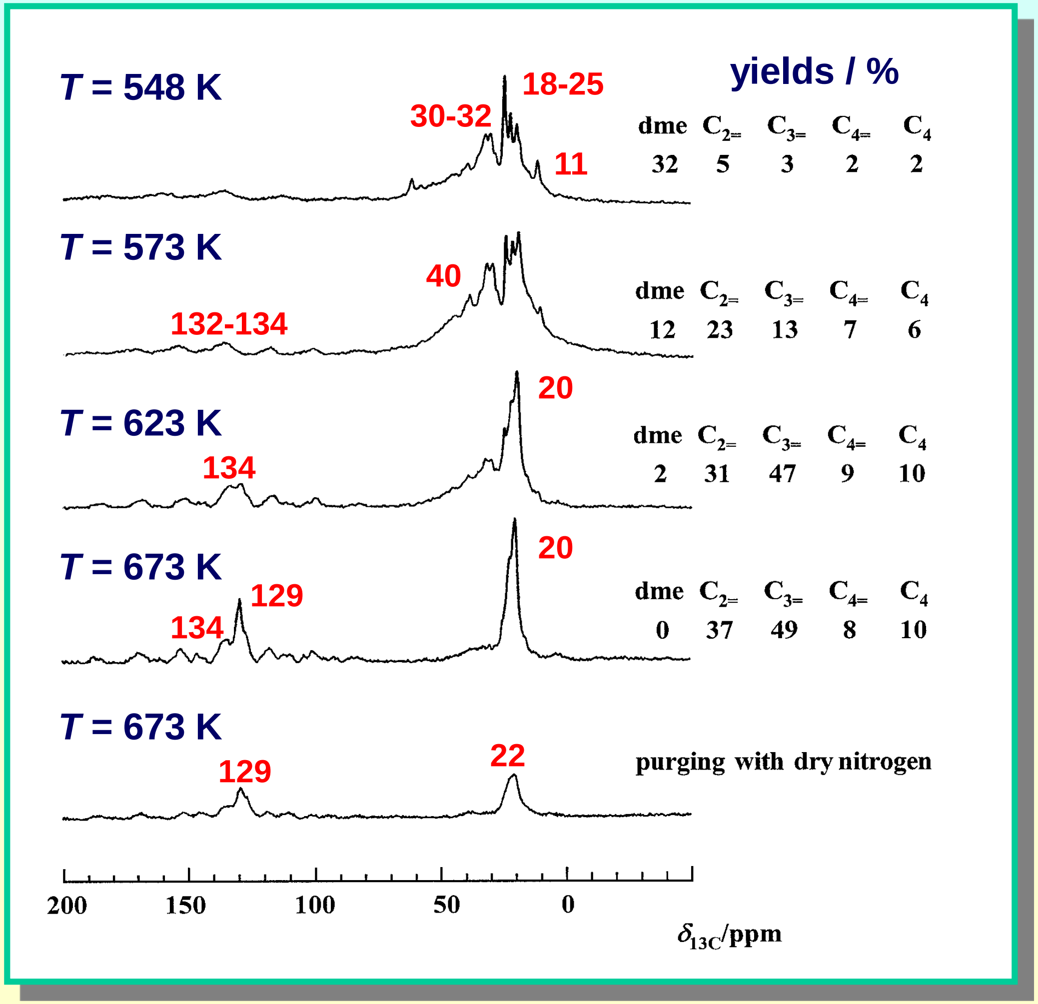
A.G. Stepanov et al., Catal. Lett. 54 (1998) 1; J. Sommer et al., J. Catal. 181 (1999) 265.

Coupling of in situ CF MAS NMR and on-line gas chromatography



M. Hunger et al., Catal. Lett. 57 (1999) 199.

Conversion of methanol on H-SAPO-34 studied by in situ ^{13}C CF MAS NMR



yields / %

	dme	$C_{2=}$	$C_{3=}$	$C_{4=}$	C_4
T = 548 K	32	5	3	2	2
T = 573 K	12	23	13	7	6
T = 623 K	2	31	47	9	10
T = 673 K	0	37	49	8	10

T = 673 K: purging with dry nitrogen

***T* < 623 K:**

→ **mixture of olefinic compounds:**

3-hexene (14.4, 25.9, 131.2 ppm)
2,3-hexadiene (17.5, 126.2, 132.5 ppm)
....

***T* > 623 K:**

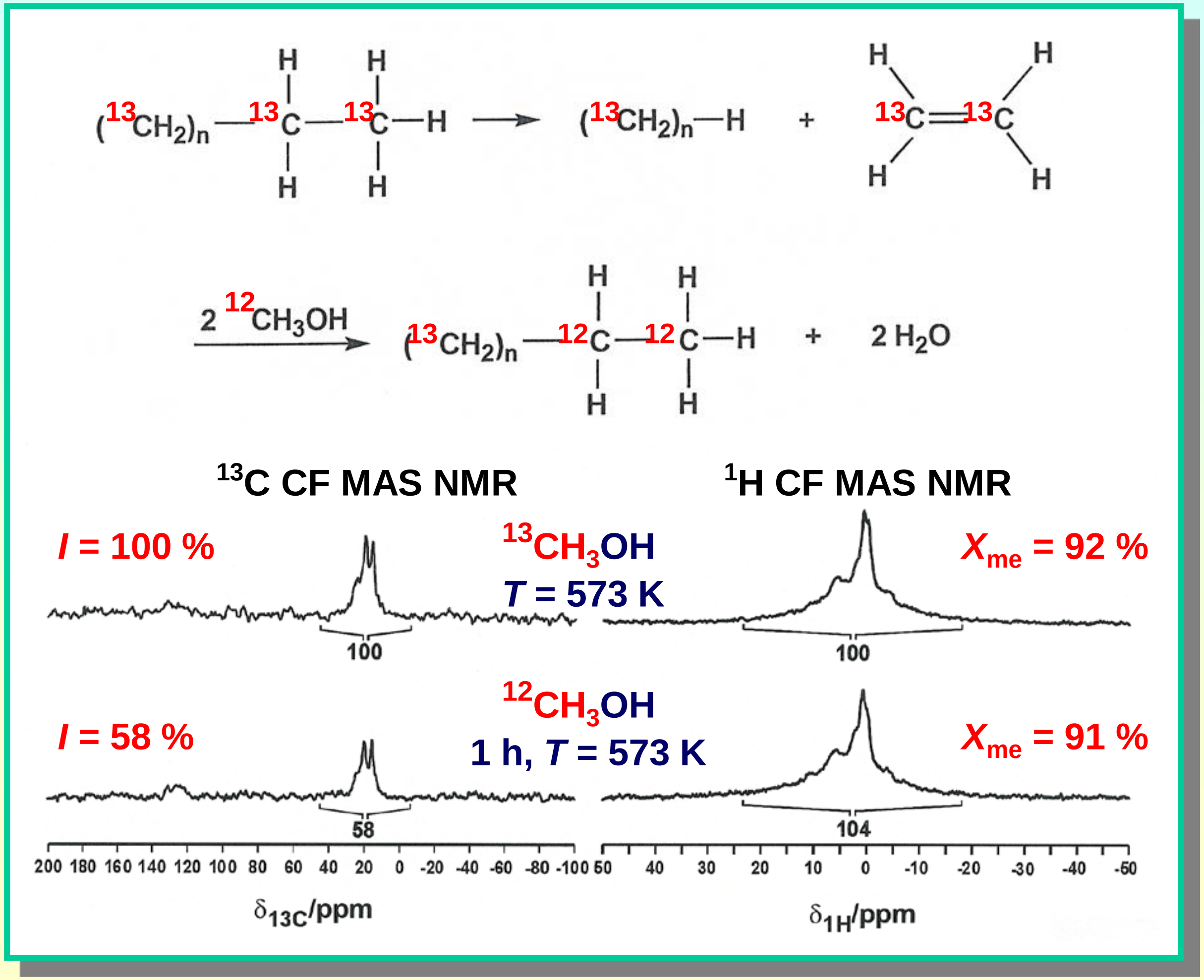
→ **domination of aromatic compounds:**

benzene (128.6 ppm)
toluene (20.3, 128.5, 129.0 ppm)
....

tetramethylbenzene (18.9, 131.1, 134 ppm)
hexamethylbenzene (17.6, 132.1 ppm)

M. Hunger, et al., Catal. Lett. 1-2 (2001) 61.

Role of the carbon pool in the MTO process on H-ZSM-5



switching of the reactant flow induces a decrease of the ^{13}C-isotopes in the alkyl groups:

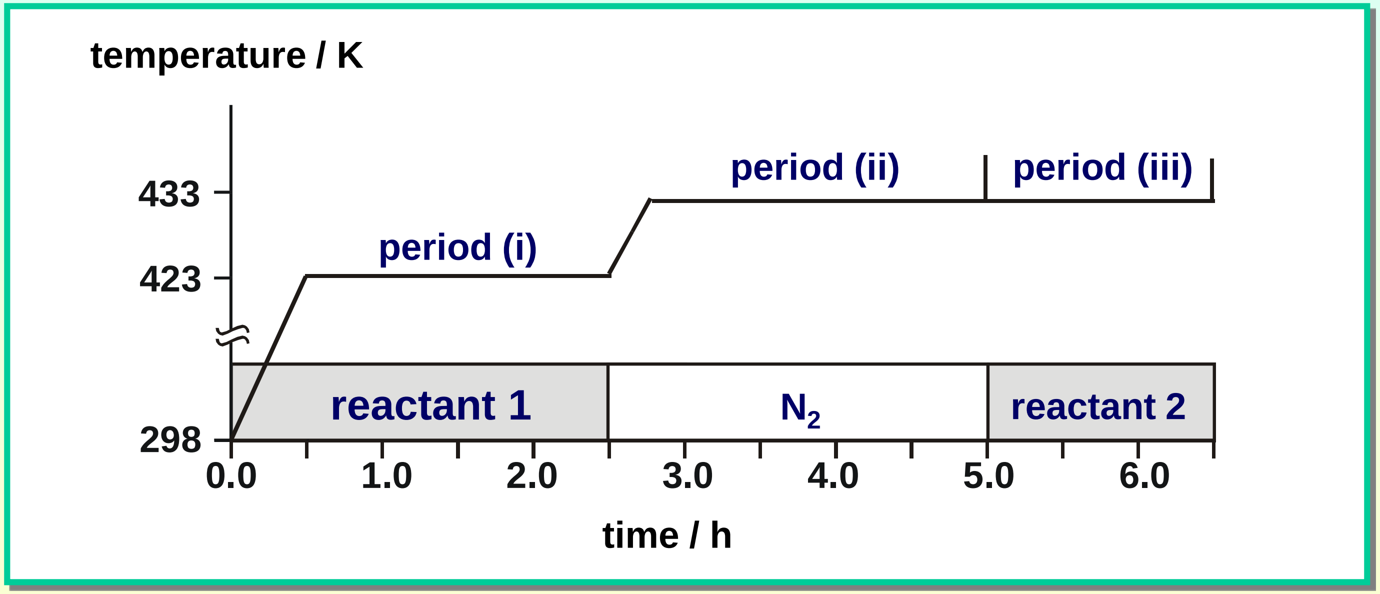
→ **alkyl groups are involved in the formation of olefins**

→ **carbon pool plays an active role in the MTO process**

M. Seiler et al., Catal. Lett. 88 (2003) 187.

Study of surface compounds by in situ SF (stopped-flow) MAS NMR

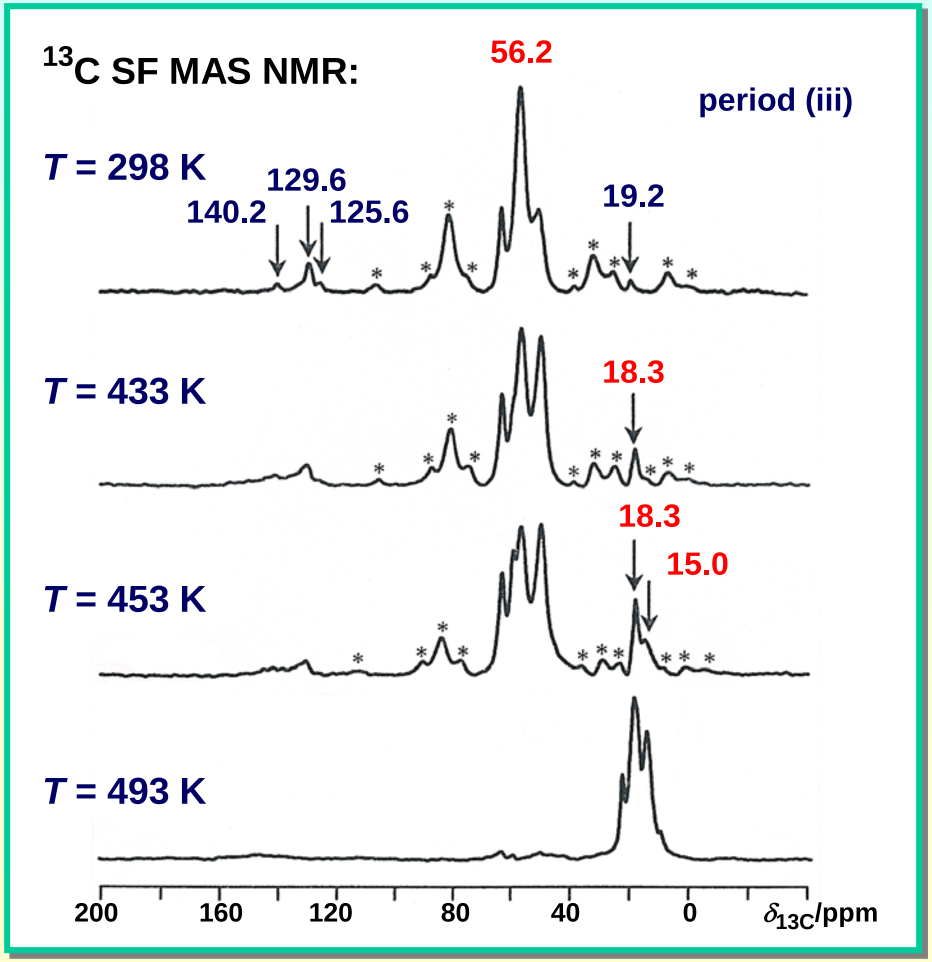
selective preparation of adsorbate complexes by purging the volatile reactants in period (ii) and study of their further reaction in period (iii)



→ **investigation of the reactivity of surface compound and intermediates**

Methylation of aromatics by surface methoxy groups

reaction of methoxy groups with toluene on zeolite H-Y



methoxy toluene

$$SiO(^{13}CH_3)Al \quad + \quad CH_3C_6H_5$$

56.2 ppm 19.2 ppm

$$\rightarrow \quad SiOHAl \; + \; CH_3C_6H_4{}^{13}CH_3$$

18.3 ppm

- **methylation of aromatics by surface methoxy groups starts at T = 433 K**

W. Wang et al., J. Am. Chem. Soc. 125 (2003) 15260.

Summary I

advantages:

FTIR:
- low costs
- commercially available
- large temperature range

UV/Vis:
- low costs
- high sensitivity
- large temperature range

ESR:
- high sensitivity
- sensitive for the local structure of adsorbates and surface sites

NMR:
- large number of NMR sensitive nuclei
- good separation of signals

disadvantages:

FTIR:
- broad and overlapping bands
- no direct quantitative evaluation
- problematic assignment of bands

UV/Vis:
- limited application
- broad and overlapping bands
- problematic assignment of bands

ESR:
- limited application
- strong line broadening at high temperatures

NMR:
- high costs
- low sensitivity
- long observation time

Summary II

applications of solid-state NMR spectroscopy in heterogeneous catalysis:

- **concentration and chemical behaviors of surface sites**
- **local structure and composition of the framework of solid catalysts**
- **structure of particles formed during the synthesis of solid catalysts**
- **intermediates and surface compounds formed upon conversion of reactants on solid catalysts**