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# ***Solid-state NMR Spectroscopy in Heterogeneous Catalysis***

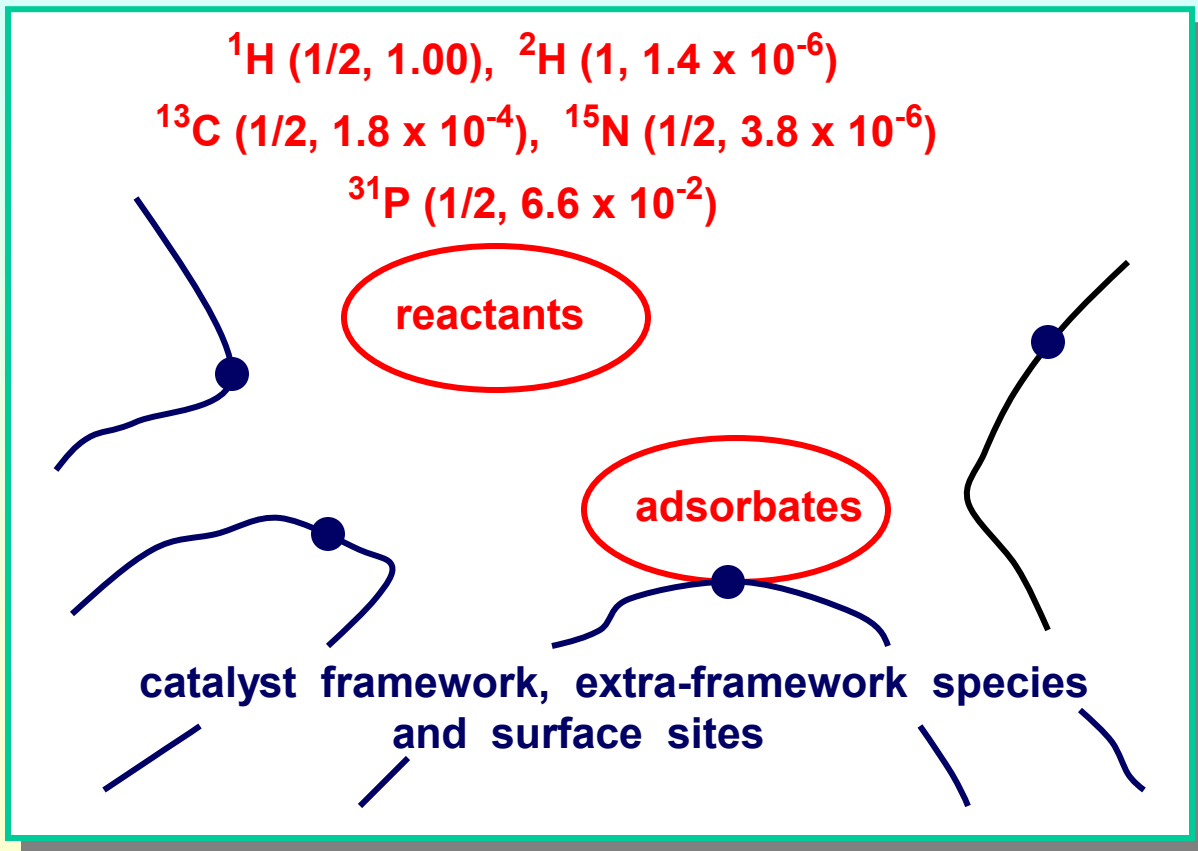
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***Lecture Series Heterogeneous Catalysis  
Fritz Haber Institute, Berlin, November 11, 2005***

# Examples of nuclei accessible for in situ NMR in heterogeneous catalysis

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



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

# ***Contents***

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- **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**

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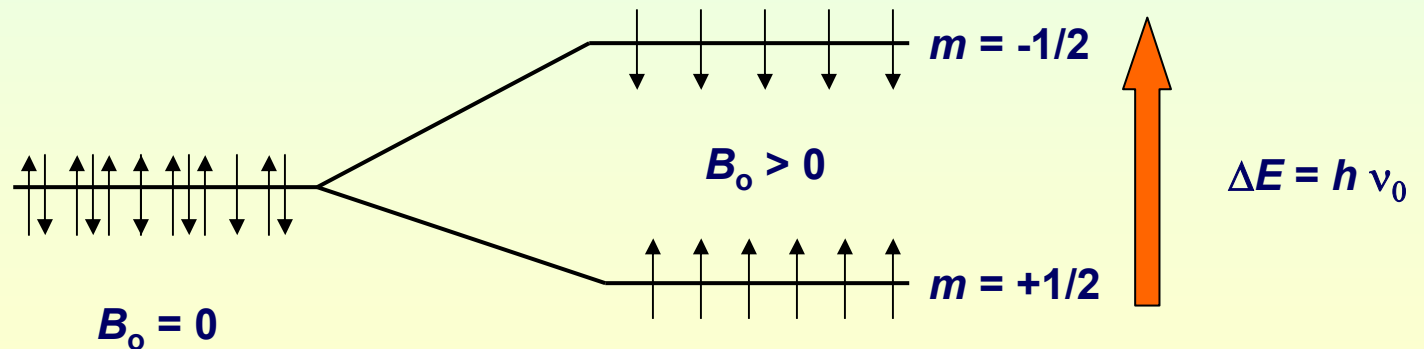
***Basics and specific problems of solid-state  
NMR spectroscopy***

# 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  $B_0$



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

# Basics of NMR spectroscopy

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

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

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

- isotropic shielding:  $\sigma_{iso}$  in ppm (parts per million)
- shielding anisotropy:  $\Delta\sigma$
- asymmetry parameters:  $\eta$
- Euler angles:  $\alpha$  and  $\beta$

- characteristic resonance positions for different local structures:
- number and type of coordinated atoms ( $\sigma_{iso}$ ,  $\delta_{iso}$ )
  - bond angle and bond lengths ( $\sigma_{iso}$ ,  $\delta_{iso}$ )
  - symmetry of local structure ( $\eta$ )

# Basics of NMR spectroscopy

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

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

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

- vector between interacting nuclei  $i$  and  $k$ :  $r_{ik}$
- angle between  $B_0$  and  $r_{ik}$ :  $\beta_{ik}$

- strength of dipolar interaction (broadening):
- distance of interacting nuclei ( $r_{ik}$ )
  - number of interacting nuclei
  - orientation of molecules and complexes in solids ( $\beta_{ik}$ )

# Basics of NMR spectroscopy

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

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

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

- electric quadrupole moment in the nuclei:  $eQ$
- z-component of the electric field gradient:  $V_{zz} = eq$
- quadrupole coupling constant:  $QCC = e^2 q Q / h$
- 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

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



# ***Problems of NMR spectroscopy on working catalysts***

**magnetization:**

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

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

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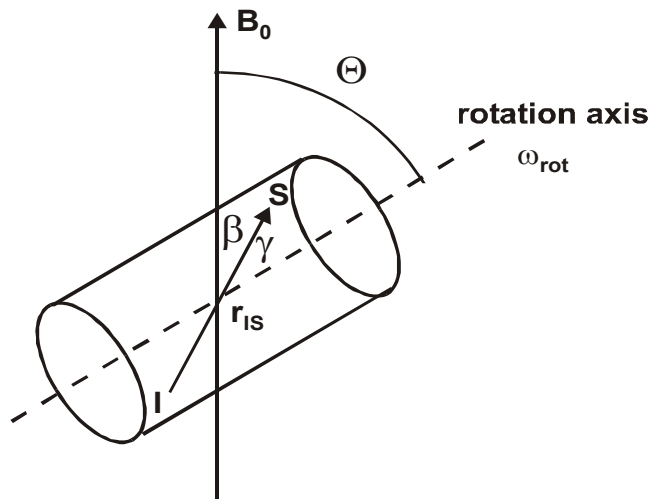
***Experimental techniques of solid-state  
NMR spectroscopy***

# High-resolution solid-state NMR techniques

spin  $I = 1/2$  :

- magic angle spinning (**MAS**)

$$\nu_{\text{CSA,DI,1QI}} = f \{3\cos^2\Theta - 1\} \rightarrow \Theta = 54.7^\circ$$

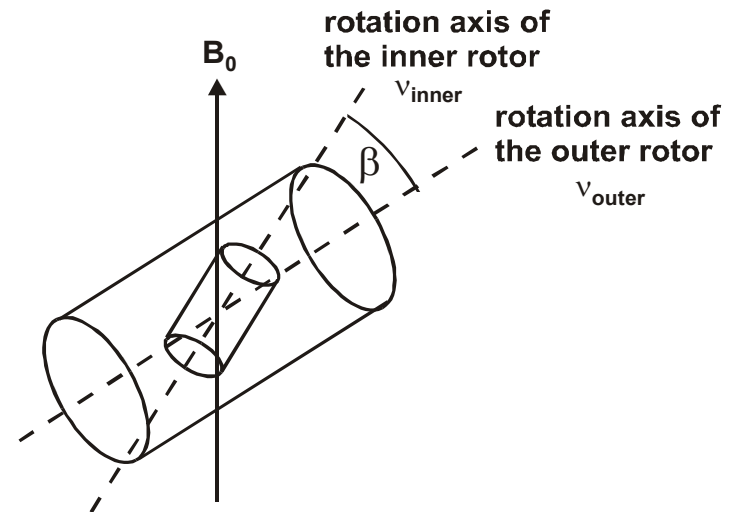


spin  $I > 1/2$  :

- double oriented rotation (**DOR**)

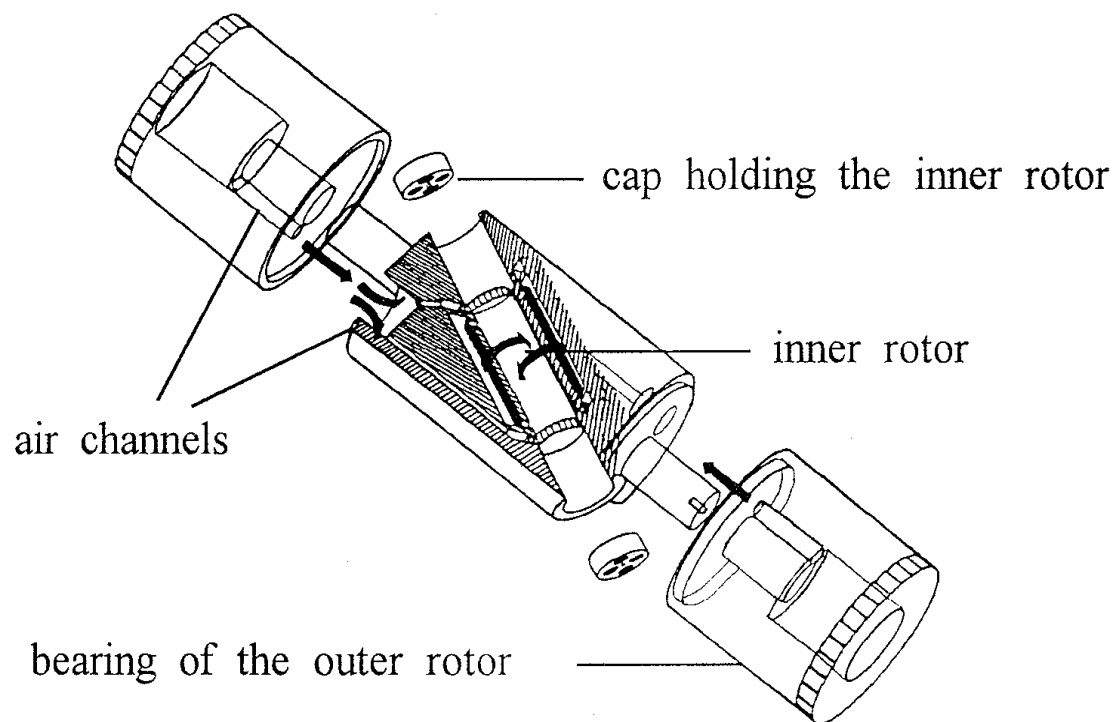
$$\nu_{2\text{QI}} = f \{35\cos^4\beta - 30\cos^2\beta + 3\}$$

$$\rightarrow \beta = 30.6^\circ, \beta = 70.1^\circ$$



# High-resolution solid-state NMR techniques

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



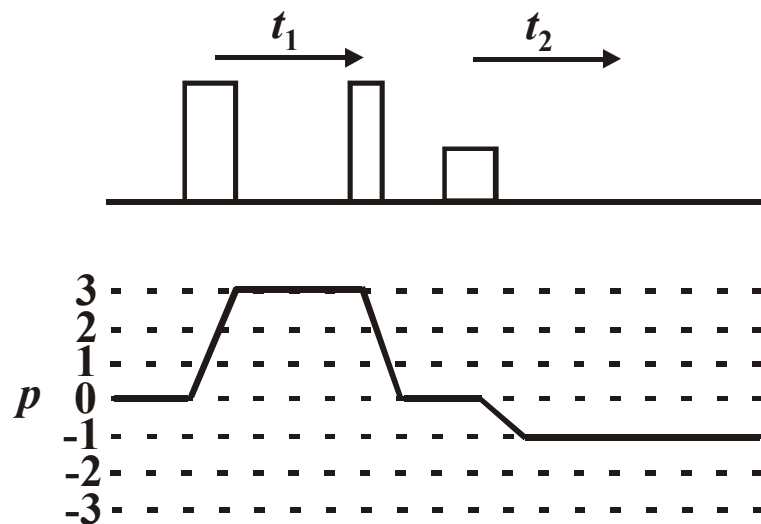
# High-resolution solid-state NMR techniques

spin  $I > \frac{1}{2}$  :

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

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

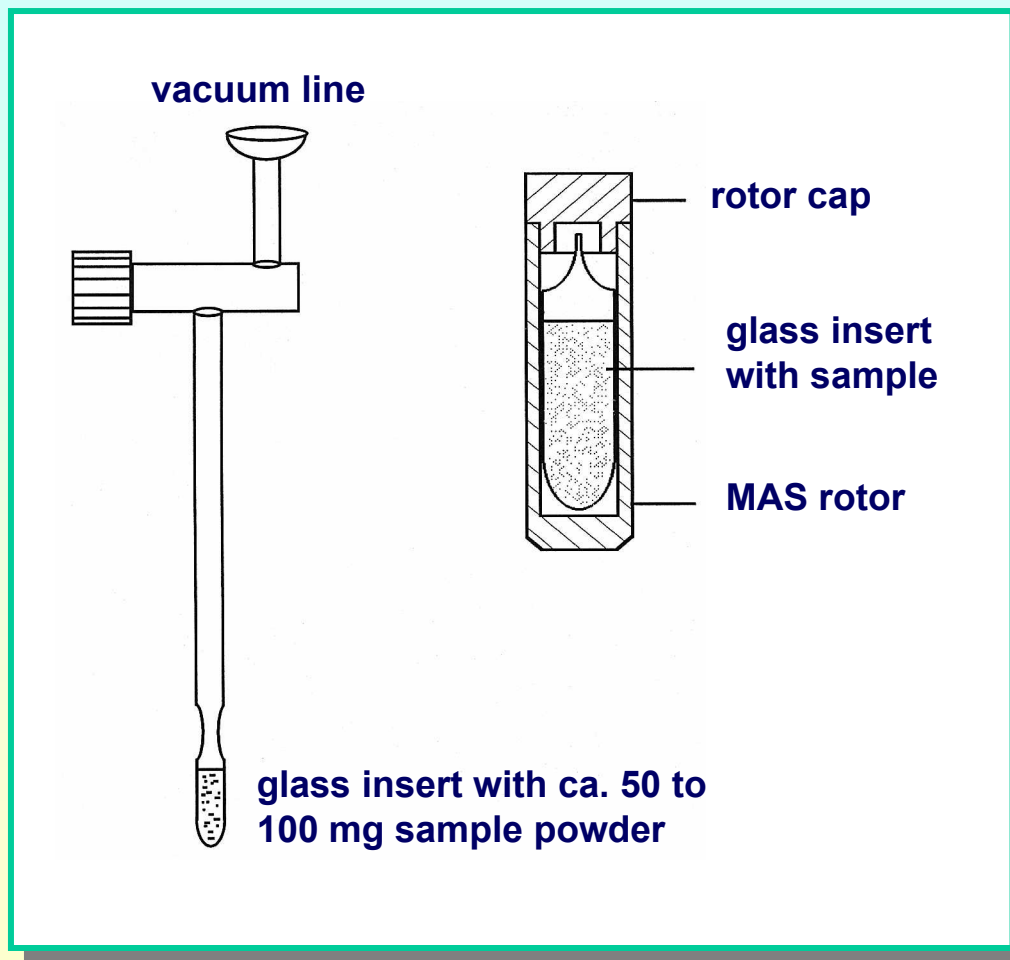
- MQMAS pulse sequence (z-filter)



with  $p$ : multiple-quantum level  
 $t_1$ : pulse delay  
 $t_2$ : echo delay

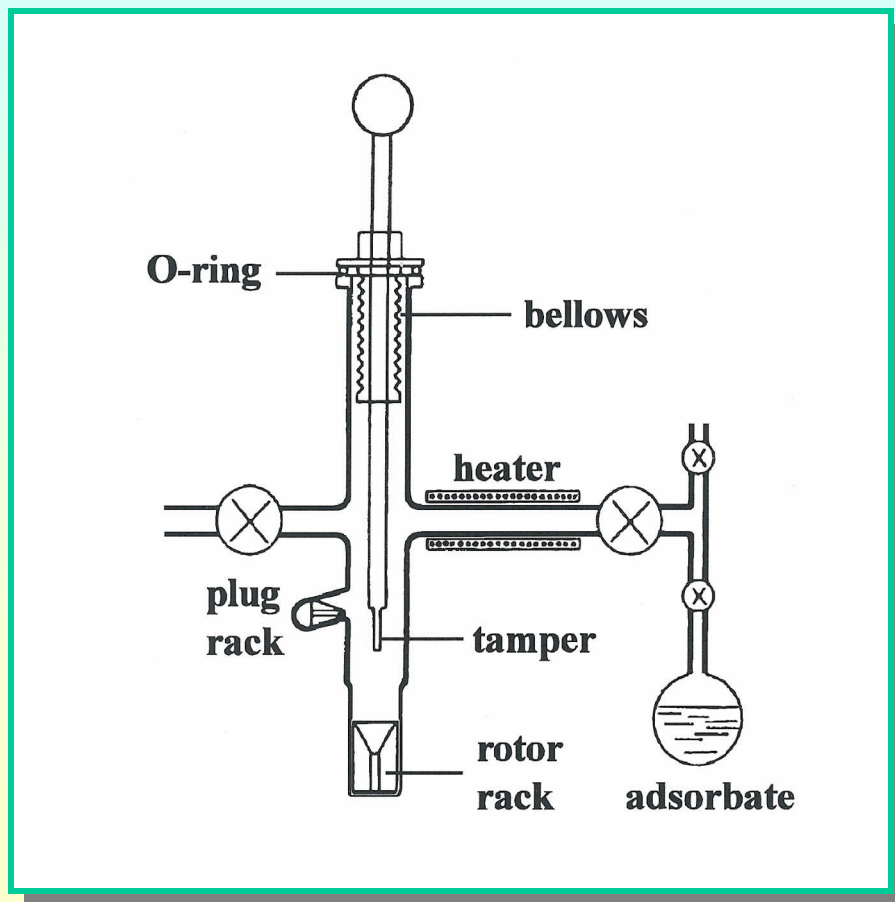
# Preparation of samples under vacuum in glass inserts

- 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

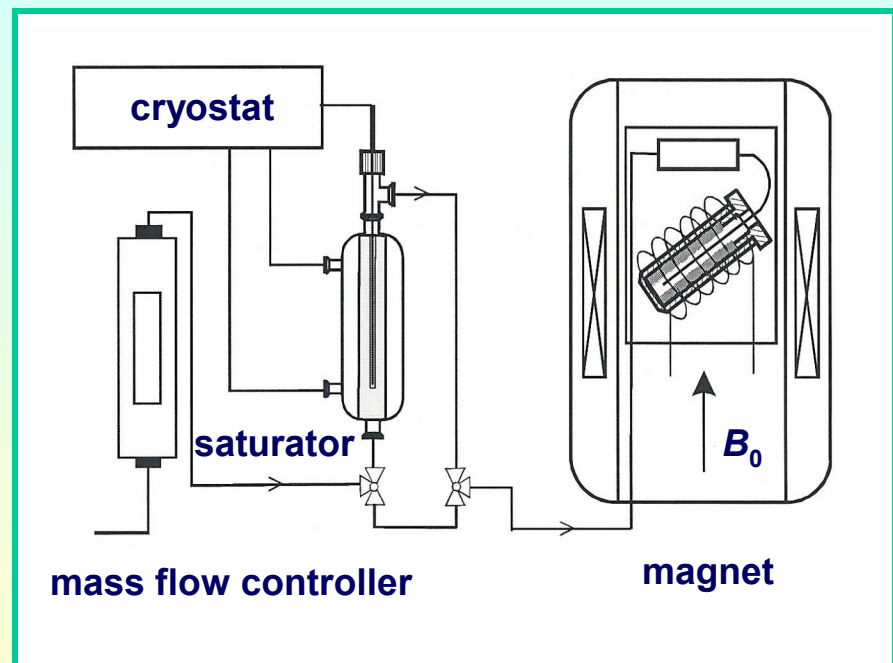
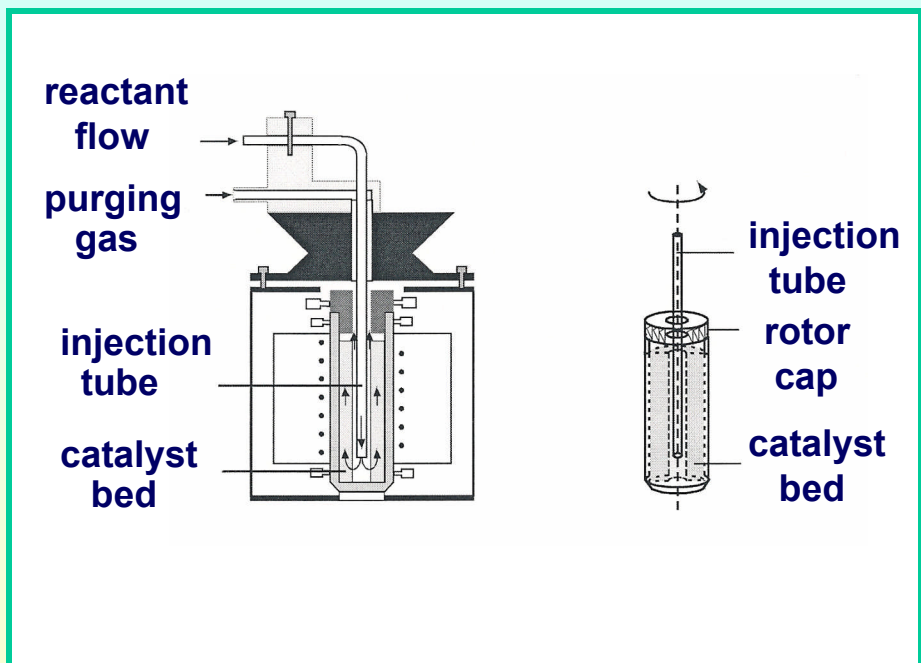


# Approach for batch and continuous-flow experiments in an external reactor

- 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



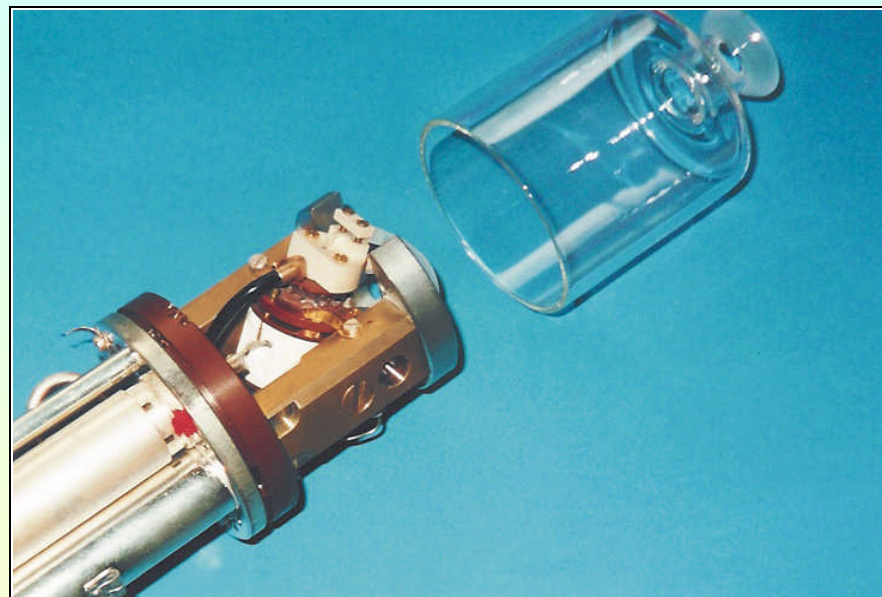
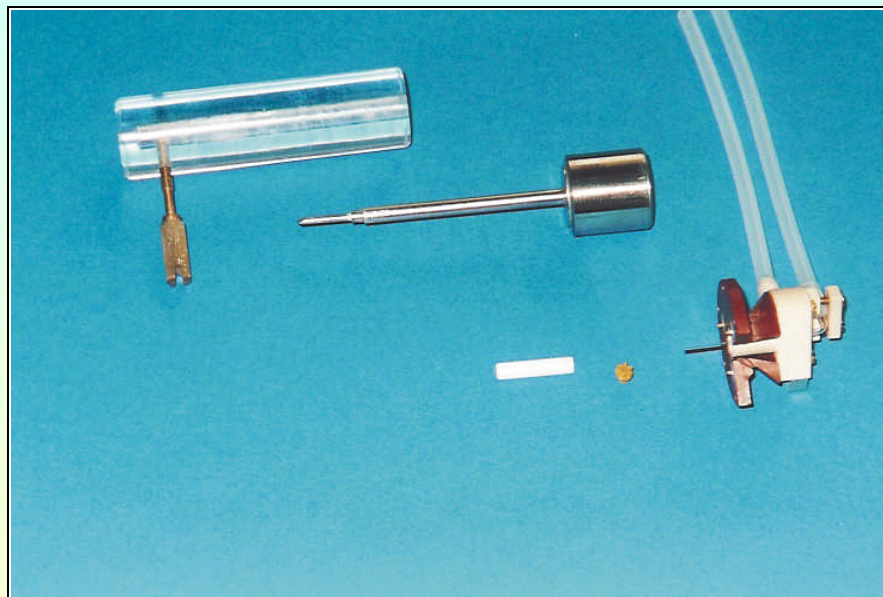
# Continuous-flow (CF) MAS NMR technique



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



## ***Continuous-flow (CF) MAS NMR technique***



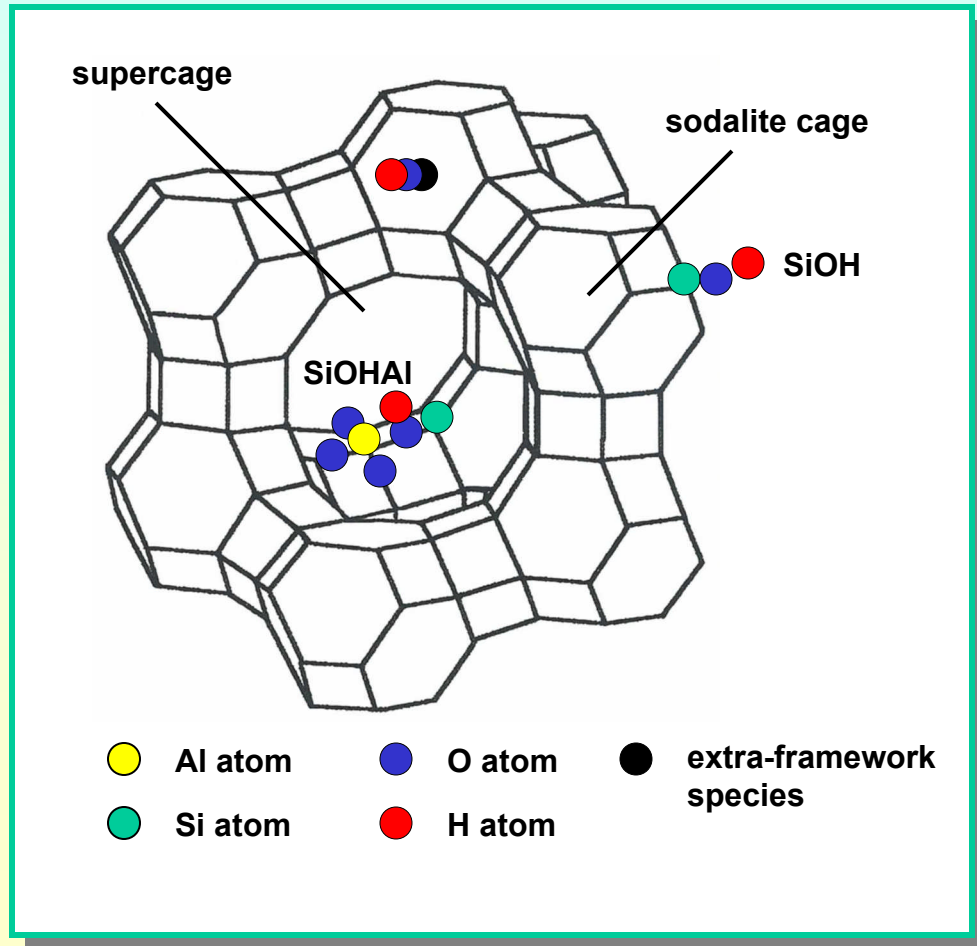
- **modified 4 mm Bruker MAS NMR probe equipped with an injection system**

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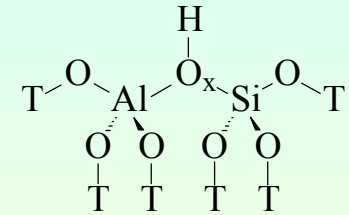
***Characterization of surface sites on solid  
catalysts***

# Surface OH groups

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



- Brønsted 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

# $^1\text{H}$ MAS NMR studies of the hydroxyl coverage

- typical  $^1\text{H}$  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

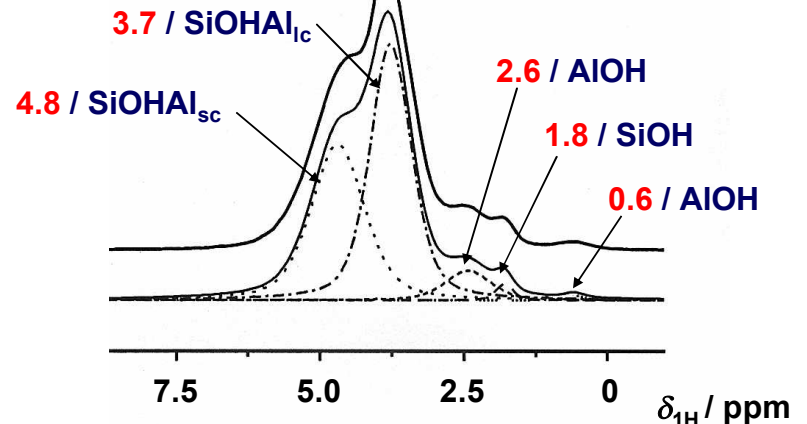
bridging OH groups in large cages and pores ( $\text{SiOHAl}_{\text{lc}}$ ):  
3.6 to 4.3 ppm

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

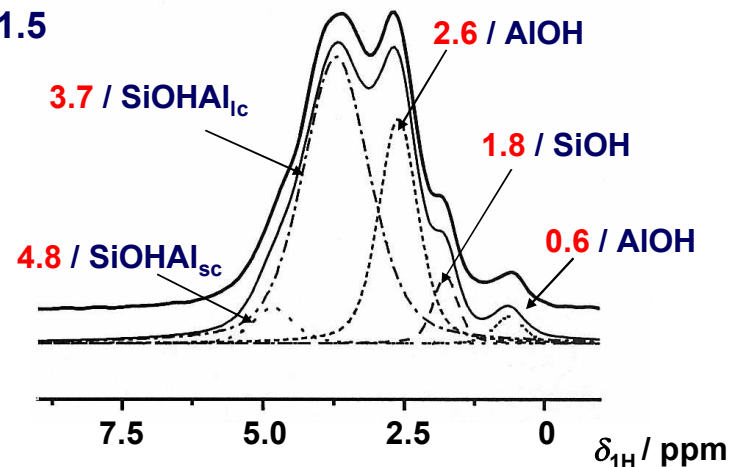
hydrogen bonded SiOH and SiOHAl groups:  
5.2 to 13 ppm

deH-Y/7.4

$^1\text{H}$  MAS NMR



deH-Y/81.5



# Quantitative studies of the hydroxyl coverage

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

total OH intensities:

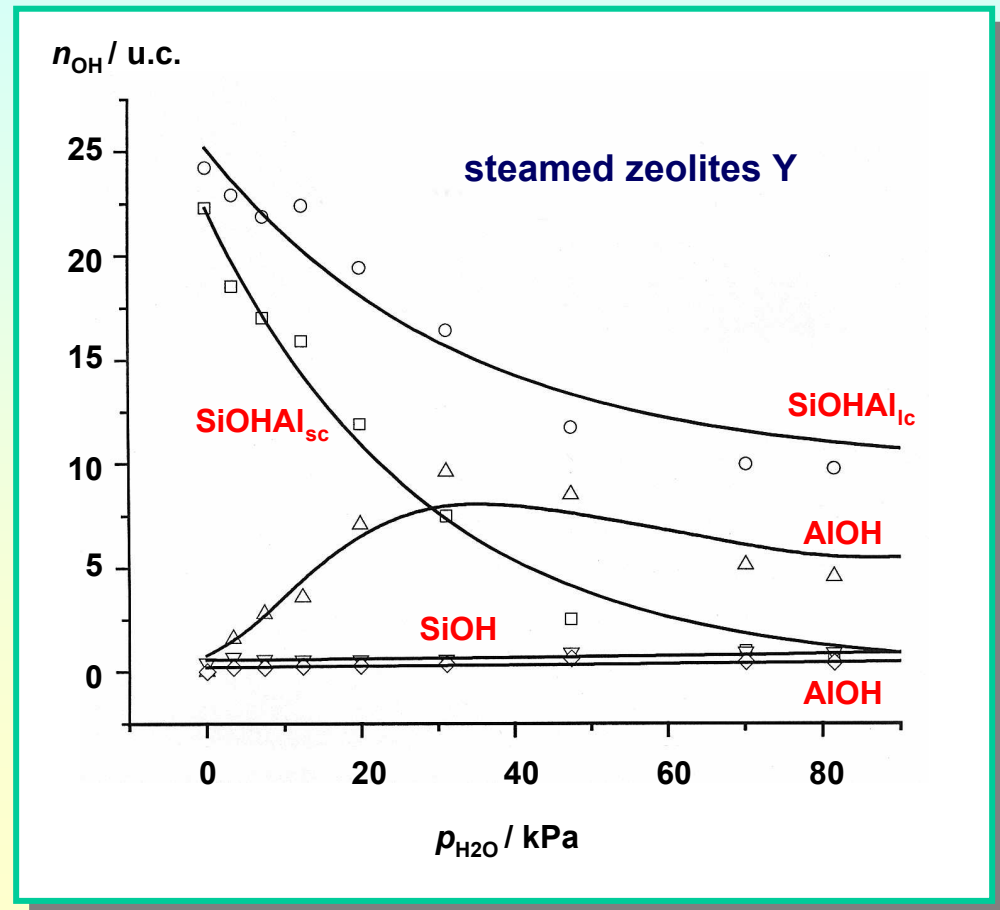
give the total OH concentrations,  
determination of the samples mass

relative OH intensities:

simulation and separation of the  
 $^1\text{H}$  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



# Study of the accessibility and strength of surface sites

Surface site	Probe molecule	Resonance / Effect
<b>Brønsted acid sites:</b>	pyridine-d <sub>5</sub>	<sup>1</sup> H: hydrogen-bonded pyridine at ca. $\delta_{1H} = 10$ ppm (SiOH) and pyridinium ions at $\delta_{1H} = 12$ to 20 ppm (SiOHAl)
	acetonitrile-d <sub>3</sub>	<sup>1</sup> H: adsorbate-induced low-field shift by $\Delta\delta_{1H} = 4.3$ (H-Y) to 7.1 ppm (H-ZSM-5)
	trichloroacetonitrile	<sup>1</sup> H: adsorbate-induced low-field shift by $\Delta\delta_{1H} = 3.0$ (H-Y) to 4.9 ppm (H-ZSM-5)
	perchloroethylene*)	<sup>1</sup> H: adsorbate-induced low-field shift by $\Delta\delta_{1H} = 0.75$ (SiOH) to 1.9 ppm (SiOHAl)
	perfluorotributyl amine	<sup>1</sup> 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	<sup>1</sup> H: H/D exchange, activation energy
	<sup>13</sup> C-2-acetone	<sup>13</sup> C: hydrogen-bonded acetone at $\delta_{13C} = 216.8$ (H-SAPO-5) to 225.4 ppm (H-ZSM-22)
	<sup>15</sup> N-pyridine*)	<sup>15</sup> N: hydrogen-bonded pyridine at $\delta_{15N} = 295$ ppm and pyridinium ions at 198 ppm

# Study of the accessibility and strength of surface sites

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<b>Lewis acid sites:</b>	$^{13}\text{C}$ -2-acetone	$^{13}\text{C}$ : adsorbed acetone at $\delta_{^{13}\text{C}} = 233$ ppm
	$^{15}\text{N}$ -pyridine*)	$^{15}\text{N}$ : adsorbed pyridine at $\delta_{^{15}\text{N}} = 265$ ppm
	trimethylphosphine oxide (TMPO)	$^{31}\text{P}$ : adsorbed TMPO at $\delta_{^{31}\text{P}} = 37$ ppm

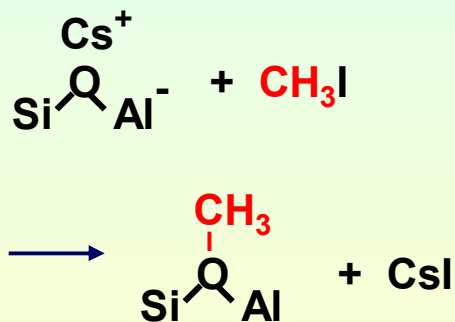
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<b>Base sites:</b>	trichloromethane	$^1\text{H}$ : hydrogen-bonded trichloromethane at $\delta_{^1\text{H}} = 7.55$ (Li-Y) to 8.23 ppm (Cs;Na-Y-90)
	pyrrole	$^1\text{H}$ : hydrogen-bonded pyrrole at $\delta_{^1\text{H}} = 8.4$ (Li-Y) to 11.5 ppm (K-X)
	chloroform	$^1\text{H}$ : hydrogen-bonded chloroform at $\delta_{^1\text{H}} = 7.45$ (H-Y) to 8.70 ppm (Na,Ge-X)
	$^{13}\text{C}$ -chloroform	$^{13}\text{C}$ : hydrogen-bonded $^{13}\text{C}$ -chloroform at $\delta_{^{13}\text{C}} = 77.9$ (H-Y) to 81.7 ppm (Na,Ge-Y)
	$^{13}\text{C}$ -methyl iodide, $^{13}\text{C}$ -methanol	$^{13}\text{C}$ : methoxy groups occurring at $\delta_{^{13}\text{C}} = 58.5$ (Na-ZSM-5) to 54.0 ppm (Cs,Na-X)

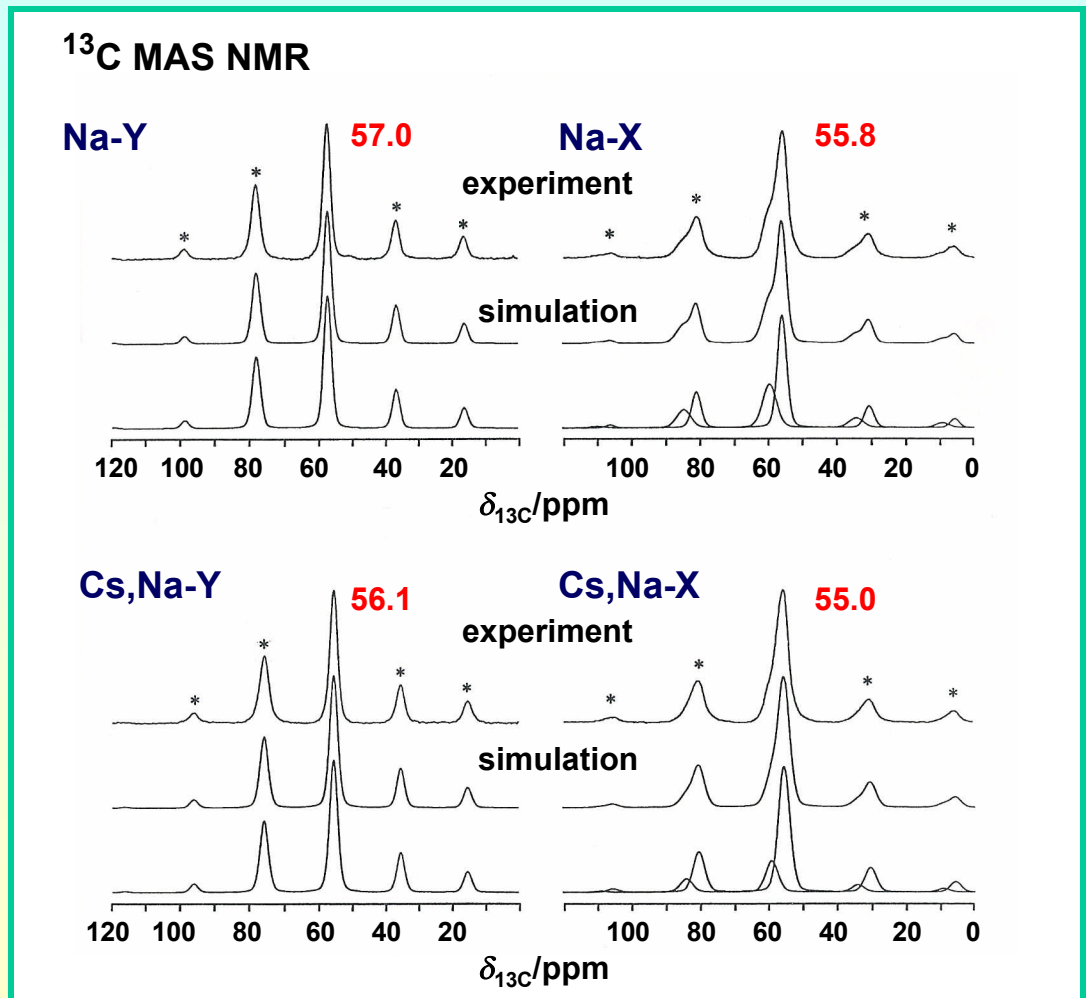
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# Characterization of basic sites on solid catalysts

- $^{13}\text{C}$  MAS NMR spectroscopy of surface methoxy groups formed on basic oxygen atoms
- conversion of  $\text{CH}_3\text{I}$  on basic zeolites:



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



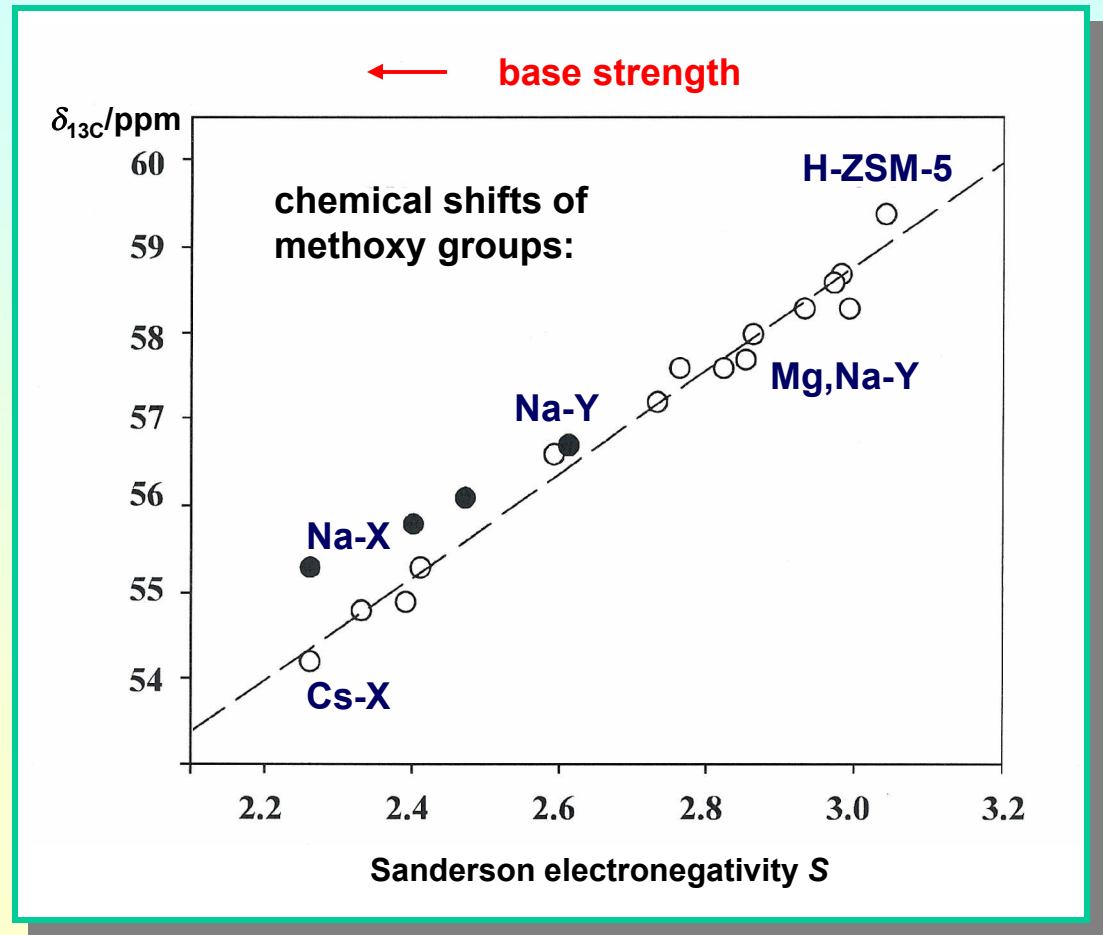


# Base strength of zeolite catalysts

- 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

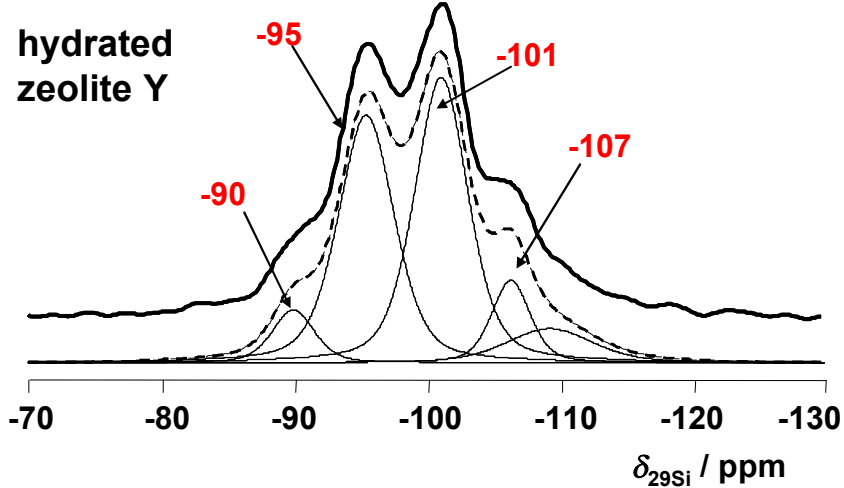


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***Investigation of the framework  
of solid catalysts***

# Determination of the framework aluminum content of zeolites by $^{29}\text{Si}$ MAS NMR

hydrated zeolite Y



hydrated zeolite Y

Si/Al ratio:

2.7

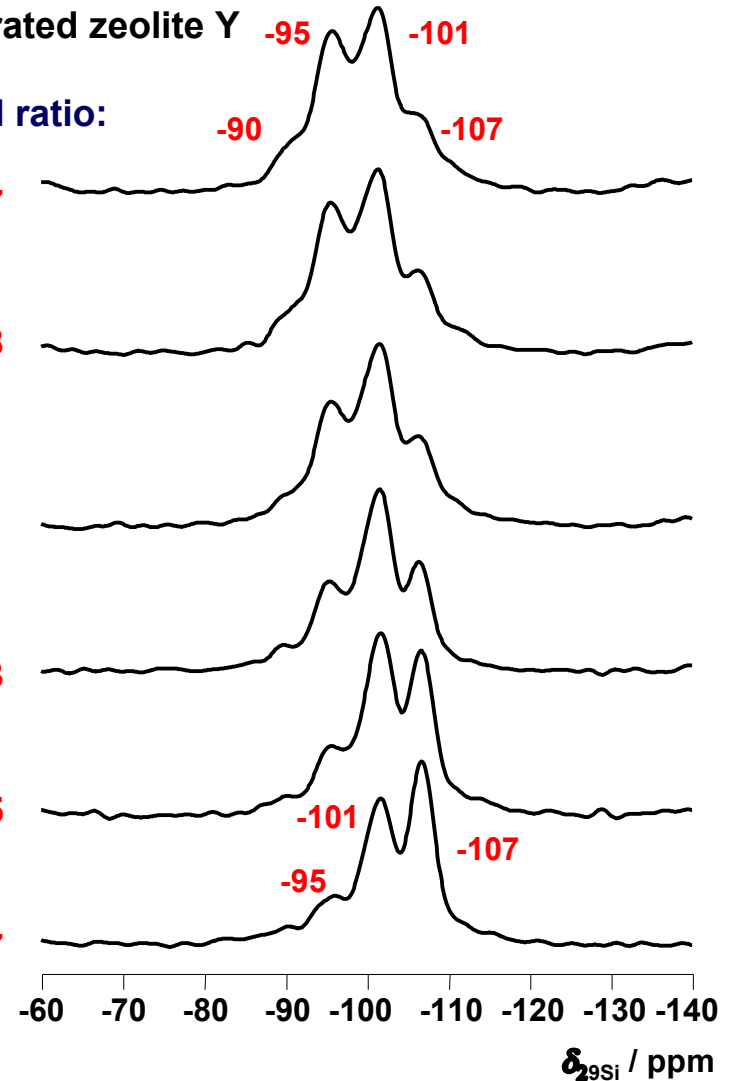
2.8

3.1

3.3

3.5

4.7



- signals of  $\text{Q}^4$  silicon atoms:

-90 ppm Si(1Si,3Al)

-95 ppm Si(2Si,2Al)

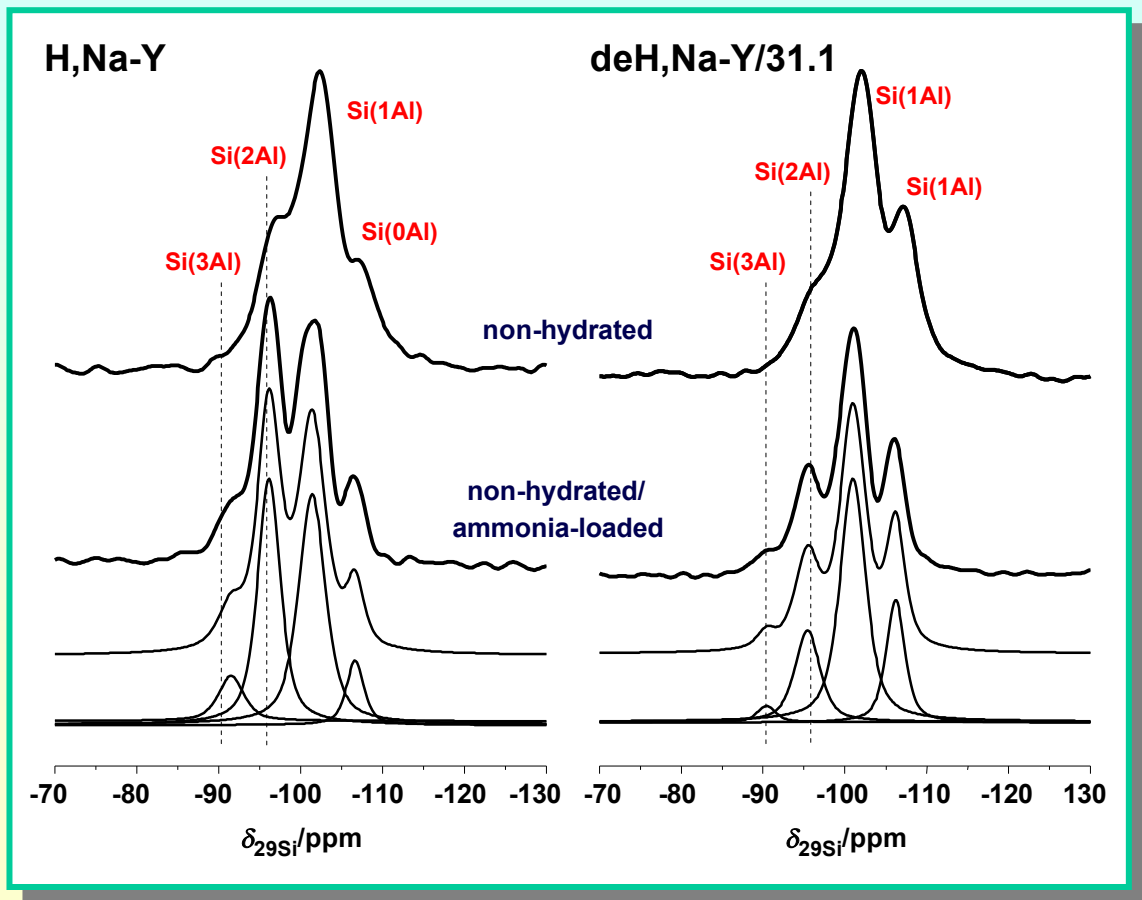
-101 ppm Si(3Si,1Al)

-107 ppm Si(4Si)

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

# $^{29}\text{Si}$ MAS NMR of non-hydrated zeolites

- determination of the framework aluminum content after loading with ammonia

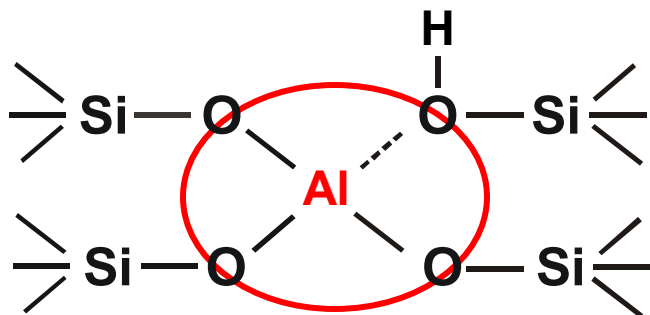


→ high-field shift of the signals of  $\text{Si}(n\text{Al})$  species upon dehydration

→ relaxation of the local structure in the vicinity of  $\text{SiO}_4$  tetrahedra upon loading of ammonia

# Quadrupolar interaction of aluminum atoms in zeolite catalysts

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



- electric field gradient:

$$V_{zz} = eq$$

- quadrupole coupling constant:

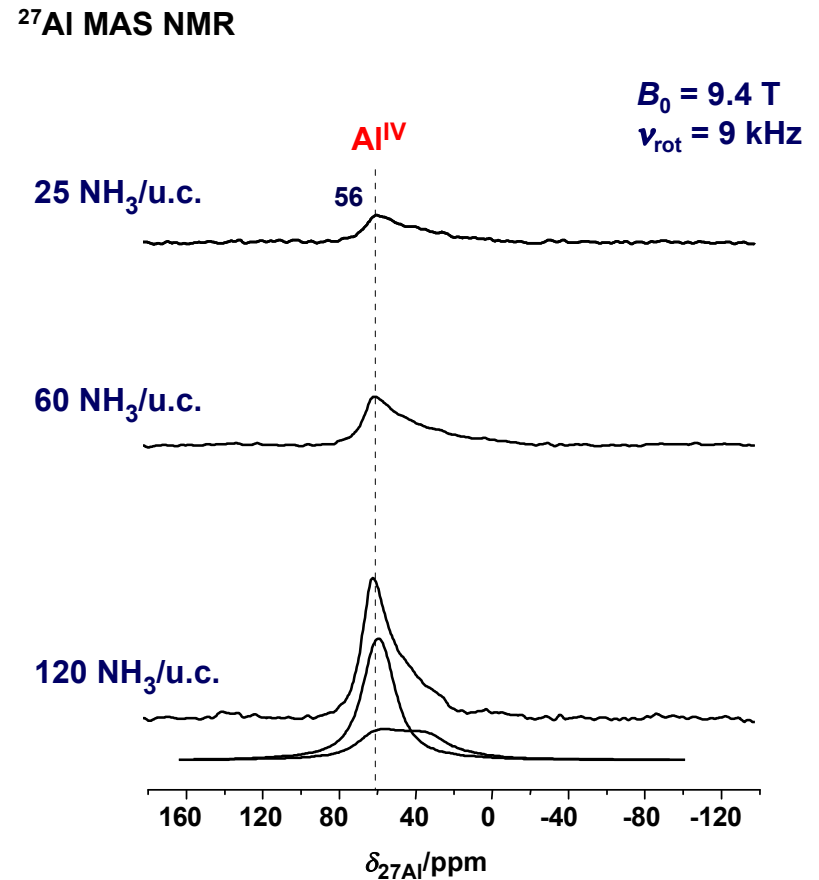
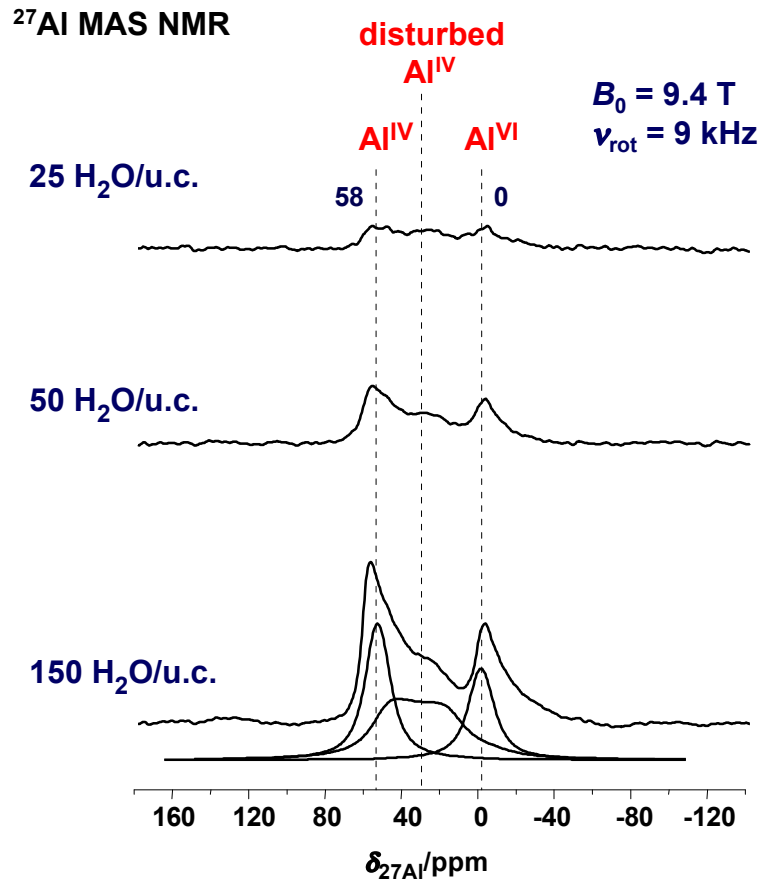
$$QCC = \frac{e^2qQ}{h}$$

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 <sup>ex</sup> 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 $^{27}\text{Al}$ MAS NMR

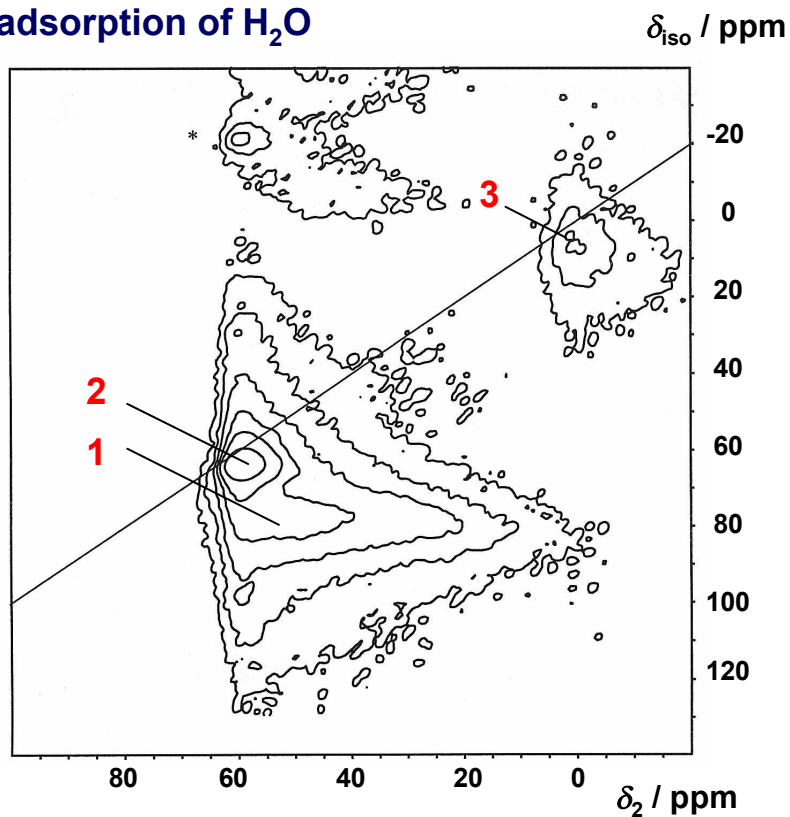
- comparison of hydrated and ammonia-loaded zeolites Y



# $^{27}\text{Al}$ MQMAS NMR of zeolite deH,Na-Y

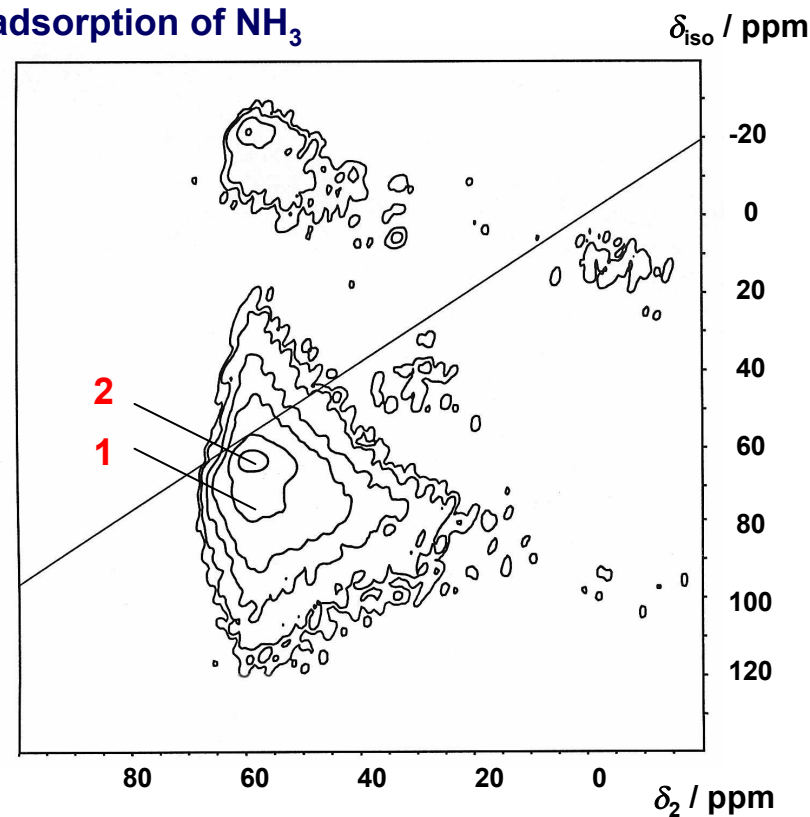
- MQMAS experiments at  $B_0 = 9.4 \text{ T}$ ,  $\nu_{\text{rot}} = 9 \text{ kHz}$

adsorption of  $\text{H}_2\text{O}$



- signal 1:  $\delta_{\text{iso}} = 75 \text{ ppm}$ , SOQE ca. 5.8 MHz
- signal 2:  $\delta_{\text{iso}} = 62 \text{ ppm}$ , SOQE = 2.6 MHz
- signal 3:  $\delta_{\text{iso}} = 3 \text{ ppm}$ , SOQE = 2.3 MHz

adsorption of  $\text{NH}_3$

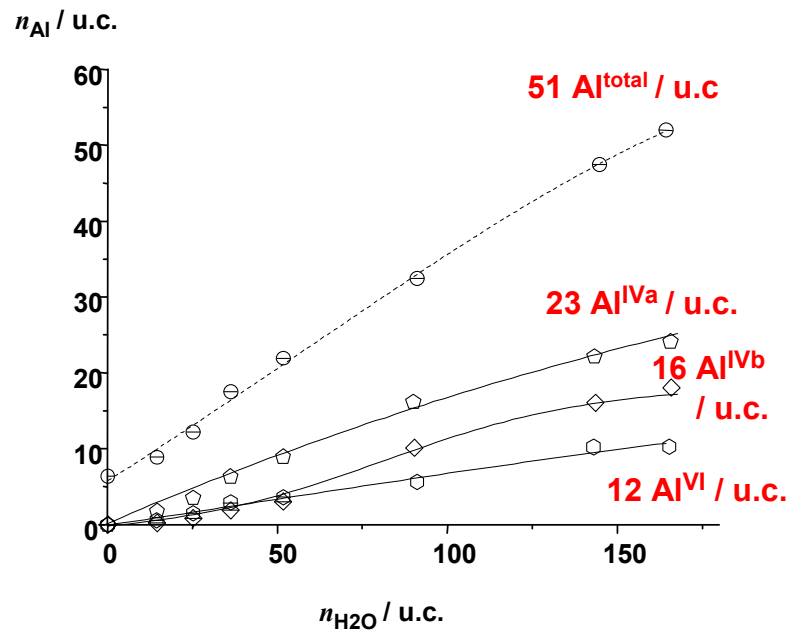


- signal 1:  $\delta_{\text{iso}}$  ca. 70 ppm, SOQE ca. 5.0 MHz
- signal 2:  $\delta_{\text{iso}} = 62 \text{ ppm}$ , SOQE = 2.6 MHz

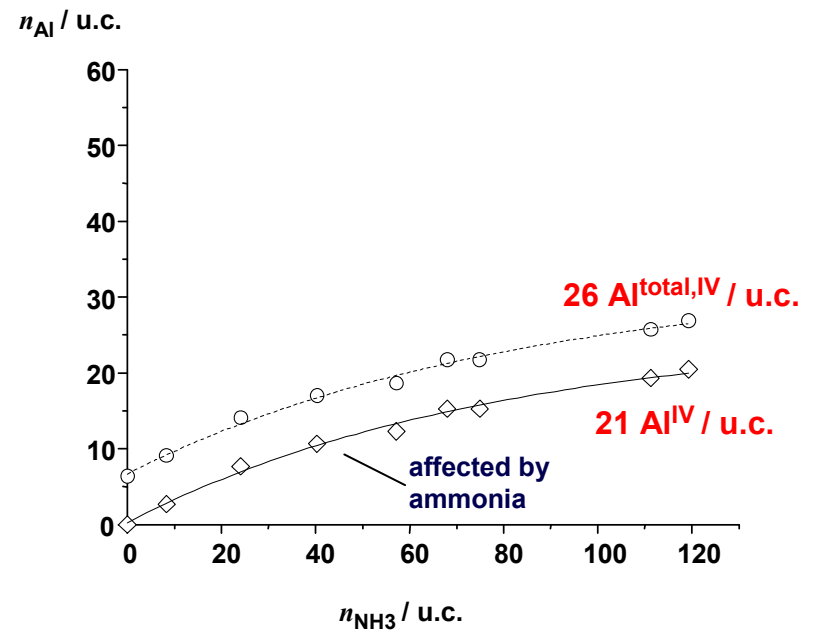
# Effect of adsorption studied by $^{27}\text{Al}$ MAS NMR

- adsorption of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  on non-hydrated deH,Na-Y/81.5

## adsorption of $\text{H}_2\text{O}$



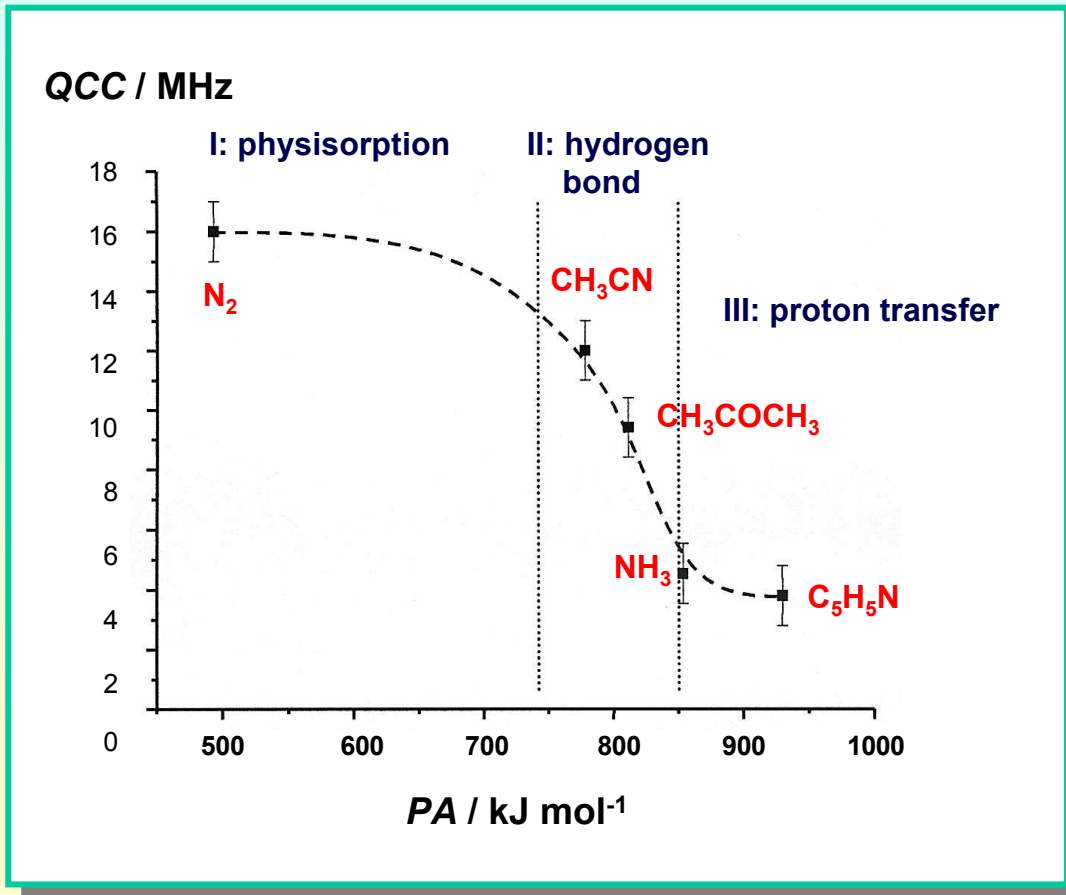
## adsorption of $\text{NH}_3$





# Effect of the base strength of the adsorbate molecules on $^{27}\text{Al}$ nuclei

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



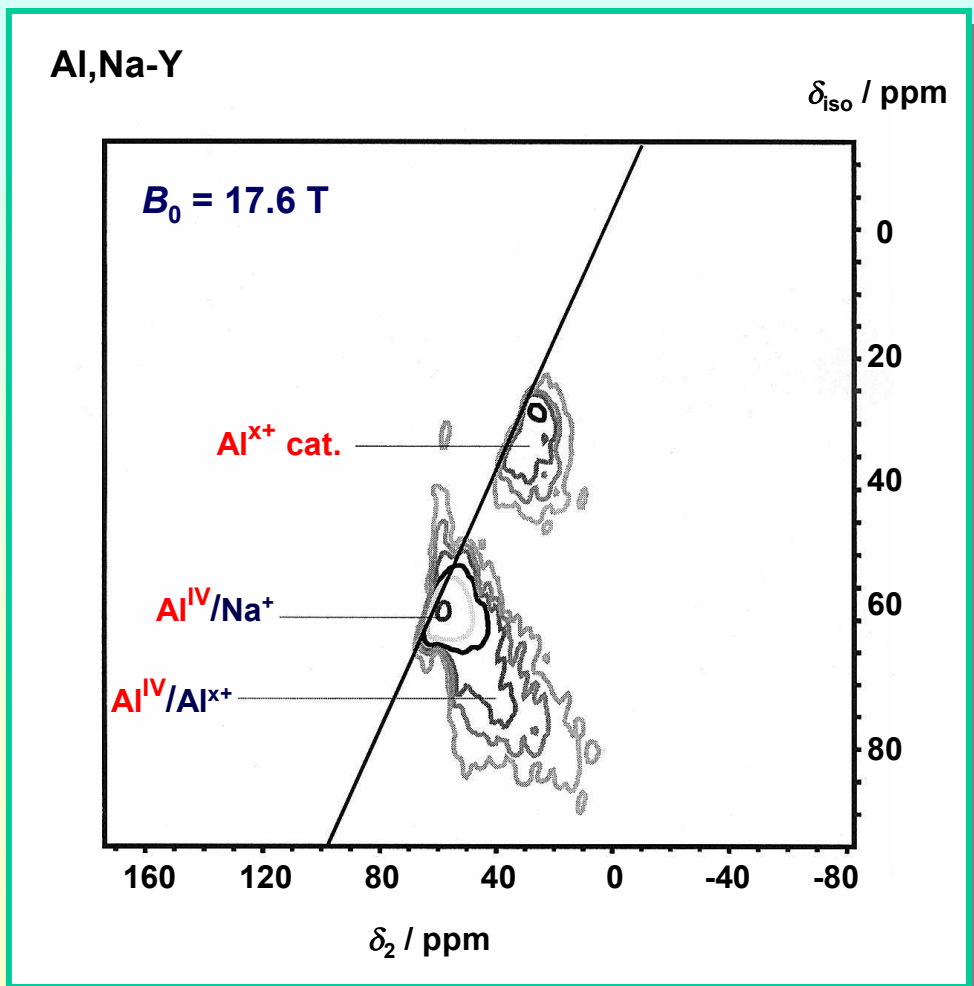
→ the QCC value of framework aluminum atoms in non-hydrated zeolite catalysts is sensitive to the adsorbate complexes formed at acid sites ( $\text{SiOHAl}$ )

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

# ***Characterization of the aluminum distribution in zeolites***

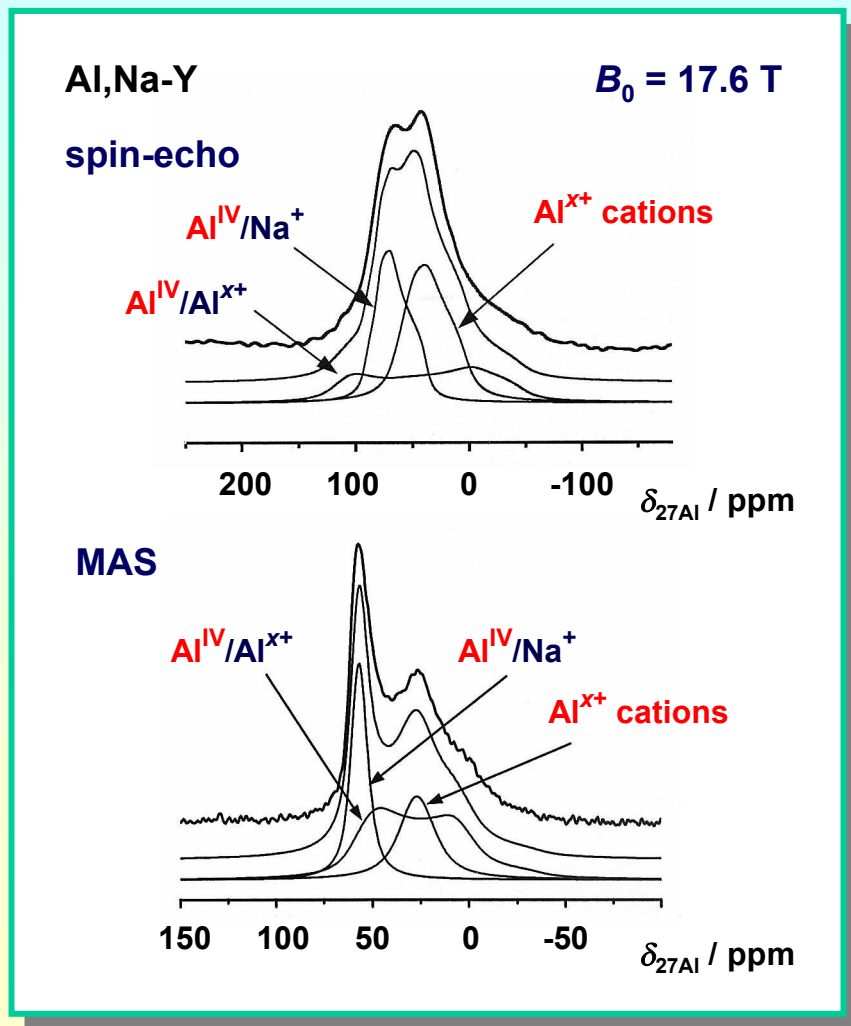
- dealuminated zeolite (non-hydrated state):
  - zeolite H,Na-Y steamed at 475°C with a water vapor pressure of 81.5 kPa
  - framework  $n_{\text{Si}}/n_{\text{Al}}$  ratio of 5.8
- reference materials (dehydrated state):
  - parent zeolite H,Na-Y
  - zeolite Al,Na-Y with a cation exchange degree of 69 %
  - X-ray amorphous  $\gamma\text{-Al}_2\text{O}_3$ , specific surface area of 150 m<sup>2</sup>/g
- spectroscopic methods:
  - <sup>27</sup>Al spin-echo NMR at  $B_0 = 9.4, 14.1, \text{ and } 17.6$  T
  - <sup>27</sup>Al high-speed MAS NMR at  $B_0 = 17.6$  T with  $\nu_{\text{rot}} = 30$  kHz
  - <sup>27</sup>Al MQMAS NMR at  $B_0 = 17.6$  T, split- $t_1$  pulse sequence

# $^{27}\text{Al}$ MQMAS NMR studies of reference materials



- parameters of signal  $\text{Al}^{\text{x}+}$  cations:
  - $\text{SOQE} = 6.0 \text{ MHz}$
  - $\delta_{\text{iso}} = 35 \pm 5 \text{ ppm}$
- parameters of signal  $\text{Al}^{\text{IV}}/\text{Na}^+$ :
  - $\text{SOQE} = 5.5 \text{ MHz}$
  - $\delta_{\text{iso}} = 60 \pm 5 \text{ ppm}$
- parameters of signal  $\text{Al}^{\text{IV}}/\text{Al}^{\text{x}+}$ :
  - $\text{SOQE} = 14.5 \text{ MHz}$
  - $\delta_{\text{iso}} = 70 \pm 5 \text{ ppm}$

# $^{27}\text{Al}$ solid-state NMR studies of reference materials



- parameters of signal  $\text{Al}^{\text{x+}}$  cat.:

- QCC = 6.0 MHz,  $\eta = 0.7$

- $\delta_{\text{iso}} = 35 \pm 5$  ppm

- $I_{\text{rel}} = 24\%$

- parameters of signal  $\text{Al}^{\text{IV}}/\text{Na}^+$ :

- QCC = 5.5 MHz,  $\eta = 0.8$

- $\delta_{\text{iso}} = 60 \pm 5$  ppm

- $I_{\text{rel}} = 28\%$

- parameters of signal  $\text{Al}^{\text{IV}}/\text{Al}^{\text{x+}}$ :

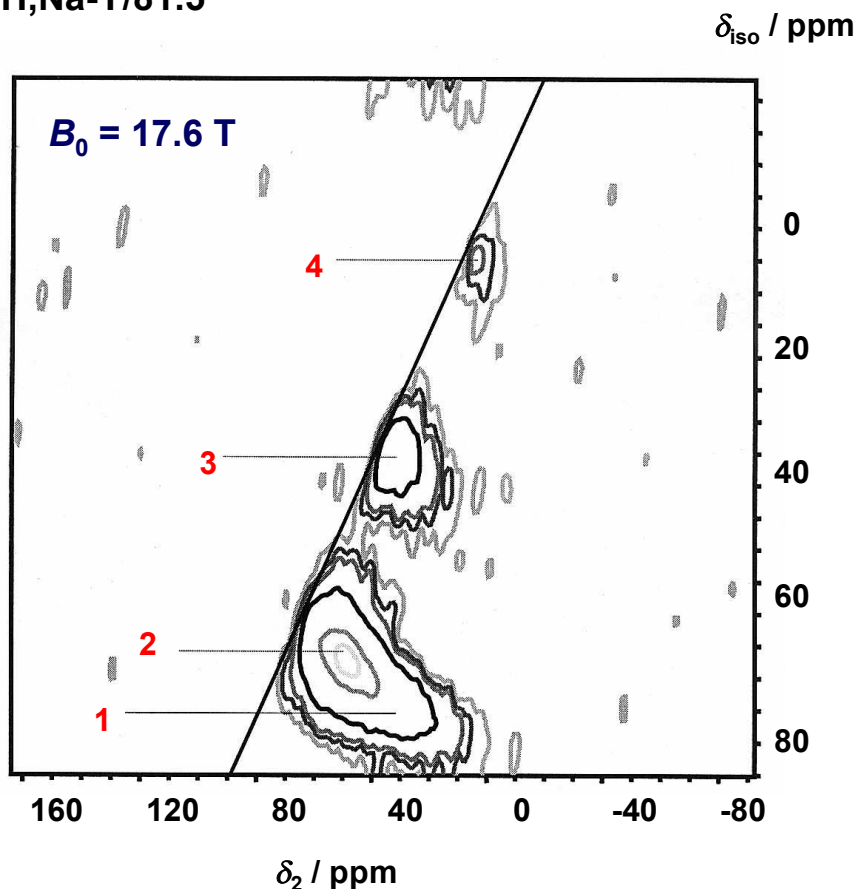
- QCC = 14.5 MHz,  $\eta = 0.3$

- $\delta_{\text{iso}} = 70 \pm 5$  ppm

- $I_{\text{rel}} = 48\%$

# $^{27}\text{Al}$ MQMAS NMR studies of dealuminated zeolite Y

deH,Na-Y/81.5



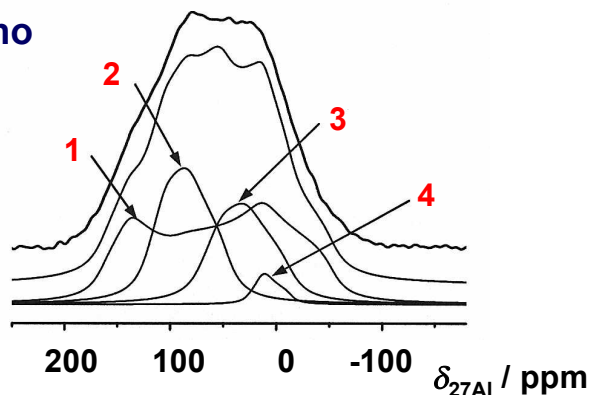
- parameters of signal **1**:
  - $\text{SOQE} = 15.0 \pm 1.0 \text{ MHz}$
  - $\delta_{\text{iso}} = 70 \pm 10 \text{ ppm}$
- parameters of signal **2**:
  - $\text{SOQE} = 8.0 \pm 0.5 \text{ MHz}$
  - $\delta_{\text{iso}} = 65 \pm 5 \text{ ppm}$
- parameters of signal **3**:
  - $\text{SOQE} = 7.5 \pm 0.5 \text{ MHz}$
  - $\delta_{\text{iso}} = 35 \pm 5 \text{ ppm}$
- parameters of signal **4**:
  - $\text{SOQE} = 5.0 \pm 0.5 \text{ MHz}$
  - $\delta_{\text{iso}} = 10 \pm 5 \text{ ppm}$

# $^{27}\text{Al}$ solid-state NMR studies of dealuminated zeolite Y

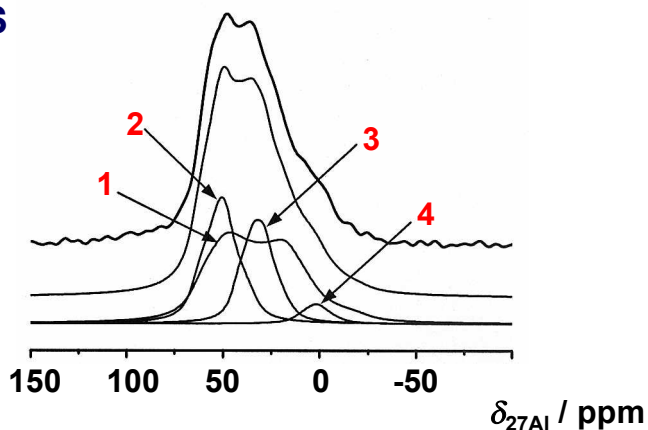
deH,Na-Y/81.5

$B_0 = 17.6 \text{ T}$

spin-echo



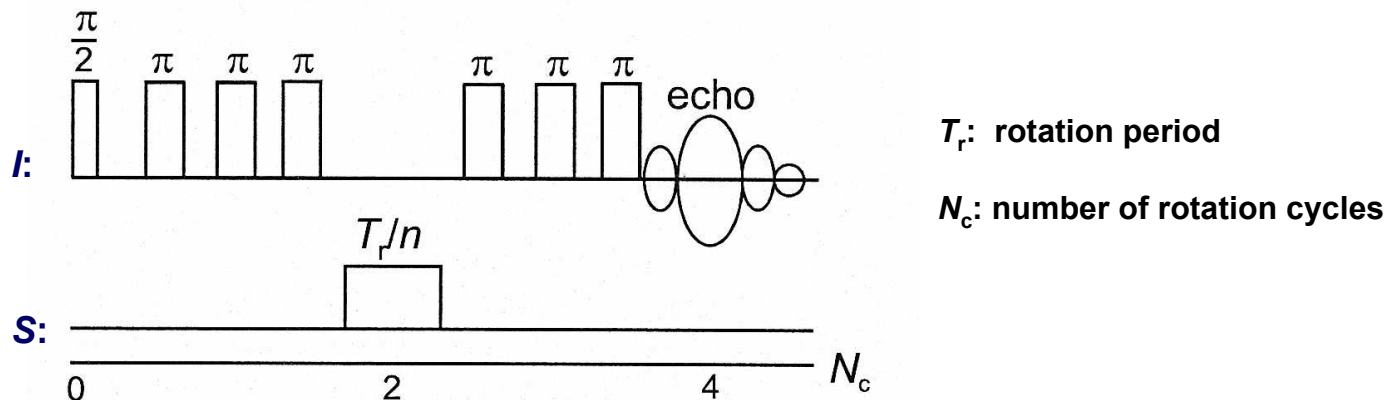
MAS



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

# Determination of the distance between resonating nuclei

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



- echo decay is described by REAPDOR fraction:

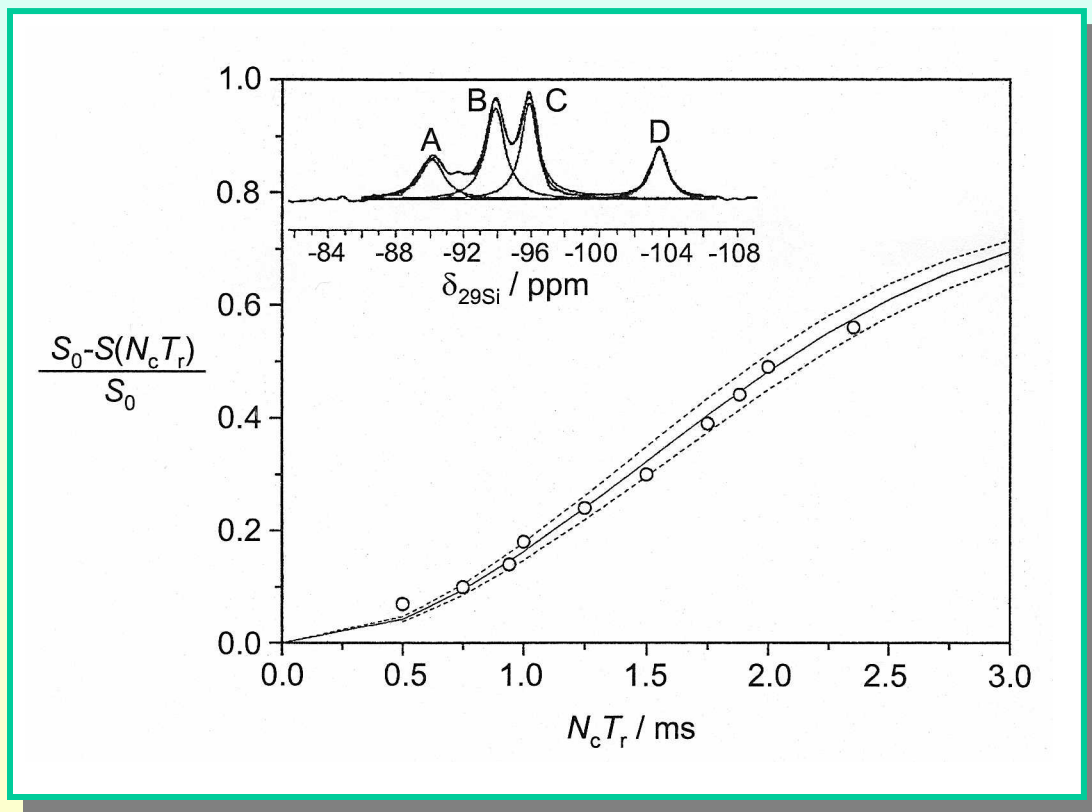
$$\frac{S_0 - S(N_c T_r)}{S_0} = \frac{1}{\pi^2 S(S+1)} (N_c T_r)^2 M_2^{\text{IS}}$$

with

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

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

- $^{29}\text{Si}/^{27}\text{Al}$  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

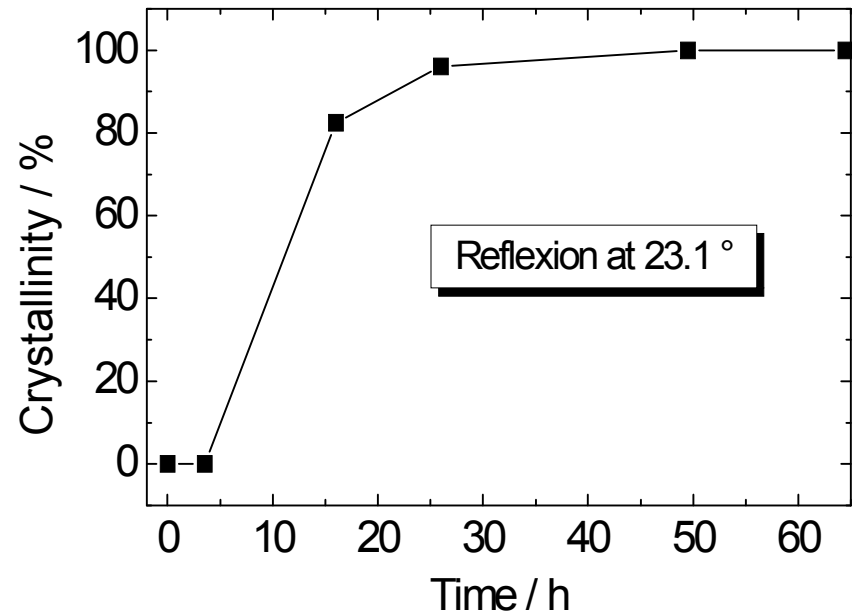
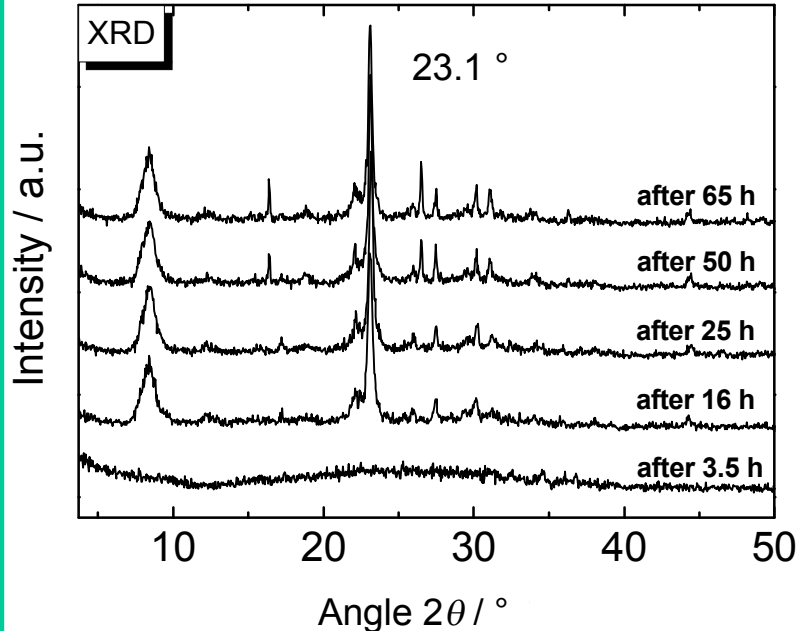


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***Local structure of particels during the  
synthesis of solid catalysts***

# 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

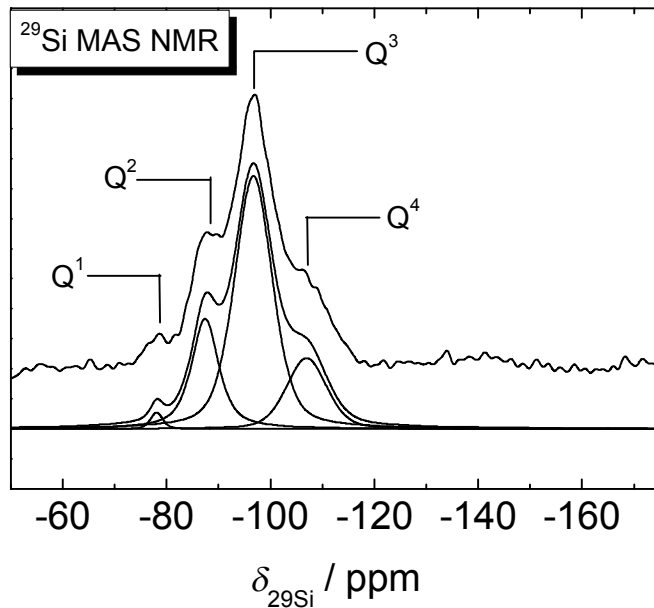


→ formation of zeolite particles already within the first 16 h

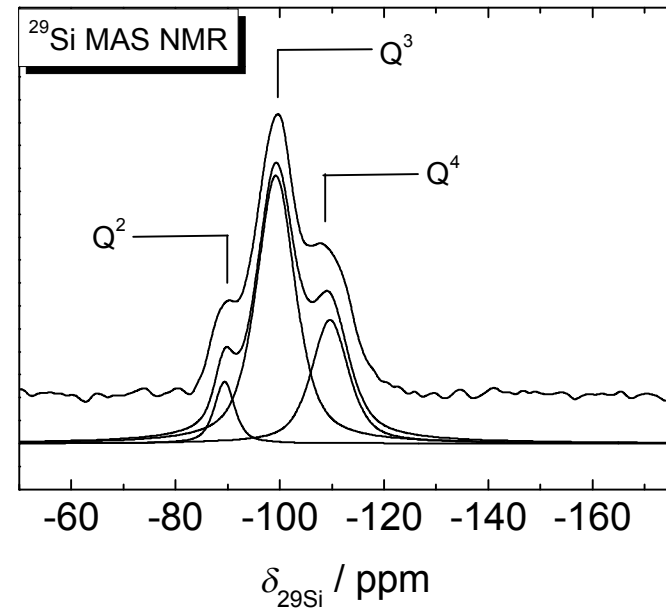
# $^{29}\text{Si}$ MAS NMR of zeolite [Ga]Beta ( $n_{\text{Si}}/n_{\text{Ga}} = 8.2$ )

- $^{29}\text{Si}$  MAS NMR spectra recorded after different conversion times

fresh dry-gel particles (0 h)



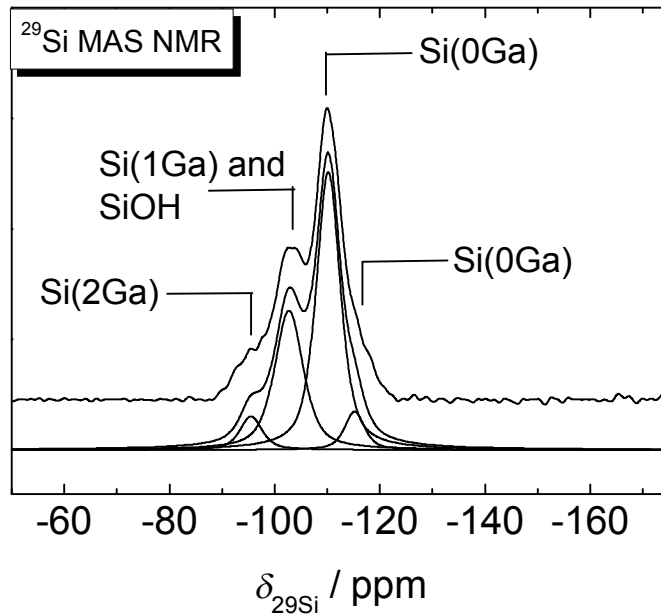
conversion time of 3.5 h



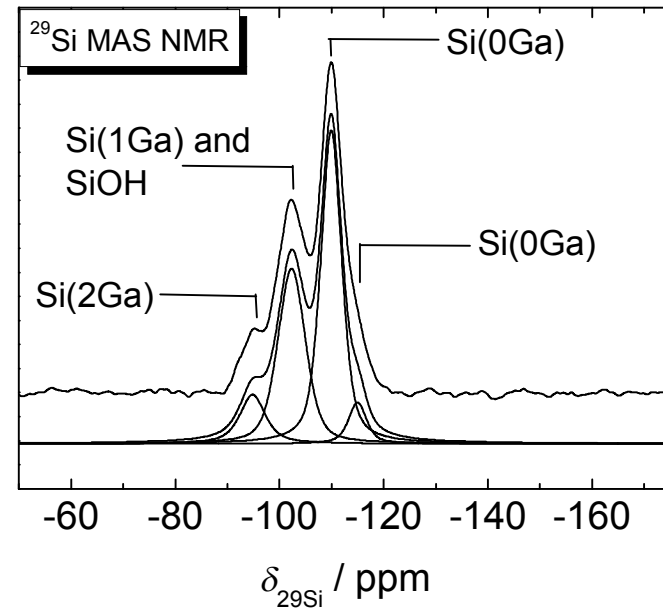
# $^{29}\text{Si}$ MAS NMR of zeolite [Ga]Beta ( $n_{\text{Si}}/n_{\text{Ga}} = 8.2$ )

- $^{29}\text{Si}$  MAS NMR spectra recorded after different conversion times

conversion time of 16 h

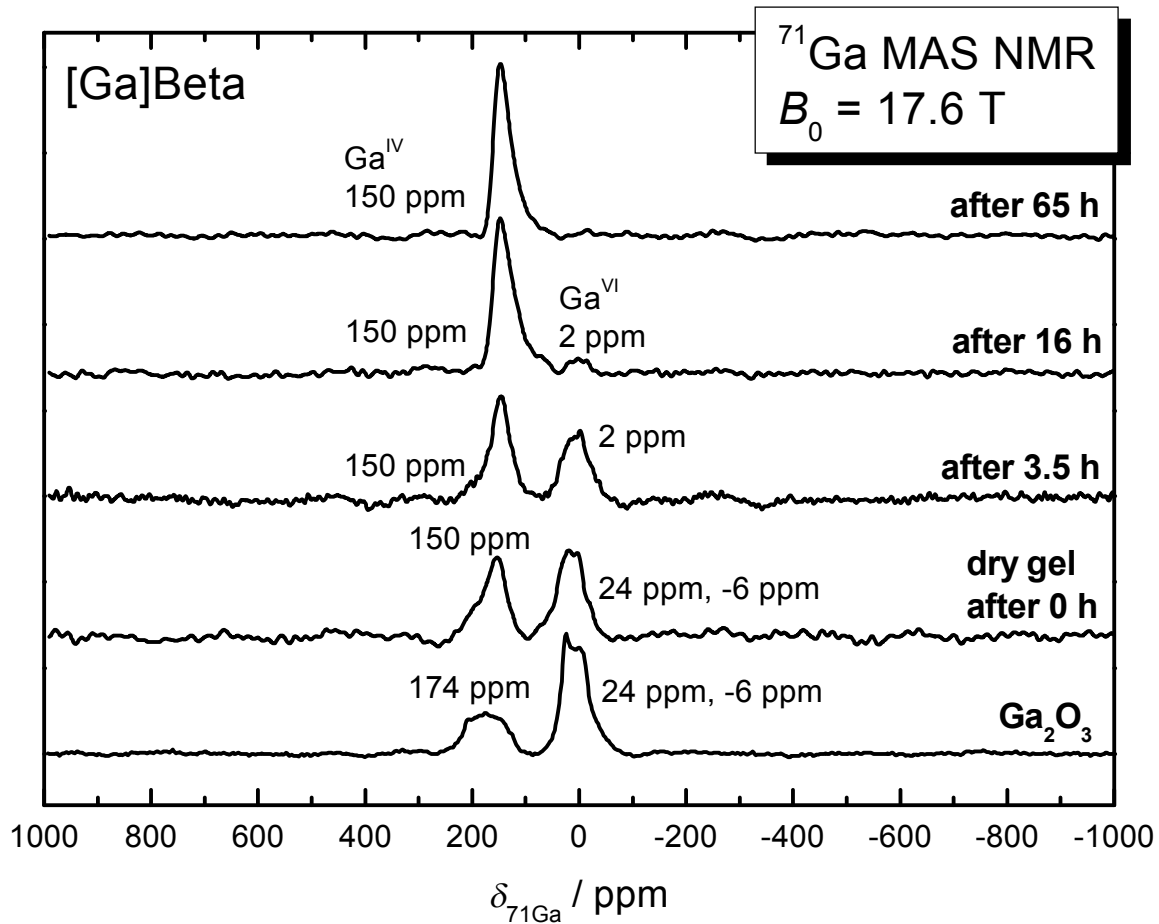


conversion time of 65 h



→ incorporation of gallium into the zeolite framework

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



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

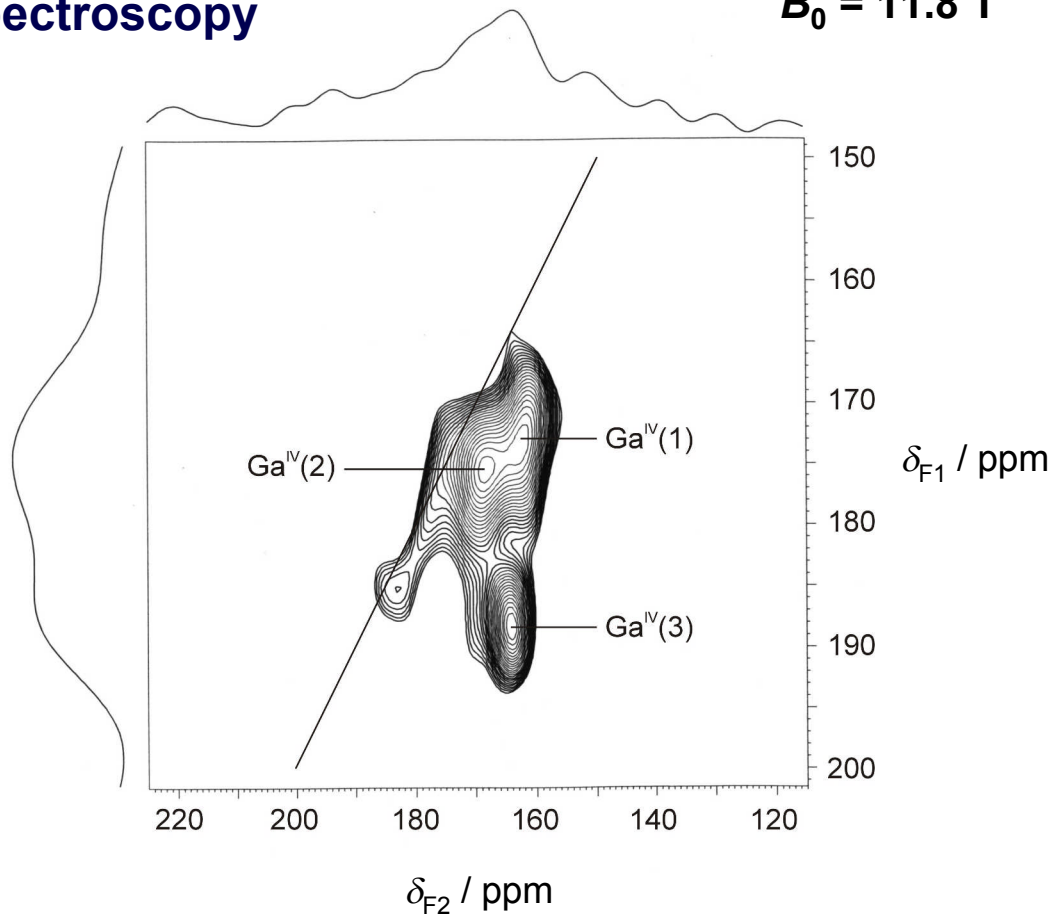
# Two-dimensional $^{71}\text{Ga}$ MQMAS NMR spectroscopy of $[\text{Ga}]\text{Beta}$ obtained after 65 h

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

$B_0 = 11.8 \text{ T}$

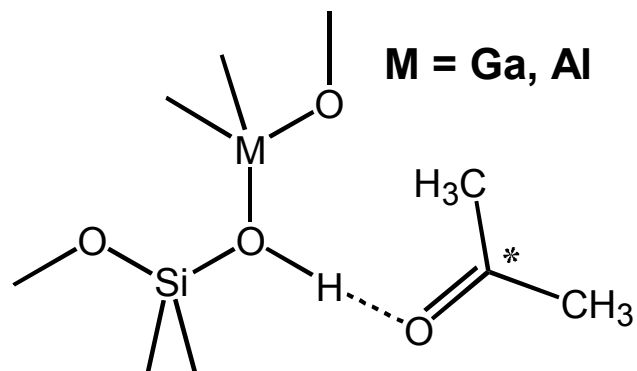
$\text{Ga}^{\text{IV}}(1, 2)$ :  
framework gallium  
species

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



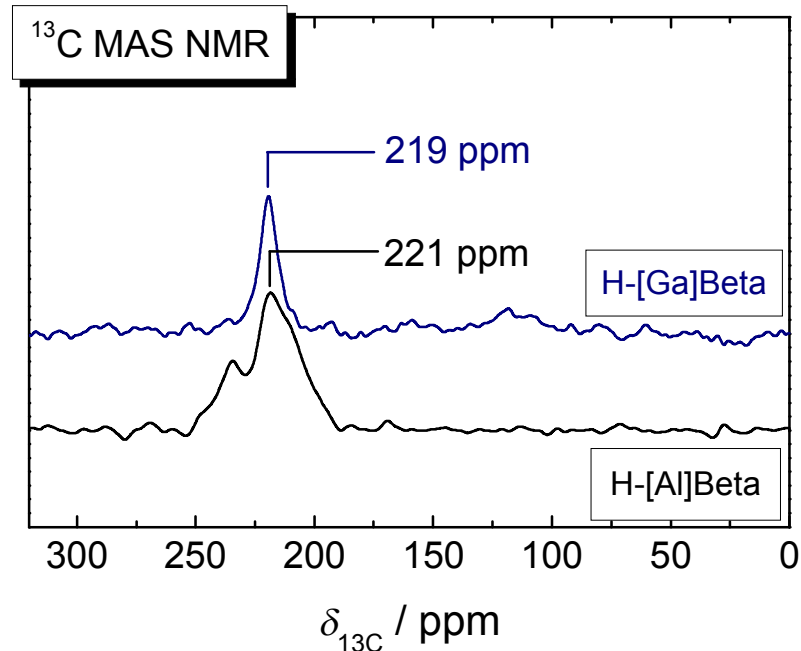
# Acid strength of zeolites Beta and EU-1

- adsorption of  $^{13}\text{C}$ -2-acetone as probe molecule



Zeolite	$\delta_{13\text{C}}$ / ppm
H-[Ga]EU-1	214
H-[Al]EU-1	215
H-[Ga]Beta	219
H-[Al]Beta	221
H-ZSM-5	223

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



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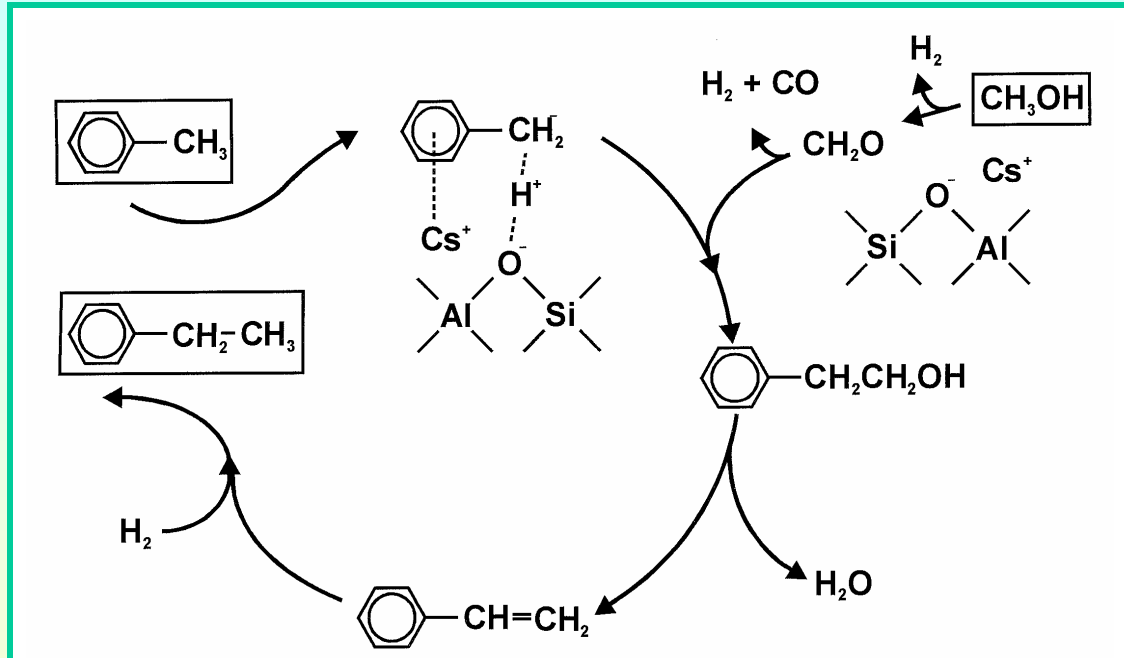
***Study of the mechanism of reactions  
catalyzed by solid materials***



# Side-chain alkylation of toluene with methanol on basic zeolites

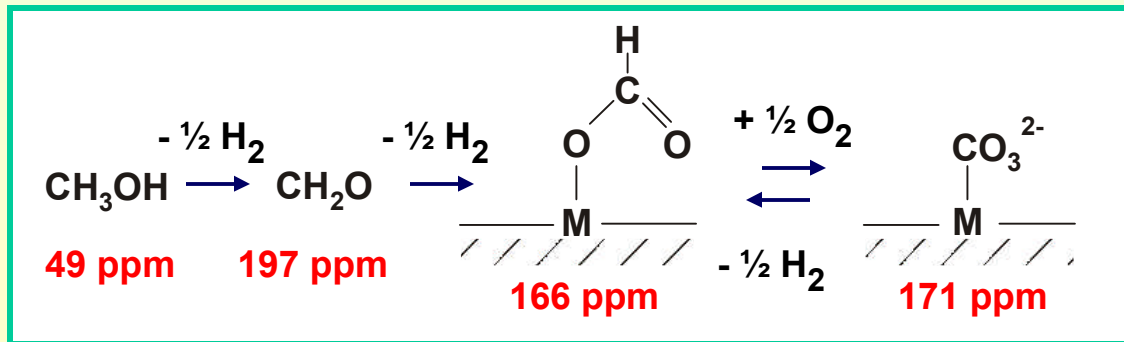
- reaction scheme proposed by Yashima et al., J. Catal. 26 (1972) 303:

- activation of toluene by adsorption on the zeolite
- conversion of methanol to formaldehyde catalyzed by base sites



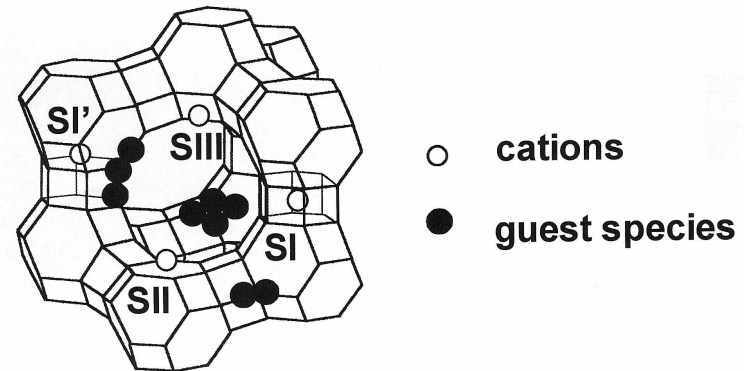
- proposed surface species:

- formate ( $\delta_{13\text{C}} = 166$  ppm)
- carbonate ( $\delta_{13\text{C}} = 171$  ppm)



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

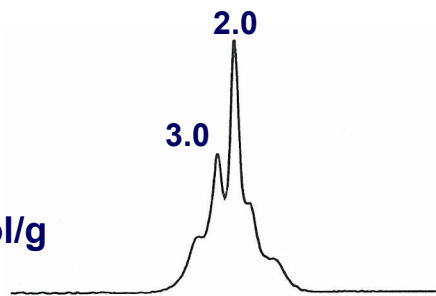
- zeolite Na-X ( $n_{\text{Si}}/n_{\text{Al}} = 1.4$ ) exchanged with cesium cations (55 %) and impregnated with cesium hydroxide (24 CsOH/u.c.)



## $^1\text{H}$ MAS NMR

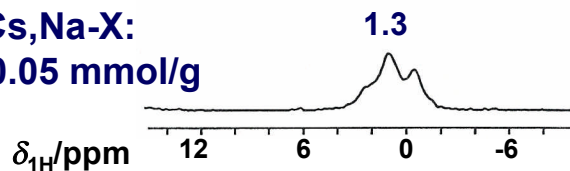
Cs,Na-X:

$c_{\text{OH}} = 0.3 \text{ mmol/g}$



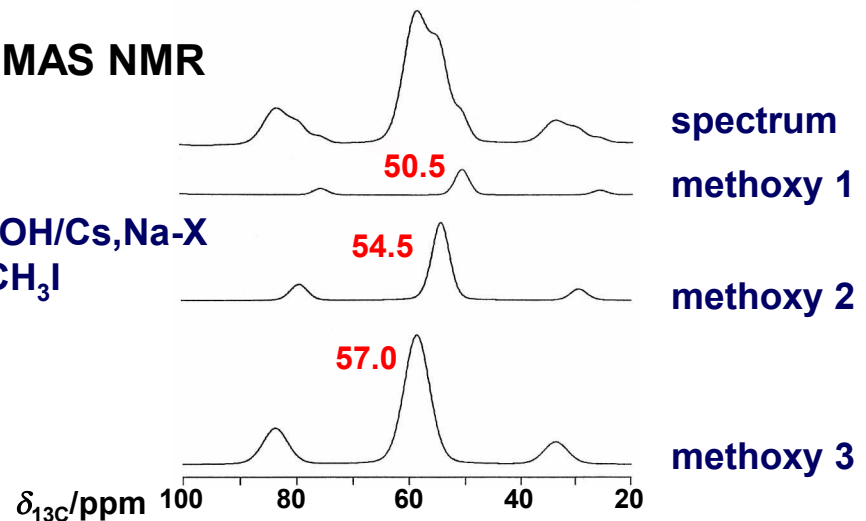
CsOH/Cs,Na-X:

$c_{\text{OH}} = 0.05 \text{ mmol/g}$



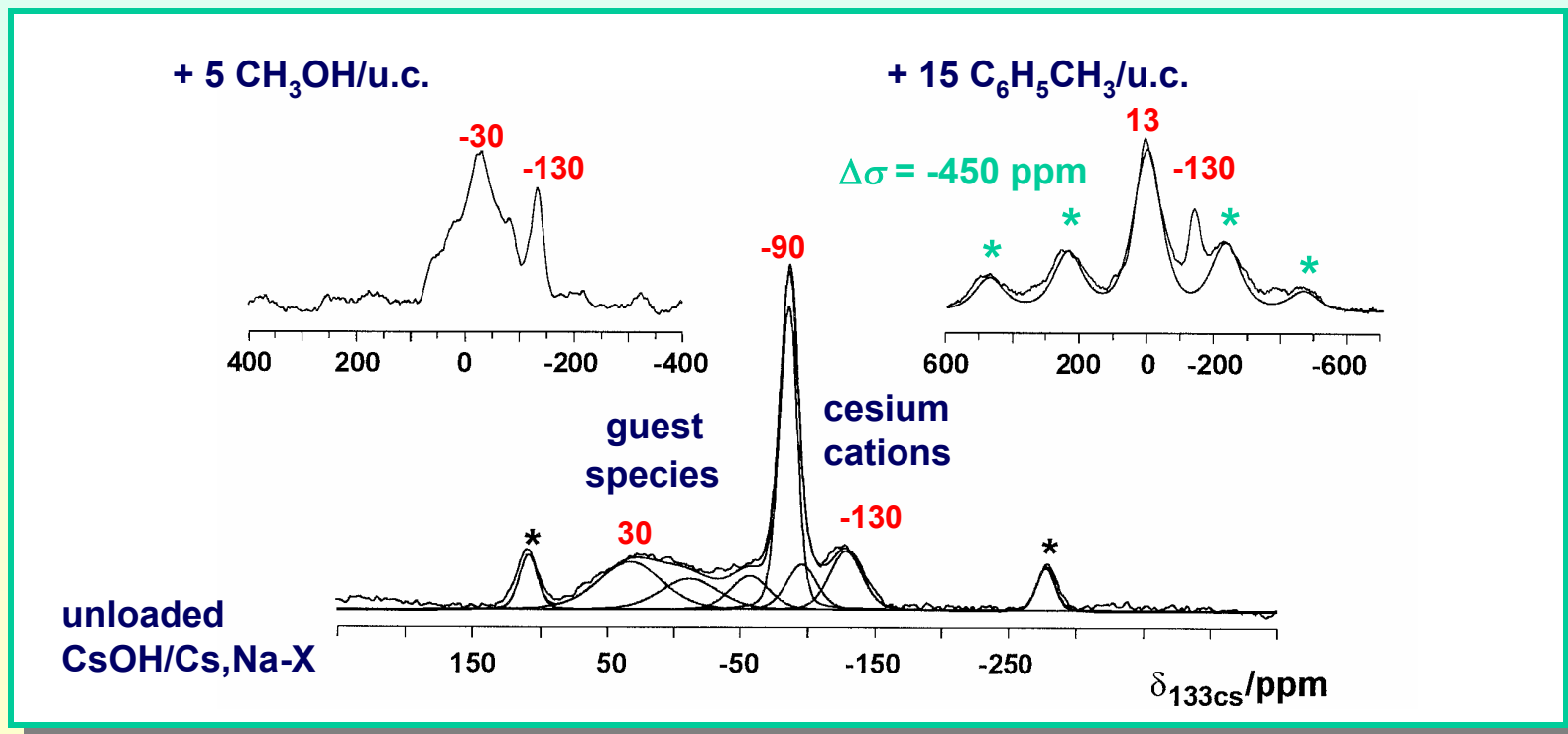
## $^{13}\text{C}$ MAS NMR

CsOH/Cs,Na-X  
+  $\text{CH}_3\text{I}$



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

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

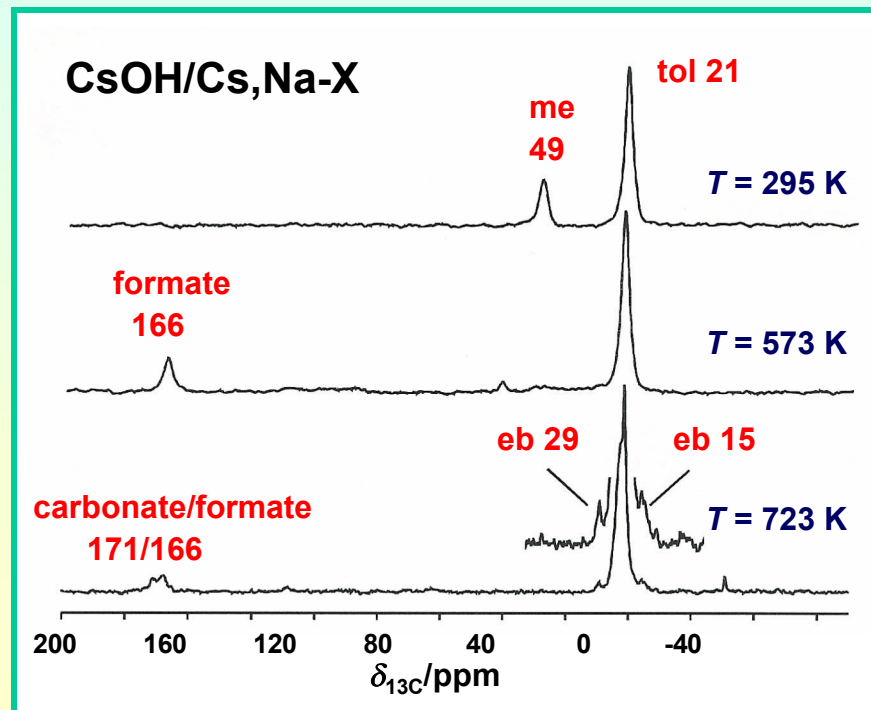
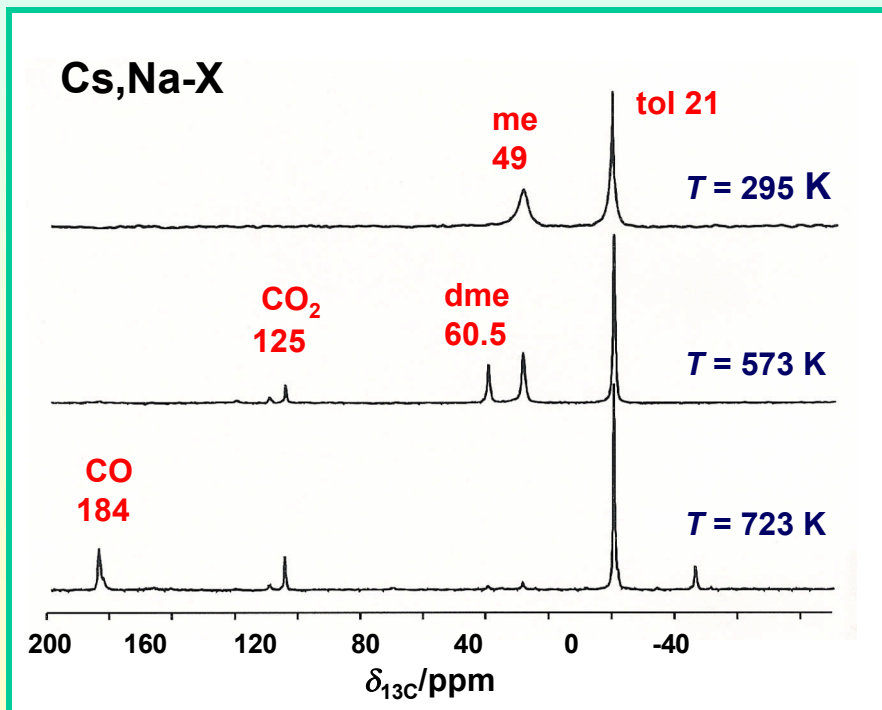


# Side-chain alkylation of toluene on basic zeolites X under batch conditions

$^{13}\text{C}$  MAS NMR spectroscopy:

15  $\text{C}_6\text{H}_5^{13}\text{CH}_3/\text{u.c.}$

5  $^{13}\text{CH}_3\text{OH}/\text{u.c.}$

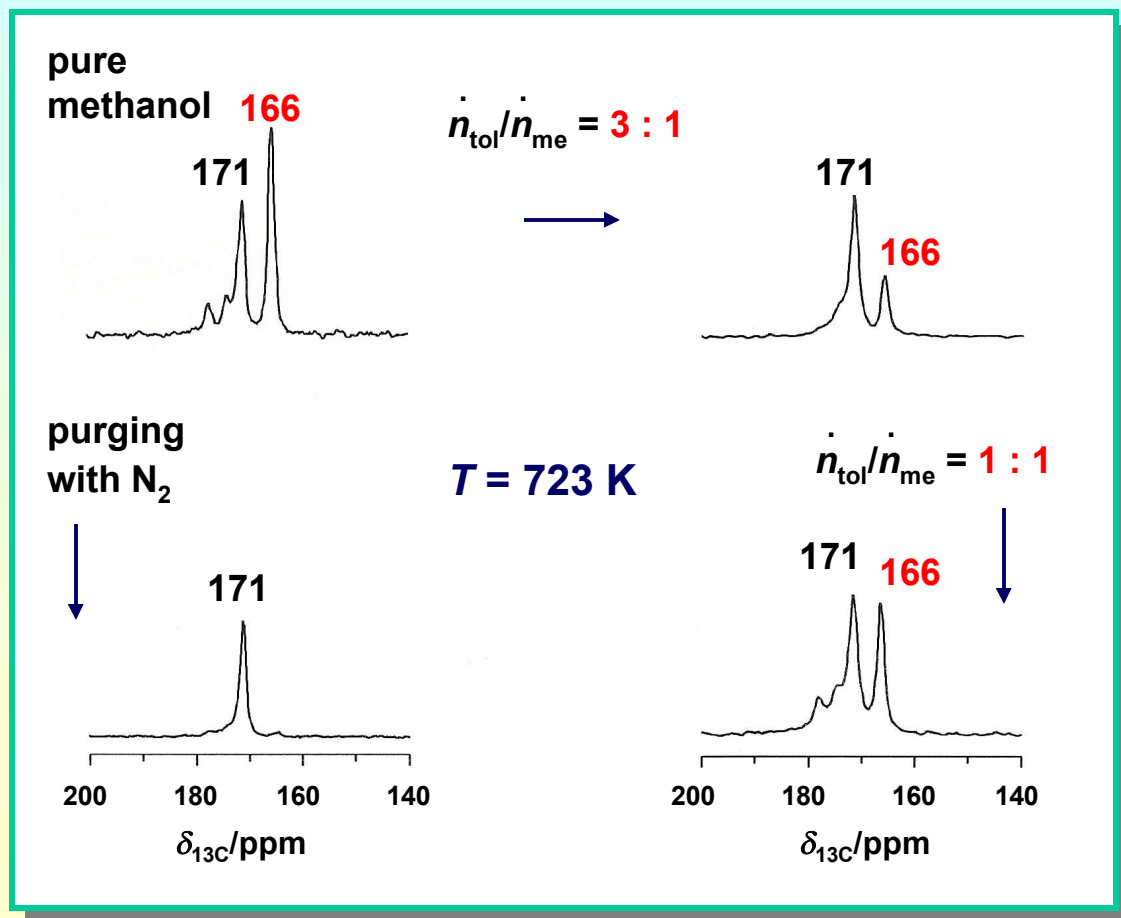


# Reactivity of formate species on zeolite CsOH/Cs,Na-X under flow conditions

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

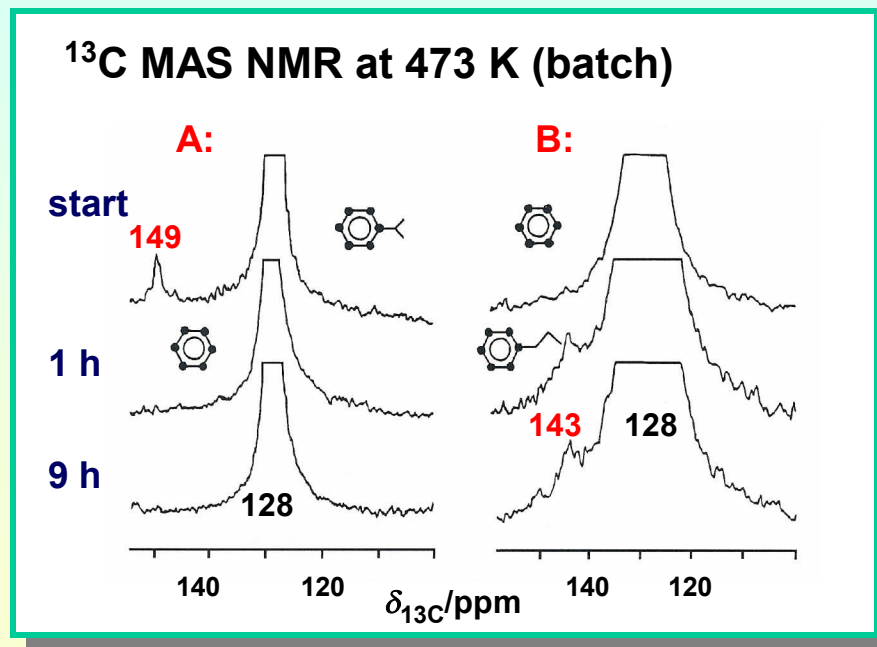
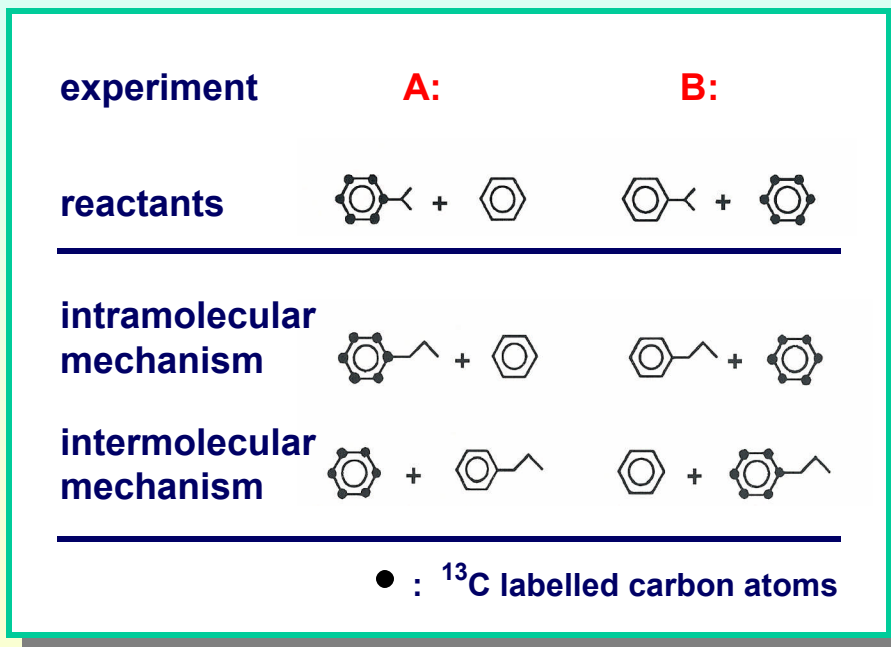
$$W_{\text{cat}}/F_{\text{me}} = 60 \text{ gh/mol}$$

- carbonate species are chemically stable
- formate species are consumed by toluene which indicates a high reactivity



# Investigation of reaction pathways by selectively labelled reactants

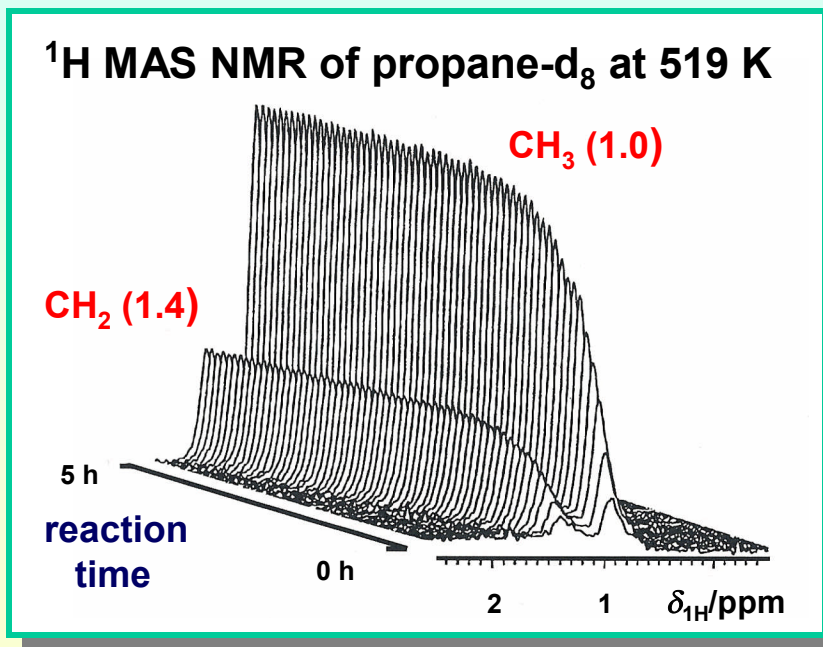
- isomerization of cumene to n-propylbenzene on zeolite H-ZSM-11 in the presence of benzene



→ experiments A and B indicate an intermolecular reaction mechanism

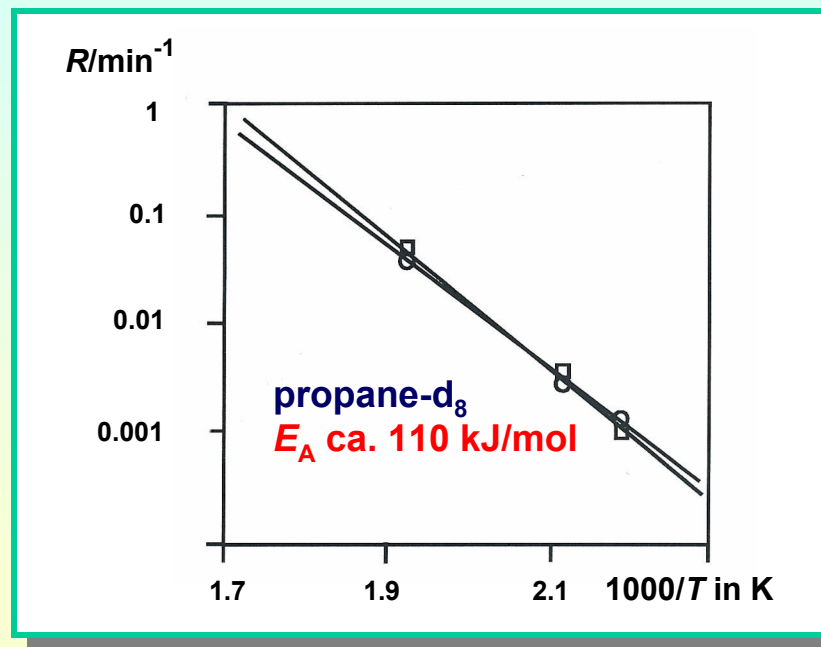
# Evaluation of reaction mechanisms by H/D exchange on acidic zeolites

- H/D exchange of propane-d<sub>8</sub> (A) and isobutane-d<sub>10</sub> (B) with SiOHAl groups on H-ZSM-5



**A:**

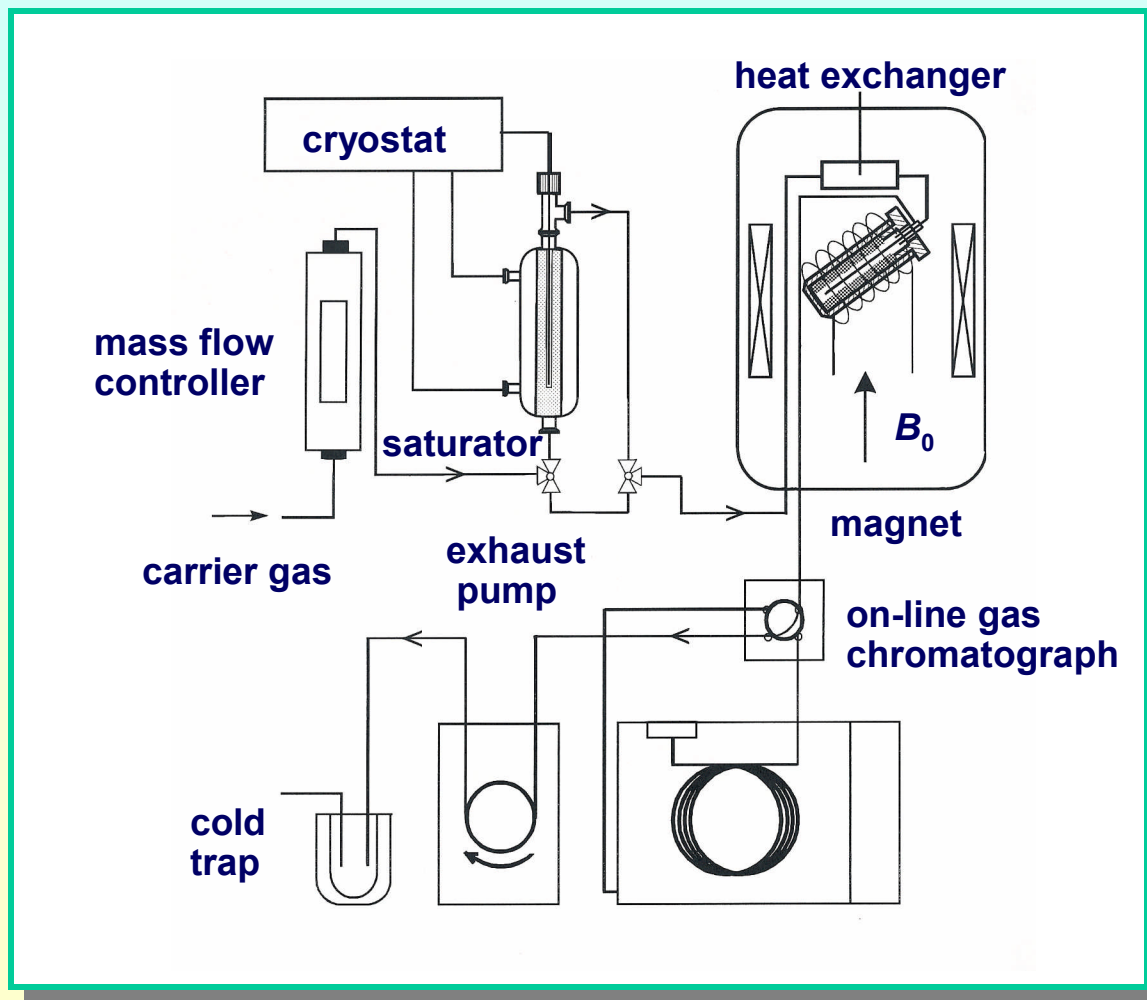
- no regiospecific H/D exchange
- $E_A$  of ca. 110 kJ/mol
- no formation carbenium ions



**B:**

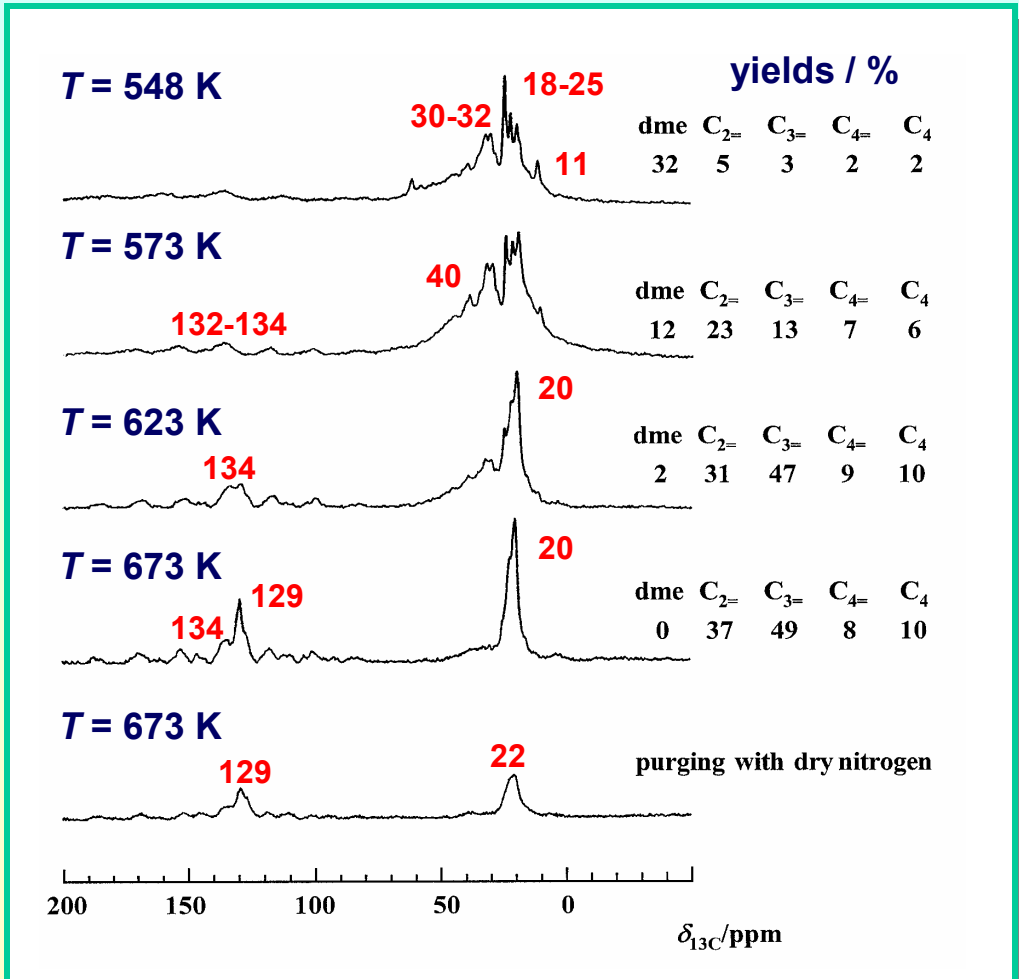
- regiospecific H/D exchange
- $E_A$  of ca. 50 kJ/mol
- formation carbenium ions

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





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



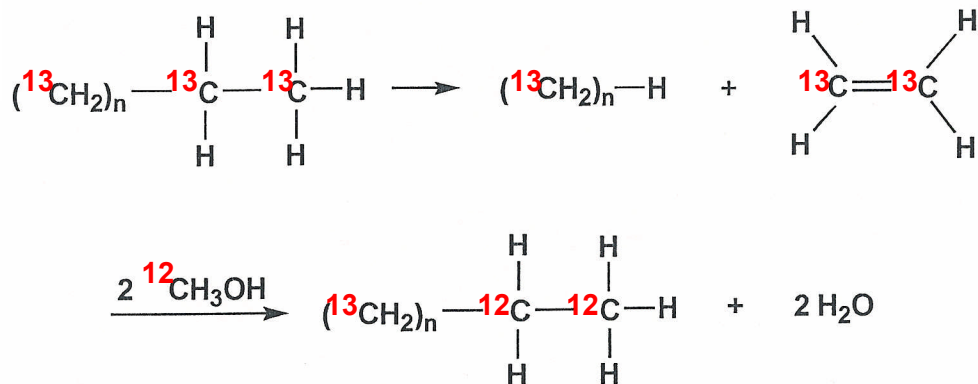
**$T < 623$  K:**

→ mixture of olefinic compounds:  
 3-hexene (14.4, 25.9, 131.2 ppm)  
 2,3-hexadiene (17.5, 126.2, 132.5 ppm)  
 ....

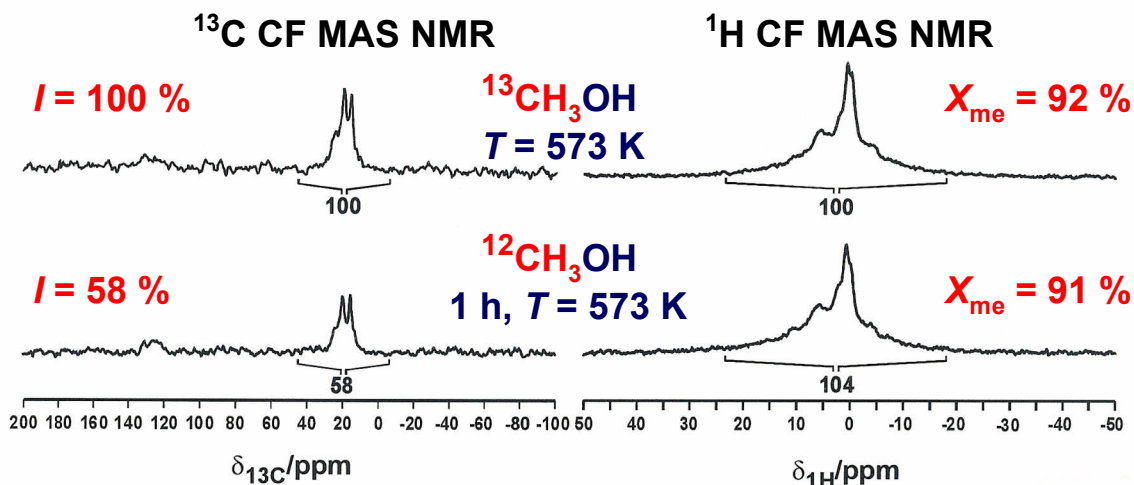
**$T > 623$  K:**

→ 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)

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



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

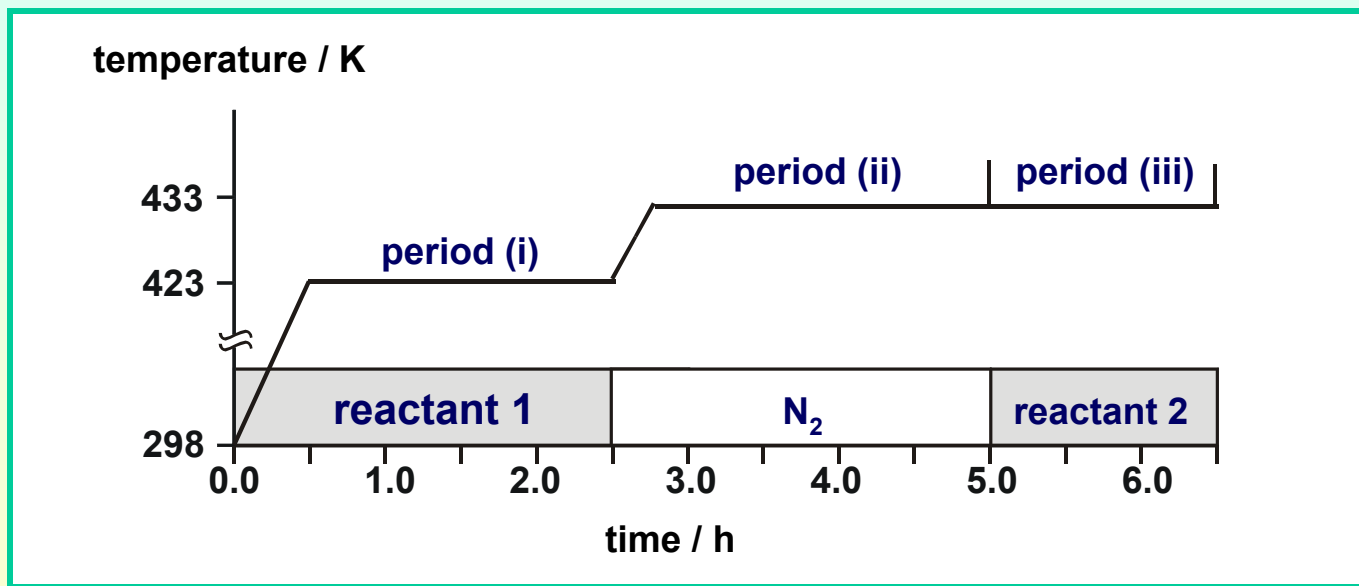


→ alkyl groups are involved in the formation of olefins

→ carbon pool plays an active role in the MTO process

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

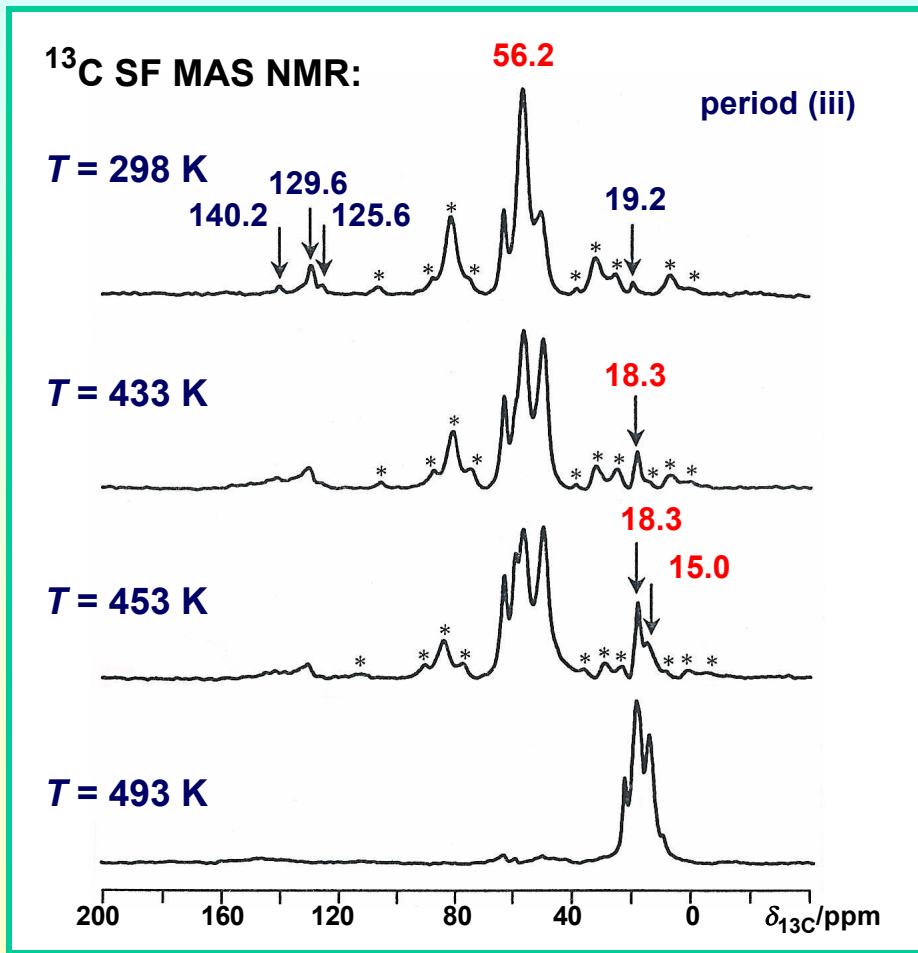
selective preparation of adsorbate complexes by purging the volatile reactants in period (ii) and study of their further reaction in period (iii)



→ investigation of the reactivity of surface compound and intermediates

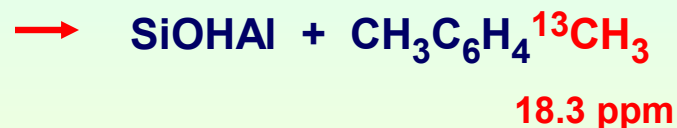
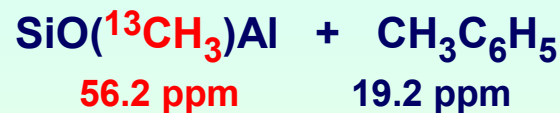
# Methylation of aromatics by surface methoxy groups

reaction of methoxy groups with toluene on zeolite H-Y



methoxy

toluene



- methylation of aromatics by surface methoxy groups starts at  $T = 433 \text{ K}$

# 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***

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### **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**