In Situ Solid-State NMR Spectroscopy in Heterogeneous Catalysis

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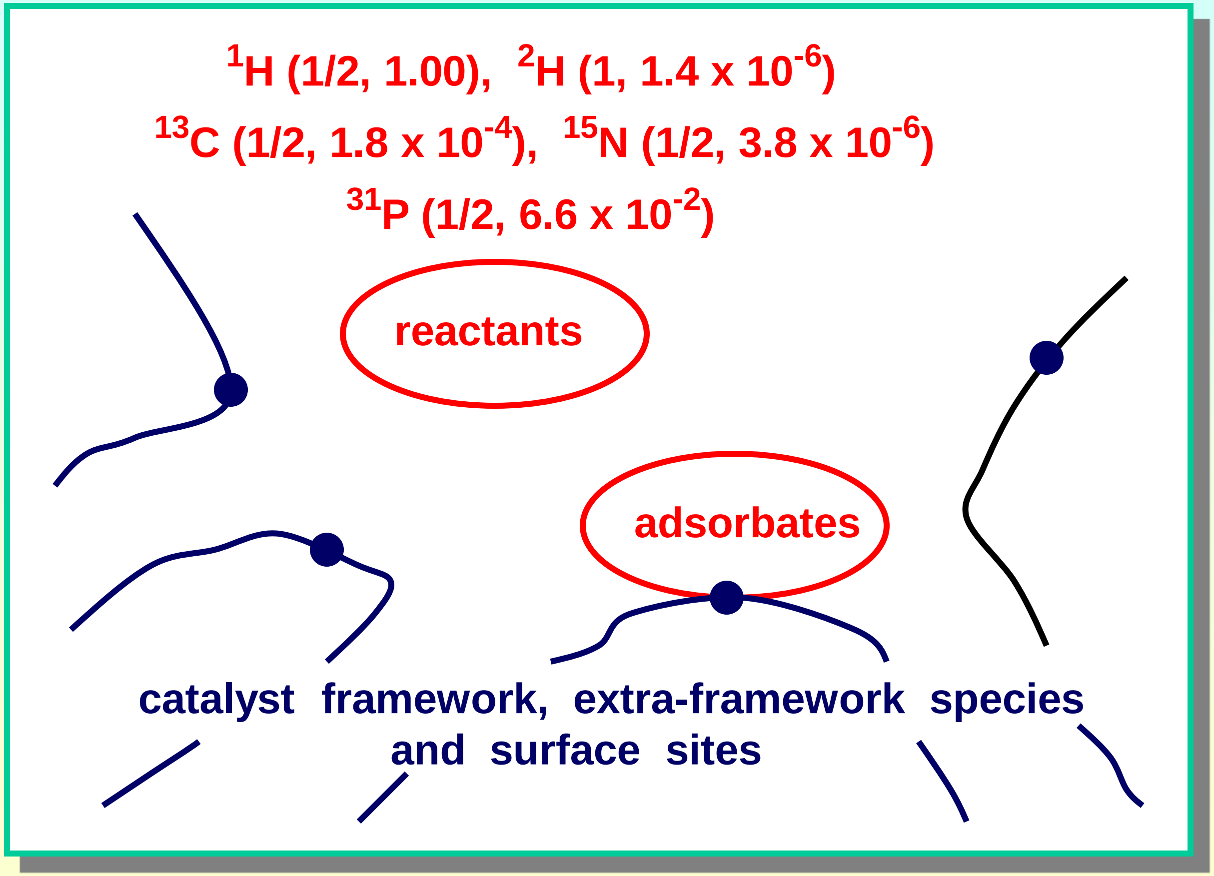
Examples of nuclei accessible for in situ NMR in heterogeneous catalysis



^{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})

isotope (nuclear spin, relative sensitivity in comparison with ^{1}H)

Contents

- specific problems of NMR spectroscopy on working catalysts

- experimental techniques applied for studies under batch and continuous-flow (CF) conditions

- solid-state NMR investigations of heterogeneous reaction systems under *in situ* conditions:

    - catalyst framework and surface sites
    - reactions catalyzed by basic zeolites
    - reactions catalyzed by acidic zeolites

Specific problems of NMR on working catalysts

magnetization:

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

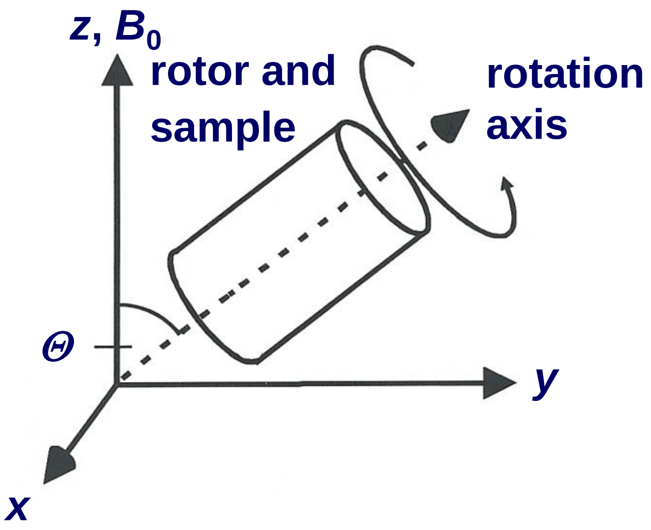
- **absolute number of spins of $N > 10^{19}$ per gram (^{1}H NMR)**
- **decrease of magnetization M_0 with increasing temperature T**
- **rapid chemical exchange of adsorbate complexes at elevated temperatures**
- **observation times of 10 ms (flow conditions) to hours (batch conditions)**
- **quenching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

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)**

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

$$\longrightarrow \begin{array}{l} \Theta = 30.6^o \\ \Theta = 70.1^o \end{array}$$

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

Experimental techniques applied for studies under batch and continuous-flow conditions

Experimental approaches

- batch experiments, external reaction
  - - sealed samples
  - - heating in an external stove
- batch experiments, *in situ* reaction
  - - sealed samples
  - - high-temperature solid-state NMR probes
  - - go-and-stop studies using a Laser heating system

characteristics:

- accessible with commercial equipments
- infinite contact times

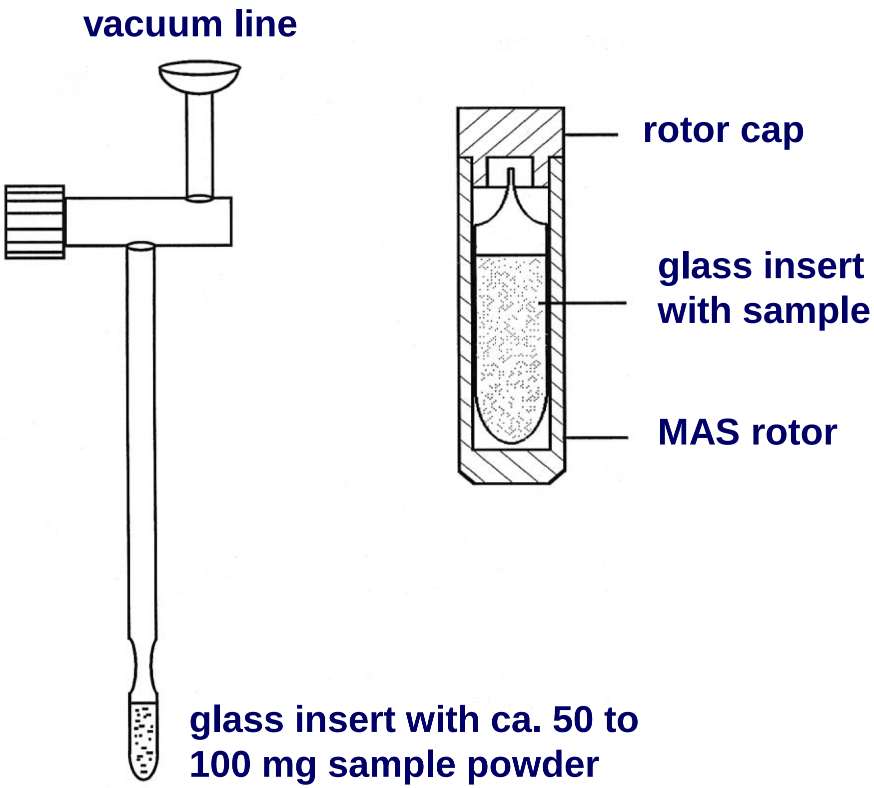
- flow experiments, external reaction
  - - reaction in an external reactor
  - - transfer of the loaded catalysts after quenching the reaction
- flow experiments, *in situ* reaction
  - - continuous injection of reactants into the MAS NMR rotor reactor
  - - high-temperature solid-state NMR probes

characteristics:

- self-made equipments
- study of reactions under staedy state conditions

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**

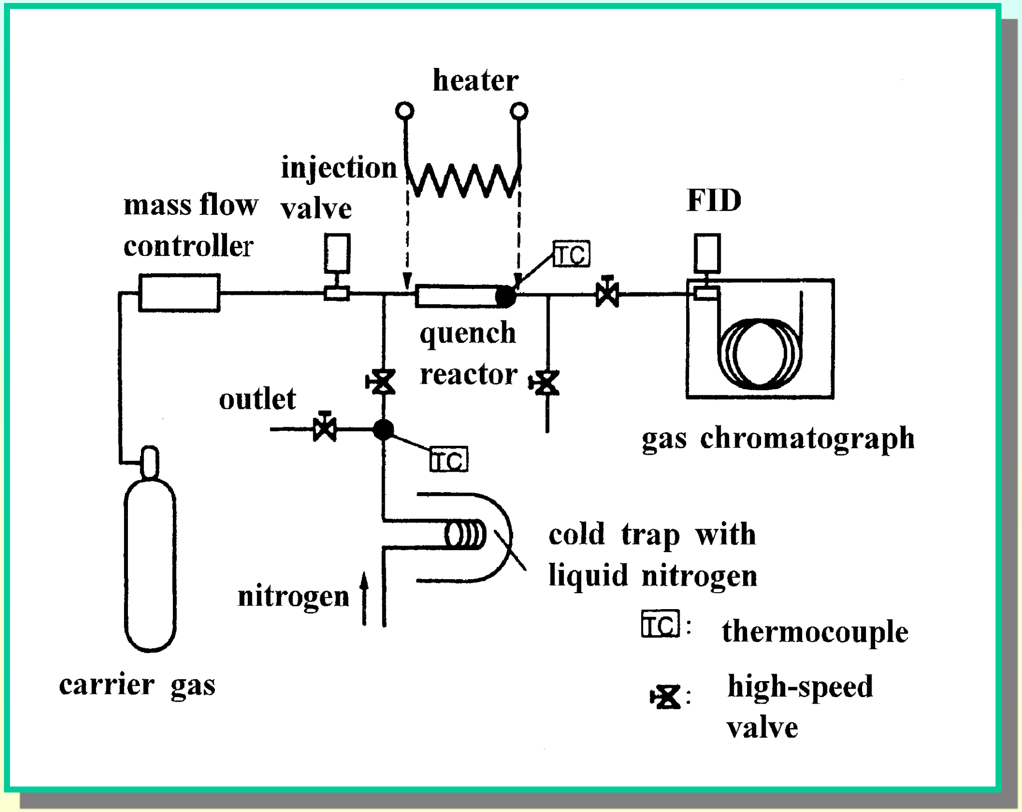


see M. Hunger et al., in: B.M. Weckhuysen, In Situ Spectroscopy of Catalysts, ASP, 2004, p. 177.

Go-and-stop experiments using an external reactor

- pulse-quench technique:
  - conversion of reactants in an external fixed-bed reactor
  - rapid stopping of the reaction by pre-cooled nitrogen gas

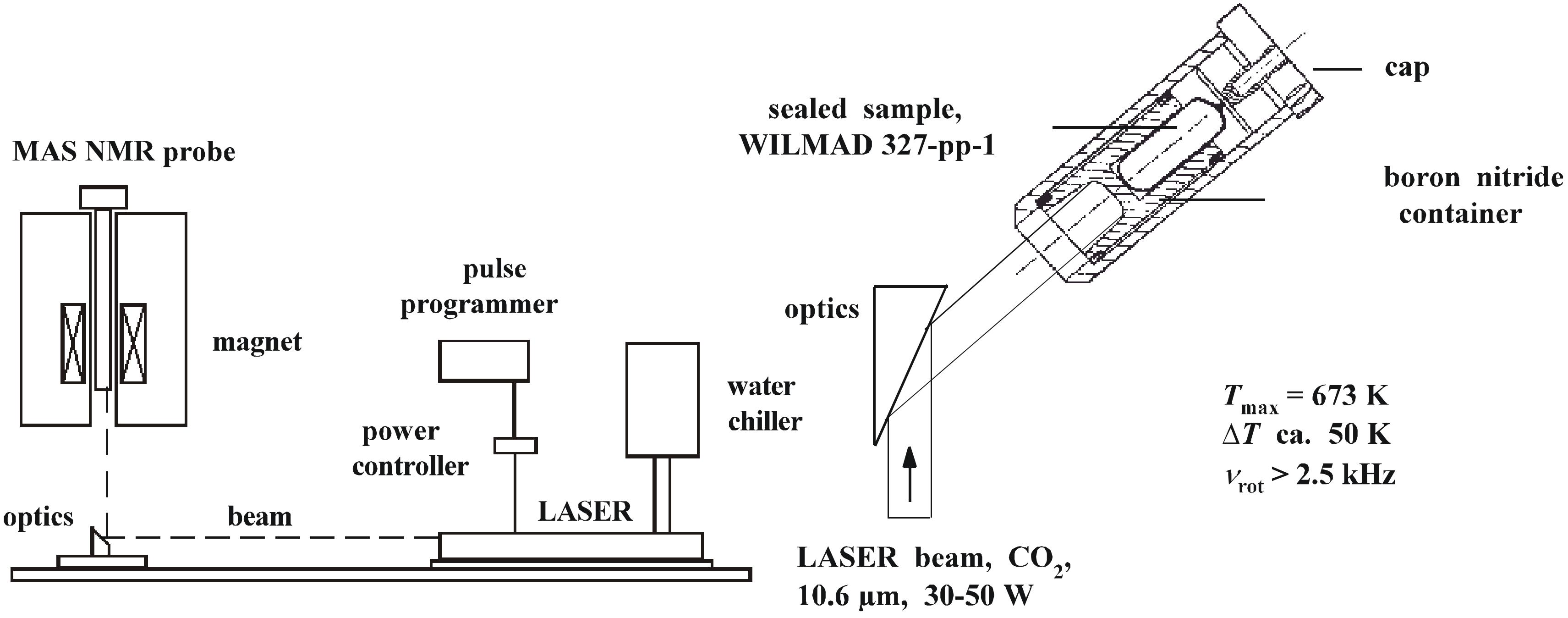
- NMR investigations:
  - transfer of the catalyst loaded with reaction products into an MAS NMR rotor
  - measurements performed at room temperature



D.H. Barich et al., J. Phys. Chem. B 102 (1998) 7163.

Go-and-stop in situ experiments using a Laser heating system

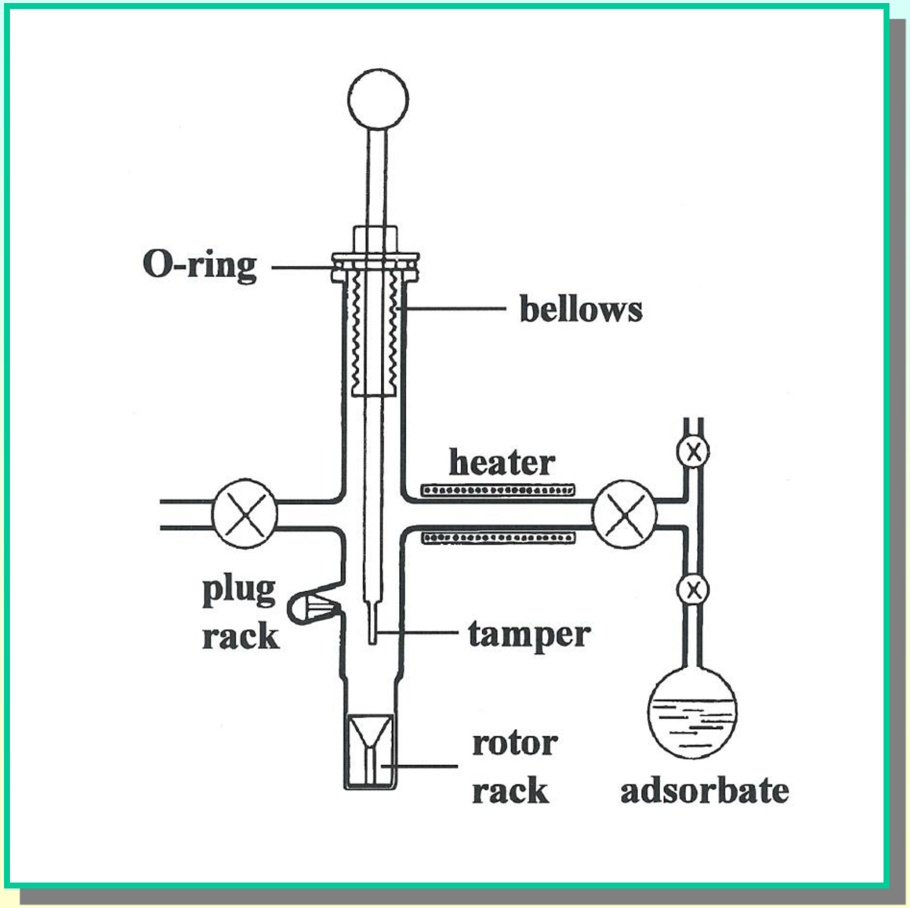
- ***in situ*** **reaction inside a high-temperature NMR probe under batch conditions**



H. Ernst et al., Solid State Nucl. Magn. Reson. 6 (1996) 147.

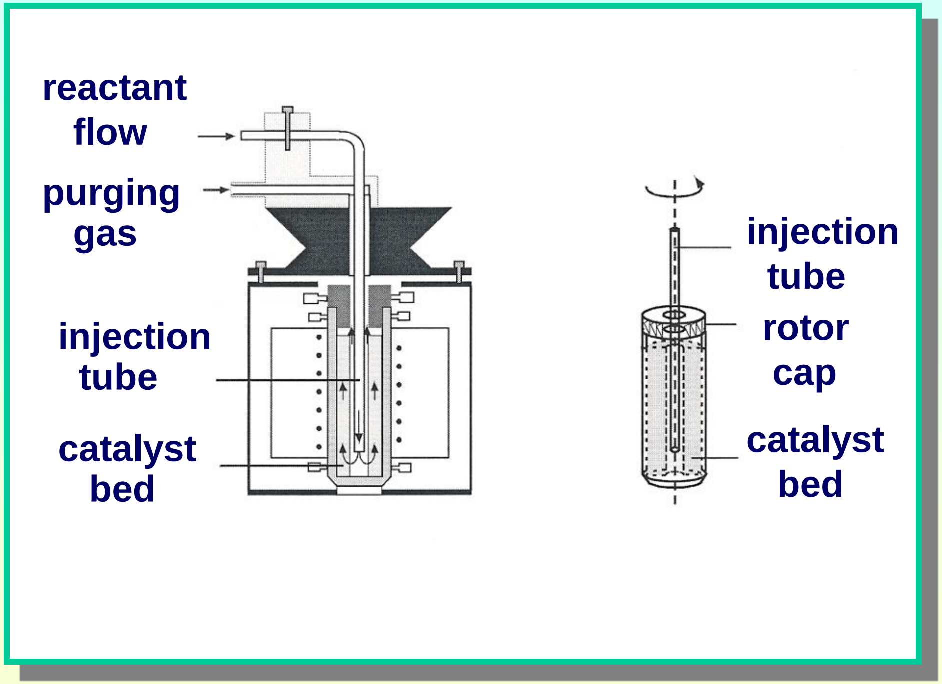
Approach for batch and continuous-flow experiments in an external reactor

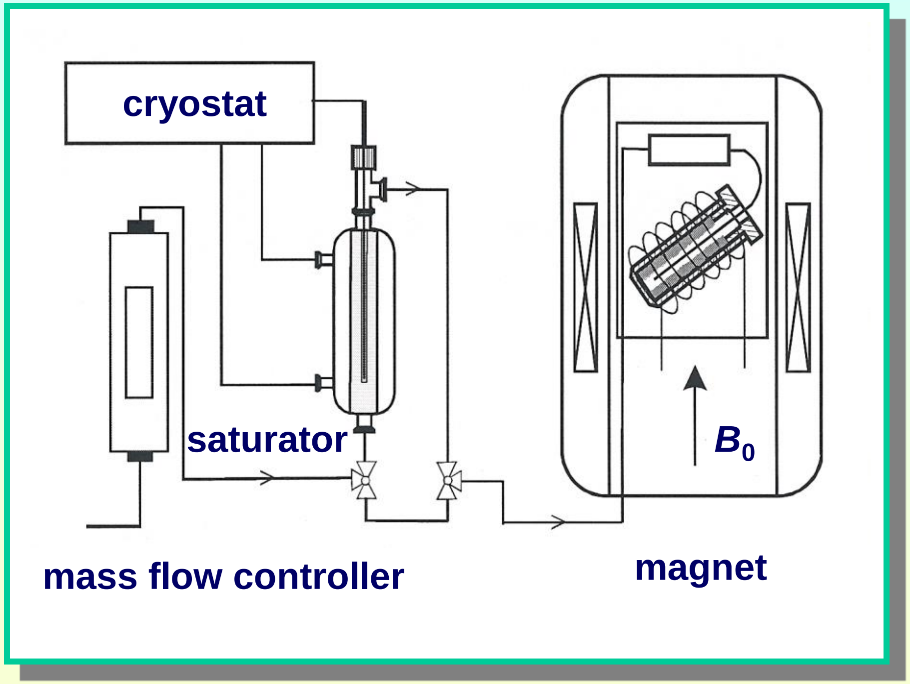
- apparatus for evacuation, loading and catalysis on solid materials in an external reactor
- no contact to air during the transfer of the catalyst material into an MAS NMR rotor
- sealing of the MAS NMR rotor inside the apparatus



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

Continuous-flow (CF) MAS NMR technique

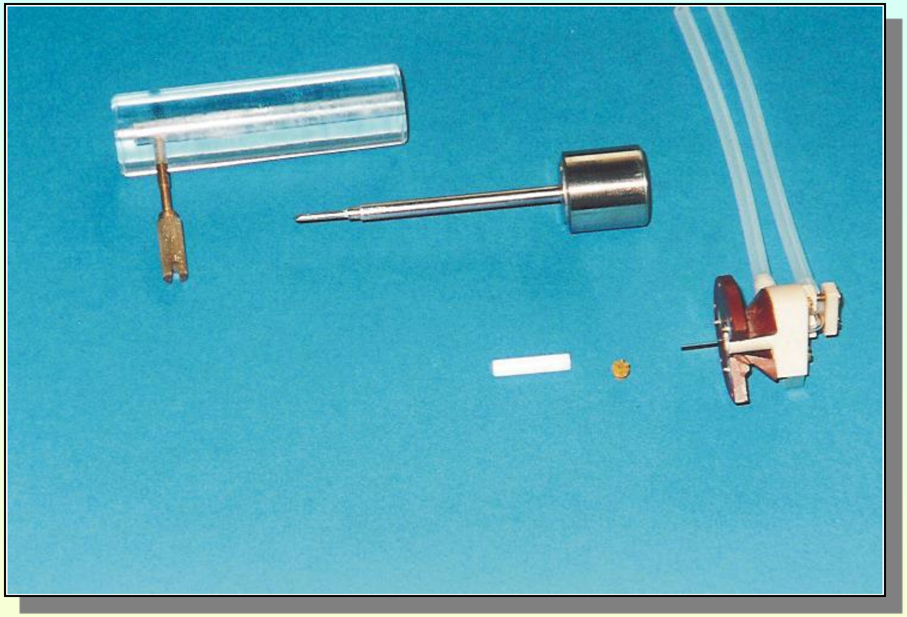


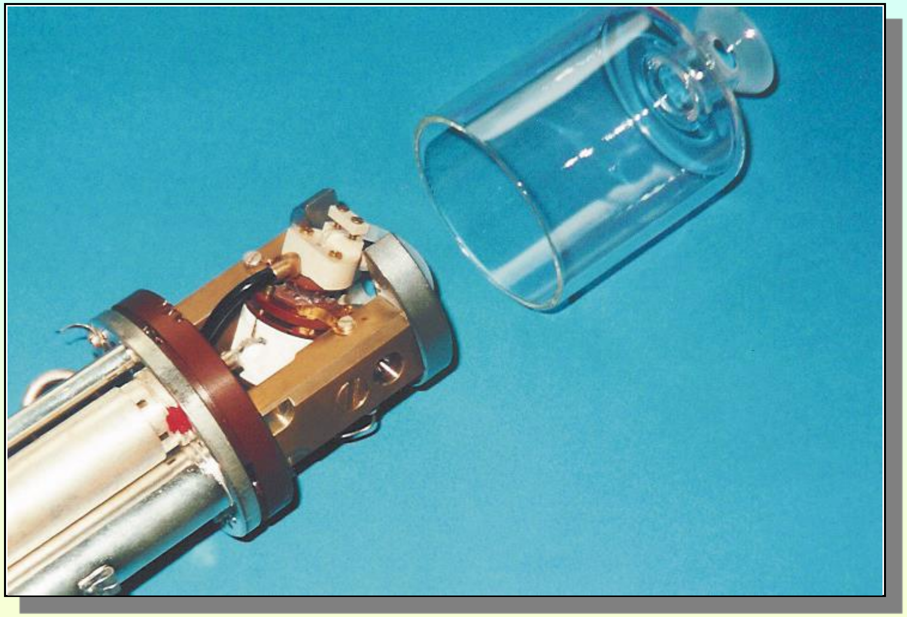


- **continuous injection of reactants into a spinning MAS NMR rotor reactor (*T* < 923 K)**

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.

Behavior of the high-temperature CF MAS NMR probe

- ^{207}Pb MAS NMR of $Pb(NO_3)_2$:

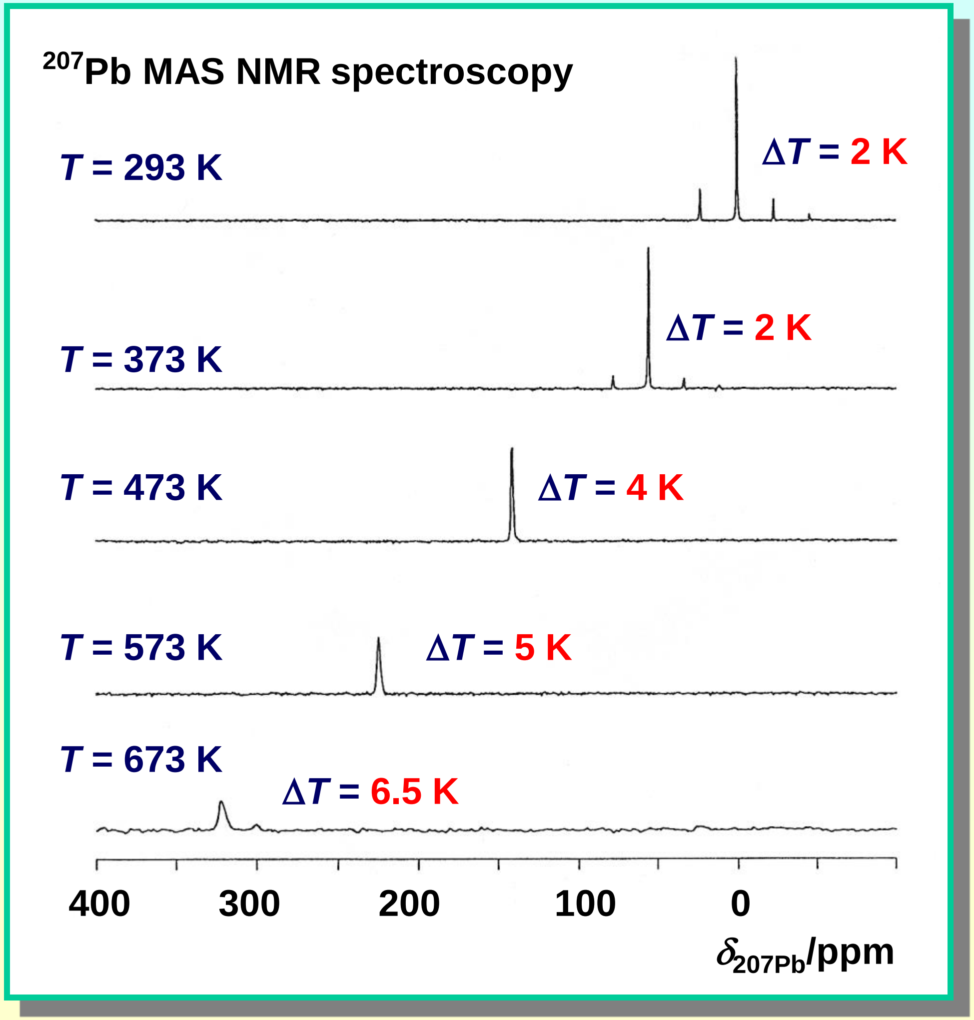
  $\Delta T / \Delta\delta$ = 1.29 K / ppm *

- modified 7 mm Doty MAS NMR probe DSI-740:

  ν_0 = 83.2 MHz

  ν_{rot} = 2.5 kHz

  F_{N2} = 15 ml/min



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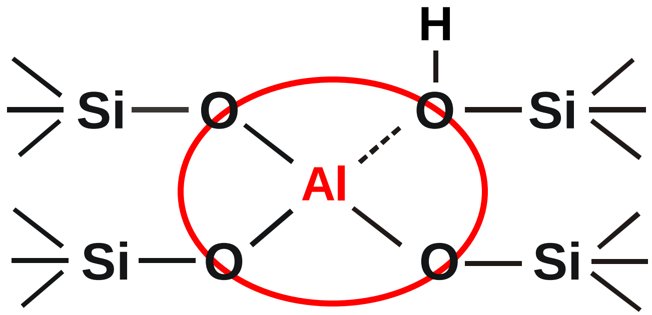
* D.B. Ferguson et al., Anal. Chem. 67 (1995) 3342.

Investigation of framework aluminum in non-hydrated zeolite catalysts

Quadrupolar interactions of aluminum atoms in non-hydrated zeolites

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



- electric field gradient:

$$V_{zz} = eq$$

- quadrupole coupling constant:

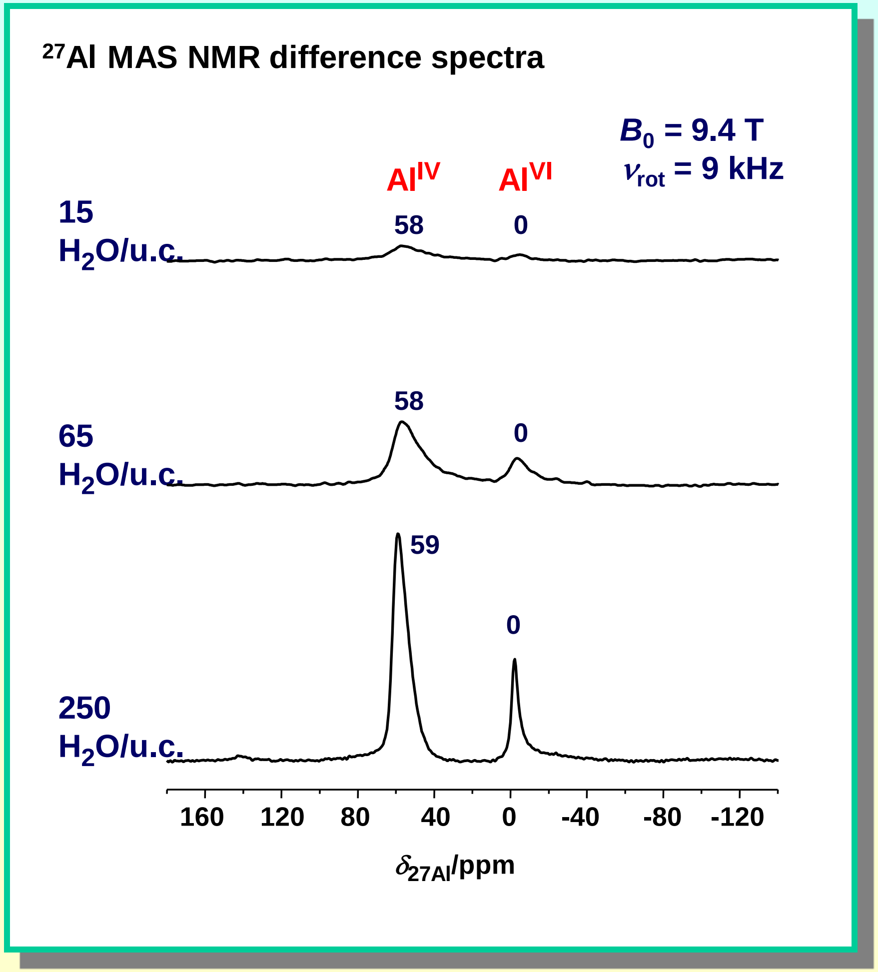
$$QCC = \frac{e^2qQ}{h}$$

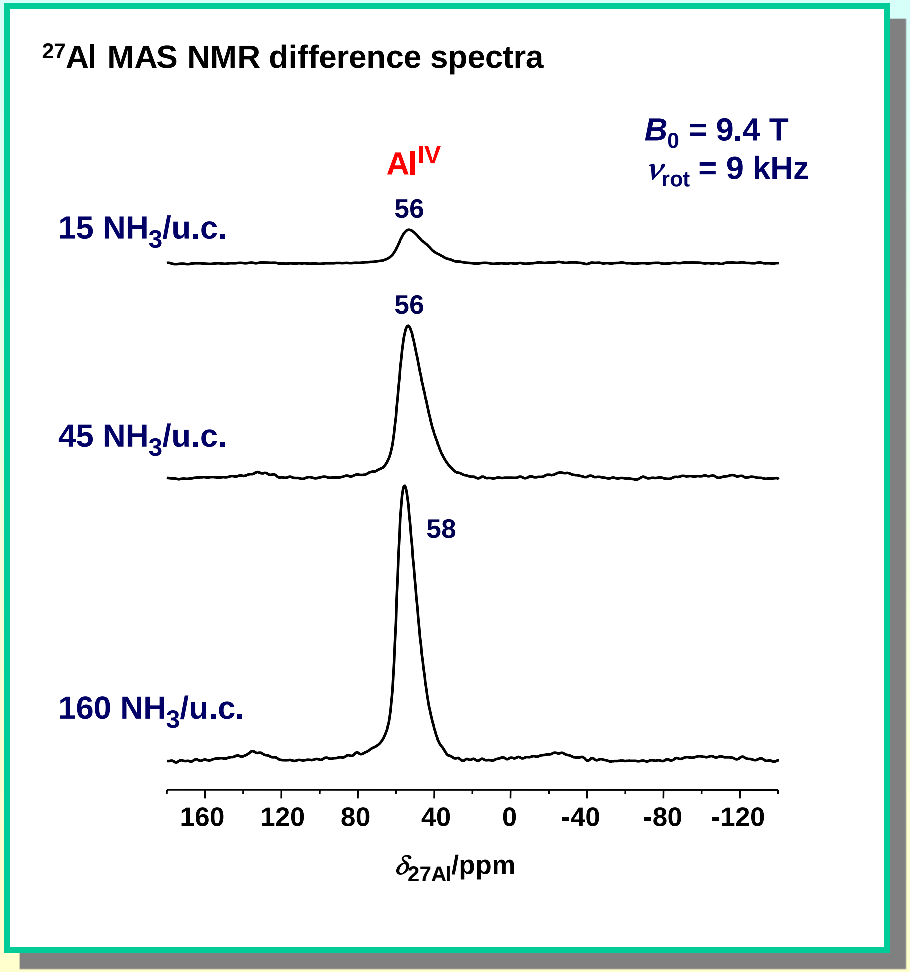
samples	*QCC* values*
hydrated H-Y and H-ZSM-5	2 MHz
non-hydrated Na-Y	5 MHz
non-hydrated H-Y	16 MHz
Al^{ex} in non-hydrated H-ZSM-5	ca. 9 MHz
pyridine-loaded H-Y	5 MHz
ammonia-loaded H-Y	5 MHz

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

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

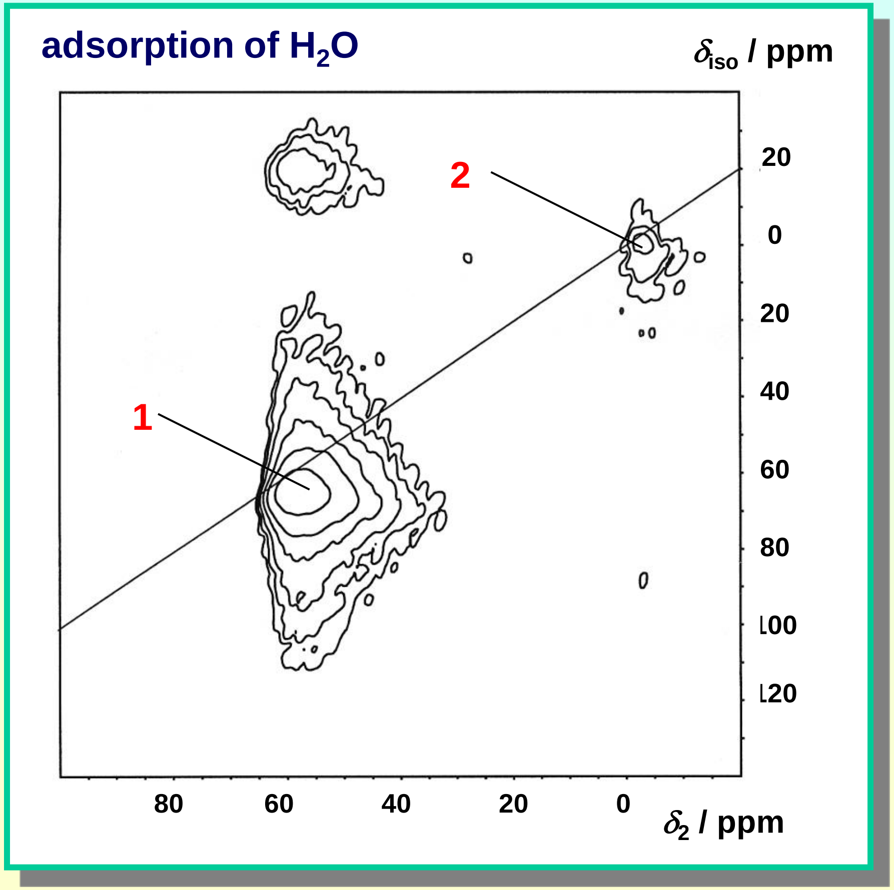
- **effect of the adsorption of H_2O and NH_3 on non-hydrated H,Na-Y**



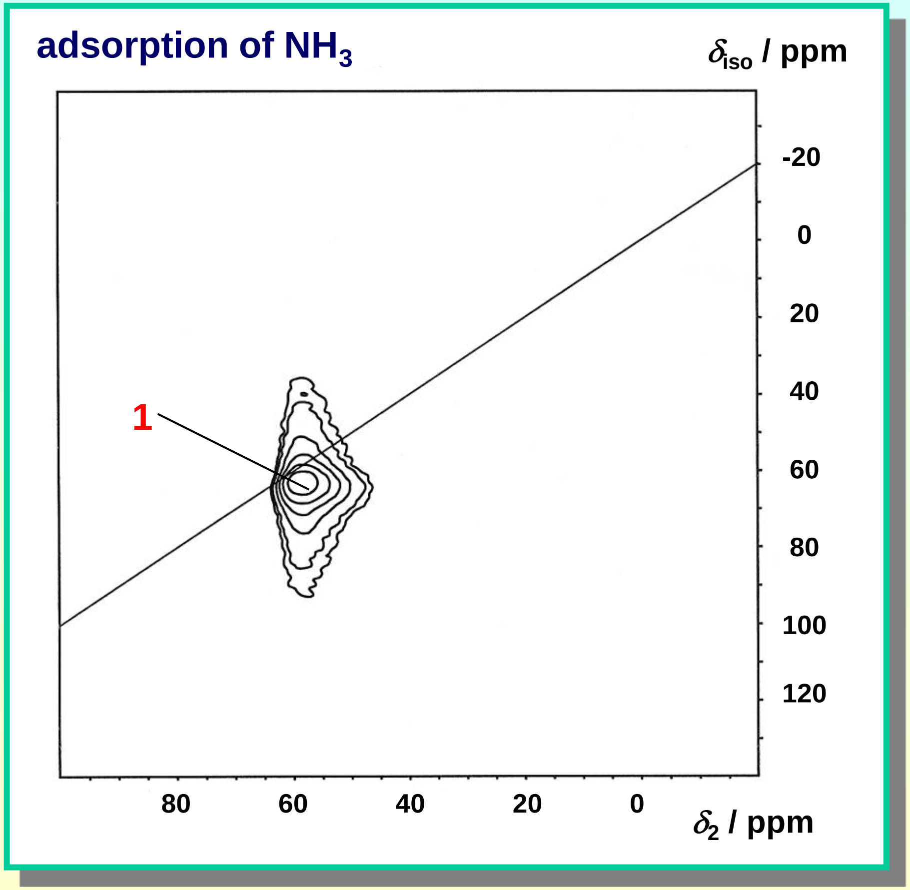


^{27}*Al MQMAS NMR of zeolite H,Na-Y*

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



adsorption of H_2O



adsorption of NH_3

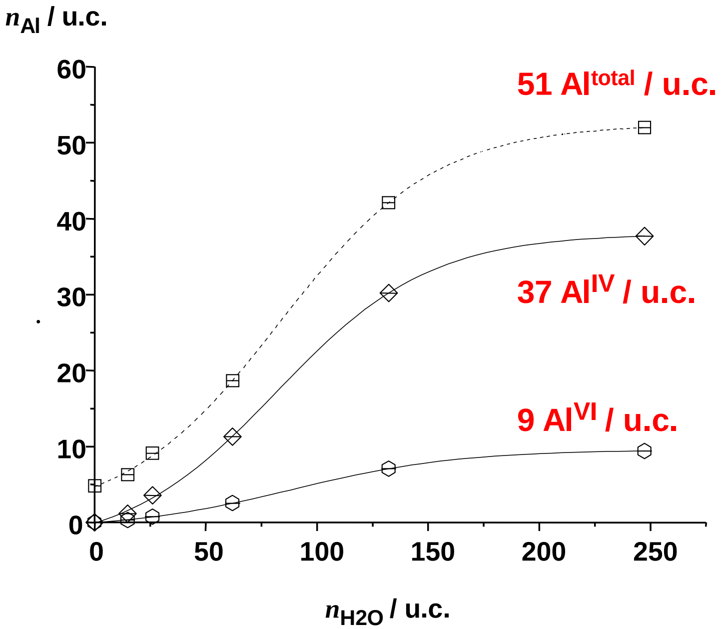
signal 1: δ_{iso} = 64 ppm, *SOQE* = 3.3 MHz
signal 2: δ_{iso} = 0 ppm, *SOQE* = 2.3 MHz

signal 1: δ_{iso} = 62 ppm, *SOQE* = 4.0 MHz

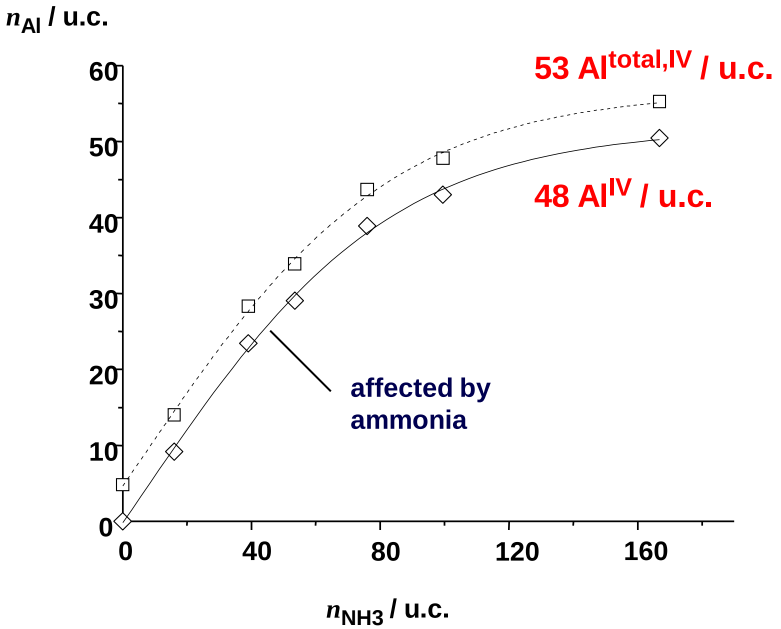
Effect of adsorption studied by ^{27}Al MAS NMR

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

adsorption of H_2O

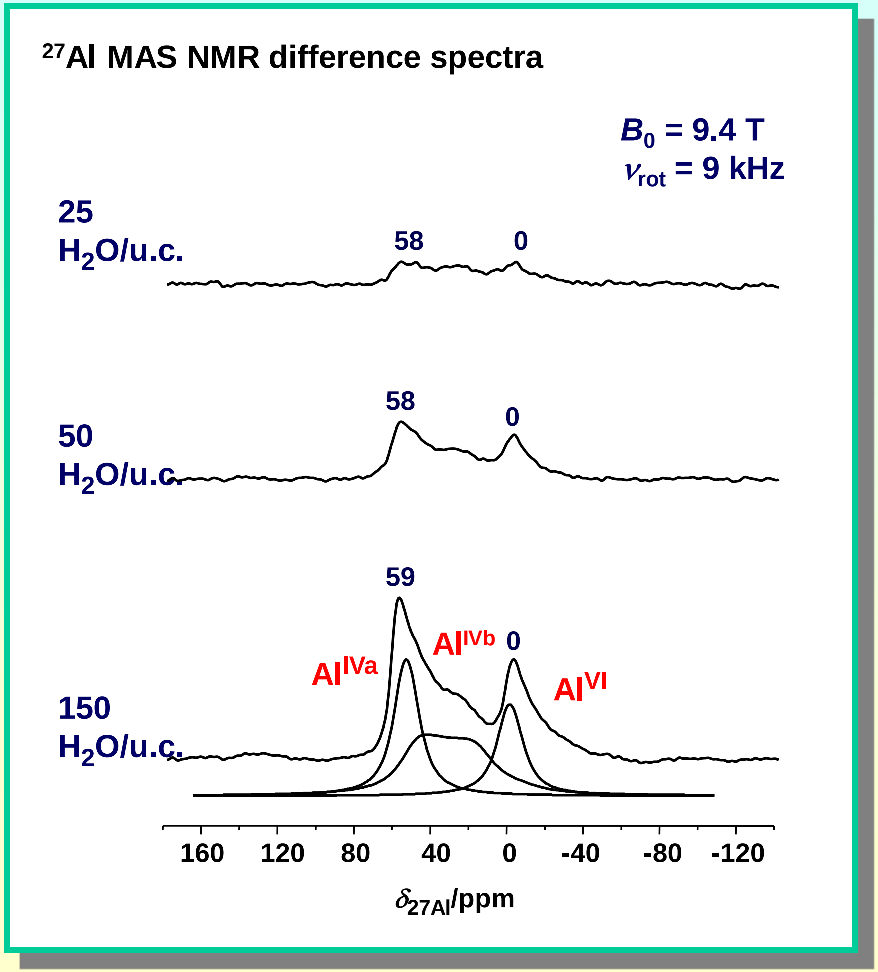


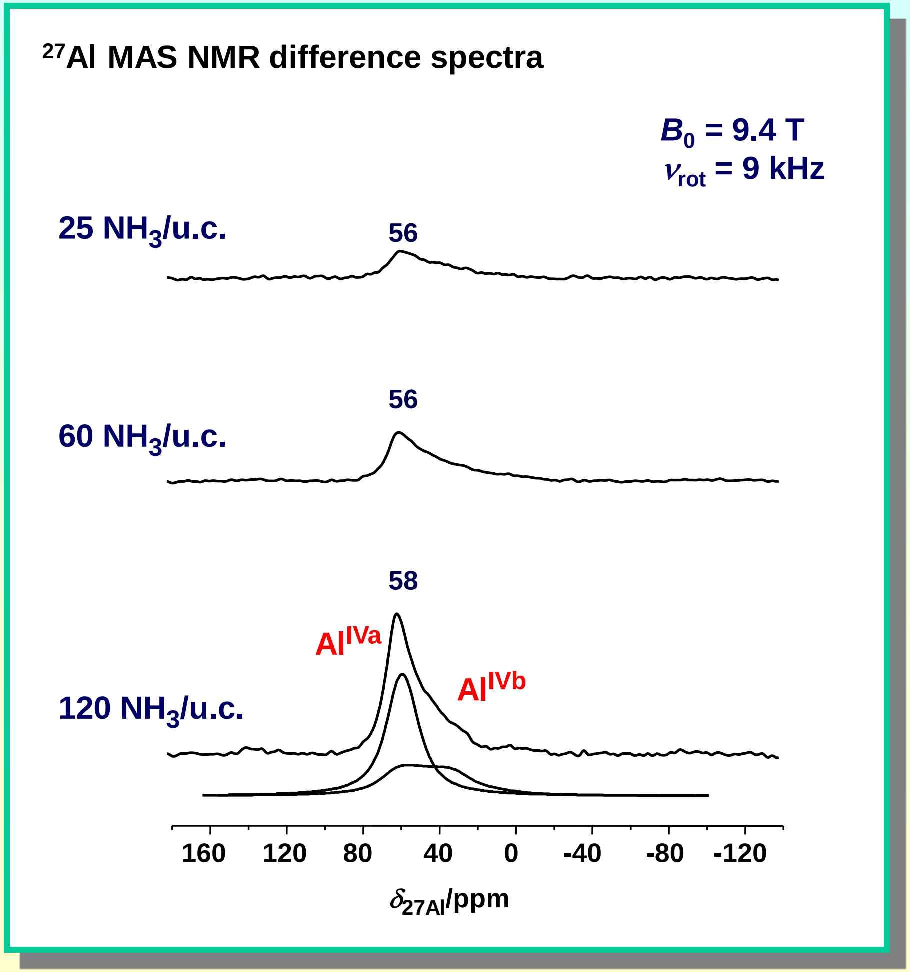
adsorption of NH_3



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

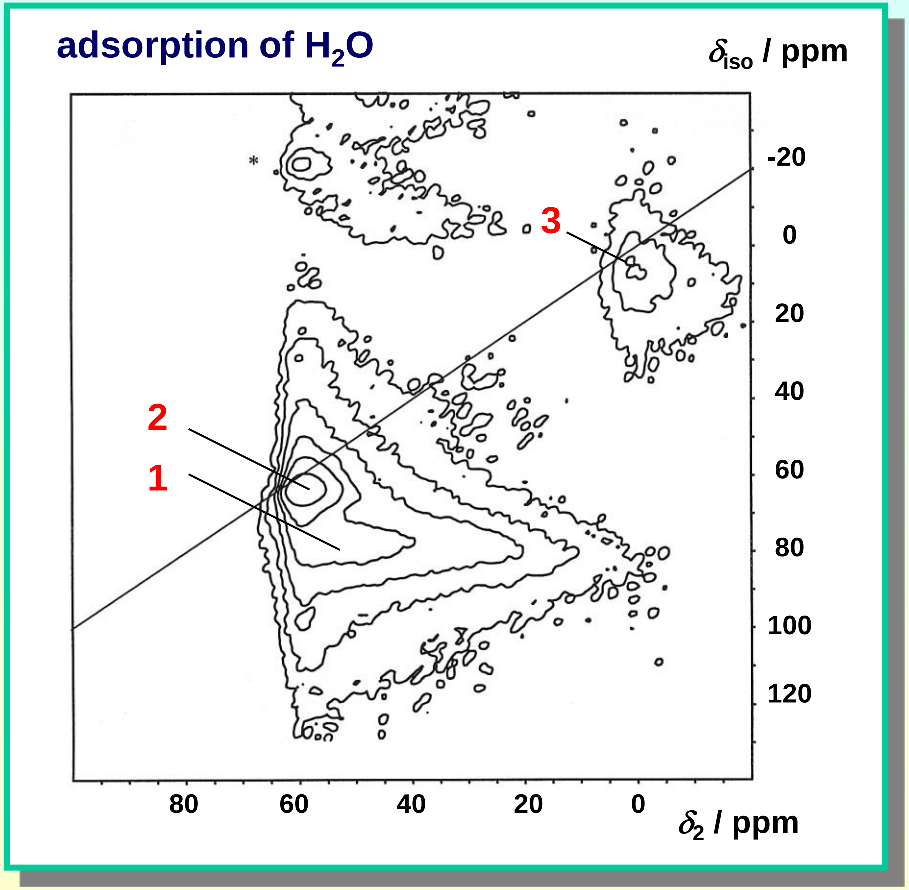
- adsorption of H_2O and NH_3 on dehydrated zeolite deH,Na-Y/81.5



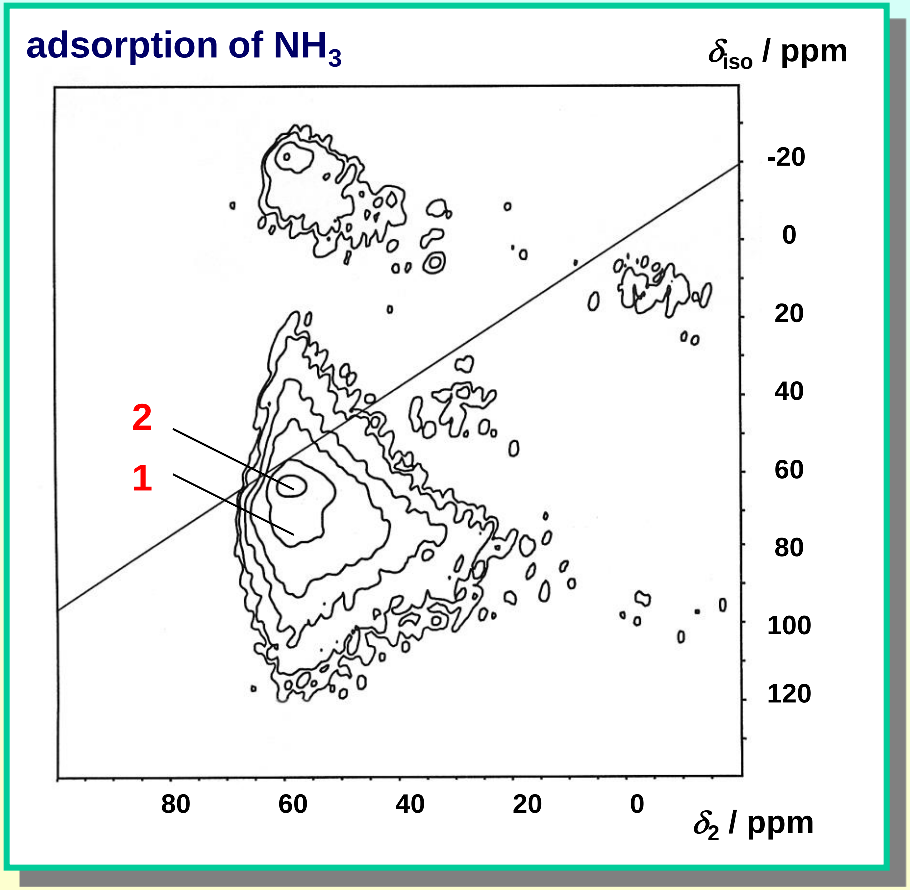


^{27}*Al MQMAS NMR of zeolite deH,Na-Y*

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



adsorption of H_2O



adsorption of NH_3

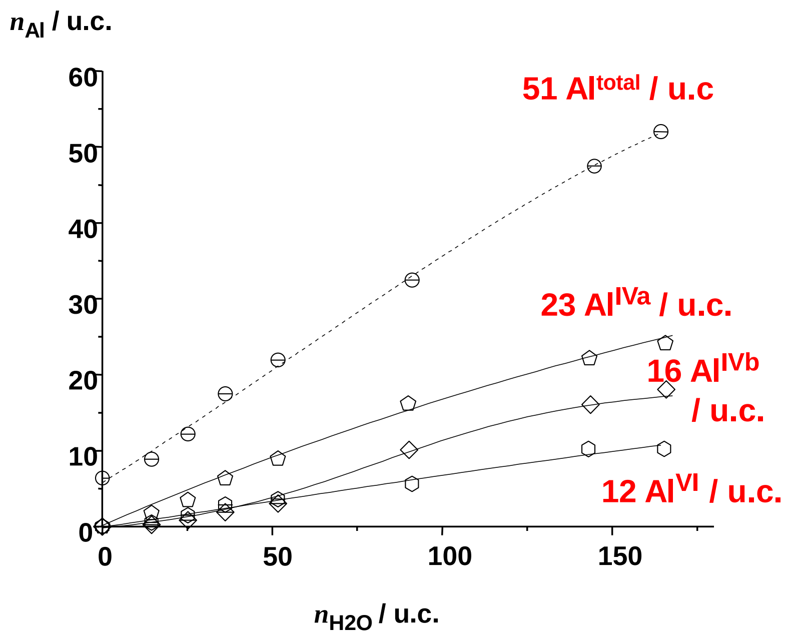
signal 1: δ_{iso} = 75 ppm, *SOQE* ca. 5.8 MHz
signal 2: δ_{iso} = 62 ppm, *SOQE* = 2.6 MHz
signal 3: δ_{iso} = 3 ppm, *SOQE* = 2.3 MHz

signal 1: δ_{iso} ca. 70 ppm, *SOQE* ca. 5.0 MHz
signal 2: δ_{iso} = 62 ppm, *SOQE* = 4.0 MHz

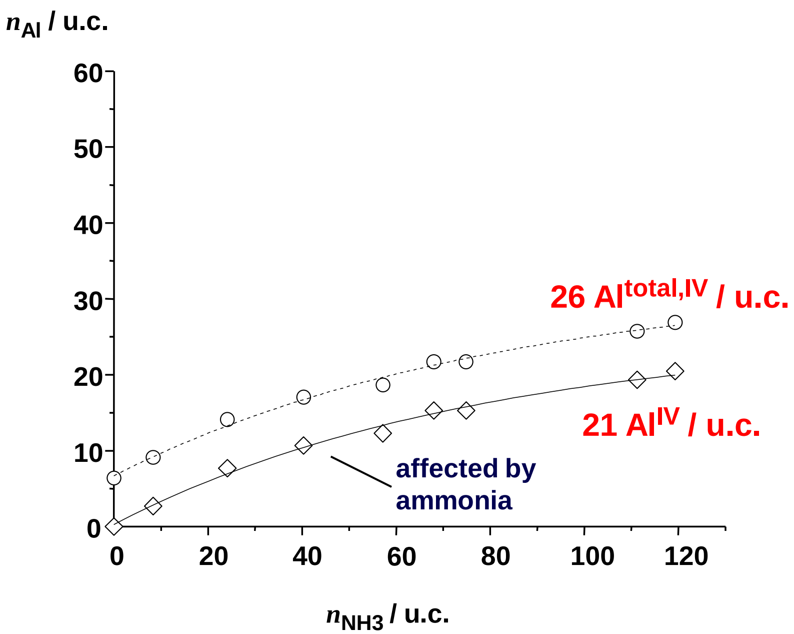
Effect of adsorption studied by ^{27}Al MAS NMR

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

adsorption of H_2O



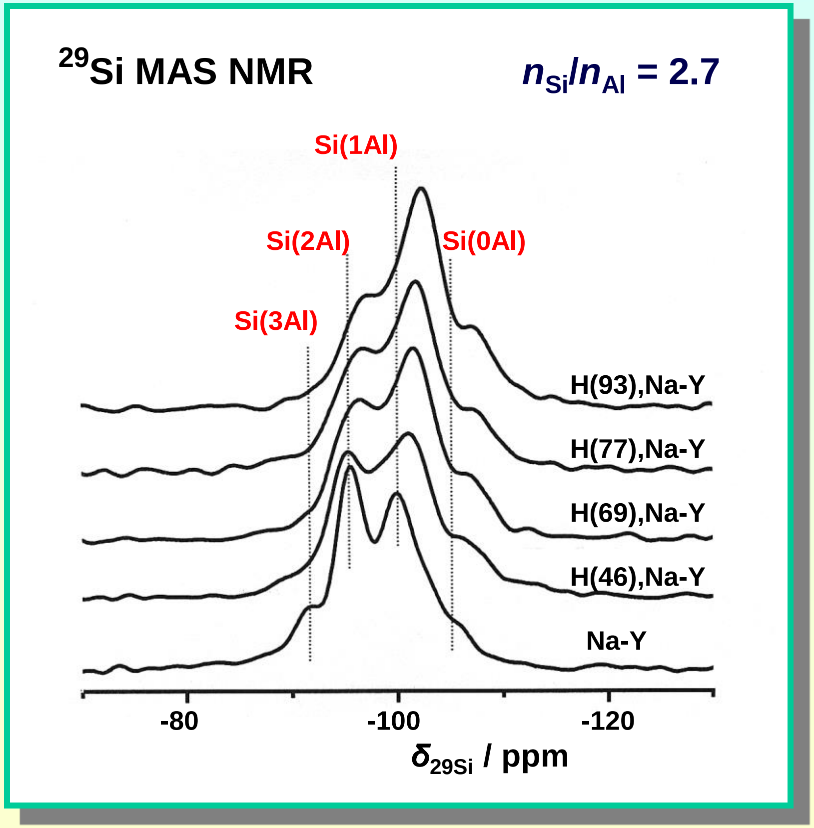
adsorption of NH_3



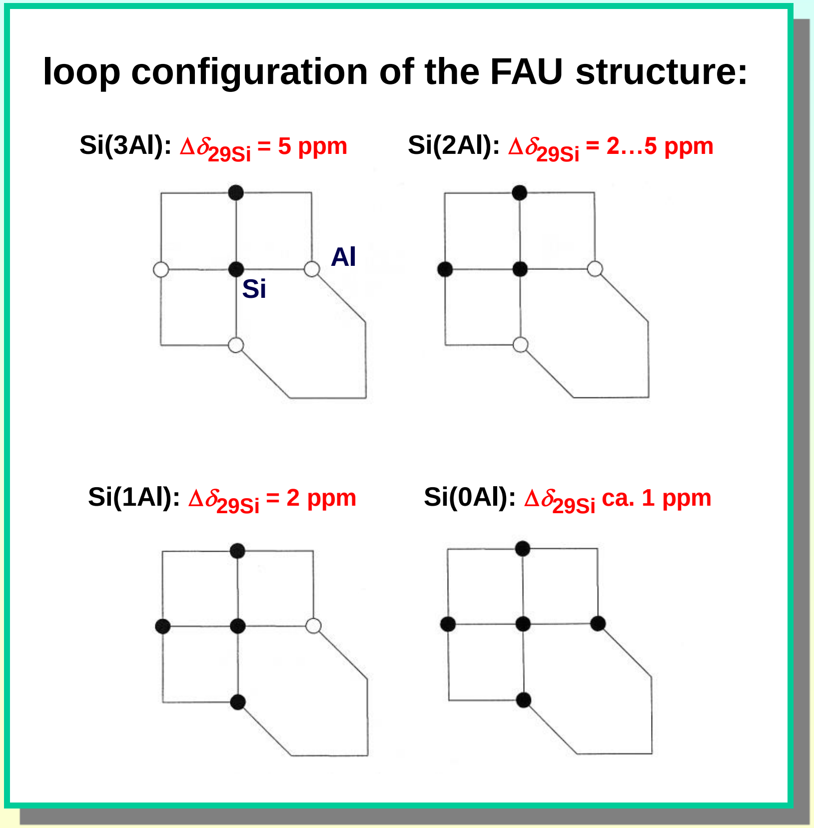
Strain of Si(nAl) tetrahedra in non-hydrated zeolites

^{29}Si MAS NMR

$n_{Si}/n_{Al} = 2.7$



loop configuration of the FAU structure:



Si(3Al): $\Delta\delta_{29Si}$ = 5 ppm

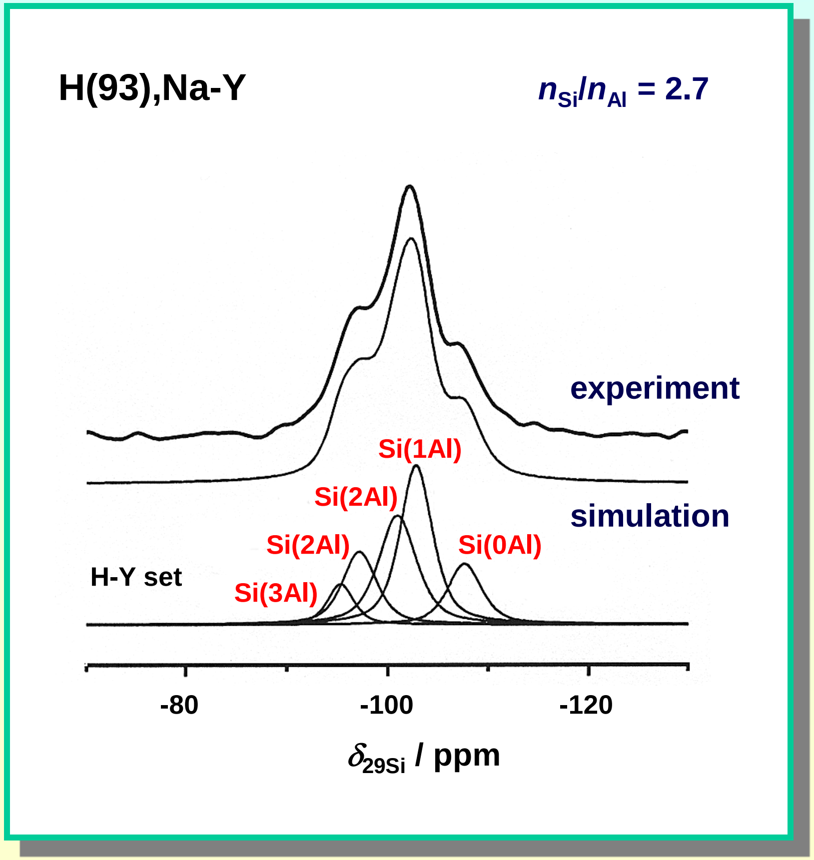
Si(2Al): $\Delta\delta_{29Si}$ = 2…5 ppm

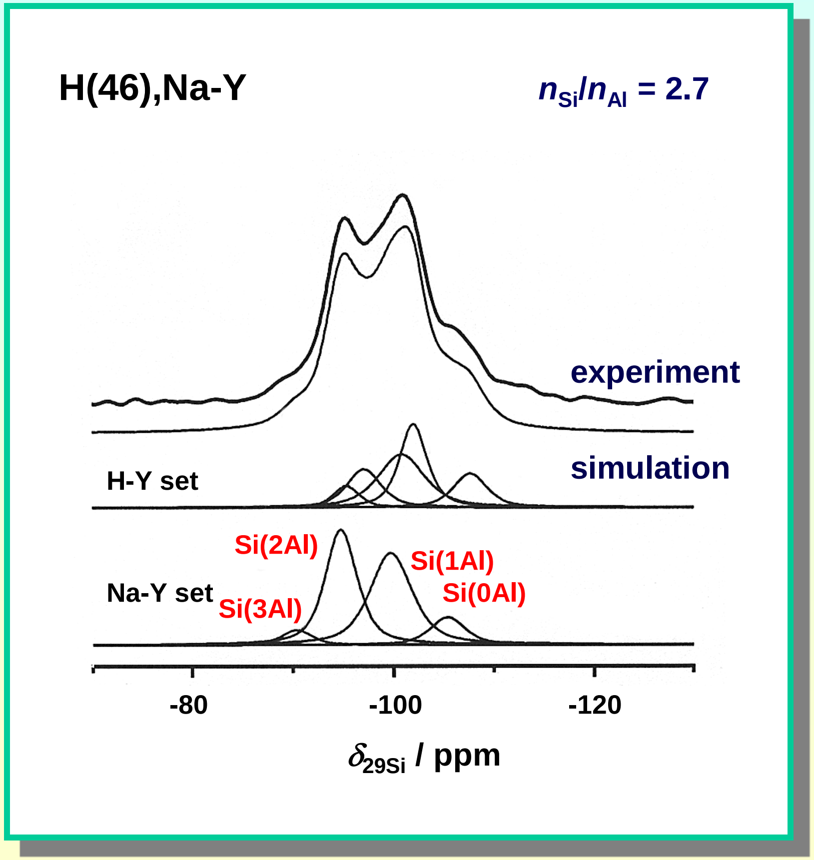
Si(1Al): $\Delta\delta_{29Si}$ = 2 ppm

Si(0Al): $\Delta\delta_{29Si}$ ca. 1 ppm

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

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

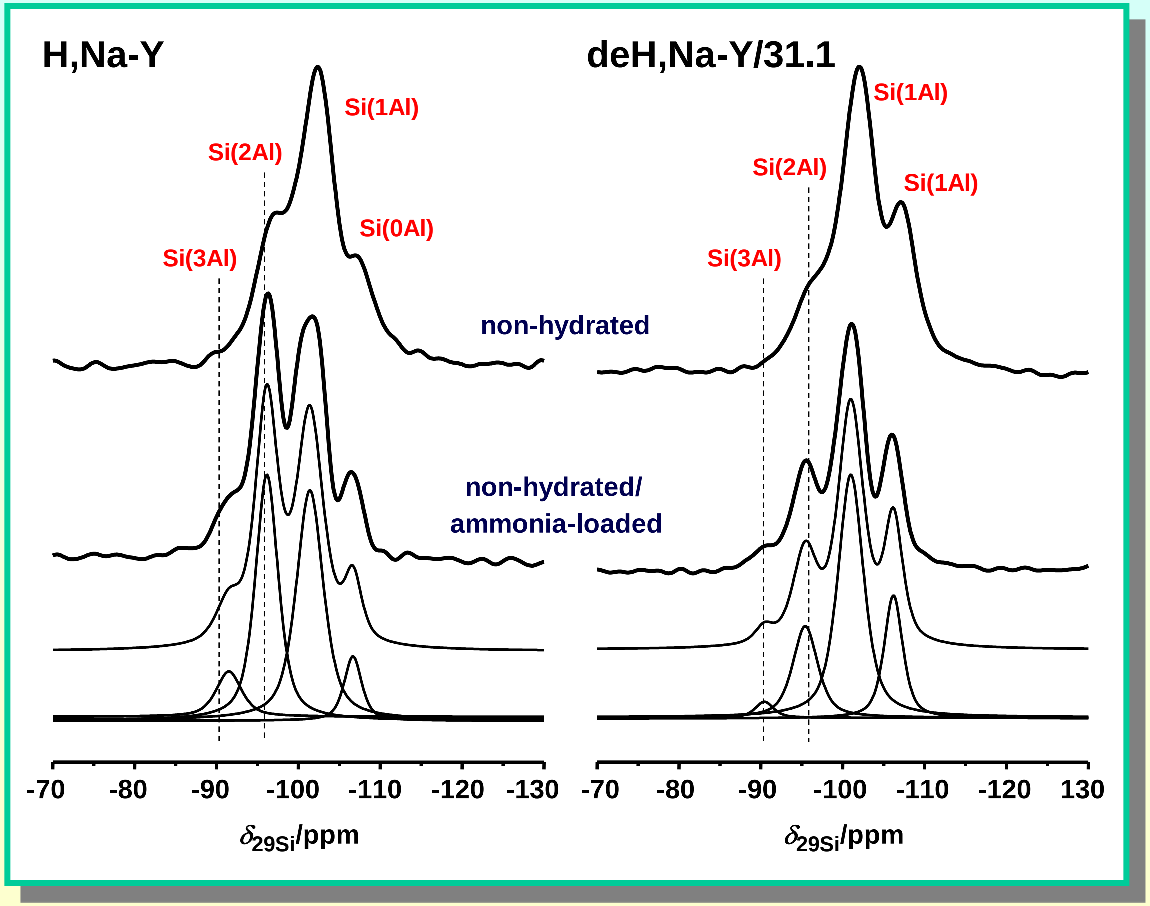




J. Jiao et al., Z. Anorg. Allg. Chem. 631 (2005) 484.

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

- determination of the framework aluminum content after loading of ammonia



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

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

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

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

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

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

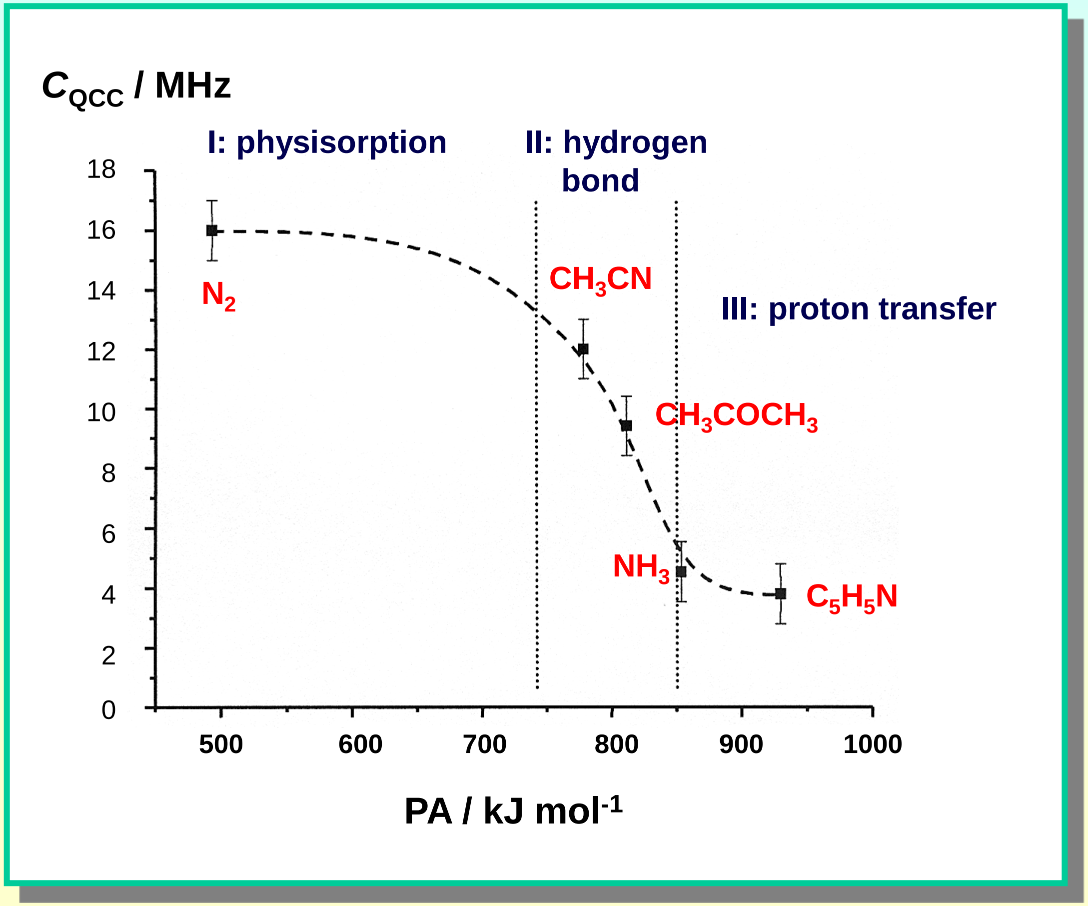
→ reasonable agreement of framework n_{Si}/n_{Al} ratios obtained for non-hydrated/ ammonia-loaded samples

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

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

Effect of the base strength of adsorbates

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



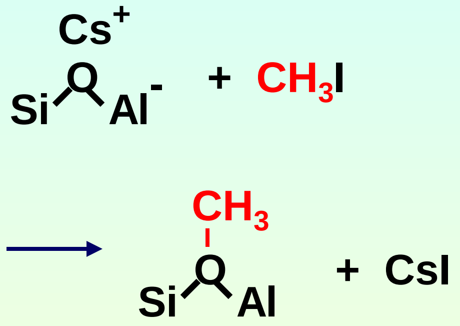
→ **the C_{QCC} value of framework aluminum atoms in non-hydrated zeolite catalysts is sensitive to the adsorbate complexes formed at acid sites (SiOHAl)**

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

Investigation of base sites and of reactions catalyzed by basic zeolites

Characterization of basic zeolites under reaction conditions

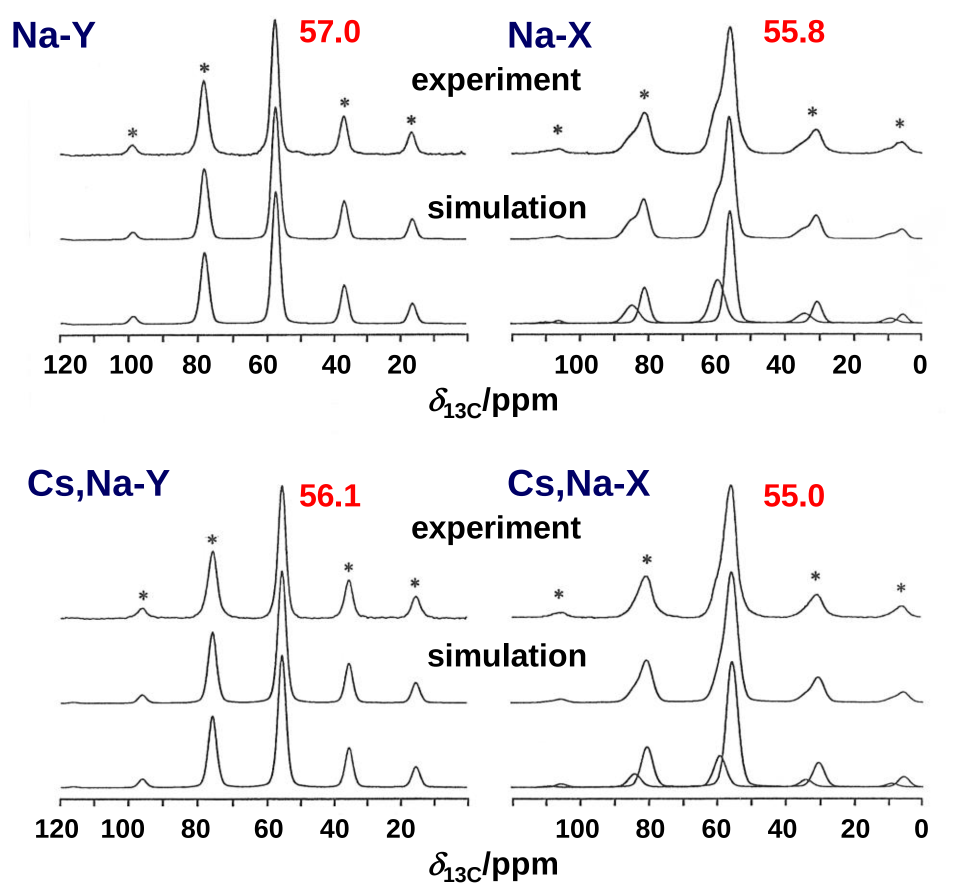
- **conversion of CH_3I on basic zeolites:**



- **^{13}C MAS NMR spectroscopy of the surface methoxy groups formed under batch conditions:**

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

^{13}C MAS NMR spectroscopy



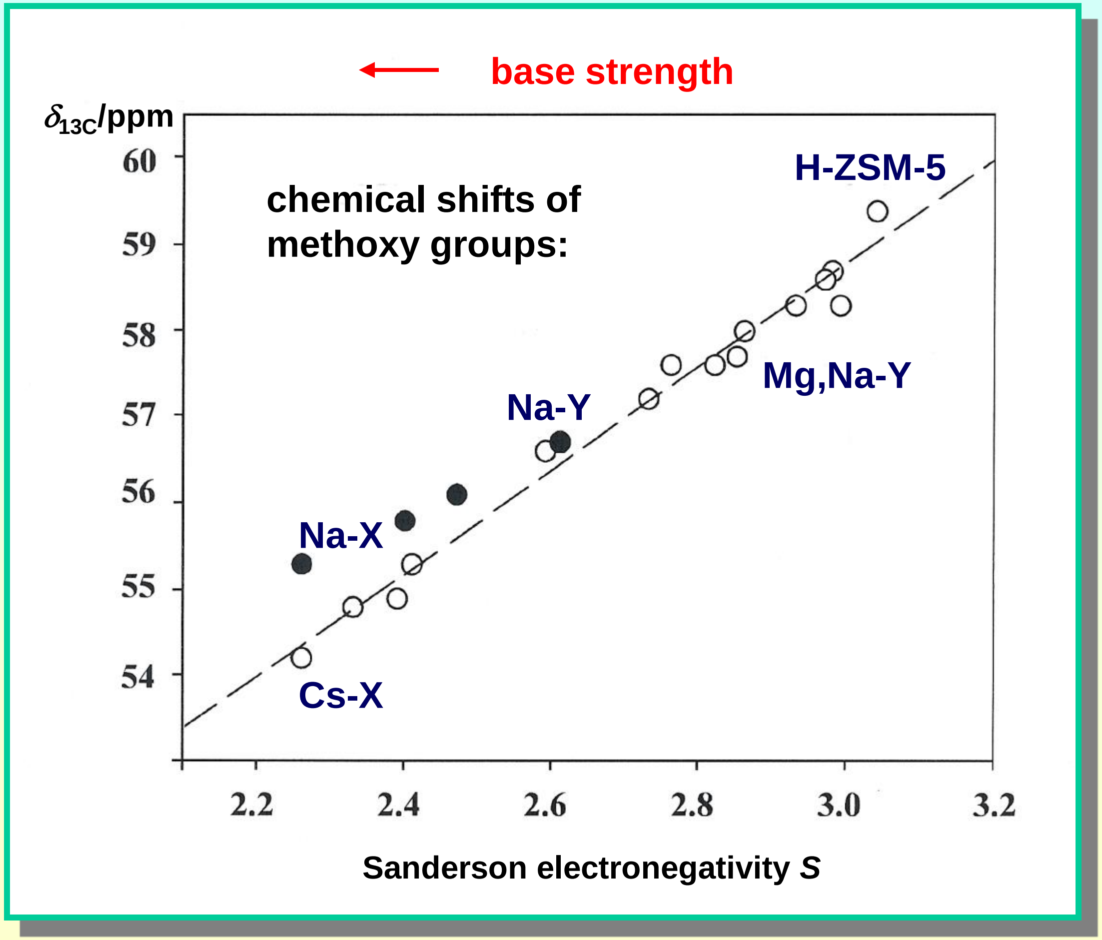
U. Schenk, PhD thesis, University of Stuttgart, 2001.

Characterization of basic zeolites under reaction conditions

- **mean Sanderson electronegativity:**

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

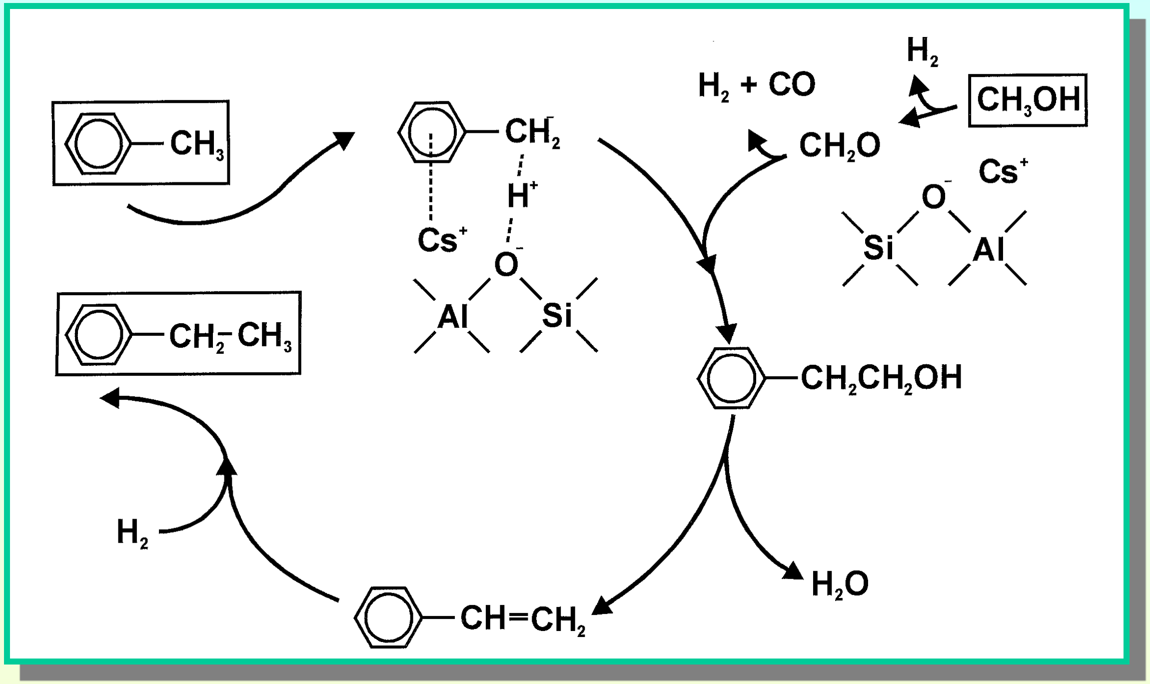
→ **decreasing ^{13}C NMR shift of surface methoxy groups with increasing base strength of the framework oxygen atoms**



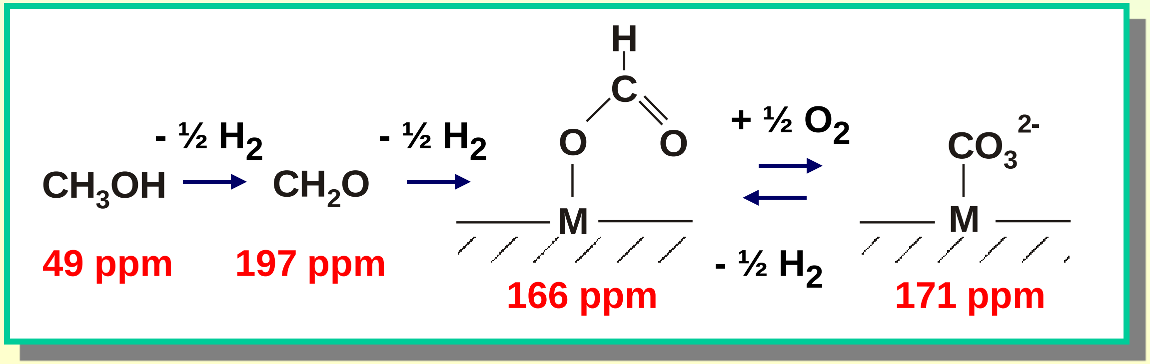
V. Bosacek et al., Z. Phys. Chem. 189 (1995) 241.

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

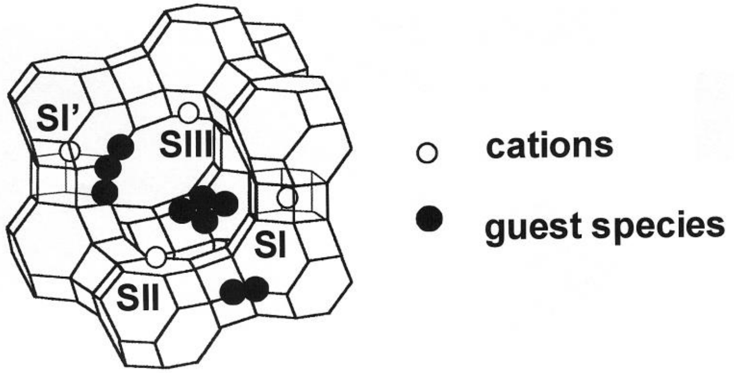


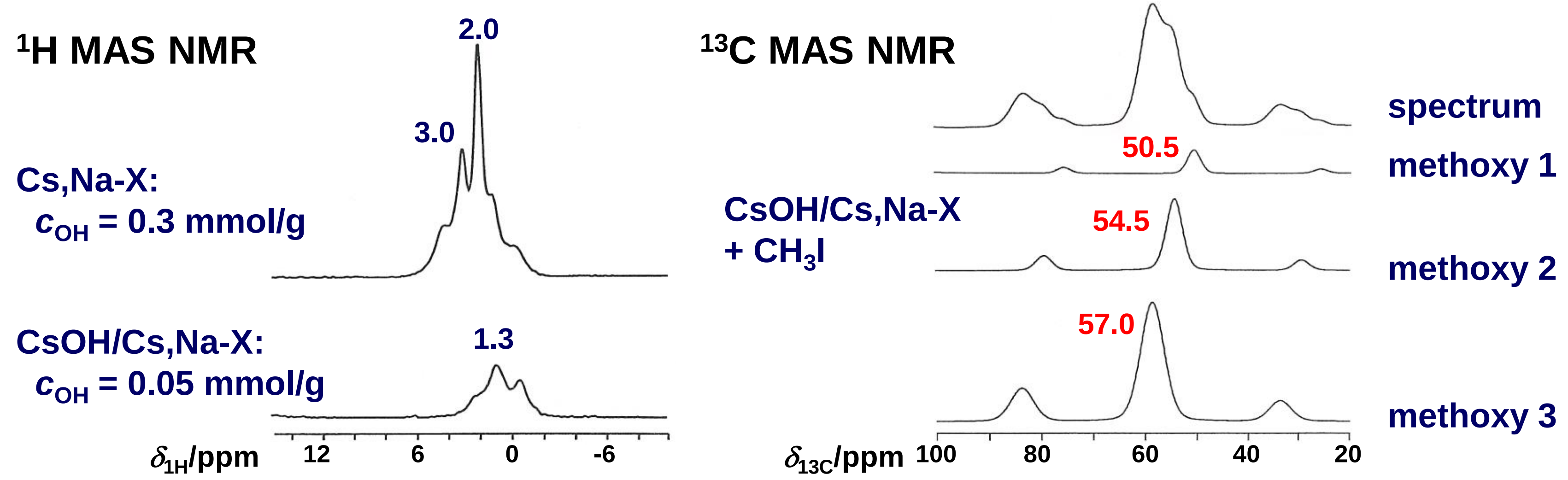
- proposed surface species:
  - formate (δ_{13C} = 166 ppm)
  - carbonate (δ_{13C} = 171 ppm)



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.)**

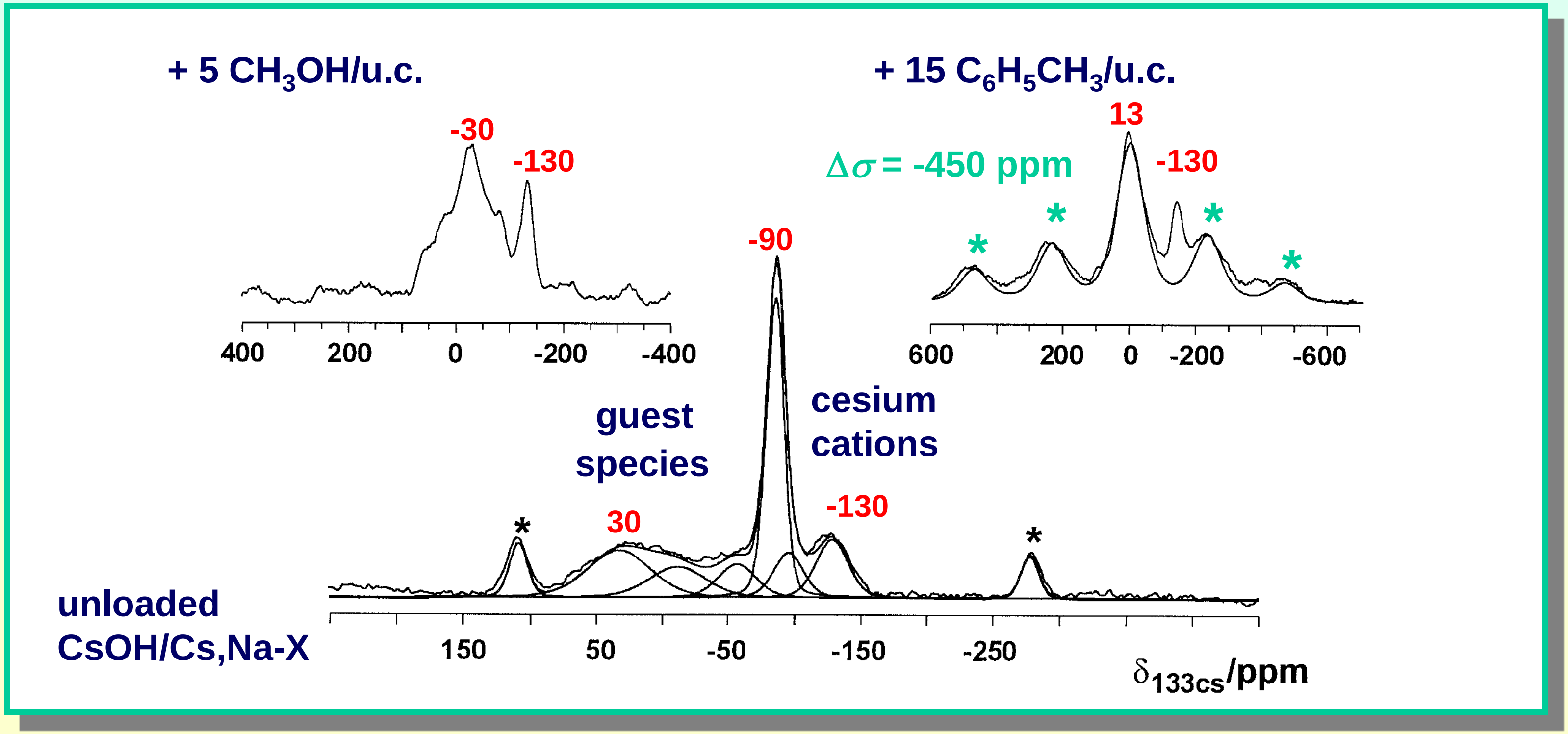




U. Schenk, PhD thesis, University of Stuttgart, 2001.

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**

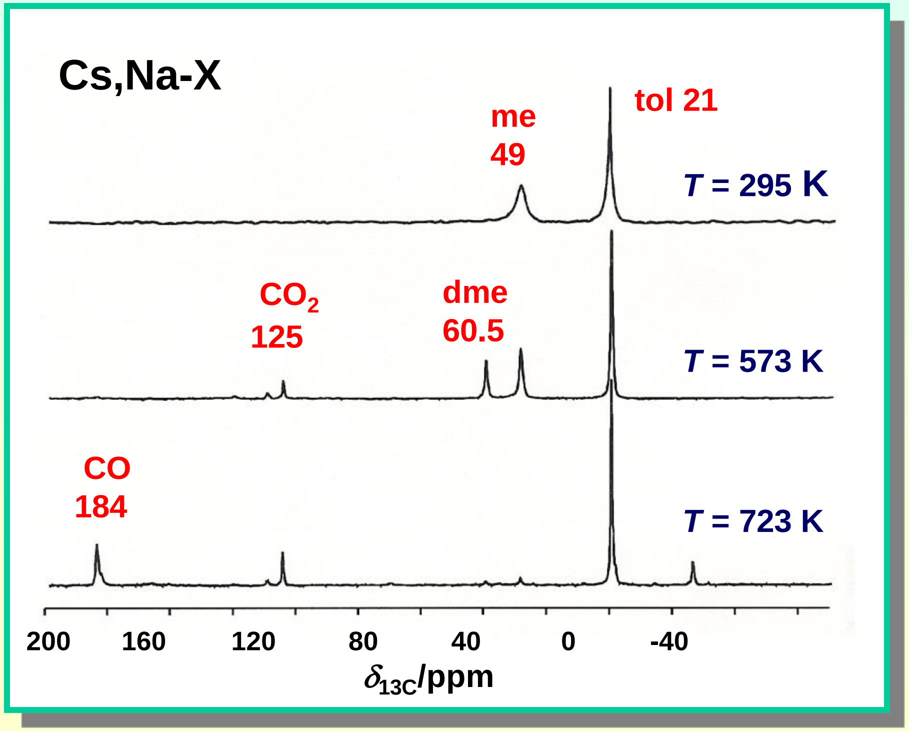


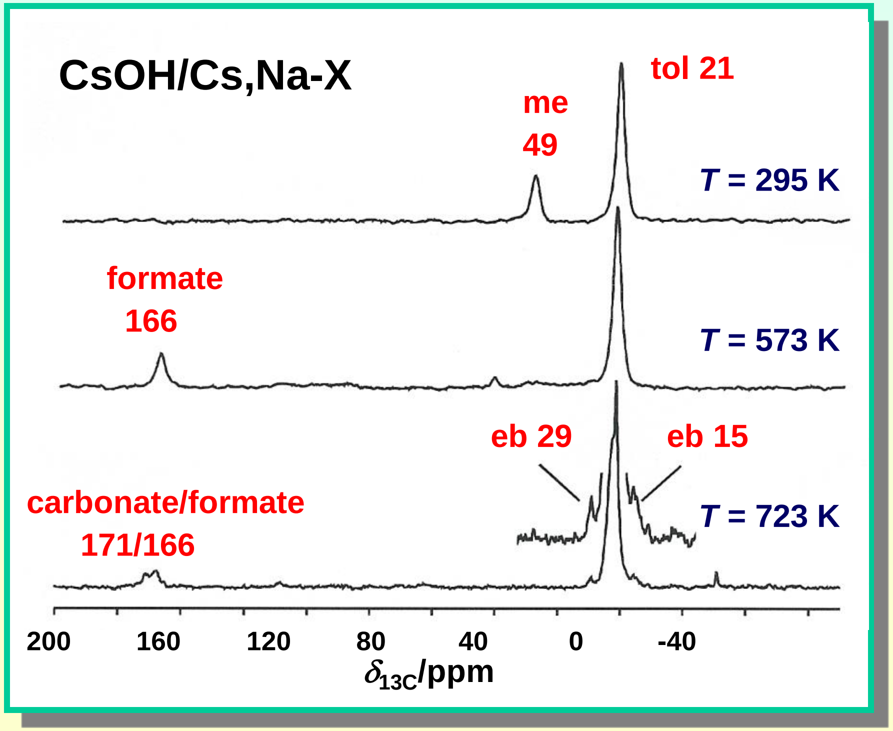
M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

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.

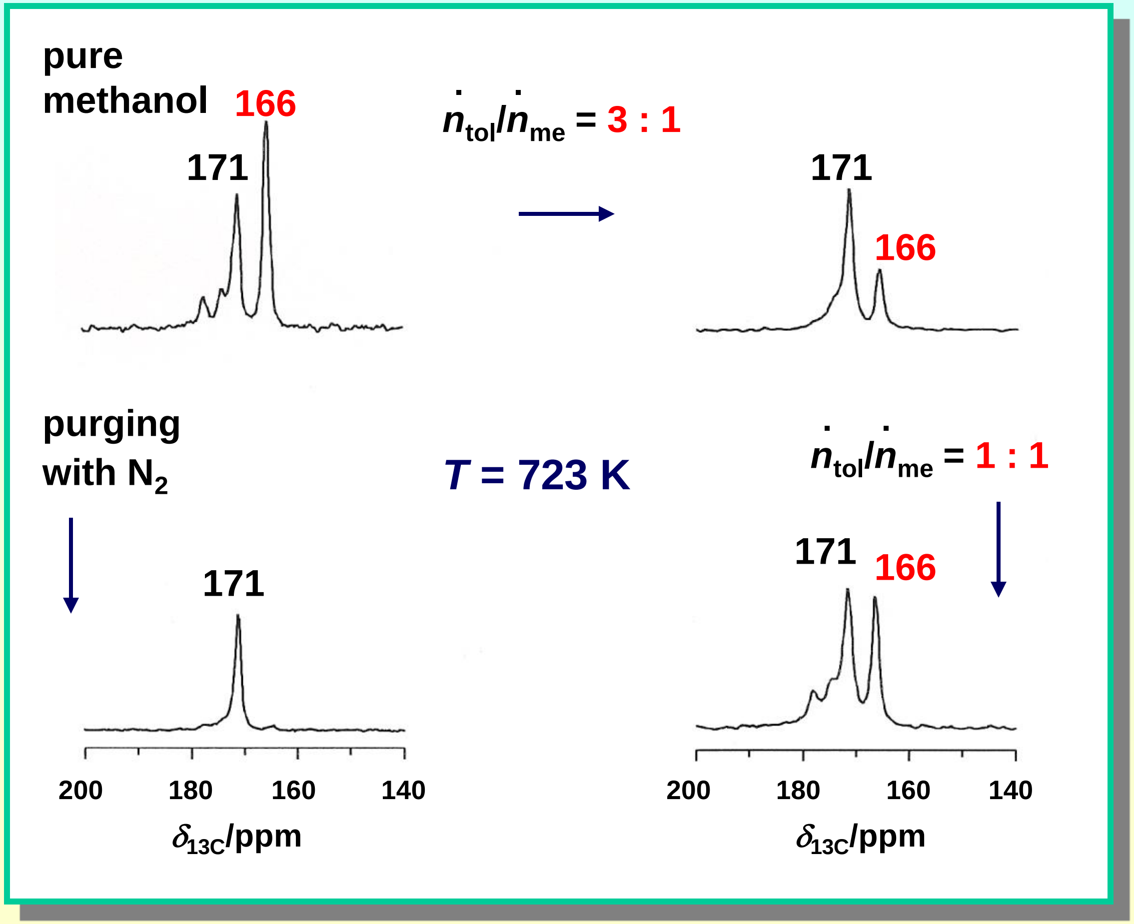
Reactivity of formate species on zeolite CsOH/Cs,Na-X under flow conditions

- ***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**

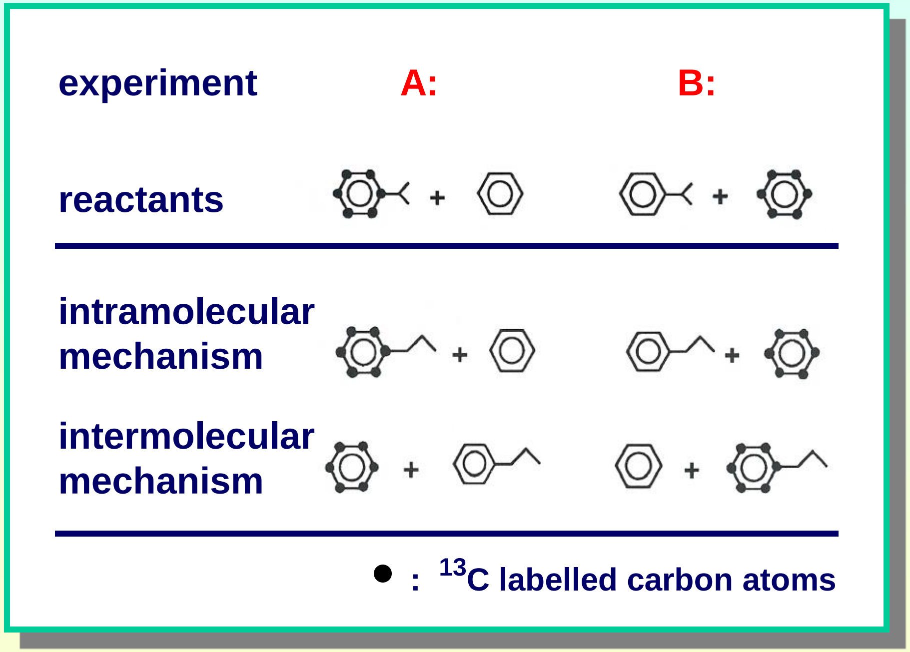


M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

Investigation of reactions catalyzed by acidic zeolites

Investigation of reaction pathways by selectively labelled reactants

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



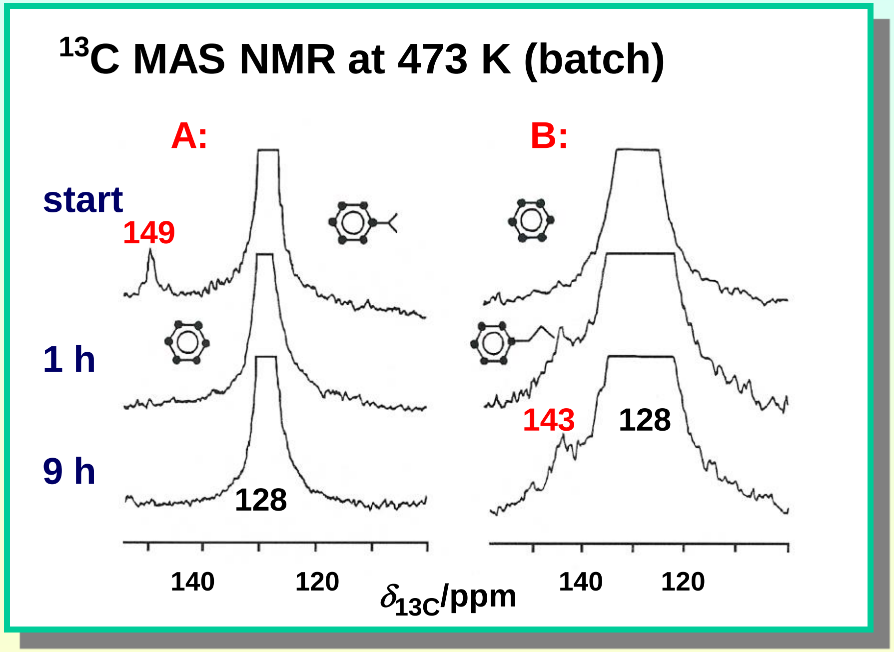
experiment A: B:

reactants

intramolecular mechanism

intermolecular mechanism

● : ^{13}C labelled carbon atoms



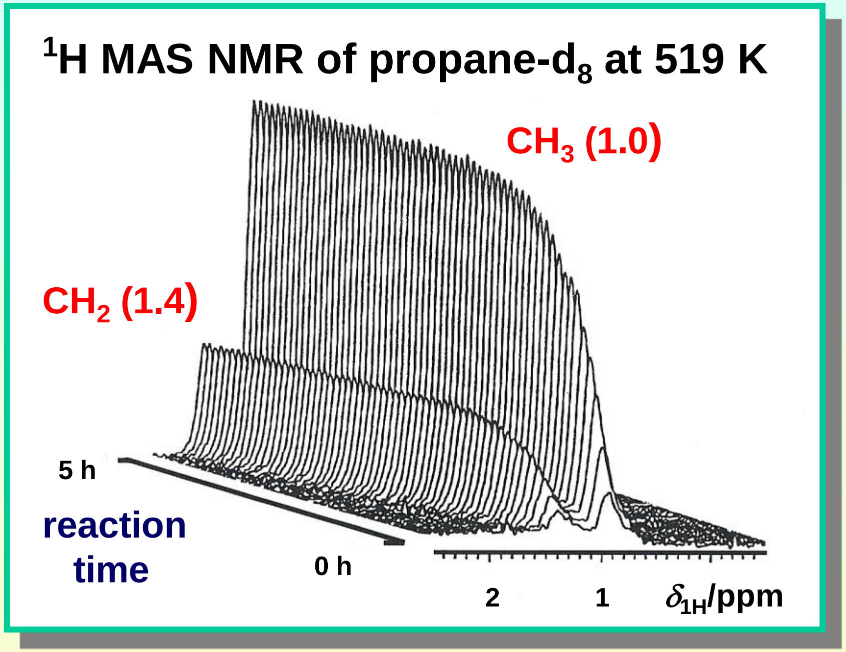
^{13}C MAS NMR at 473 K (batch)

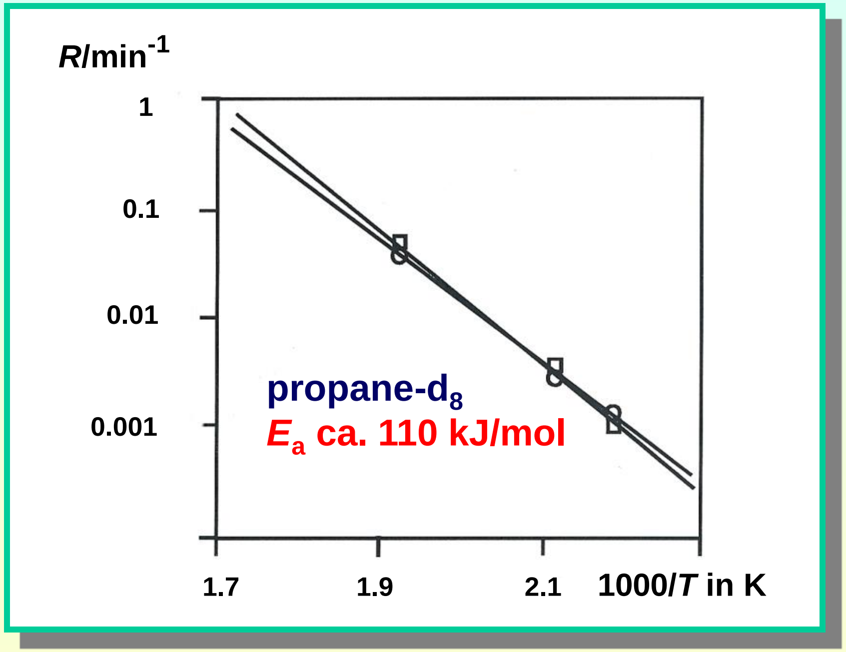
→ experiments A and B indicate an intermolecular reaction mechanism

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**





A:

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

→ no formation carbenium ions

B:

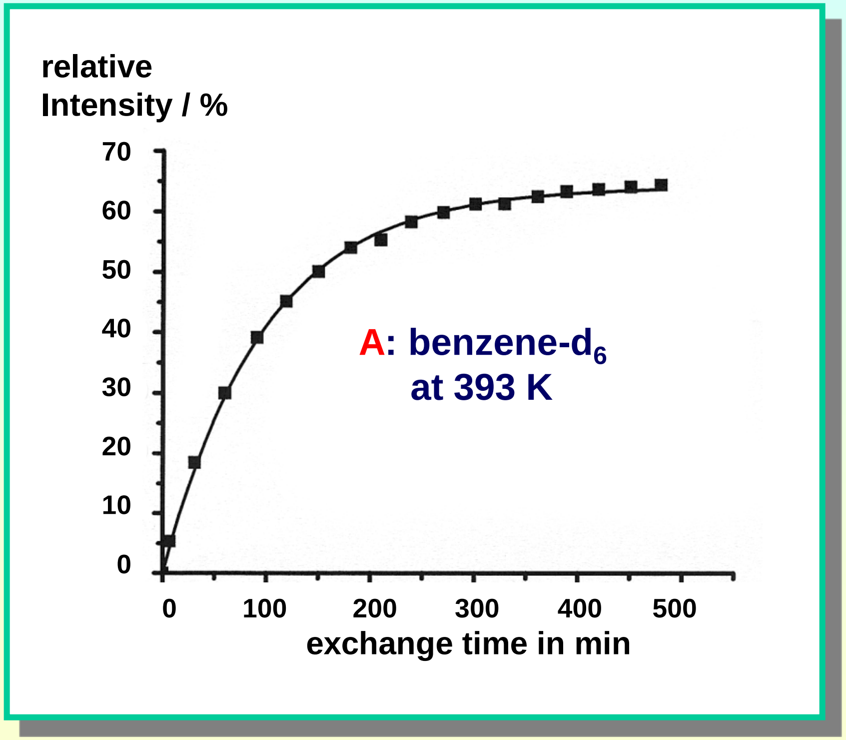
- **regiospecific H/D exchange**
- **E_a of ca. 50 kJ/mol**

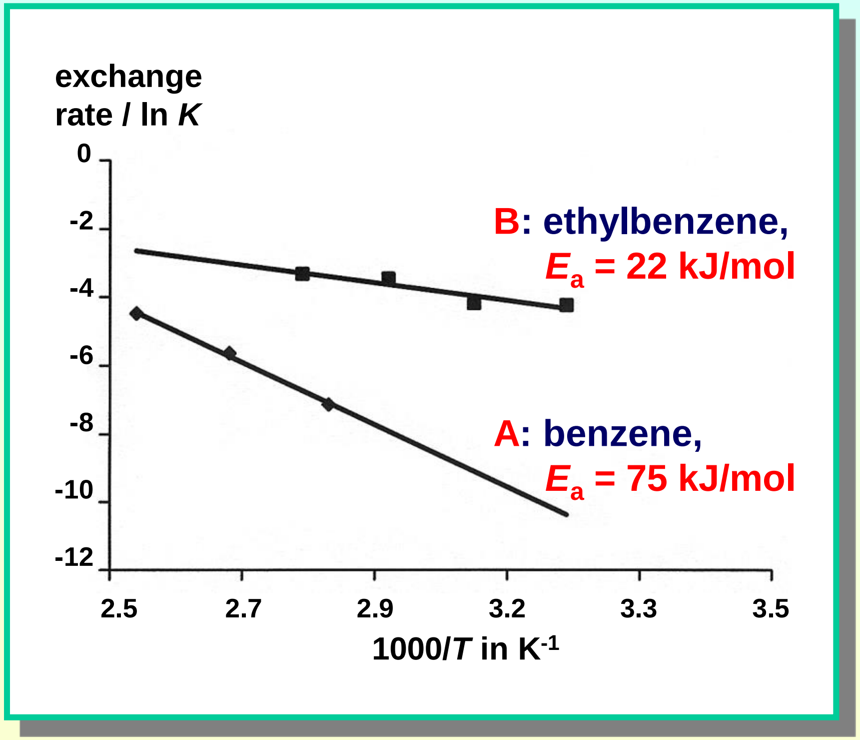
→ formation carbenium ions

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

H/D exchange of aromatic compounds on acidic zeolites

- **H/D exchange of benzene-d_6 (A) and ethylbenzene-d_{10} (B) with SiOHAl groups on H-Y**



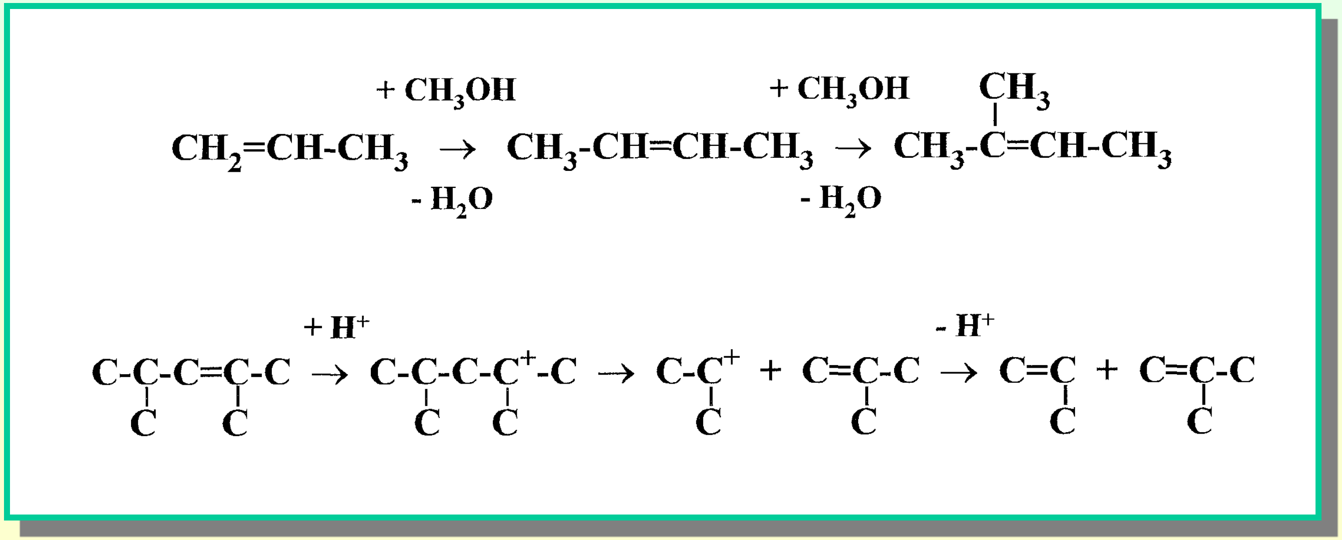


→ **H/D exchange occurs selectively with H atoms at the aromatic ring and the activation energy decreases strongly for alkylated aromatics**

Methanol to olefin (MTO) conversion on acidic zeolites

reaction mechanisms proposed in the literature:

- **carbene mechanism (Swabb and Gates)**
- **oxonium ylide mechanism (Berg and Olah)**
- **carbon-pool mechanism (Haag, Hoelderich)**

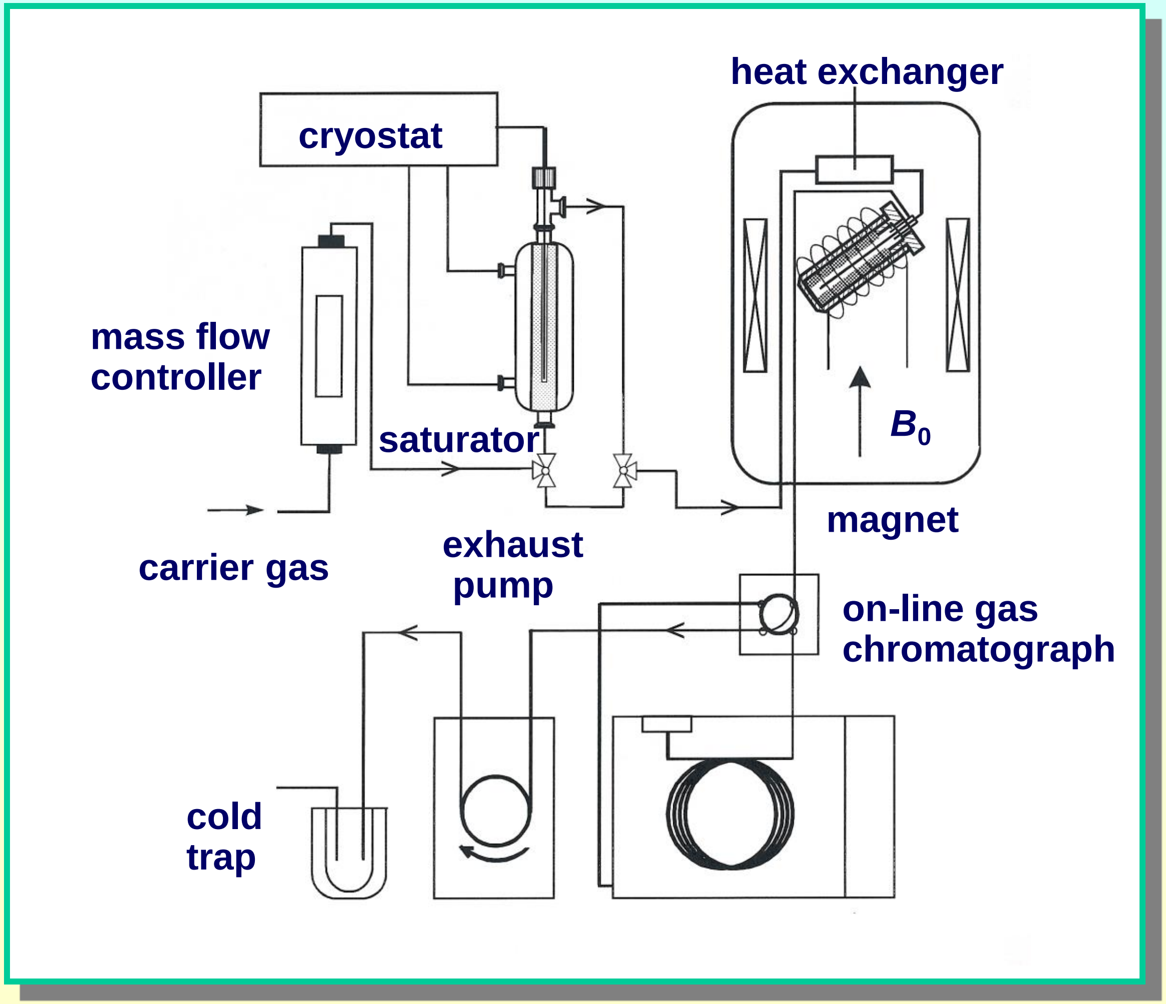


$$CH_2{=}CH{-}CH_3 \xrightarrow[-H_2O]{+CH_3OH} CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[-H_2O]{+CH_3OH} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3$$

$$C{-}\underset{\underset{C}{|}}{C}{-}C{=}\underset{\underset{C}{|}}{C}{-}C \xrightarrow{+H^+} C{-}\underset{\underset{C}{|}}{C}{-}C{-}\underset{\underset{C}{|}}{C^+}{-}C \rightarrow C{-}\underset{\underset{C}{|}}{C^+} + C{=}\underset{\underset{C}{|}}{C}{-}C \xrightarrow{-H^+} C{=}\underset{\underset{C}{|}}{C} + C{=}\underset{\underset{C}{|}}{C}{-}C$$

H. Schulz, M. Wei, Microporous Mesoporous Mater. 29 (1999) 205.

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

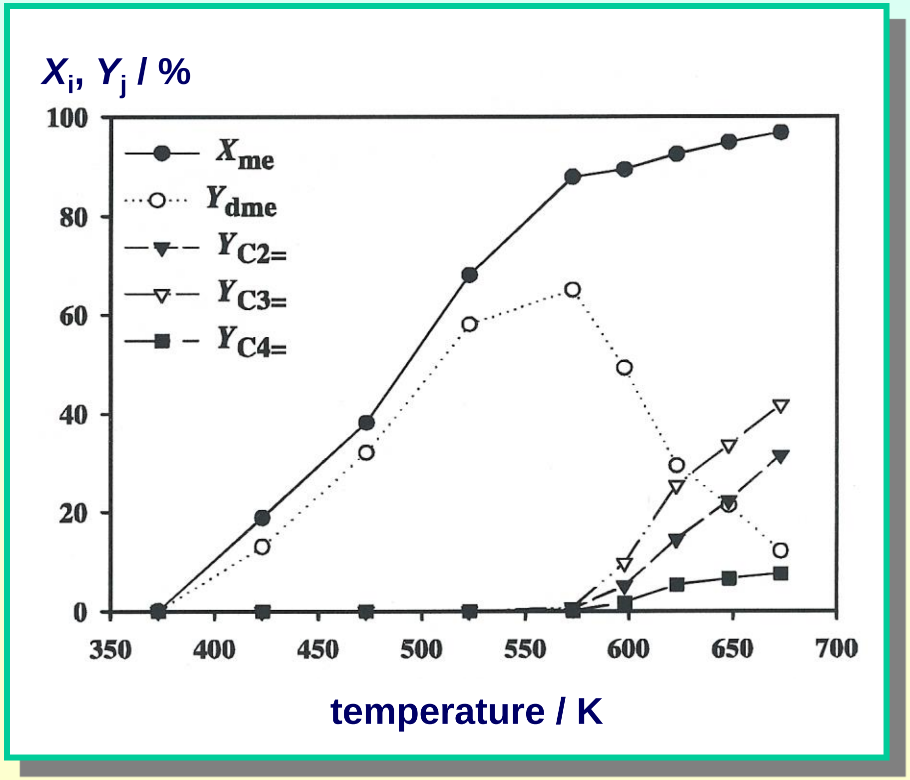


M. Hunger et al., Catal. Lett. 57 (1999) 199.

Conversion of methanol on H-ZSM-5 in a fixed-bed and in an MAS NMR rotor reactor

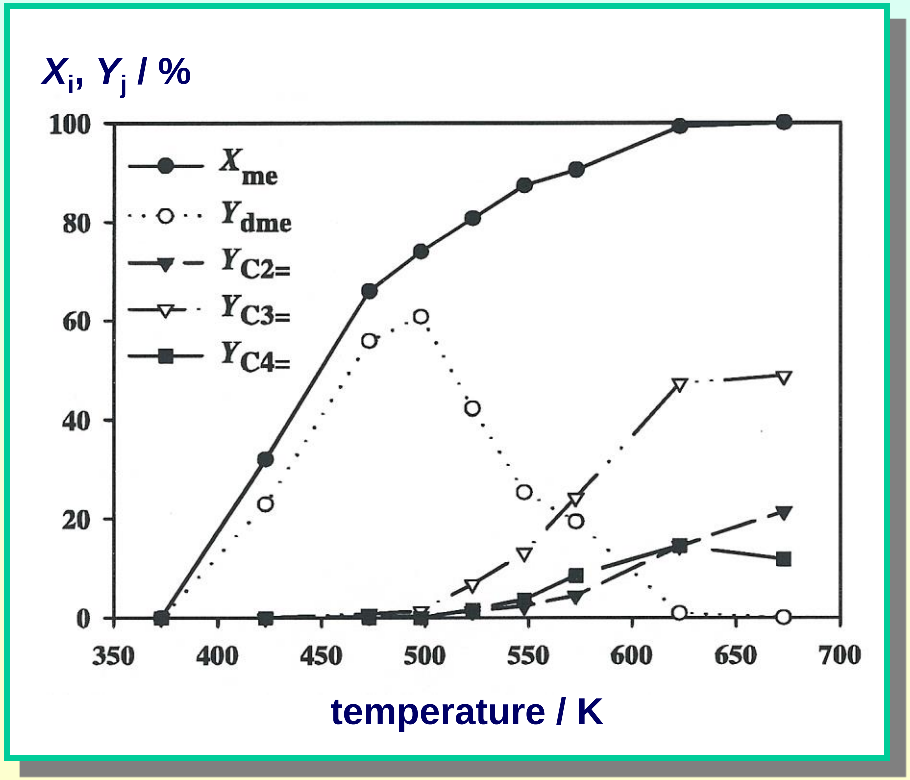
fixed-bed reactor

W_{cat}/F_{me} = 25 gh/mol



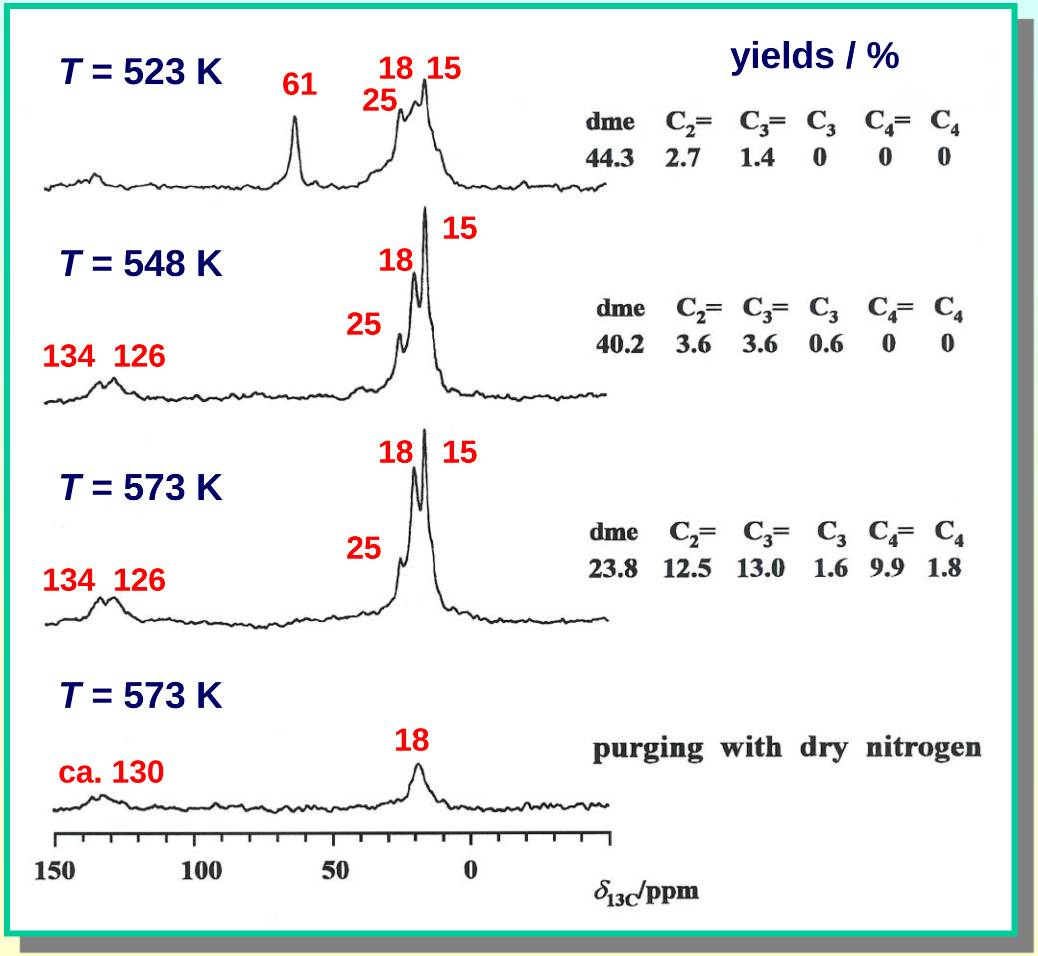
spinning (2 kHz) MAS NMR rotor reactor

W_{cat}/F_{me} = 25 gh/mol



A. Buchholz, diploma thesis, University Stuttgart, 2000.

Conversion of methanol on H-ZSM-5 studied by in situ ^{13}C CF MAS NMR



dme	C_2=	C_3=	C_3	C_4=	C_4
44.3	2.7	1.4	0	0	0

dme	C_2=	C_3=	C_3	C_4=	C_4
40.2	3.6	3.6	0.6	0	0

dme	C_2=	C_3=	C_3	C_4=	C_4
23.8	12.5	13.0	1.6	9.9	1.8

→ **aliphatic intermediates, e.g.:**

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

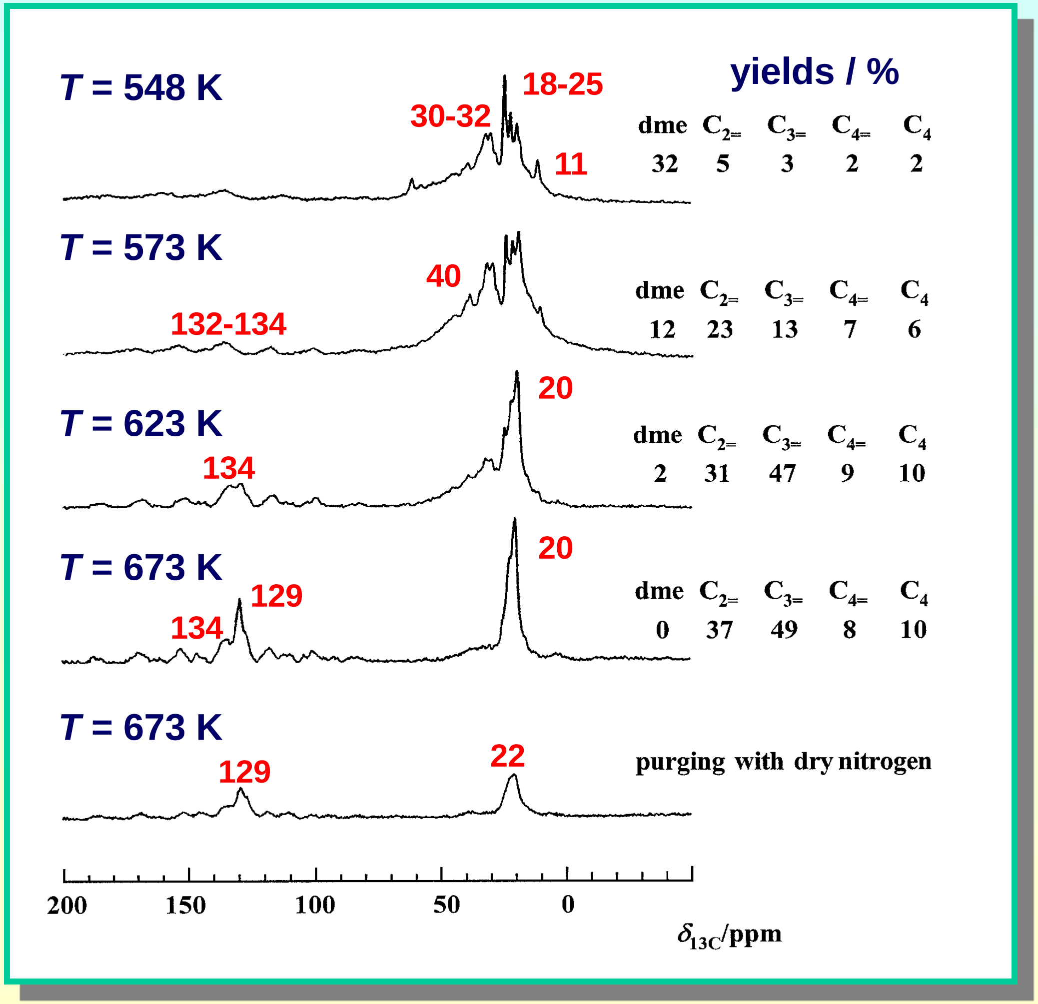
→ **olefin pool with carbon numbers of *n* > 6**

→ **aromatic adsorbates remaining after purging:**

benzene (128.6 ppm)
....
hexamethylbenzene (17.6, 132.1 ppm)

M. Seiler, et al., Catal. Lett. 62 (1999) 139.

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



yields / %

T = 548 K

dme	$C_{2=}$	$C_{3=}$	$C_{4=}$	C_4
32	5	3	2	2

T = 573 K

dme	$C_{2=}$	$C_{3=}$	$C_{4=}$	C_4
12	23	13	7	6

T = 623 K

dme	$C_{2=}$	$C_{3=}$	$C_{4=}$	C_4
2	31	47	9	10

T = 673 K

dme	$C_{2=}$	$C_{3=}$	$C_{4=}$	C_4
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:**

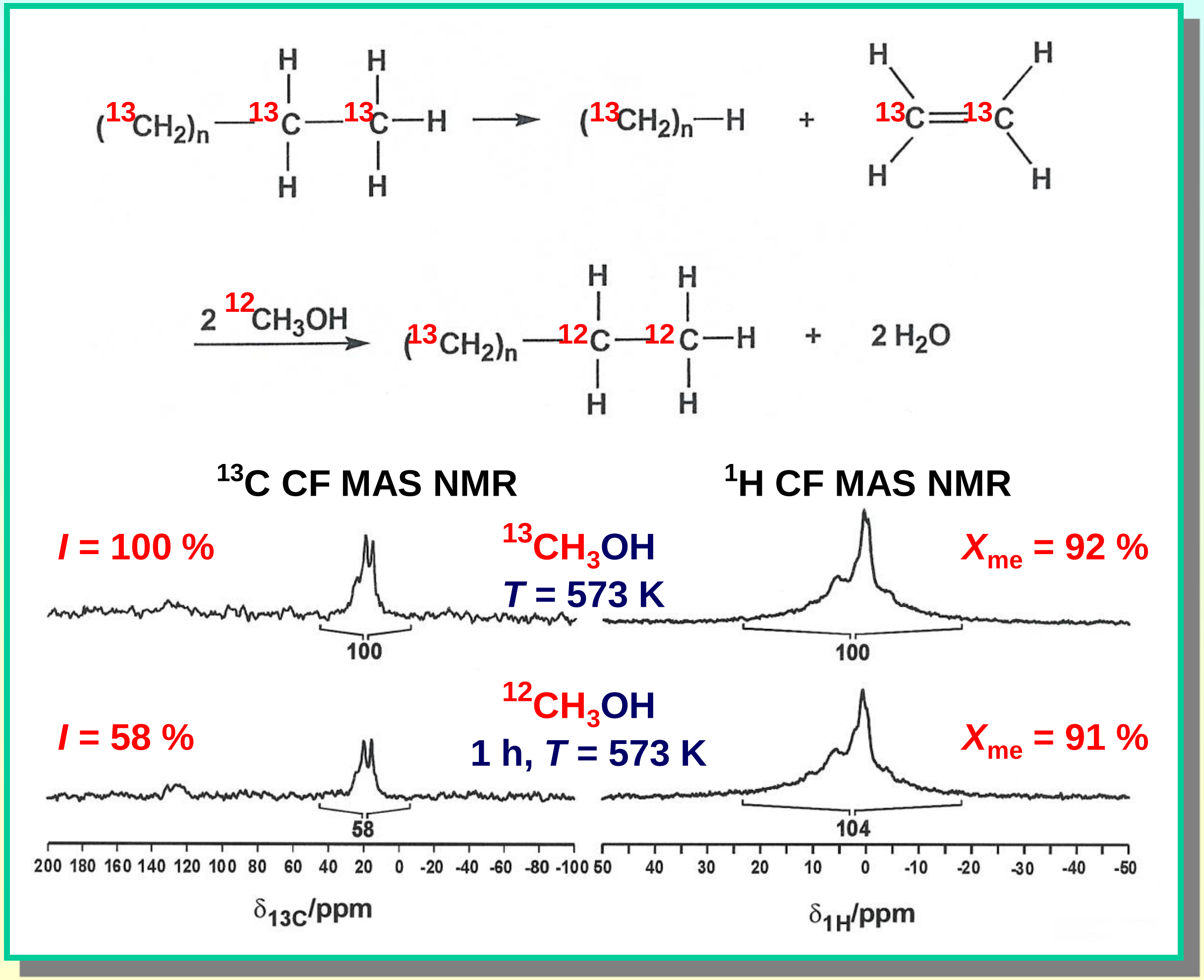
→ **domination of aromatic compounds:**

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:

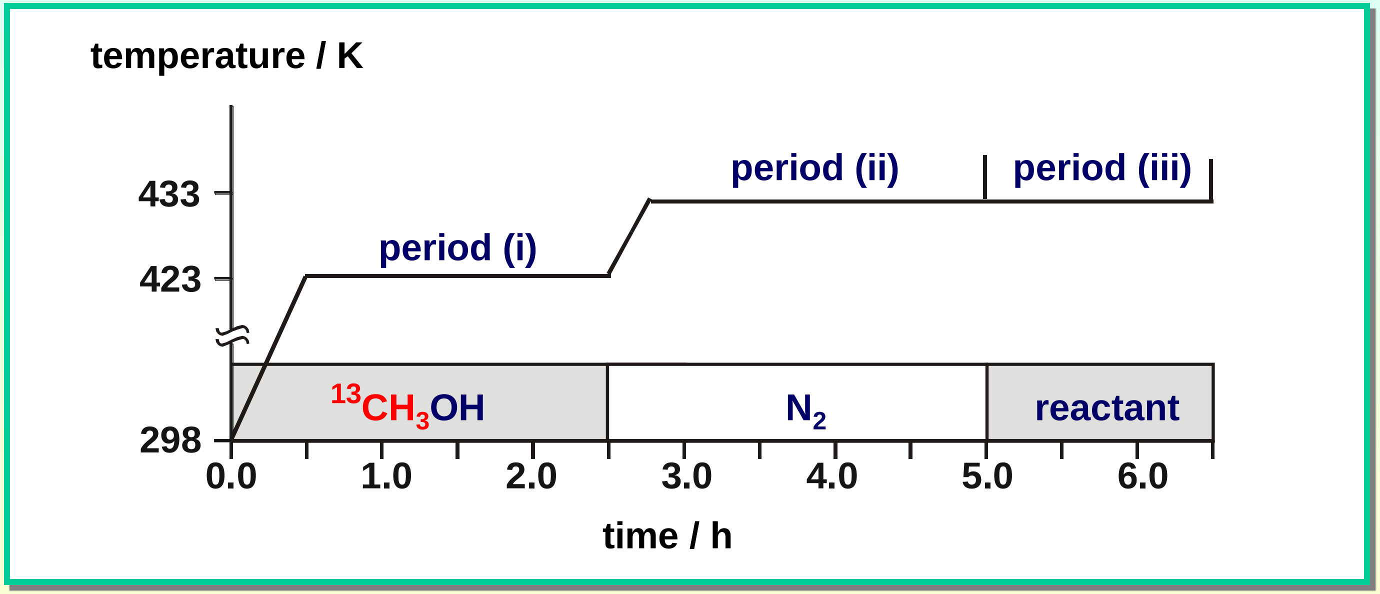
→ **alkyl groups are involved in the formation of olefins**

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

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

Study of surface methoxy groups 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)

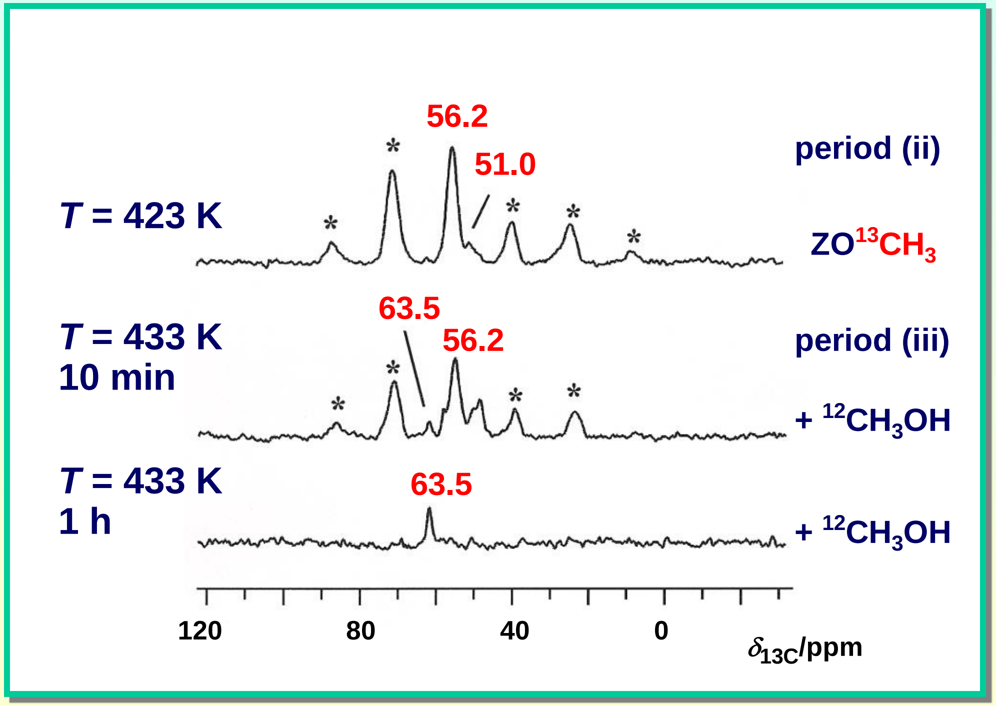


→ **investigation of the reactivity of intermediates**

W. Wang et al., J. Phys. Chem. B 105 (2001) 12553.

Reaction of methoxy groups with methanol on acidic zeolites

^{13}C SF MAS NMR investigation of methoxy groups on zeolite H-Y



methanol

$^{13}CH_3OH$ + ZOH

49.0 ppm

$\xrightarrow{-H_2O}$

methoxy

$ZO^{13}CH_3$

56.2 ppm

$\xrightarrow[-H_2O]{+\ ^{12}CH_3OH}$

dme

$^{12}CH_3OH^{13}CH_3$

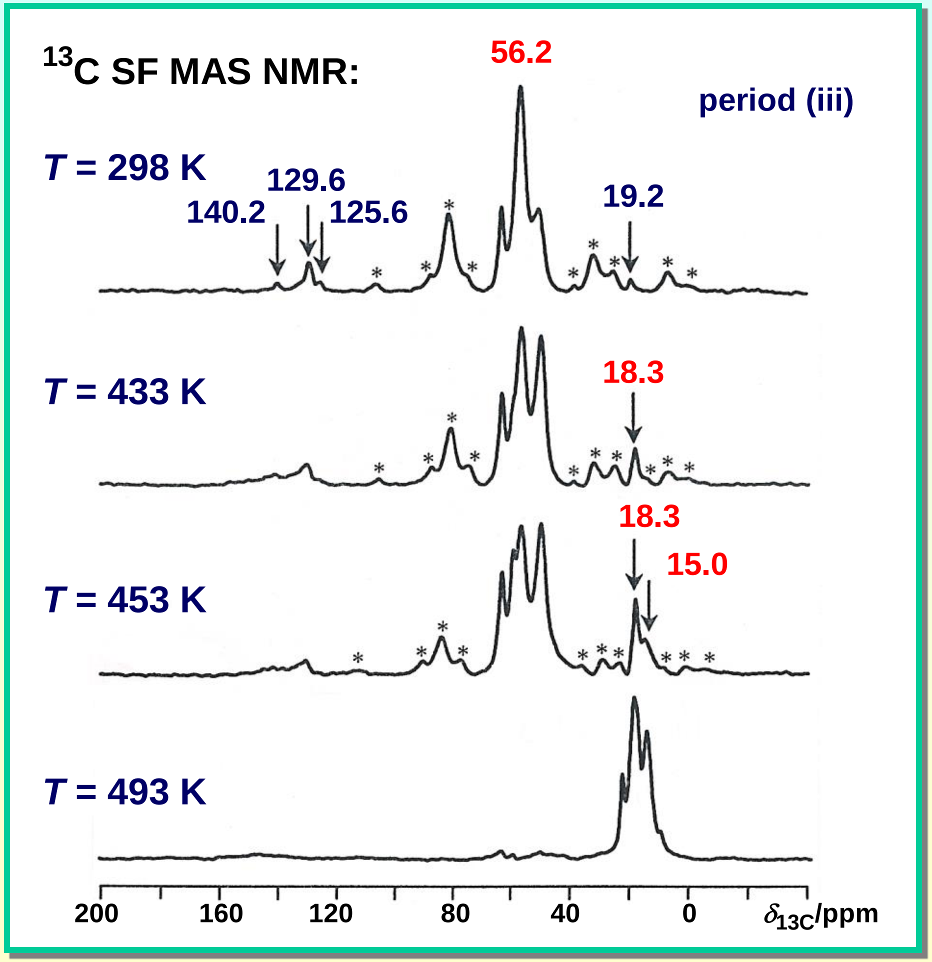
63.5 ppm

→ ^{13}C-labelled methoxy groups contribute to the formation of dimethyl ether

W. Wang et al., J. Phys. Chem. B 105 (2001) 12553.

Methylation of aromatics by surface methoxy groups

reaction of methoxy groups with toluene on zeolite H-Y



methoxy		toluene
$SiO(^{13}CH_3)Al$	+	$CH_3C_6H_5$
56.2 ppm		19.2 ppm

→ $SiOHAl + CH_3C_6H_4{}^{13}CH_3$

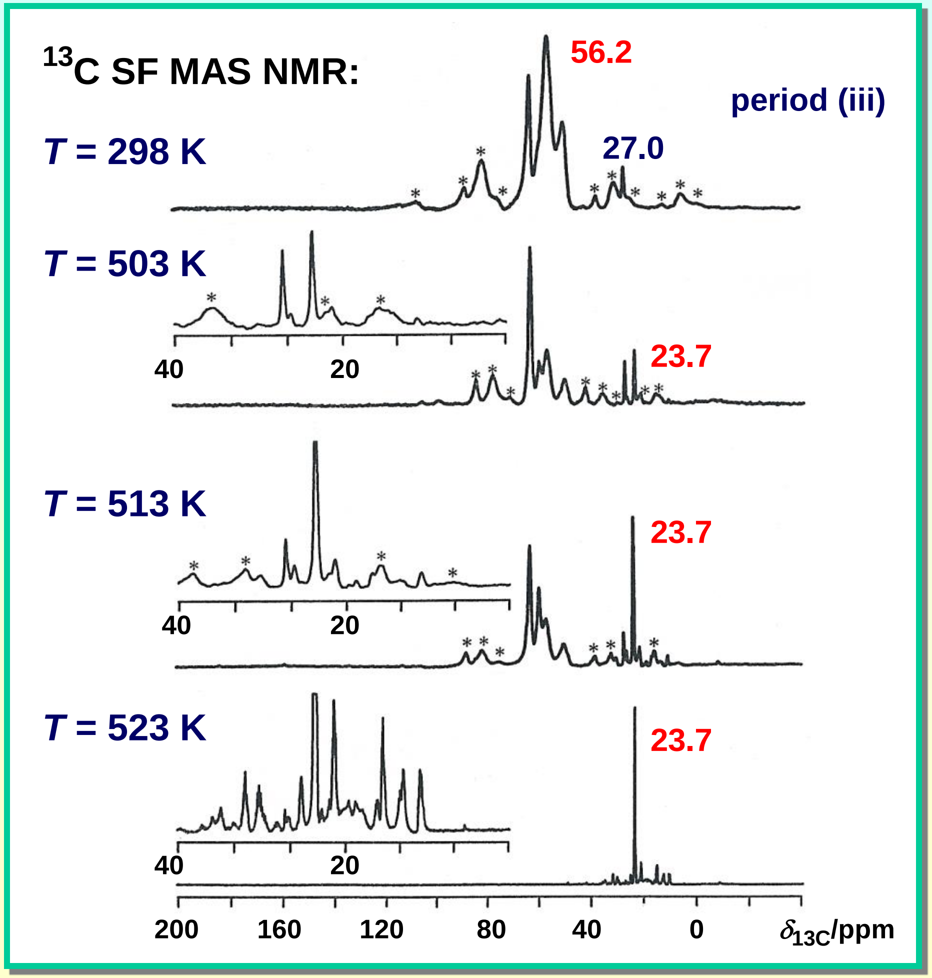
18.3 ppm

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

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

Methylation of alkanes by surface methoxy groups

reaction of methoxy groups with cyclohexane on zeolite H-Y



methoxy cyclohexane

$SiO({}^{13}CH_3)Al + C_6H_{12}$

56.2 ppm 27.0 ppm

→ $SiOHAl + {}^{13}CH_3C_6H_{11}$

23.7 ppm

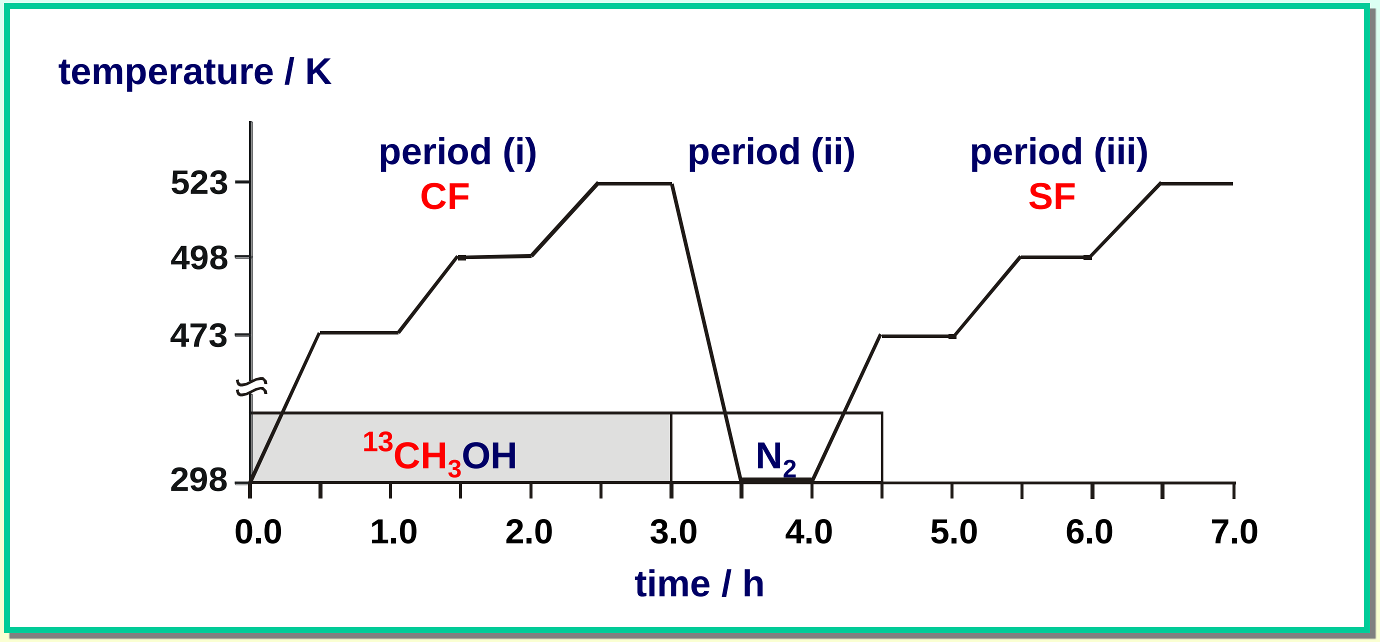
methylcyclohexane

- methylation of alkanes by surface methoxy groups starts at *T* = 503 K
- intermediates of ylide or carbene nature

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

Initiation of the MTO process by surface methoxy groups on acidic zeolites

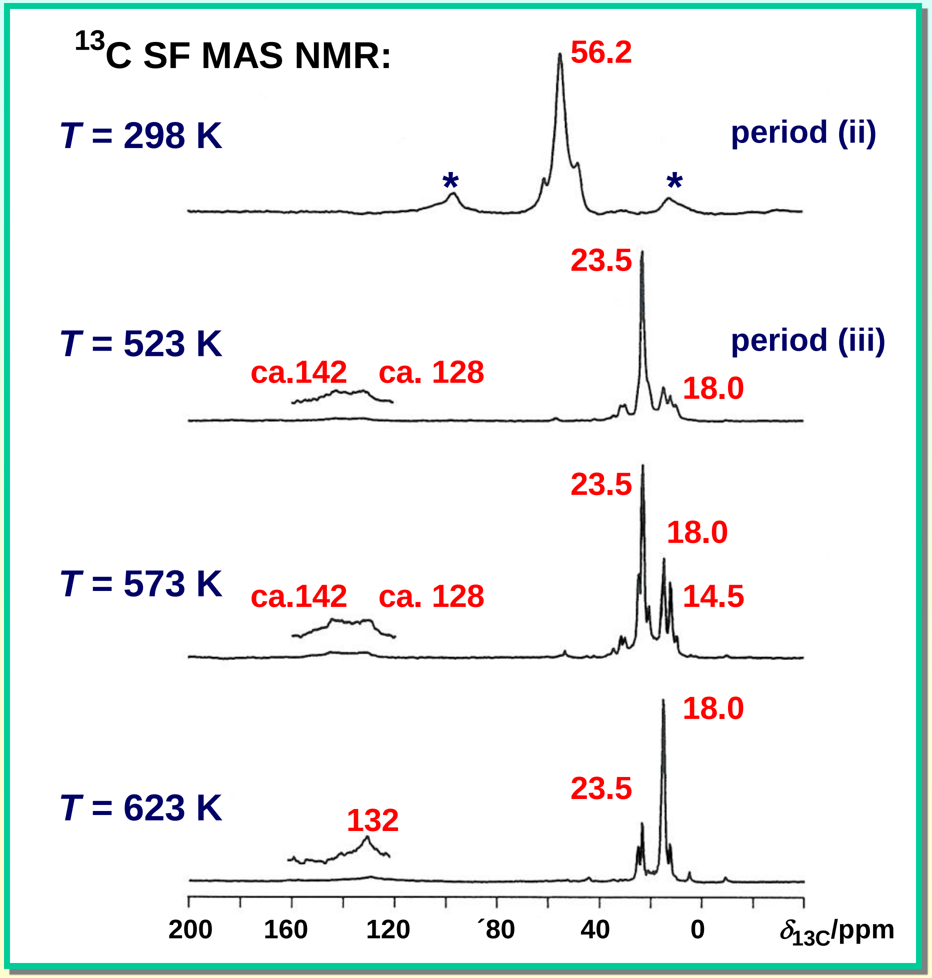
- **reaction of pure methoxy groups on zeolite H-Y at elevated temperatures**



W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc., in press.

Initiation of the MTO process by surface methoxy groups on acidic zeolites

- stopped-flow conversion of methoxy groups on zeolite H-Y



- initiation of the hydrocarbon formation at *T* = 523 K

- formation of aliphatics:

→ isobutane (23.3, 24.6 ppm)
isobutene (23.7, 119.5, 141.4 ppm)
dimethylbutadiene (20.1, 111.3, 142.1 ppm)
....

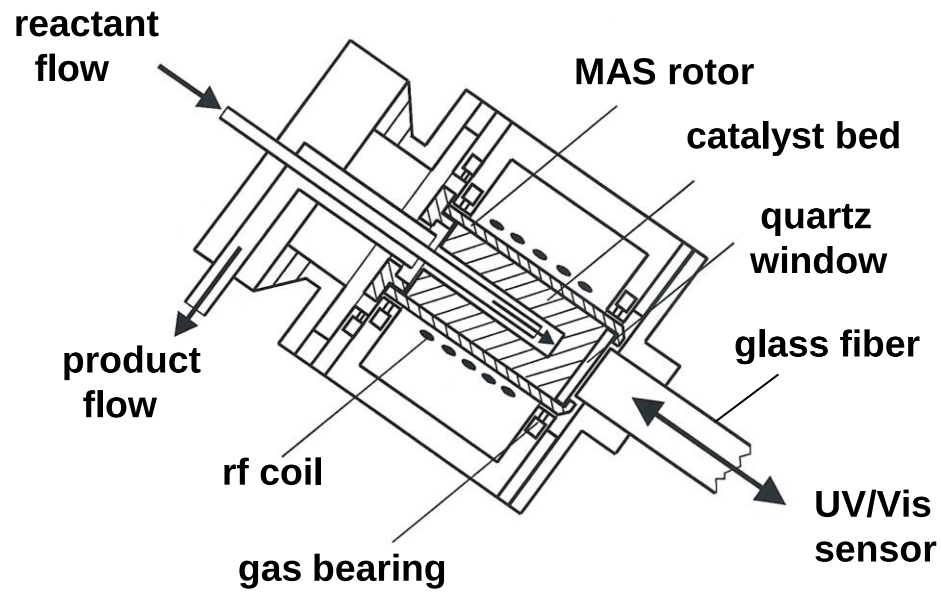
and aromatic compounds:

→ benzene (128.6 ppm)
....
hexamethylbenzene (17.6, 132.1 ppm)

W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc., in press.

MAS NMR-UV/Vis coupling

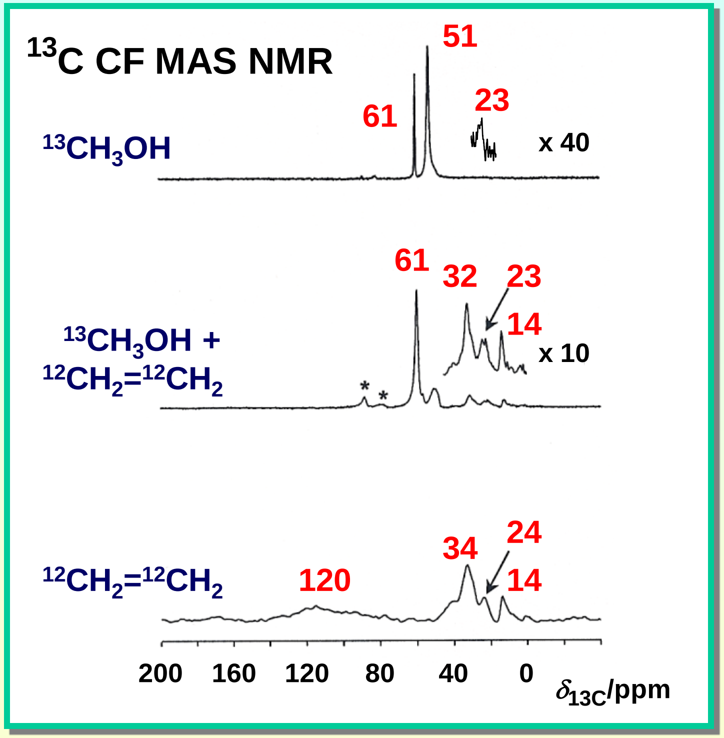
installation of a quartz fiber optic at the bottom of the CF MAS NMR stator

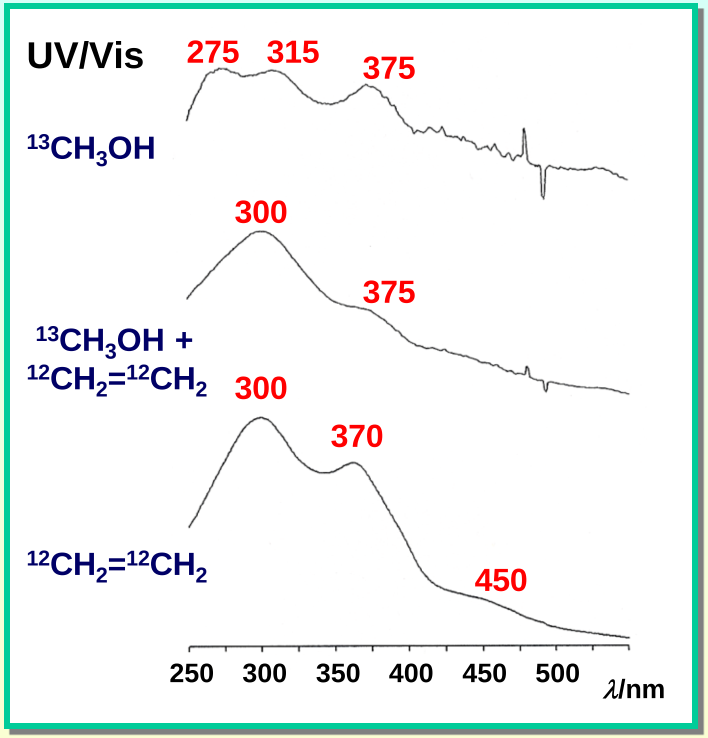


M. Hunger, W. Wang, Chem. Commun. (2004) 584.

MAS NMR-UV/Vis coupling

conversion of $^{13}CH_3OH$ on dealuminated H-ZSM-5 at 423 K





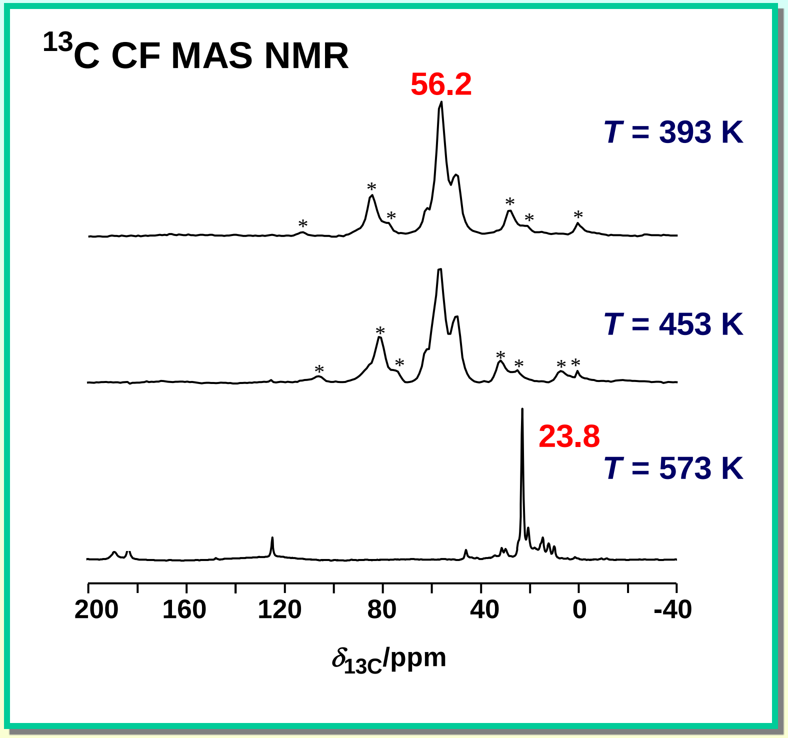
→ **275 nm: neutral aromatics**
315 nm: monoenyl carbenium ions

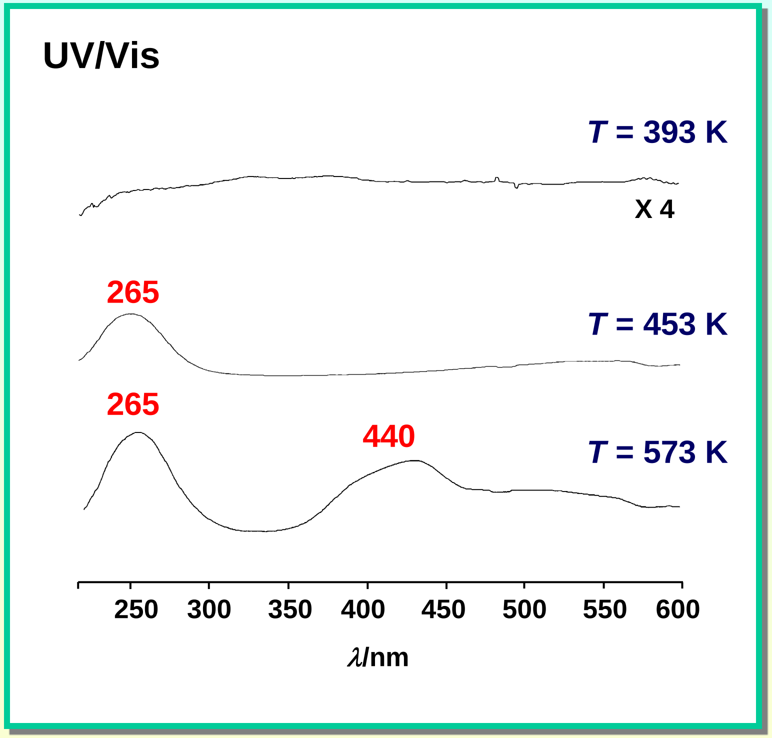
375 nm: dienyl carbenium ions
450 nm: polyaromatics

M. Hunger, W. Wang, Chem. Commun. (2004) 584.

MAS NMR-UV/Vis coupling

conversion of surface methoxy groups on zeolite H-Y





→ **23.8 ppm: isobutane**
ca. 130 ppm: aromatics

265 nm: neutral aromatics
440 nm: polyaromatics,
trienylcarbenium ions

Summary I

applications of *in situ* NMR spectroscopy in zeolite catalysis:

- **chemical behavior and local structure of active sites under reaction conditions**
- **origin of the catalyst deactivation under steady state conditions**
- **reaction pathways using labelled reactants**
- **activation energies of reaction steps**
- **reactivity of surface complexes and intermediates formed under reaction conditions**

Summary II

further developements in the field of *in situ* NMR spectroscopy:

- increase of the temperature range up to 1023 K
- application of modern solid-state NMR techniques such as MQMAS for the study of surface sites under reaction conditions
- significant enhancement of signal intensities by a continuous injection of Laser-polarized ^{129}Xe into CF MAS NMR probes
- improvement of the time-resolution of *in situ* NMR investigations by an introduction of pulsed-flow experiments
- combination of NMR spectroscopy with other spectroscopic techniques such as MS

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Max-Buchner-Forschungsstiftung

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