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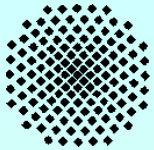
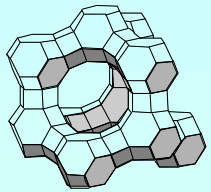




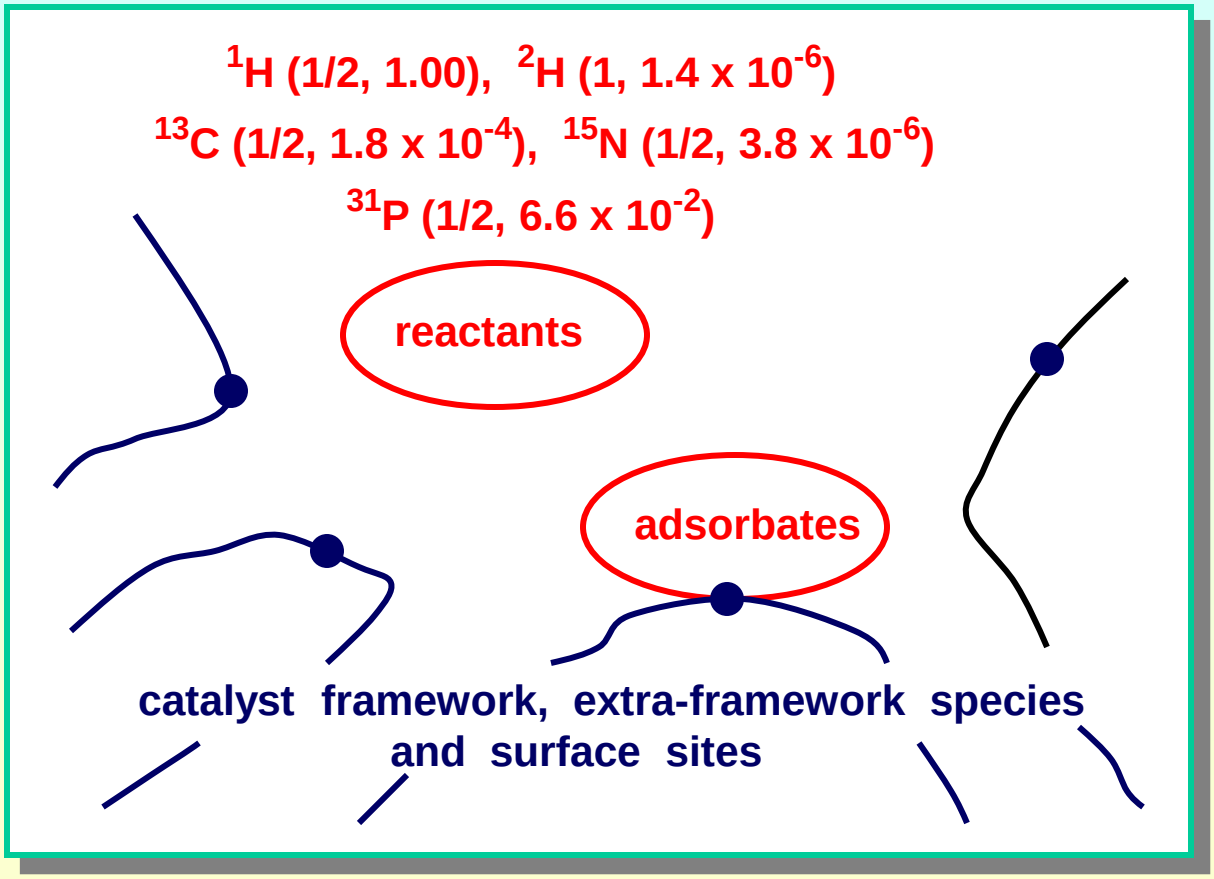
Ex Situ and In Situ Solid-State NMR Investigations of Activated Zeolite Catalysts and Heterogeneous Reaction Systems

37th Polish Conference on Catalysis
Krakow, March 15-18, 2005

Michael Hunger

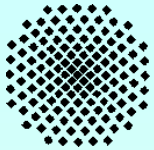
Institute of Chemical Technology
University of Stuttgart, Germany

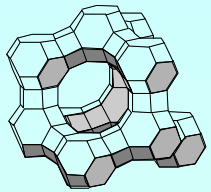
Examples of Nuclei Accessible for NMR Spectroscopy



^{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)

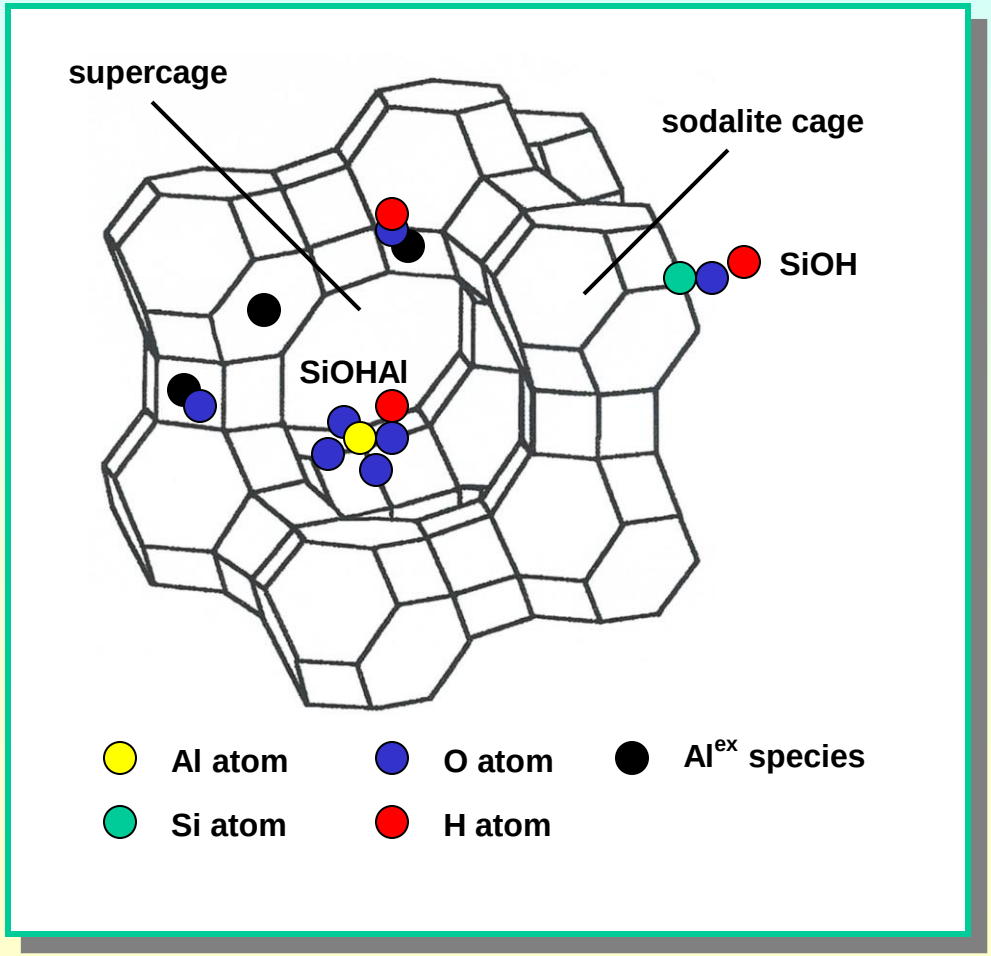




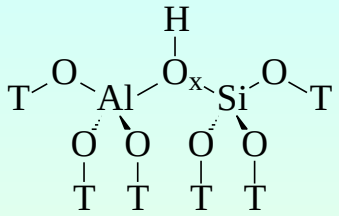
I. NMR Investigations of Non-Hydrated Zeolite Catalysts

Dealumination of Zeolites

- **dealuminated zeolite Y:**



- **Broensted-acid sites:**



bridging OH group (SiOHAl)

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

Aims of Recent Studies

NMR studies of non-hydrated zeolite catalysts:

- **possibilities and limitations of NMR spectroscopy for the study of non-hydrated solid catalysts**
- **quantitative determination of the hydroxyl coverage as a function of the steaming conditions**
- **number and coordination of framework aluminum atoms in steamed zeolite catalysts**
- **number and nature of extra-framework aluminum species in steamed zeolite catalysts**

Preparation of Samples

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

ammonium exchange →

NH_4-Y (exchange degree of 93 %)

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

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

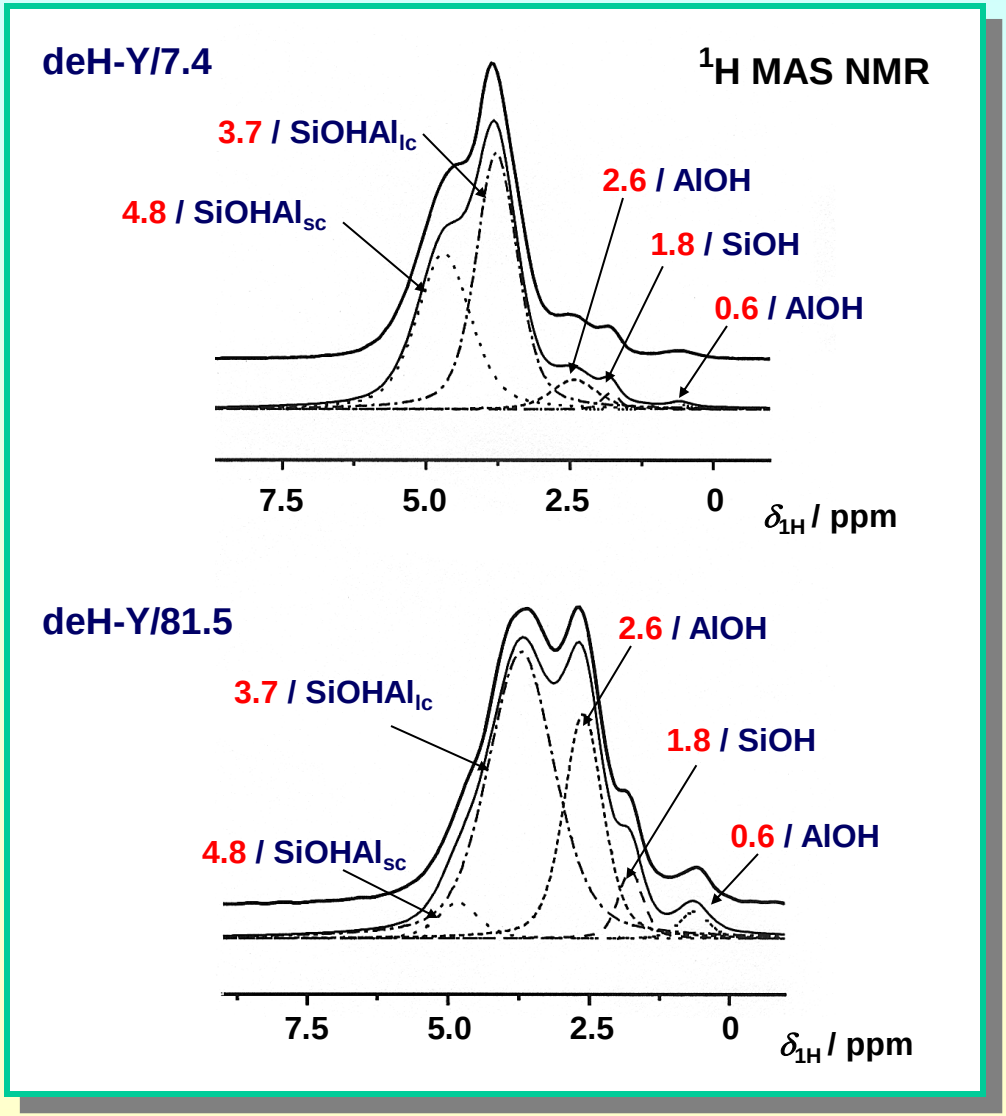
→ transfer into gas-tight glass tubes and MAS NMR rotors →

NMR characterization in the non-hydrated state

Experimental Techniques

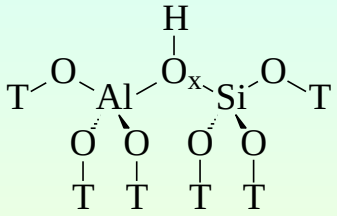
- **AES**: Perkin Elmer Plasma 400, total numbers of atoms
- **^{1}H MAS NMR**: MSL 400, quantitative determination of the hydroxyl coverage
- **^{29}Si MAS NMR:** MSL 400, determination of the framework aluminum species
- **^{1}H and ^{27}Al CF MAS NMR**: MSL 400, adsorption of probe molecules, determination of framework aluminum species
- **^{27}Al spin-echo NMR**: MSL 400, Avance 600WB, Avance 750WB, direct characterization of framework and extra-framework aluminum species

Investigation of the Hydroxyl Coverage



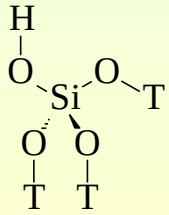
- **types of hydroxyl groups:**

  - SiOHAl$_{lc}$: bridging OH groups in large cages (supercages)



  - SiOHAl$_{sc}$: bridging OH groups in sodalite cages

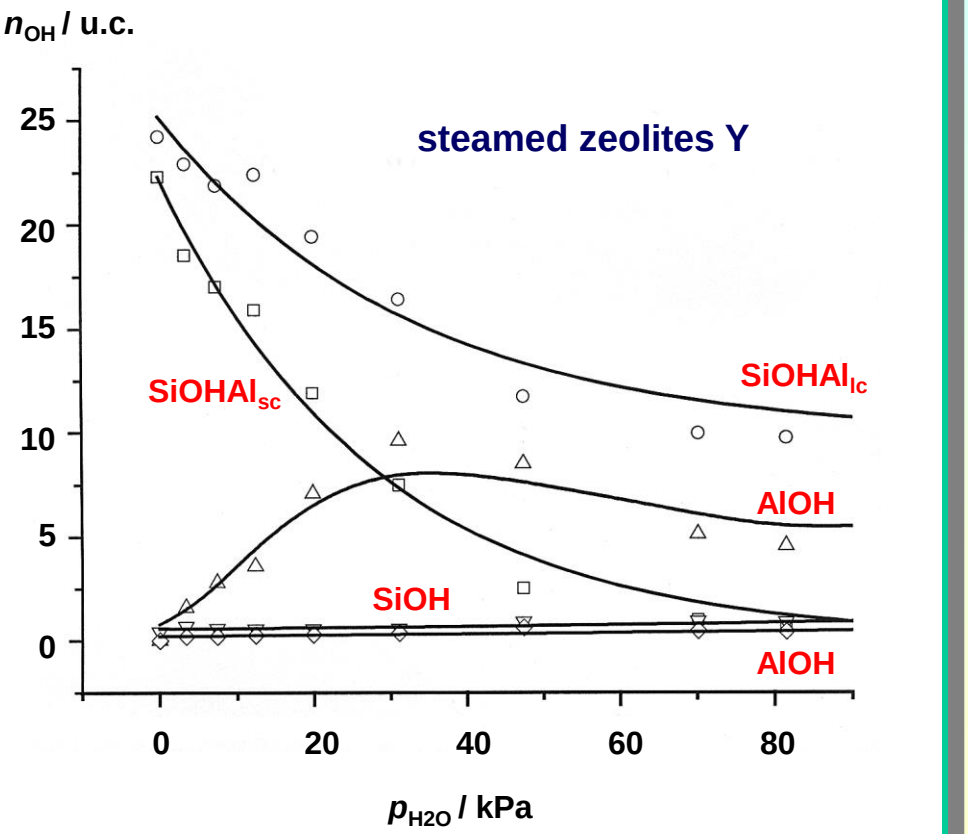
  - SiOH: defect OH groups



  - AlOH: $AlO_m(OH)_n^{x+}$ species

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

Hydroxyl Coverage as a Function of the Water Vapor Pressure

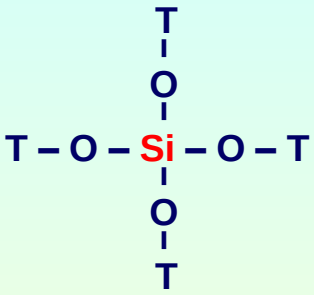


- **weak steaming:**
  strong increase of hydrogen-bound AlOH groups at 2.6 ppm
- **strong steaming:**
  stronger dehydroxylation of SiOHAl groups in sodalite cages than in supercages
- **whole range:**
  only weak formation of defect SiOH groups at 1.8 ppm and AlOH groups at 0.6 ppm

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

Determination of the Framework Aluminum Content by ^{29}Si MAS NMR spectroscopy

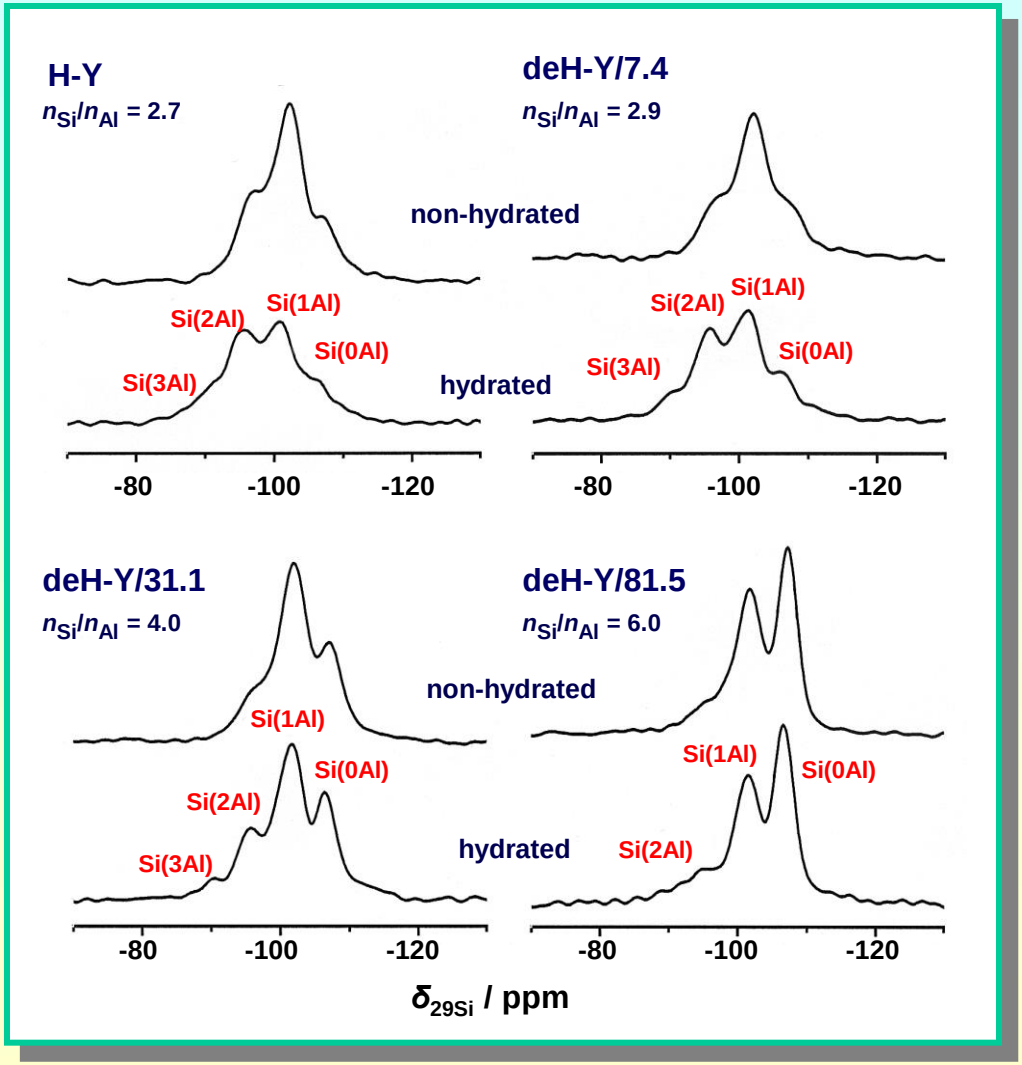
- **Q^4 silicon species:**



T: Si or Al

- **^{29}Si NMR signals of Q^4 species:**

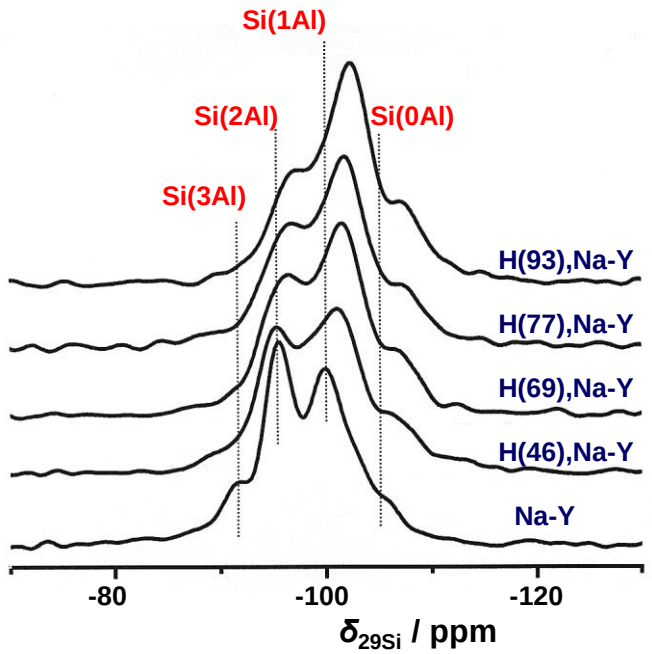
-90 ppm	Si(3Al)
-95 ppm	Si(2Al)
-101 ppm	Si(1Al)
-107 ppm	Si(0Al)



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

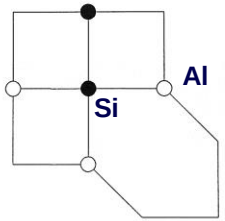
Strain of Si(nAl) Tetrahedra in Non-Hydrated Zeolites H,Na-Y

^{29}Si MAS NMR $n_{Si}/n_{Al} = 2.7$

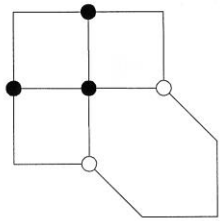


loop configuration of the FAU structure:

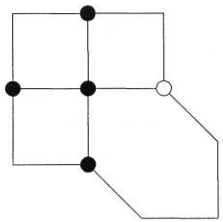
Si(3Al): $\Delta\delta_{29Si}$ = 5 ppm



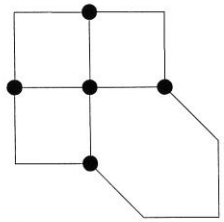
Si(2Al): $\Delta\delta_{29Si}$ = 2…5 ppm



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

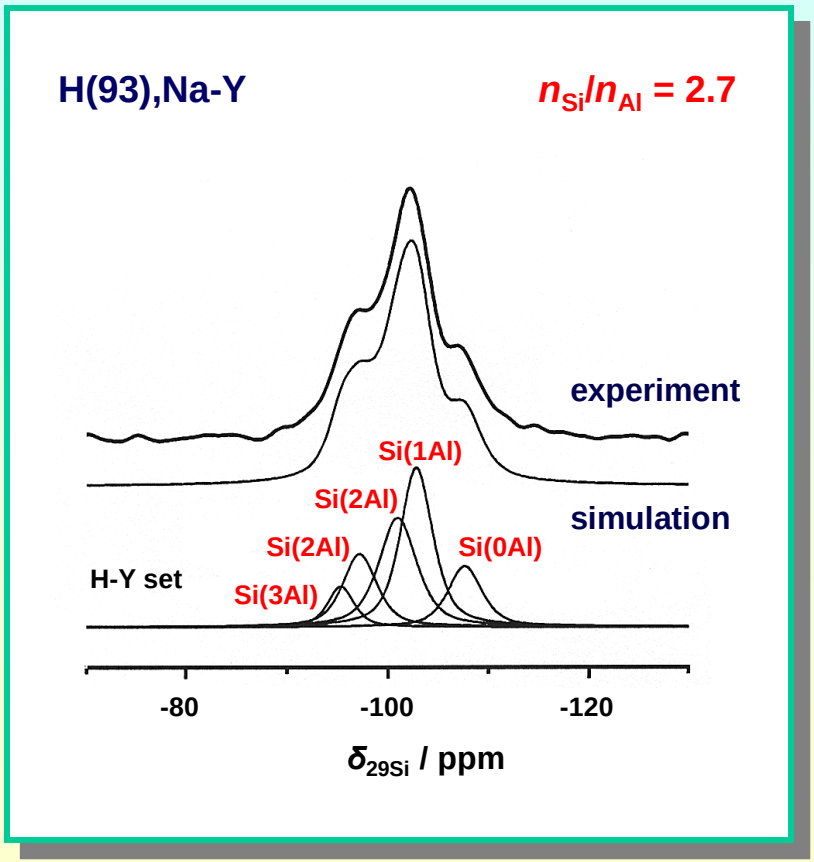


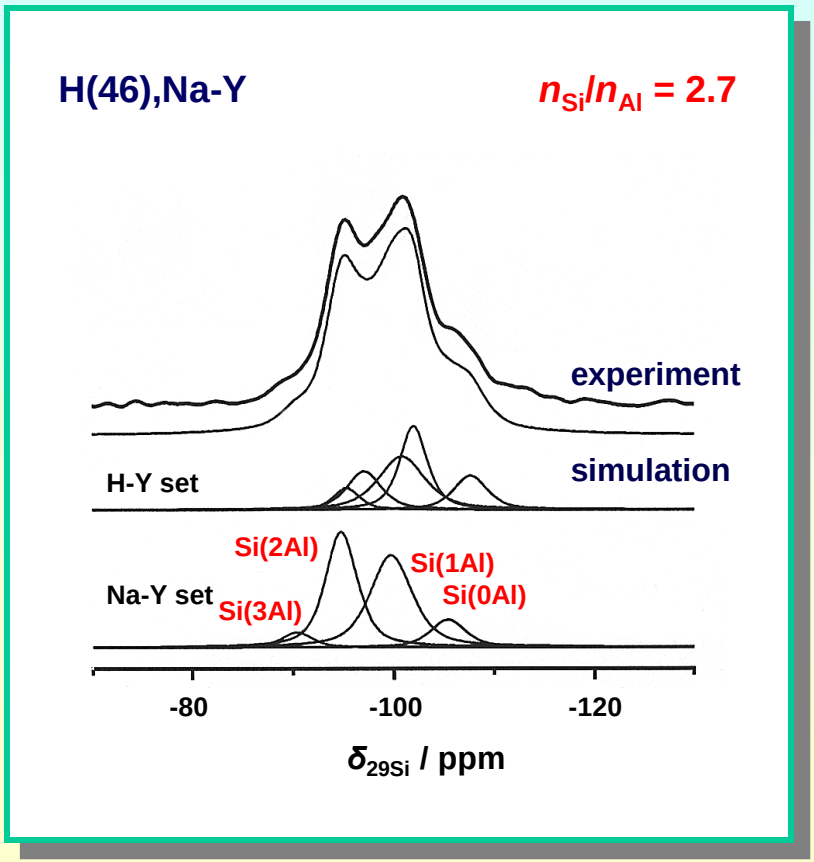
Si(0Al): $\Delta\delta_{29Si}$ ca. 1 ppm



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

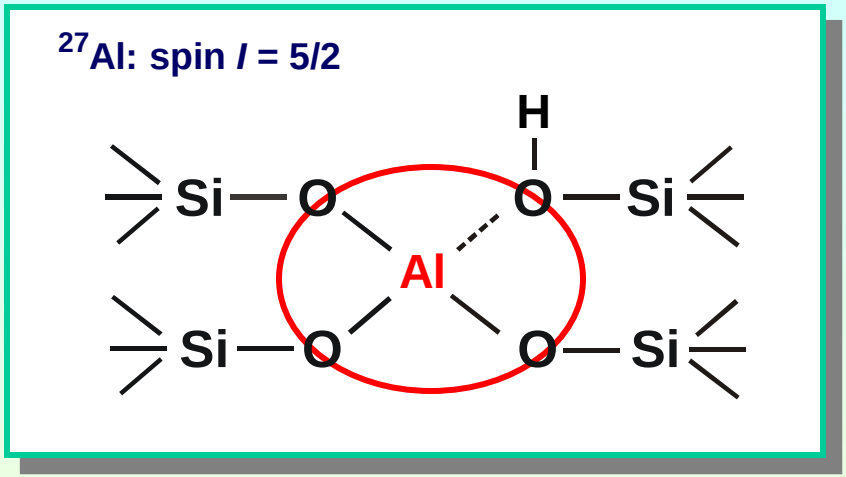
Simulation of ^{29}Si MAS NMR Spectra of Non-Hydrated Zeolites Y





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

Quadrupolar Interactions of Aluminum Atoms in Non-Hydrated Zeolites



- electric field gradient :

$$V_{zz} = eq$$

- quadrupole coupling constant:

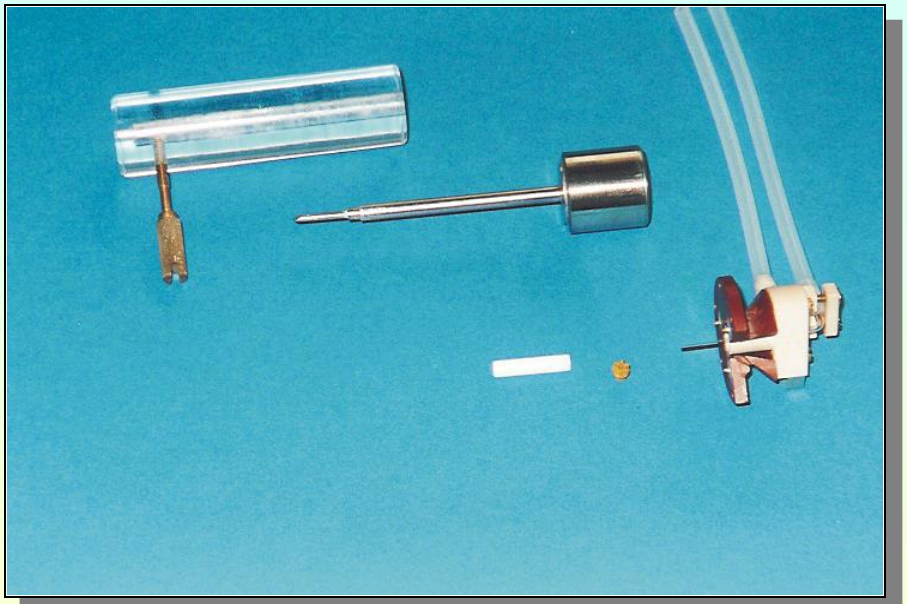
$$QCC = \frac{e^2qQ}{h}$$

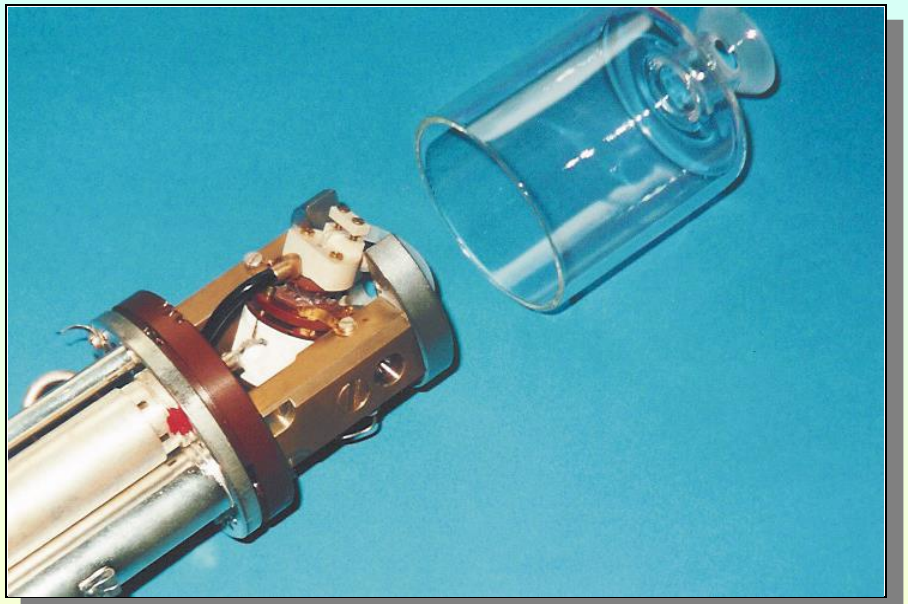
sample	*QCC* value	$\Delta\nu_{1/2}^{MAS*}$
hydrated H-Y	2 MHz	0.6 kHz / 5.5 ppm
non-hydrated H-Y	15 MHz	36 kHz / 350 ppm

*) B_0 = 9.4 T

K.U. Gore et al. J. Phys. Chem. B 106 (2002) 6115;
W. Wang et al., Chem. Phys. Lett. 370 (2003) 88.

Continuous-flow (CF) MAS NMR Probe

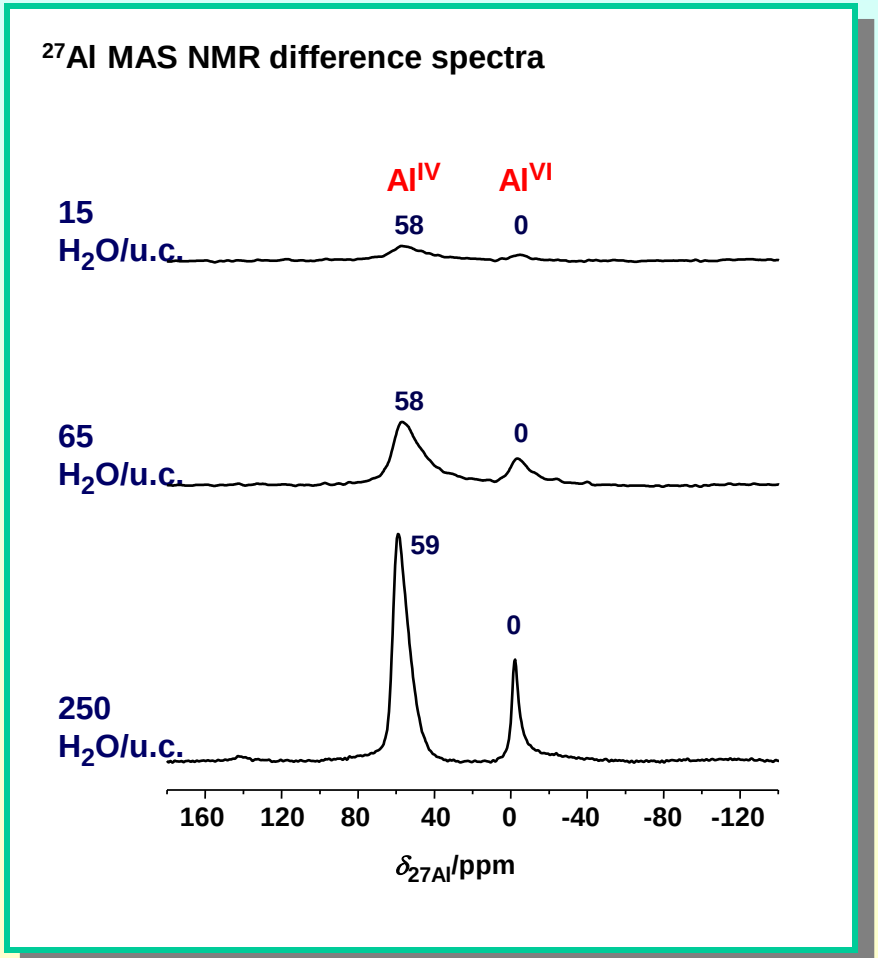


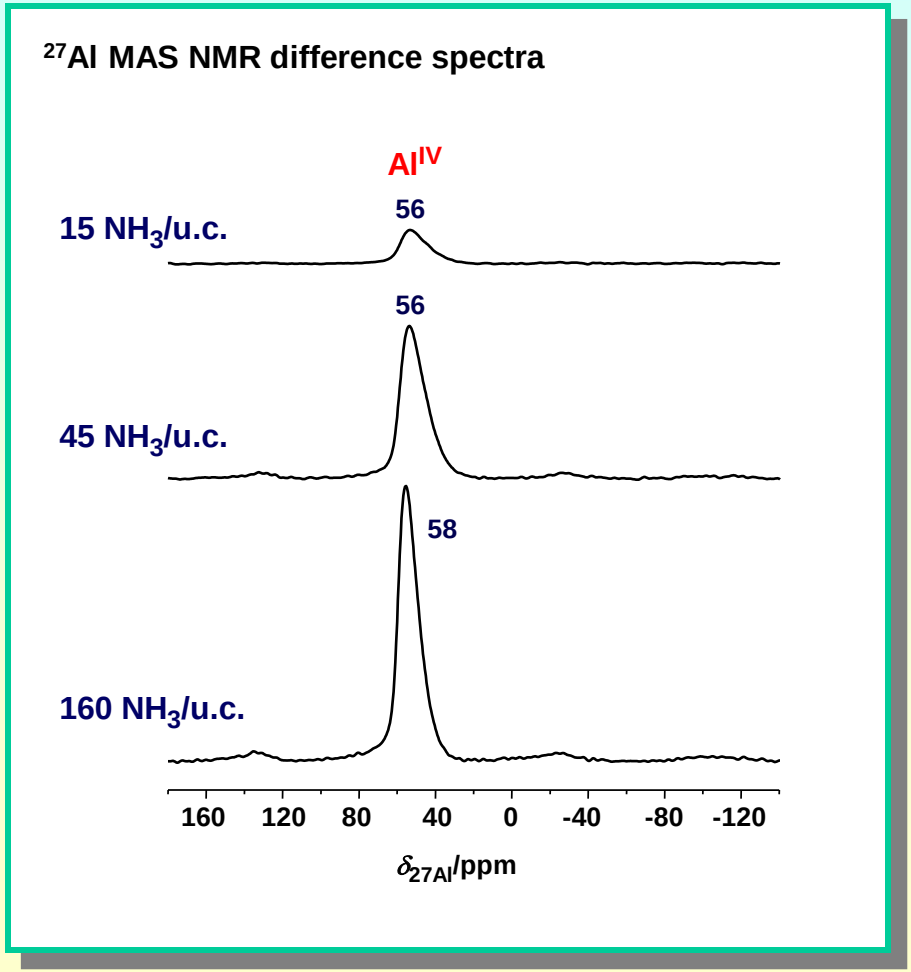


A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.

Adsorption Studied by ^{27}Al MAS NMR

- **effect of the adsorption of H_2O and NH_3 on Al species in non-hydrated H-Y (n_{Si}/n_{Al} = 2.7)**



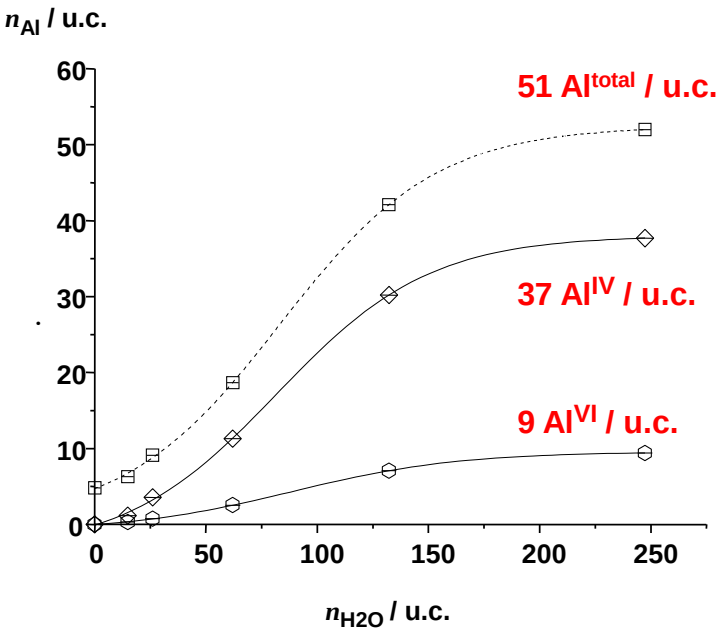


Adsorption Studied by ^{27}Al MAS NMR

- **evaluation of the adsorption of H_2O and NH_3 on non-hydrated H-Y (52.0 Al^{IV}/u.c.)**

adsorption of H_2O

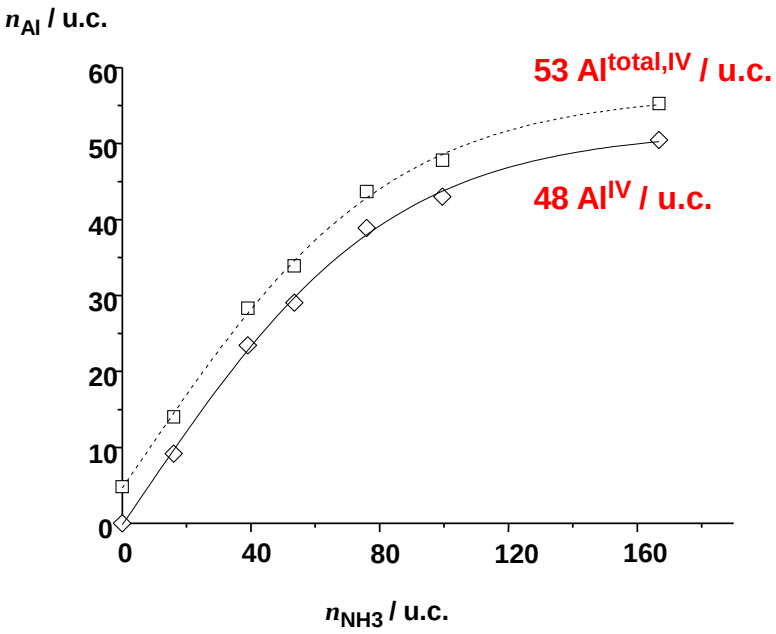
^{27}Al MAS NMR



^{1}H MAS NMR

adsorption of NH_3

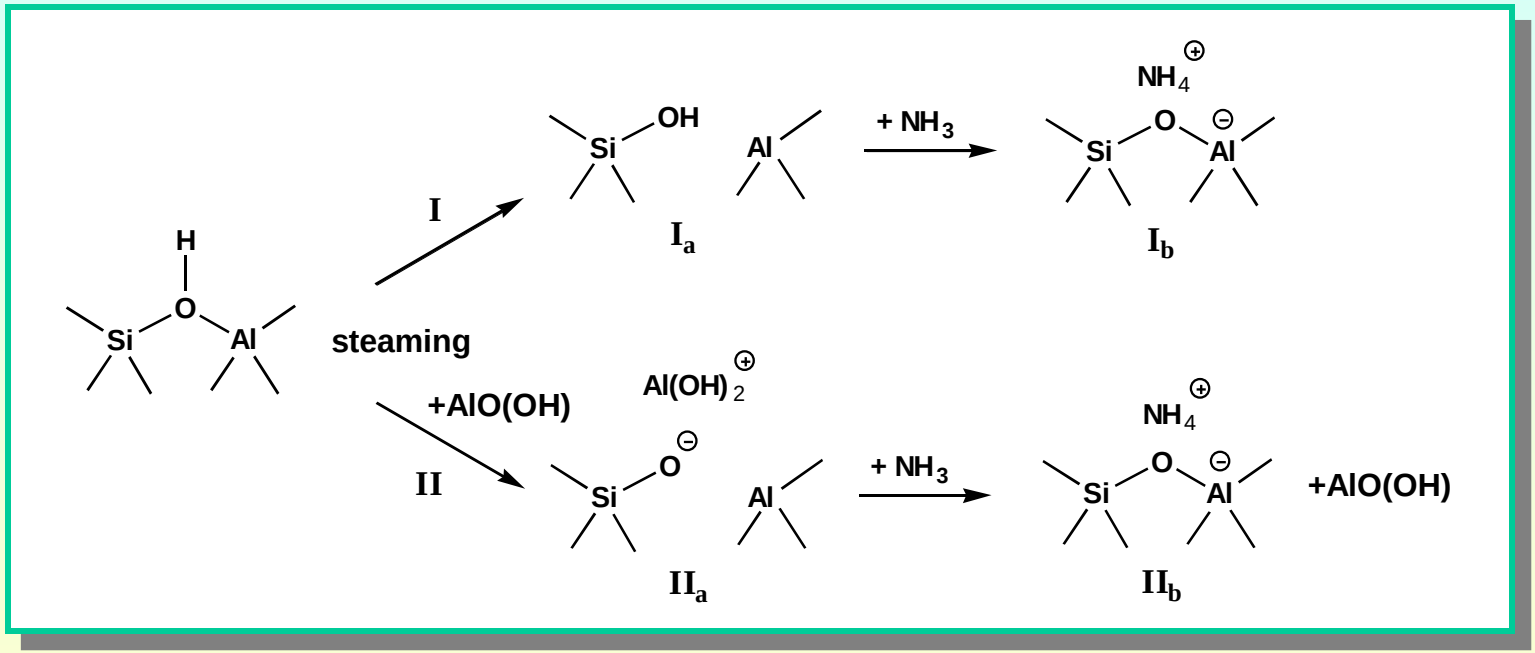
^{27}Al MAS NMR



^{1}H MAS NMR

Reversible Coordination Change of Framework Aluminum Atoms

- **proposed mechanism:**

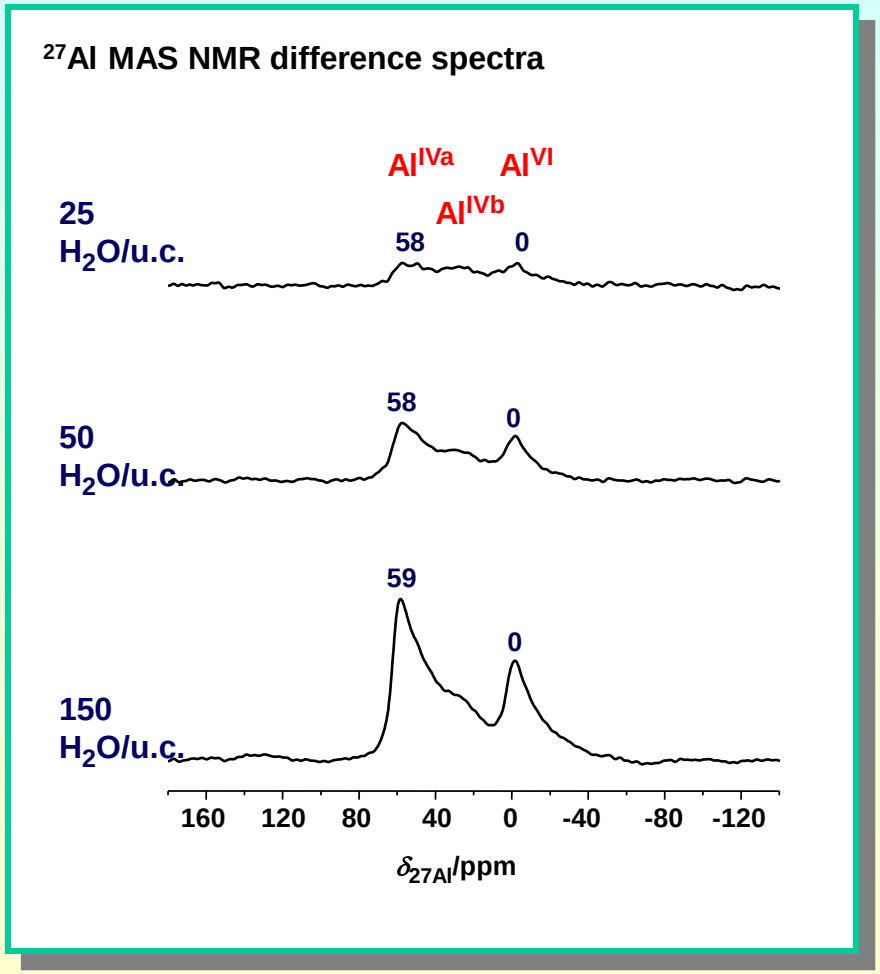


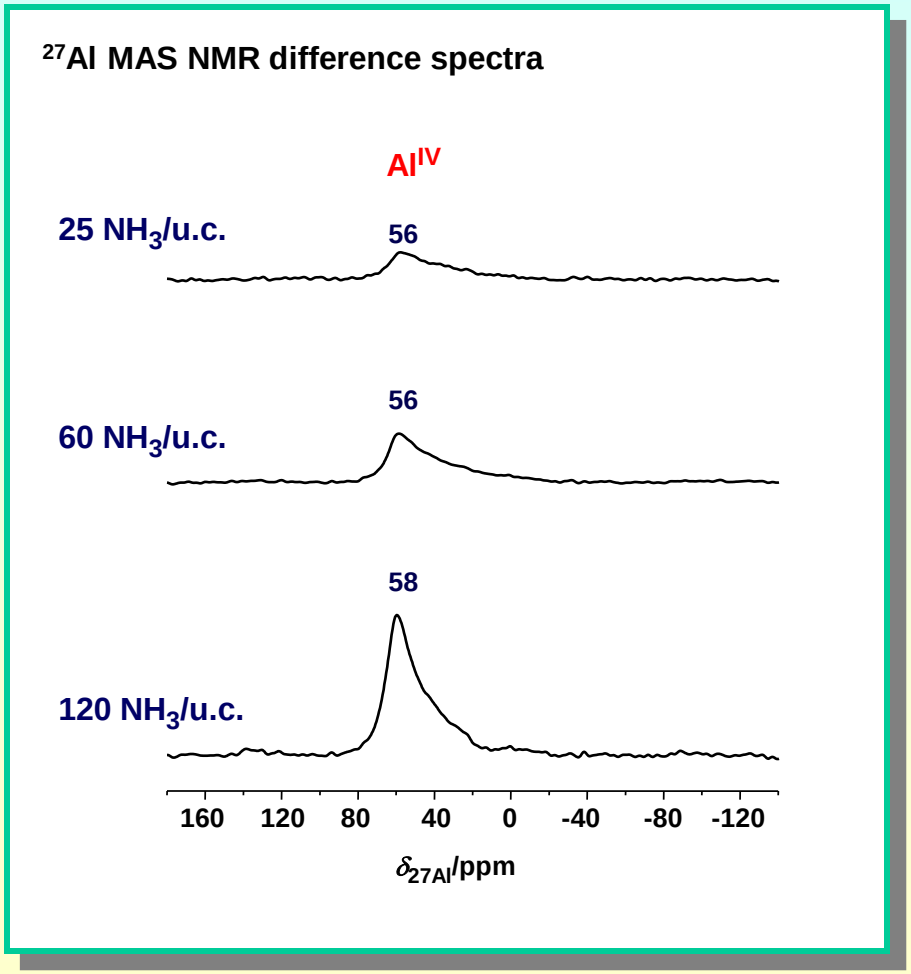
→ **adsorption of ammonia transforms Al atoms at framework defects into tetrahedrally coordinated Al atoms**

A. Omegna et al., J. Phys. Chem. B 107 (2003) 8854; J. Jiao et al., J. Phys. Chem B. 108 (2004) 14305.

Adsorption Studied by ^{27}Al MAS NMR

- **adsorption of H_2O and NH_3 on Al species in dehydrated zeolite deH-Y/81.5 (n_{Si}/n_{Al} = 6.0)**



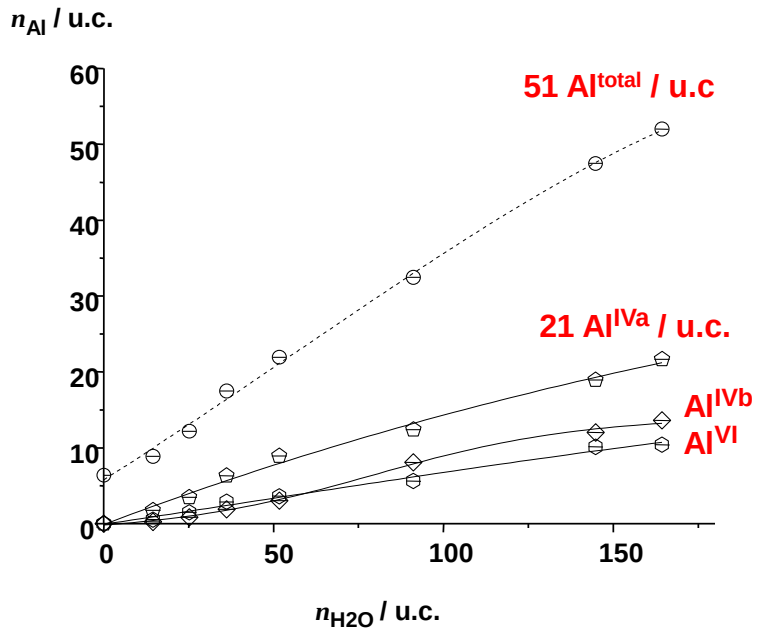


Adsorption Studied by ^{27}Al MAS NMR

- **evaluation of the adsorption of NH_3 and H_2O on non-hydrated deH-Y/81.5 (27.4 Al^{IV}/u.c.)**

adsorption of H_2O

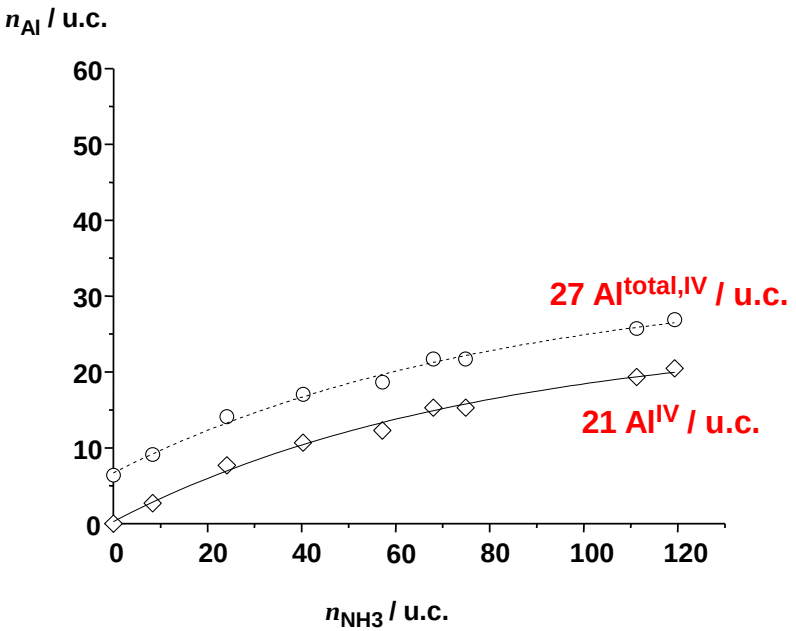
^{27}Al MAS NMR



^{1}H MAS NMR

adsorption of NH_3

^{27}Al MAS NMR



^{1}H MAS NMR

Mean Cationic Charge of Extra-Framework Aluminum Species

- effect of steaming on zeolite H-Y (3.5 residual sodium cations per u.c.)

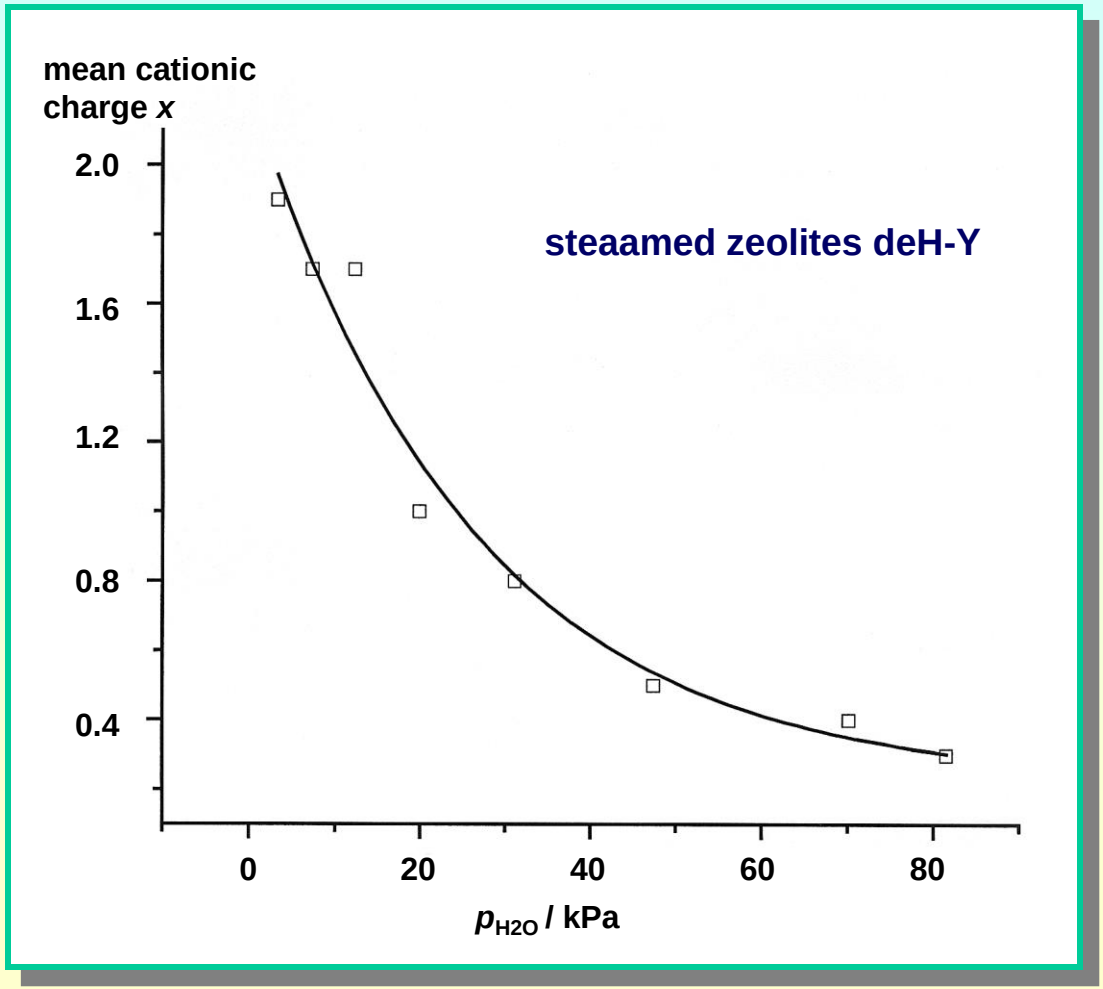
sample	n_{Si}/n_{Al}	$n_{Al^{IV}}$ / u.c.	n_{SiOHAl} / u.c.	$n_{Al^{ex}}$ / u.c.	*x*
H-Y	2.7	52.0	46.5	0	0
deH-Y/3.4	2.8	50.1	43.0	1.9	1.9+
deH-Y/7.4	2.9	48.6	39.2	3.4	1.7+
deH-Y/19.9	3.3	44.6	34.4	7.4	1.0+
deH-Y/31.1	4.0	38.4	25.7	13.6	0.7+
deH-Y/81.5	6.0	27.4	17.3	24.6	0.3+

- mean charge per extra-framework aluminum atom in non-hydrated zeolites deH-Y:

$$x = (n_{Al^{IV}} - n_{Na} - n_{SiOHAl}) / n_{Al^{ex}}$$

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

Mean Cationic Charge of Extra-Framework Aluminum Species



→ **formation of:**

$AlO_m(OH)_n^{x+}$

- **value *x*:**
  ca. 2 to 0.3/Al^{ex}

- **value *n*:**
  1.0 to 0.25/Al^{ex}

→ **weak steaming:**

- **species with mean cationic charge of ca. 2+**

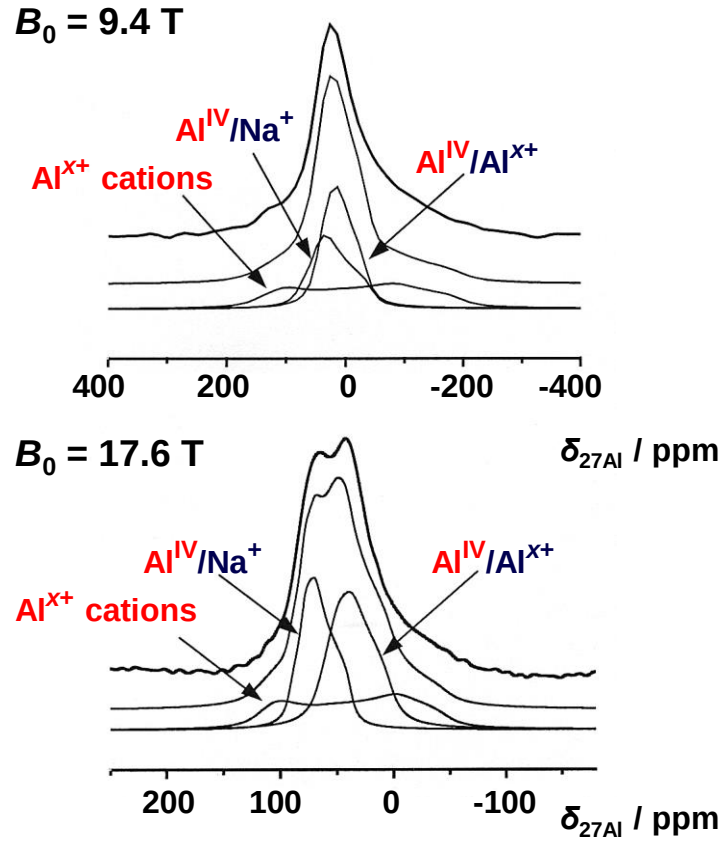
strong steaming:

- **mixture of different species**

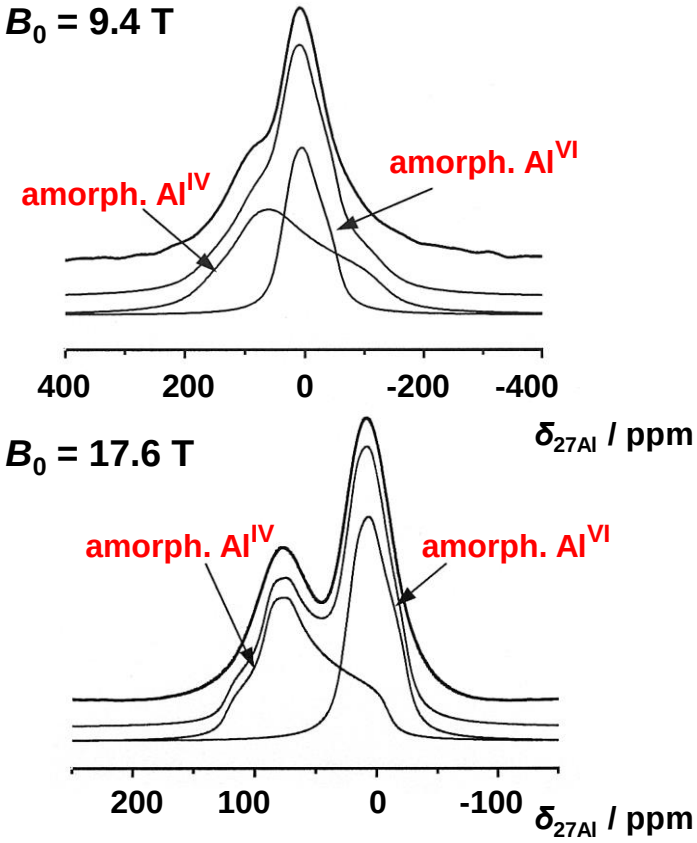
J. Jiao et al., J. Phys. Chem B. 108 (2004) 14305.

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

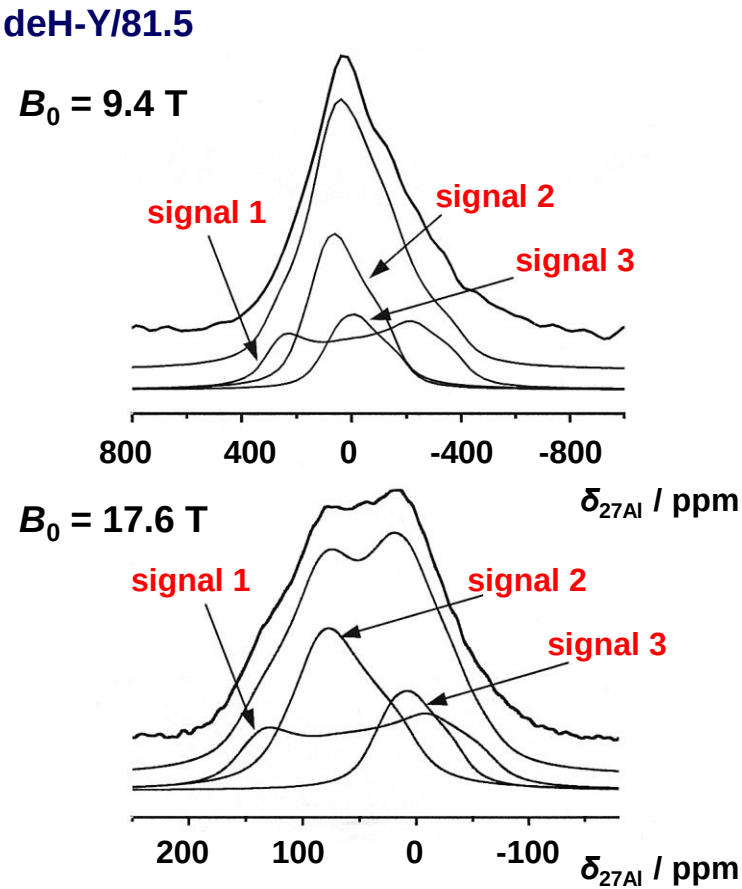
Al,Na-Y



γ-Al_2O_3



^{27}Al Spin-Echo NMR Studies of Strongly Steamed Zeolite Y



- **signal 1:**
  - QCC = 14.8 MHz, η = 0.3, δ_{iso} = 65±5 ppm
  - signals of Al^{IV}/H^{+} and Al^{x+} cations
- **signal 2:**
  - QCC = 9.0 MHz, η = 0.8, δ_{iso} = 65±5 ppm
  - signals of Al^{IV}/Na^{+}, Al^{IV}/Al^{x+}, and amorph. Al^{IV}
- **signal 3:**
  - QCC = 8.0 MHz, η = 0.7, δ_{iso} = 5±5 ppm
  - signal of amorph. Al^{VI}

→ **zeolite deH-Y/81.5 contains:**
- 8 amorph. Al^{IV} per u.c.
- 10 amorph. Al^{VI} per u.c.
- 4.5 Al^{x+} cations per u.c., $Al(OH)^{2+}$

Summary I

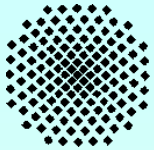
Study of steamed zeolites Y in the non-hydrated state:

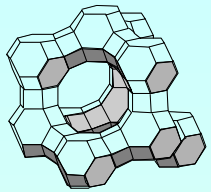
- **^{1}H MAS NMR:**
  - **preferred dehydroxylation of bridging OH groups in the sodalite cages**

- **^{29}Si MAS NMR, ^{1}H MAS NMR, and AES:**
  - **formation of Al^{ex} species with a *mean* cationic charge of ca. 2+ for weakly steamed materials and 0.3+ for strongly steamed materials**

- **^{27}Al MAS NMR studies of the adsorption of water and ammonia:**
  - **quantitative determination of the number of framework Al^{IV} species**
  - **Al^{VI} species in rehydrated zeolite H-Y may be due to framework aluminum atoms at defect sites**

- **^{27}Al spin-echo NMR, ^{1}H MAS NMR, and AES:**
  - **Al^{ex} species in strongly steamed zeolites Y are a mixture of tetrahedrally and octahedrally coordinated Al atoms in oxidic clusters and $Al(OH)^{2+}$ cations**



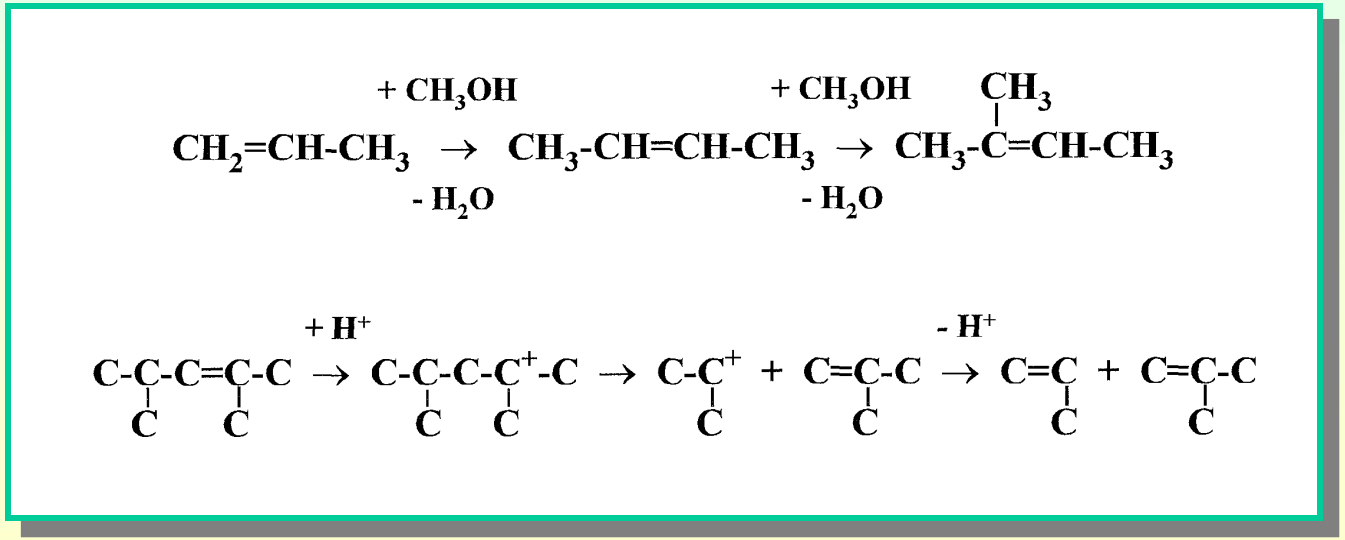


II. NMR Investigations of the Methanol to Hydrocarbon Conversion on Acidic Zeolite Catalysts

Methanol to Olefin (MTO) Conversion on Acidic Zeolite Catalysts

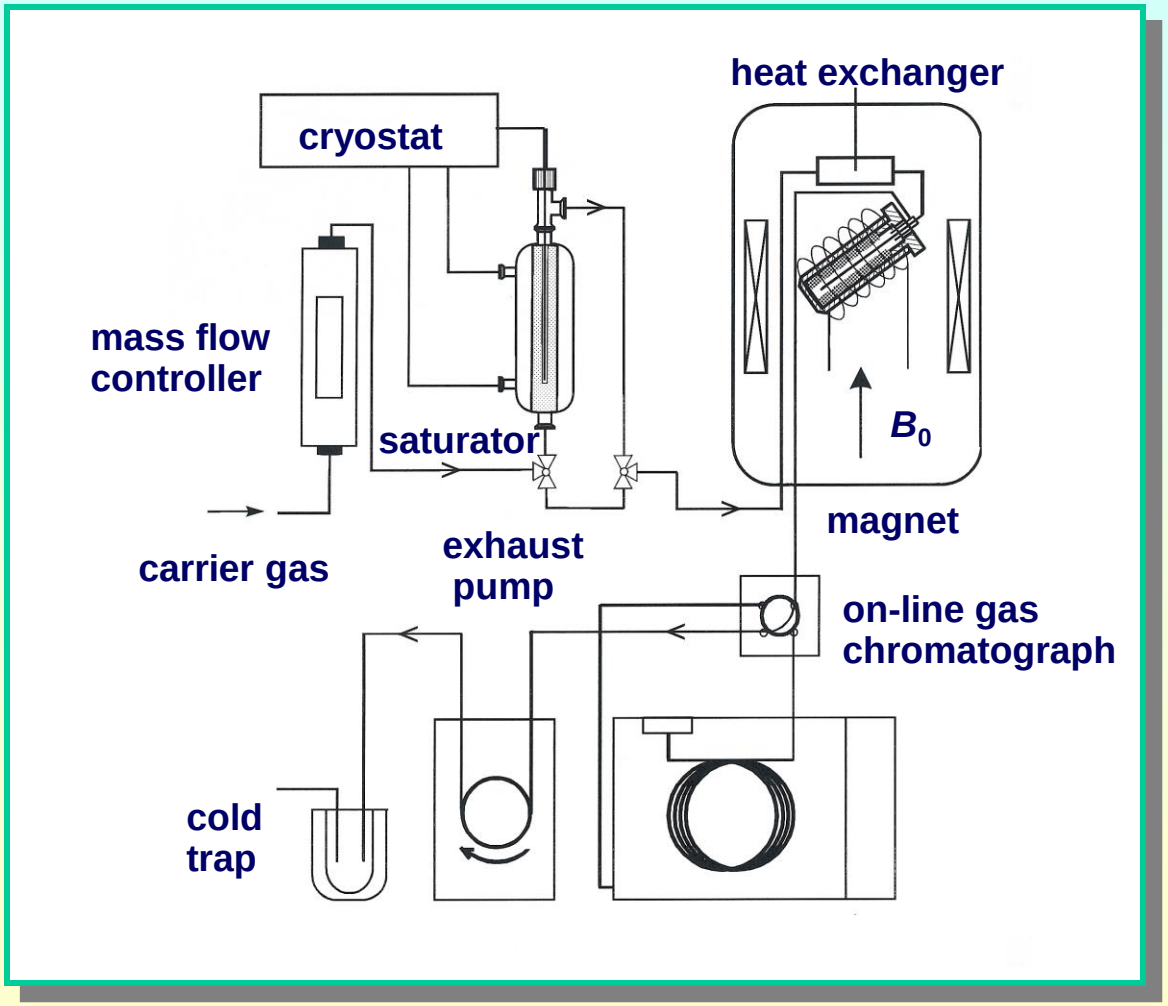
reaction mechanisms proposed in the literature:

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



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

Coupling of In Situ CF MAS NMR and On-Line Gas Chromatography

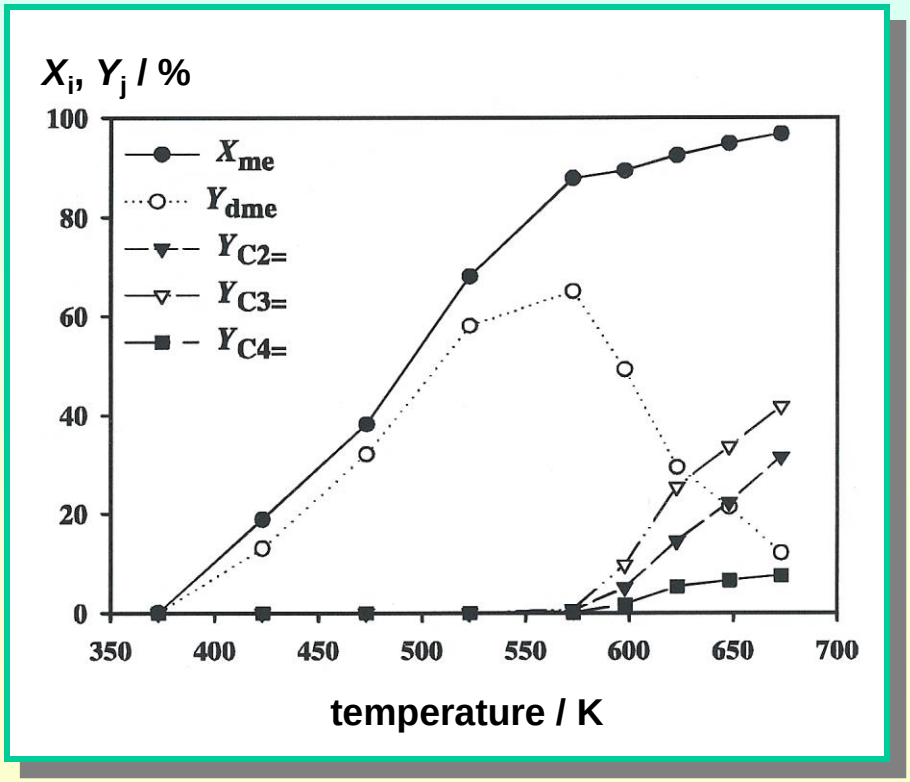


M. Hunger et al., Catal. Lett. 57 (1999) 199.

Conversion of Methanol on H-ZSM-5 in a Fixed-Bed and in an MAS NMR Rotor Reactor

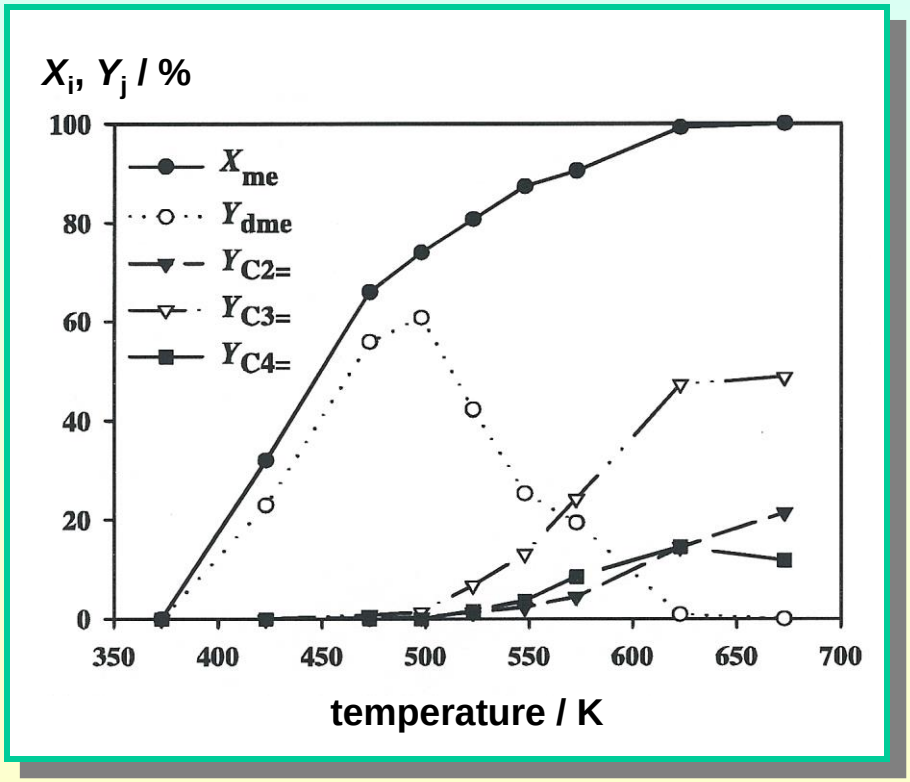
fixed-bed reactor

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



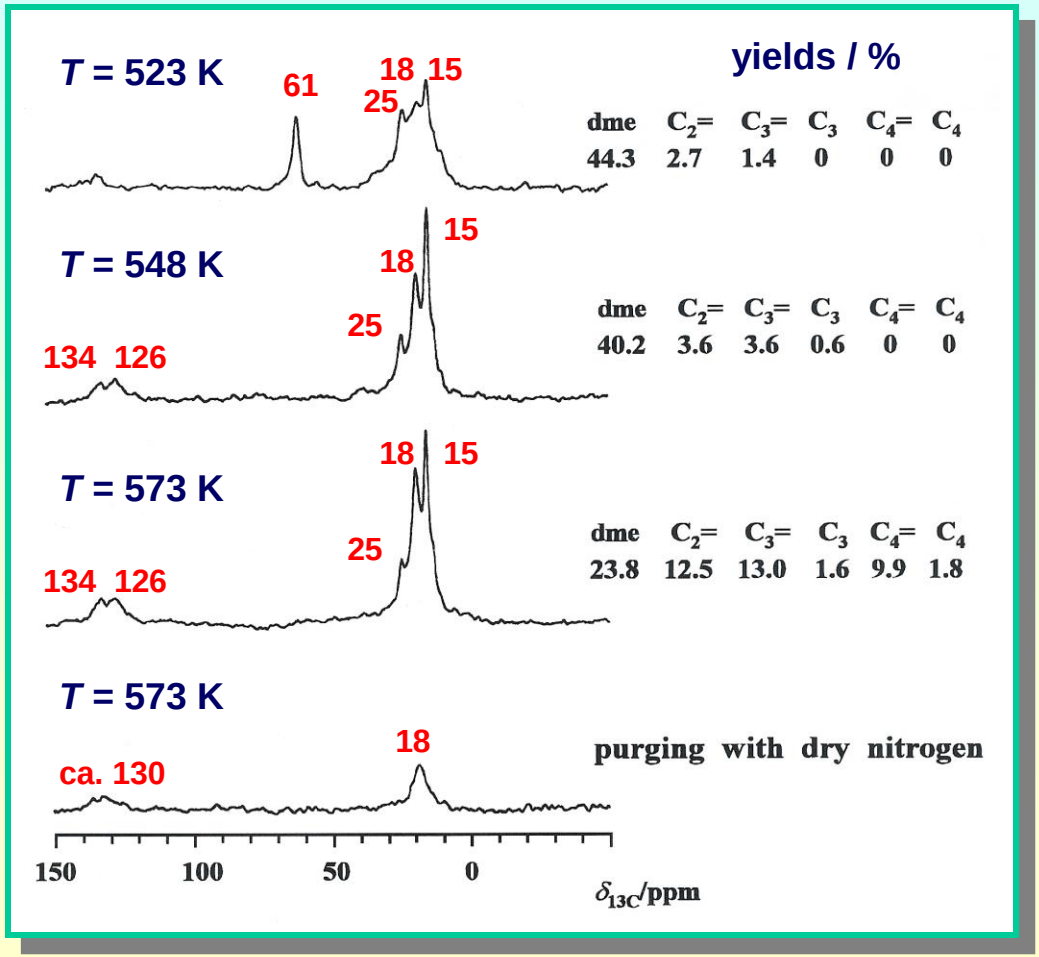
spinning (2 kHz) MAS NMR rotor reactor

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



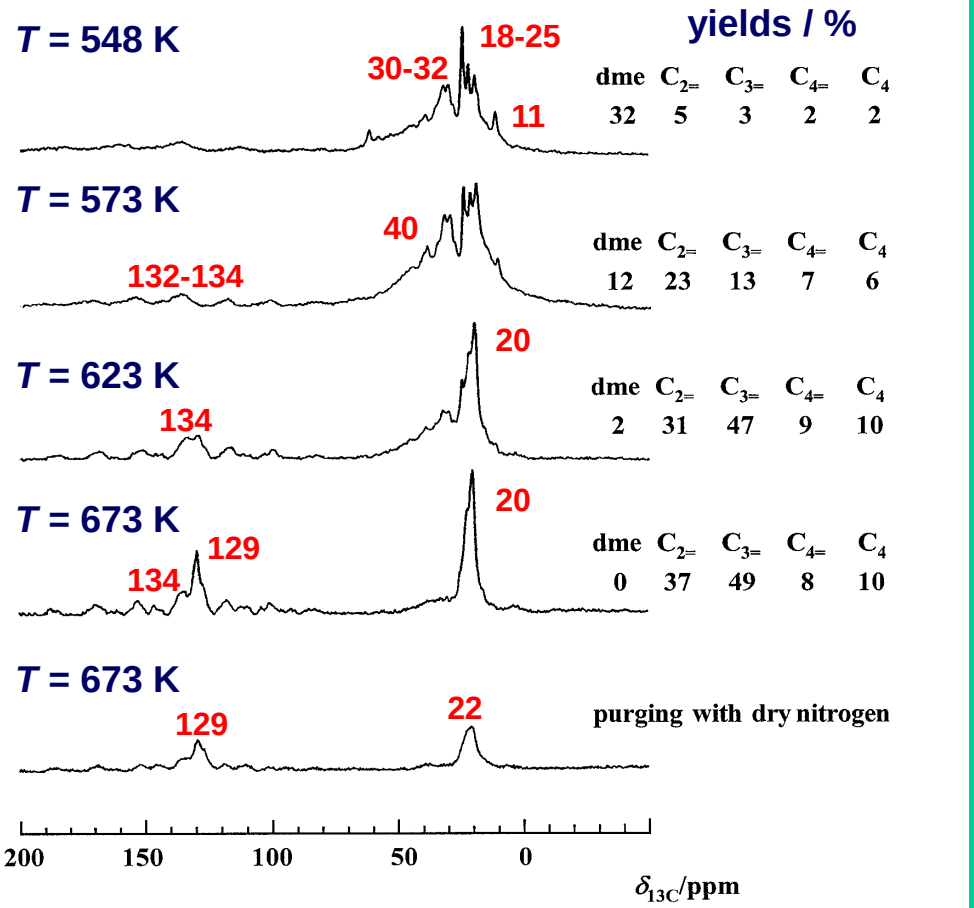
→ **olefinic deposites, e.g.:**
3-hexene (14.4, 25.9, 131.2 ppm)
2,3-hexadiene (17.5, 126.2, 132.5 ppm)
....

→ **mixture of olefins with carbon numbers of *n* > 6**

→ **domination of aromatics after purging with dry nitrogen:**
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



***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)
- ....

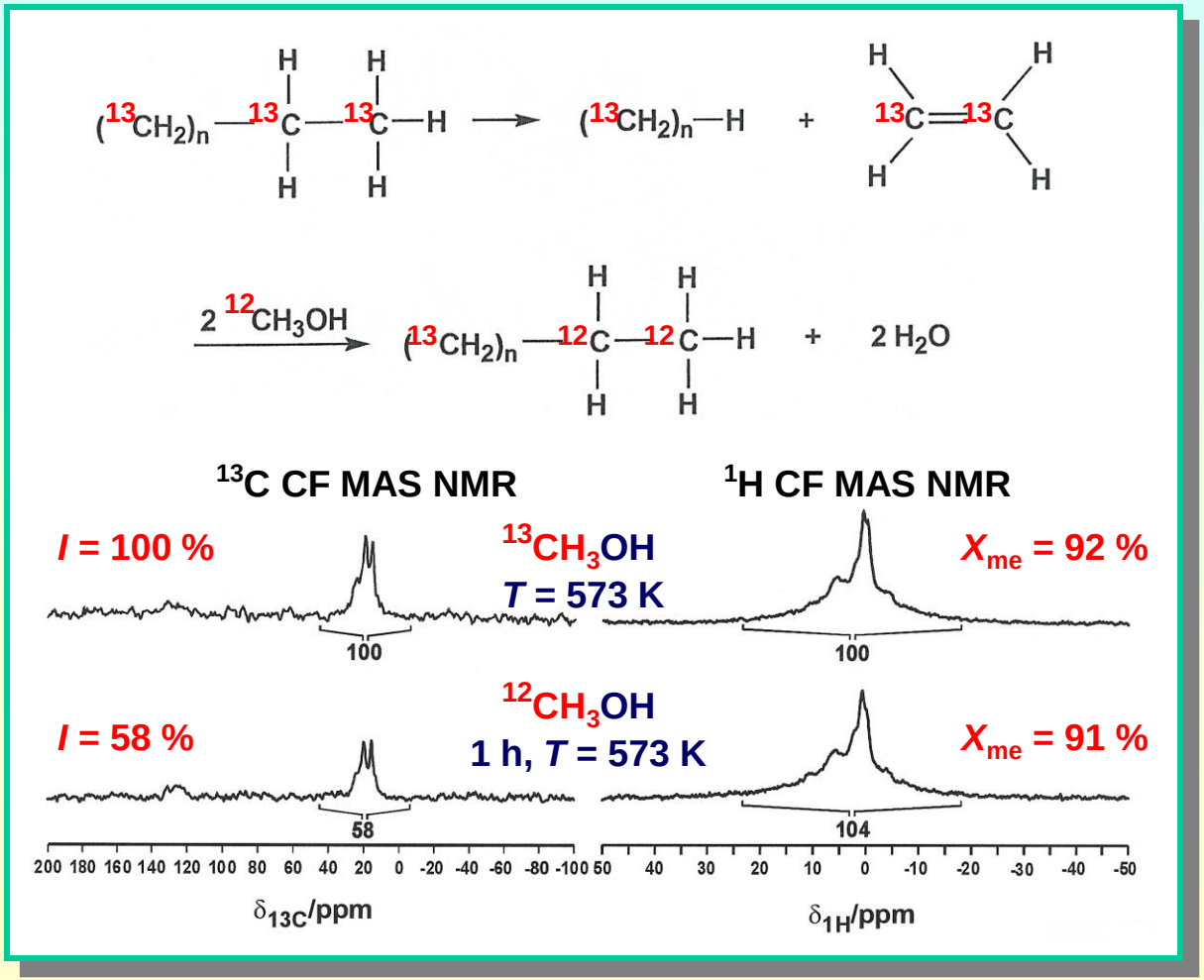
***T* > 623 K:**

→ **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:

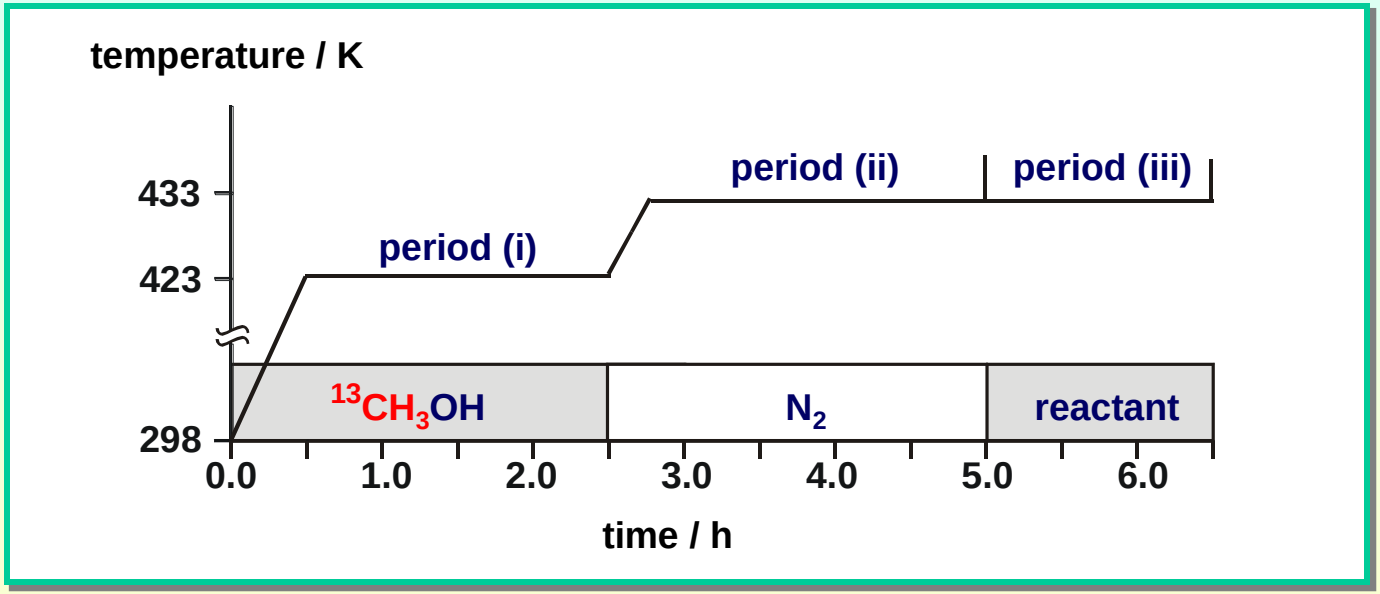
→ **alkyl groups are involved in the conversion of methanol**

→ **the 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)

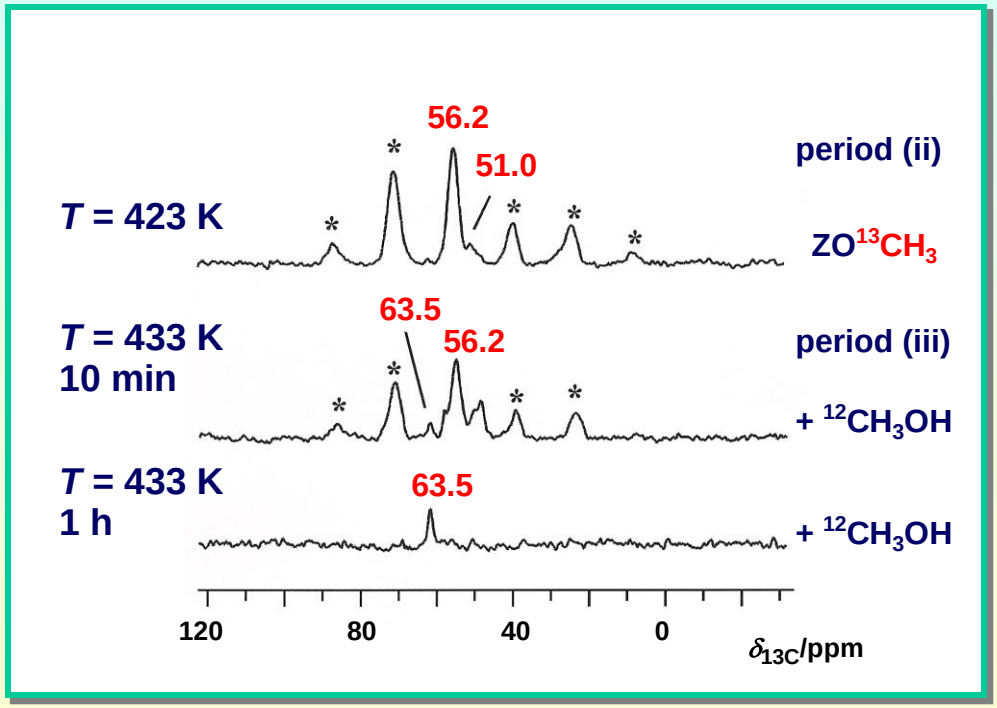


→ **investigation of the reactivity of intermediates**

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

$- H_2O$ →

methoxy

$ZO^{13}CH_3$

56.2 ppm

$+ {}^{12}CH_3OH$ →

$- H_2O$

dme

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

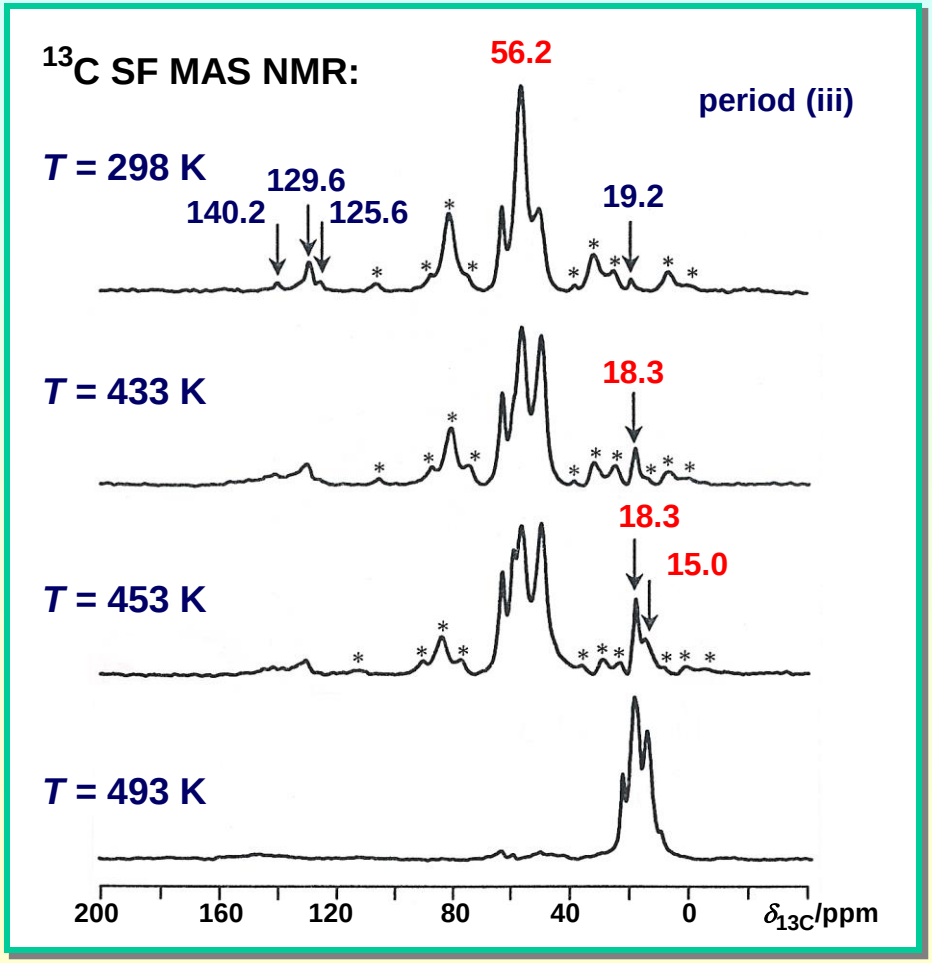
63.5 ppm

→ ^{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

→ $SiOHAl + CH_3C_6H_4{}^{13}CH_3$

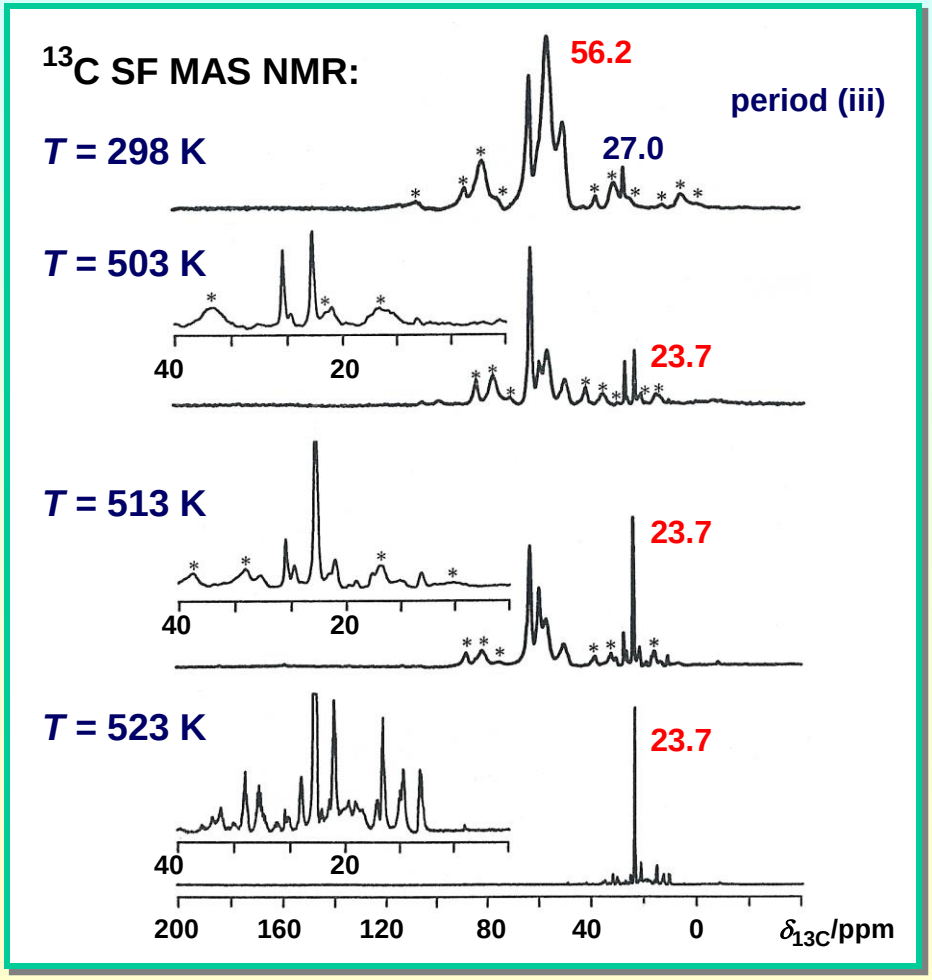
18.3 ppm

- 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

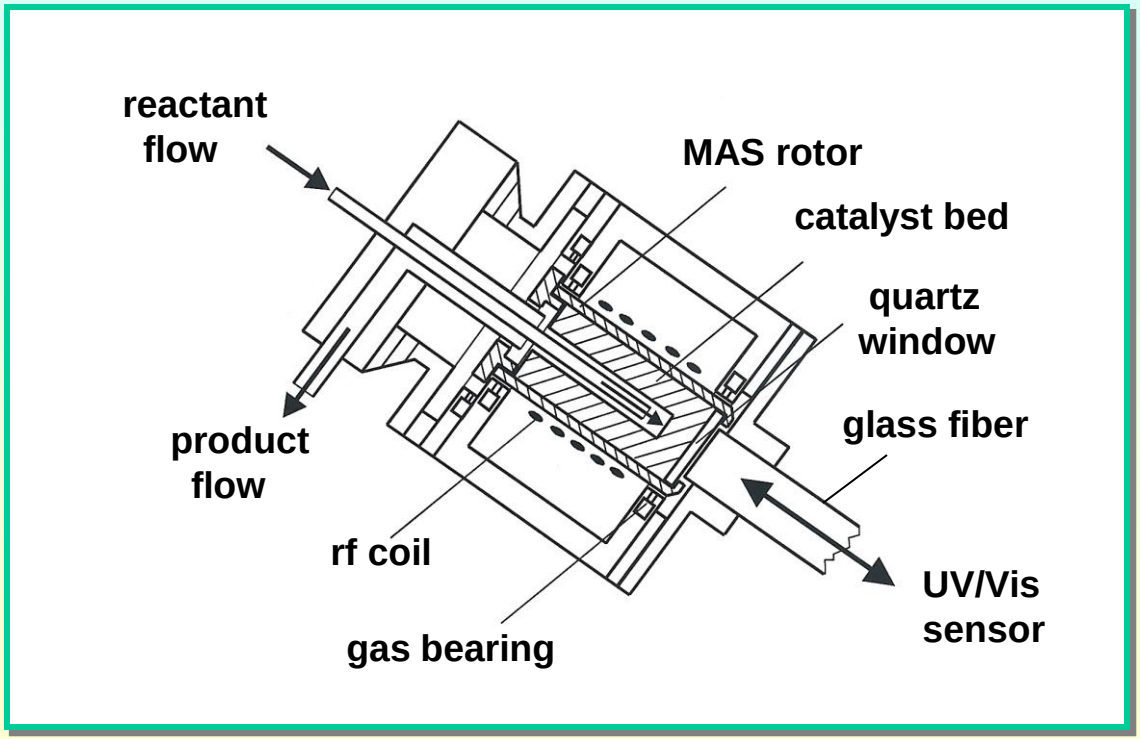
methylcyclohexane

- 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.

MAS NMR-UV/Vis Coupling

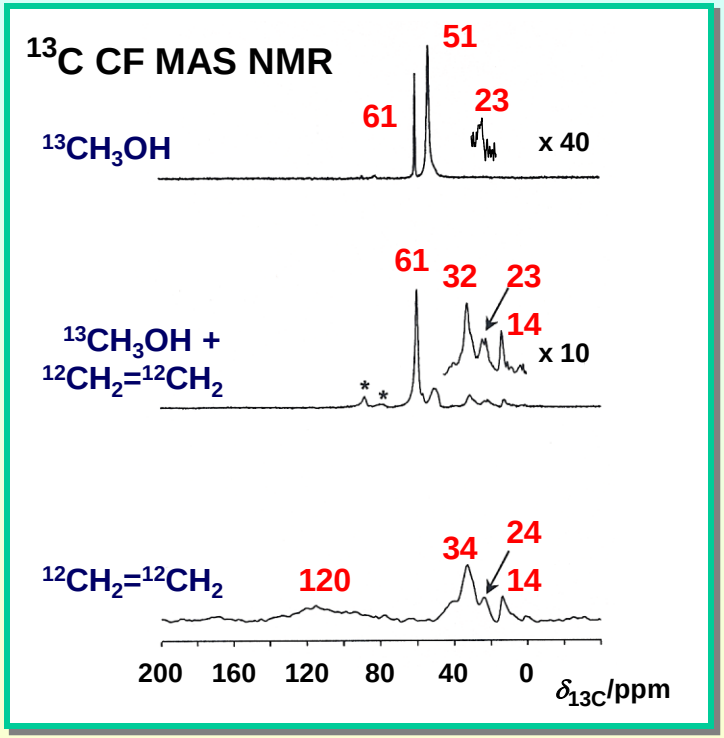
installation of a quartz fiber optic at the bottom of the CF MAS NMR stator

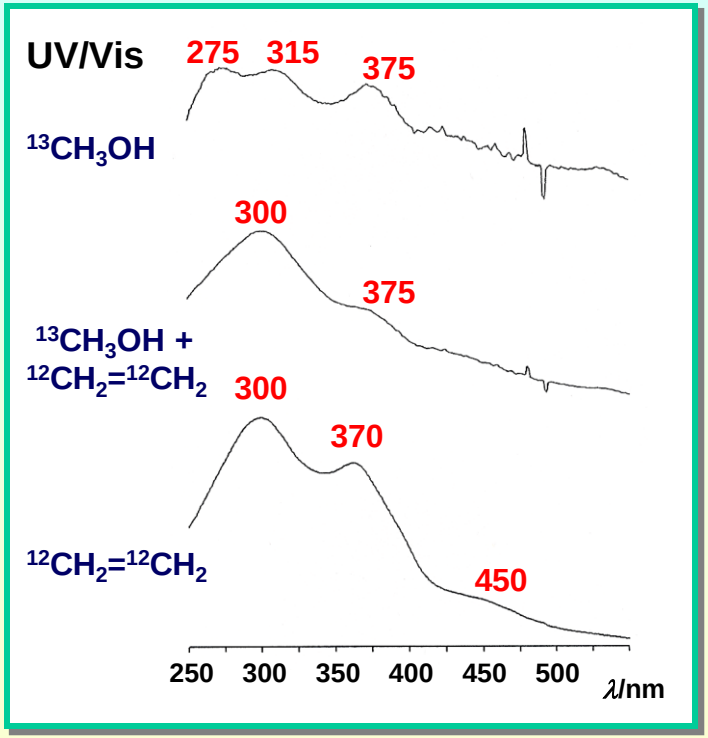


M. Hunger, W. Wang, Chem. Commun. (2004) 584.

MAS NMR-UV/Vis Coupling

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





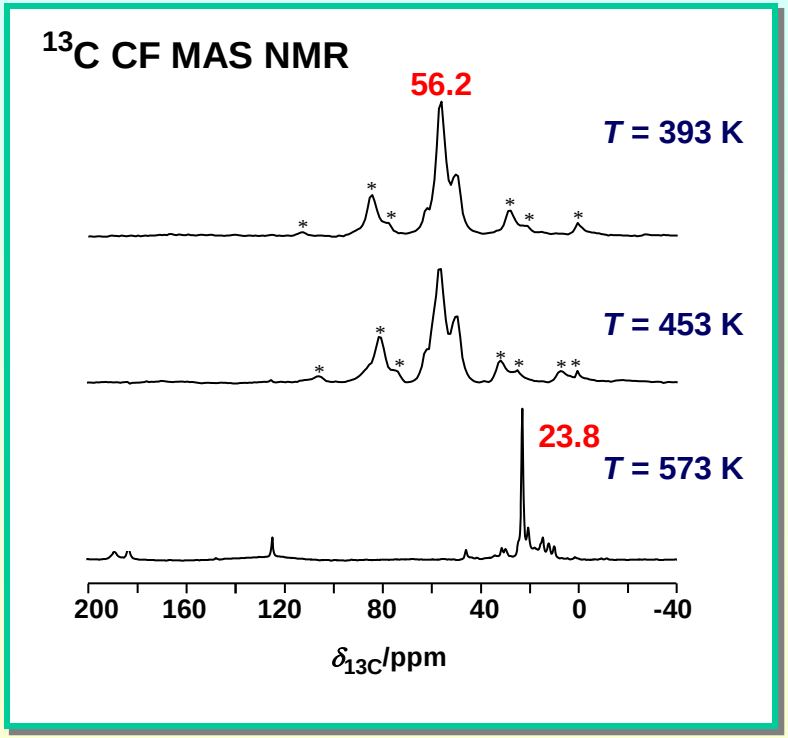
275 nm: neutral aromatics
315 nm: monoenyl carbenium ions

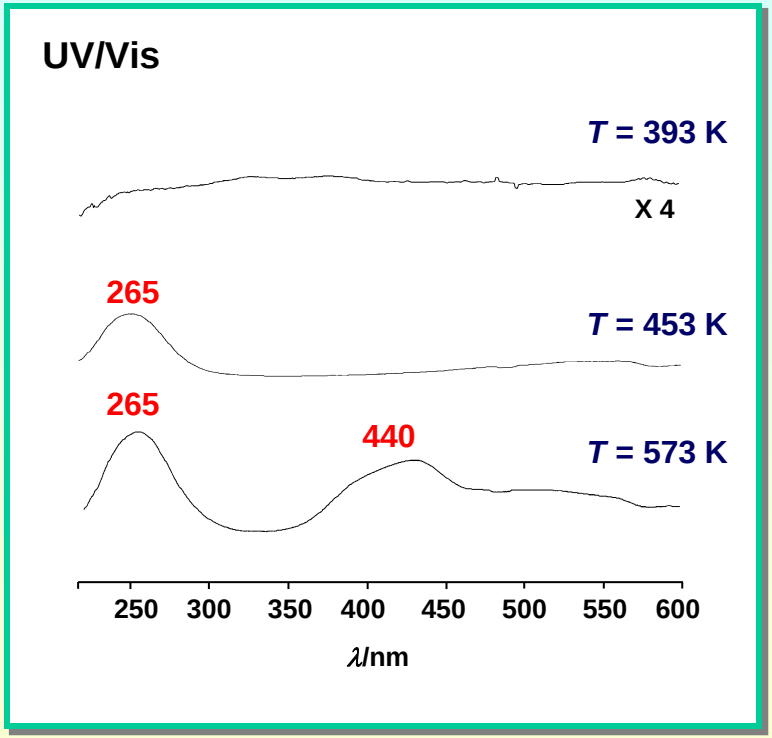
375 nm: dienyl carbenium ions
450 nm: polyaromatics

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 II

Study of the methanol-to-olefin conversion on acidic zeolites:

- **under steady-state conditions, mixtures of polyalkylated olefins and aromatics are formed in the zeolite pores**
- **composition of this carbon pool depends on the reaction conditions and on the catalyst**
- **alkyl groups of the carbon pool contribute to the conversion of methanol**
- **surface methoxy groups may be responsible for the formation of first hydrocarbons during the induction period of the MTO process**
- **aromatics are formed immediately after starting the conversion of methanol or methoxy groups on acidic zeolite catalysts**

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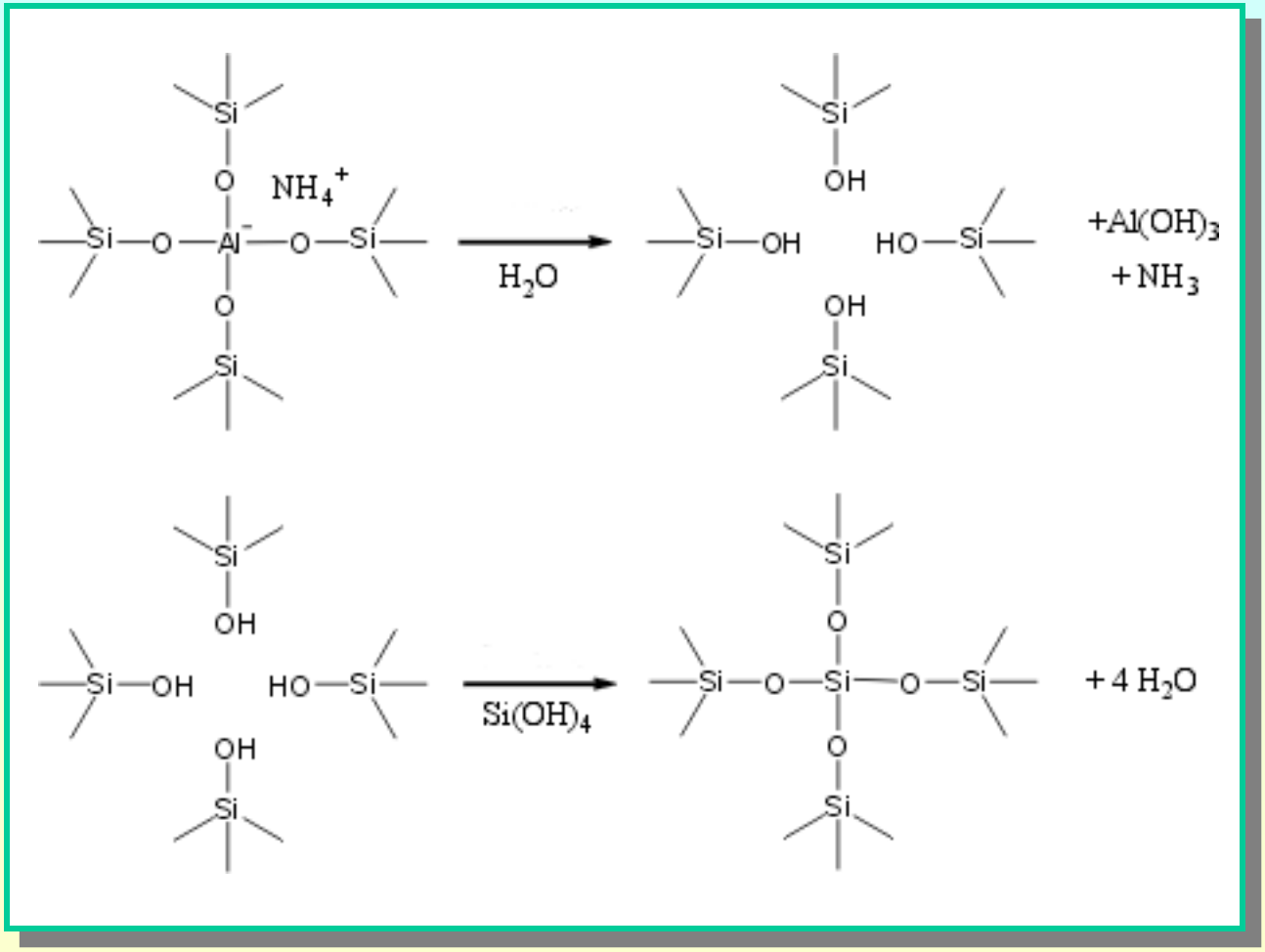
Volkswagen-Stiftung Hannover

Max-Buchner-Forschungs-stiftung

Fonds der Chemischen Industrie

Proposed Dealumination Mechanisms I

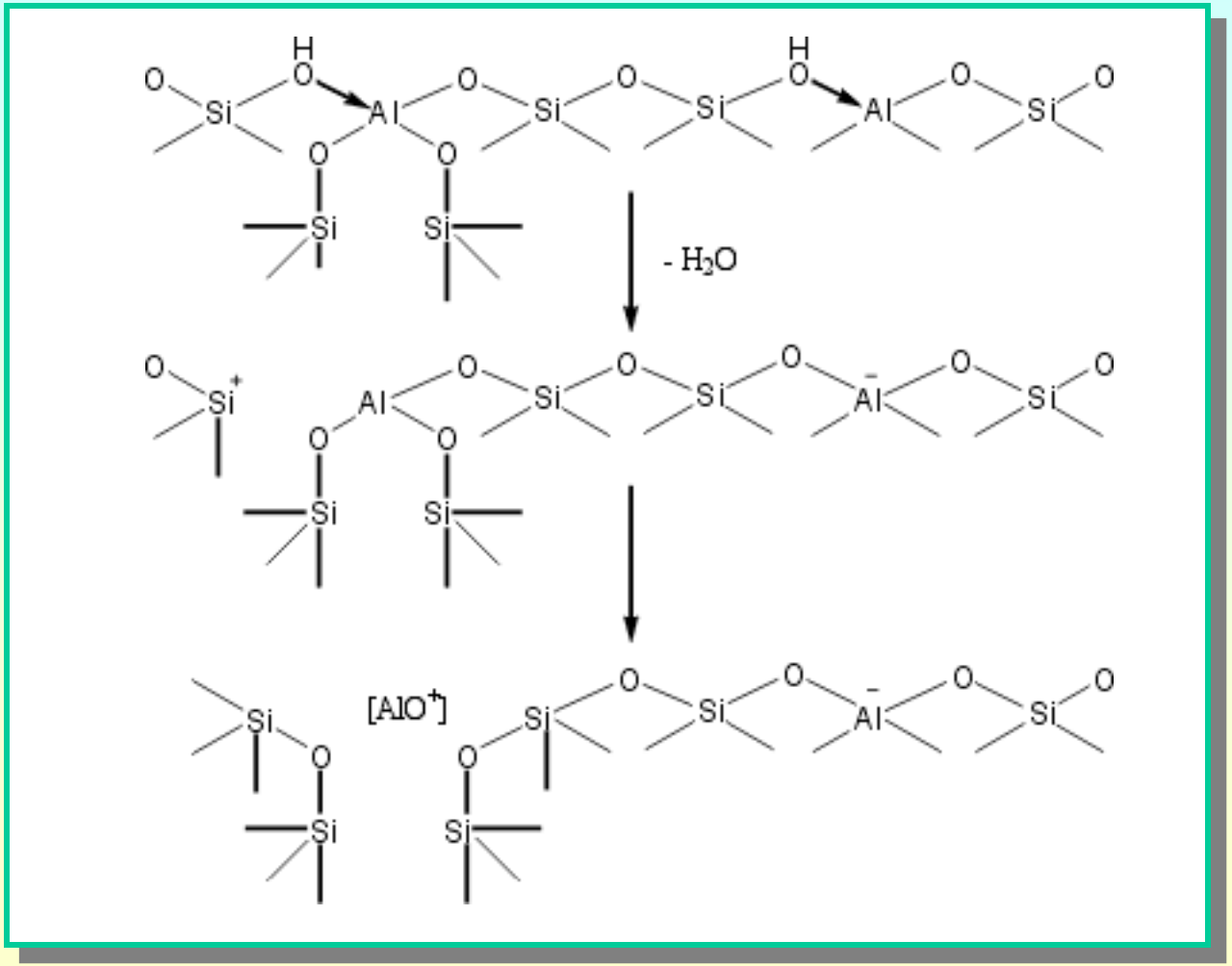
Kerr, 1974:



G.T. Kerr, in: W.M. Meier, J.B. Uytterhoeven (Eds.), Molecular Sieves, Advances in Chemistry Series, Vol. 121, American Chemical Society, Washington, 1974, p. 219-229.

Proposed Dealumination Mechanisms II

Kuehl, 1977:



G.H. Kuehl, J. Phys. Chem. Solids 38 (1977) 1259-1269.