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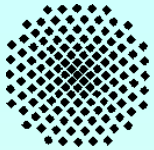
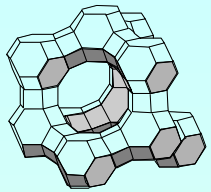


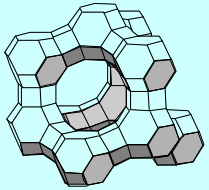


In situ NMR spectroscopy in heterogeneous catalysis

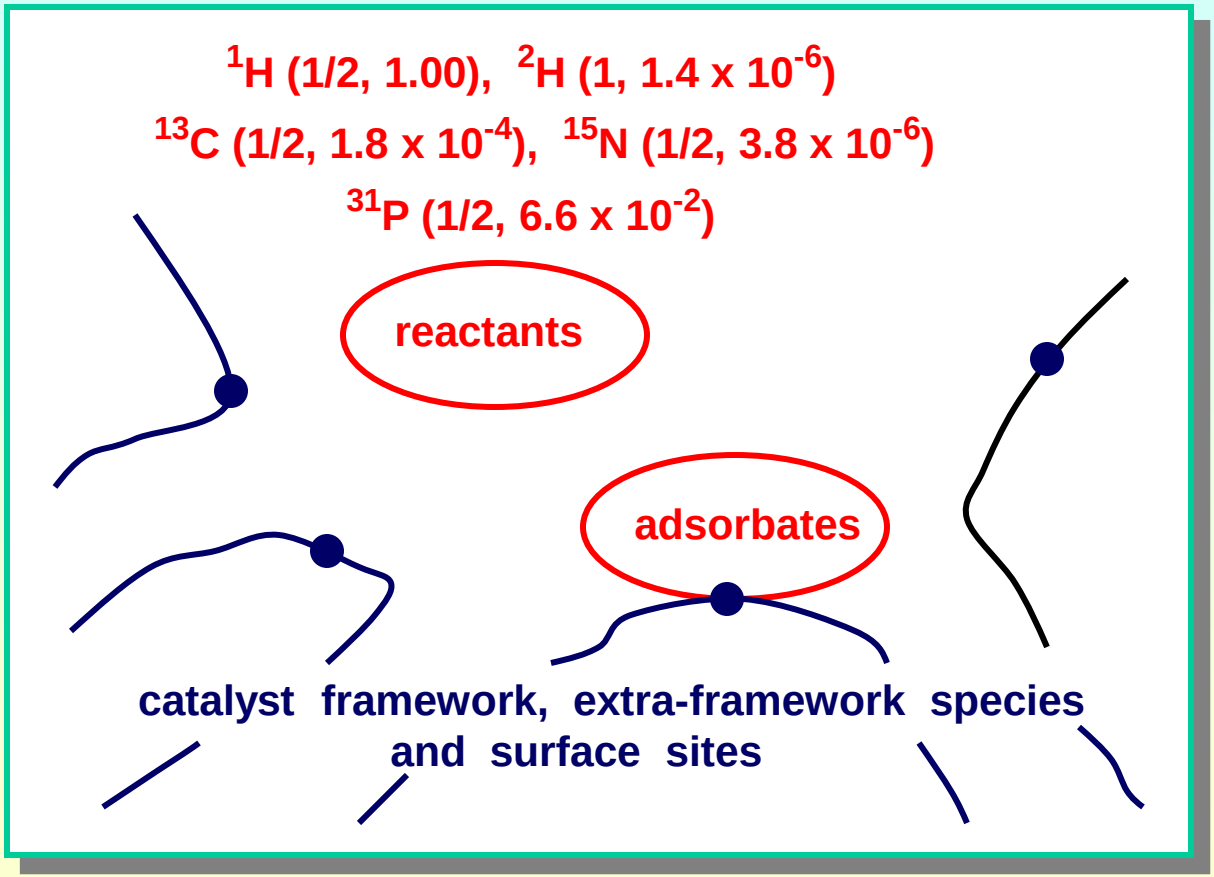
Michael Hunger

Institute of Chemical Technology

University of Stuttgart, Germany

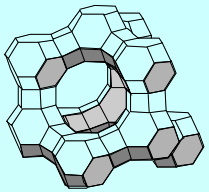


Examples of nuclei accessible for in situ NMR in heterogeneous catalysis



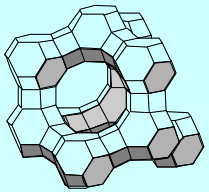
^{7}Li (3/2, 0.27)
^{11}B (3/2, 0.13)
^{17}O (5/2, 1.1 x 10^{-5})
^{23}Na (3/2, 9.2 x 10^{-2})
^{27}Al (5/2, 0.21)
^{29}Si (1/2, 3.7 x 10^{-4})
^{31}P (1/2, 6.6 x 10^{-2})
^{51}V (7/2, 0.38)
^{67}Zn (5/2, 1.2 x 10^{-2})
^{71}Ga (3/2, 5.6 x 10^{-2})
^{133}Cs (7/2, 4.7 x 10^{-2})

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:**
  - **zeolite framework and surface sites**
  - **reactions catalyzed by basic zeolites**
  - **reactions catalyzed by acidic zeolites**



Specific problems of NMR on working catalysts

magnetization:

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

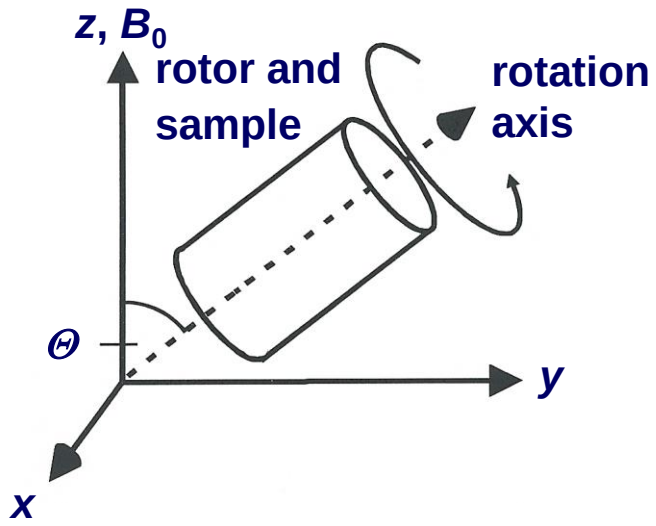
- **absolute number of spins of $N > 10^{19}$ per gram (^{1}H NMR)**
- **decrease of magnetization M_0 with increasing temperature T**
- **rapid chemical exchange of adsorbate complexes at elevated temperatures**
- **observation times of 10 ms (flow conditions) to hours (batch conditions)**
- **quenching 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)**

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



spin *I* > ½ :

- **double oriented rotation (DOR)**

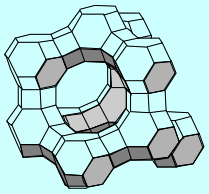
$\nu_{2QI} = f\{35\cos^4\Theta - 30\cos^2\Theta + 3\}$

$\Theta = 30.6^o$

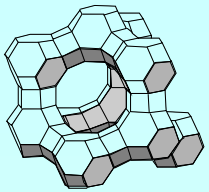
$\rightarrow$

$\Theta = 70.1^o$

- **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

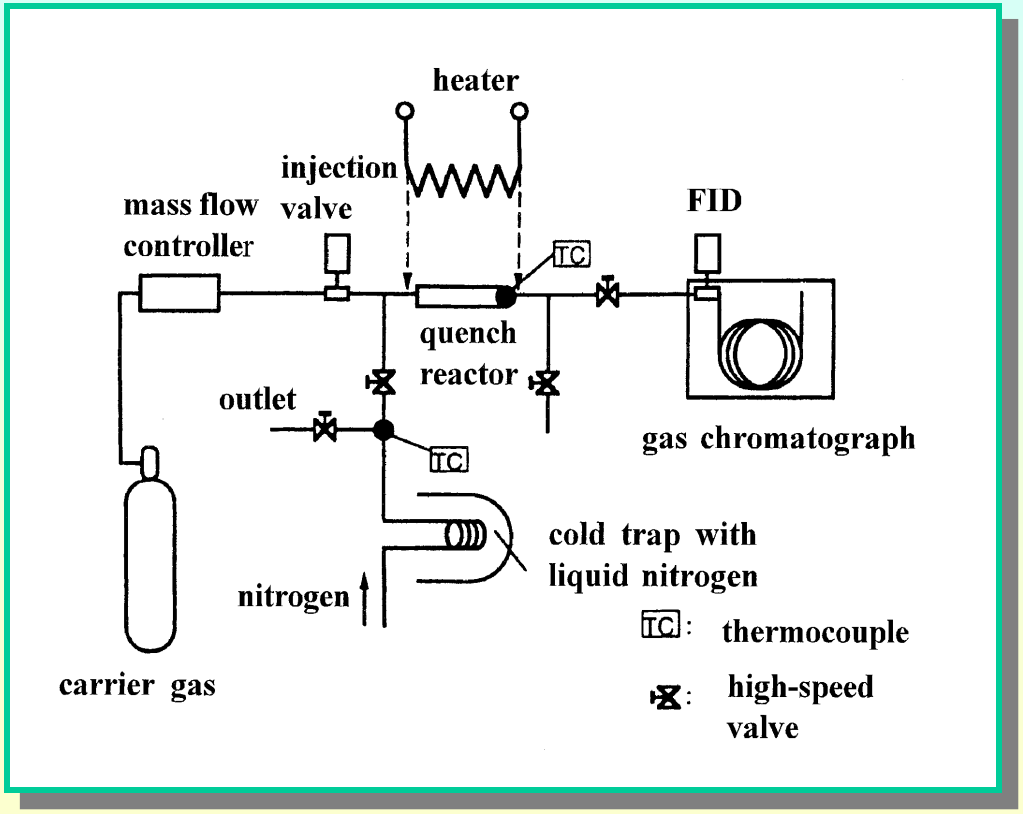
- flow experiments, *in situ* reaction
  - continuous injection of reactants into the MAS NMR rotor reactor
  - high-temperature solid-state NMR probes

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

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**

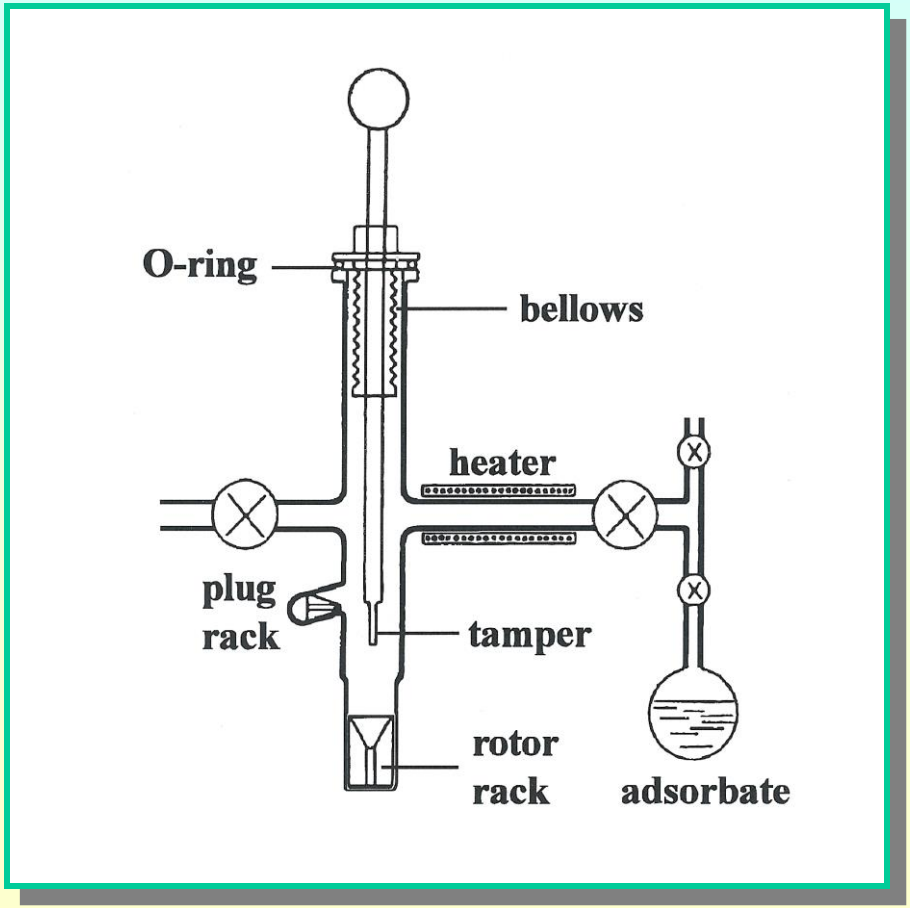
- **NMR investigations:**
  - **transfer of the catalyst loaded with reaction products into an MAS NMR rotor**
  - **measurements performed at room temperature**



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

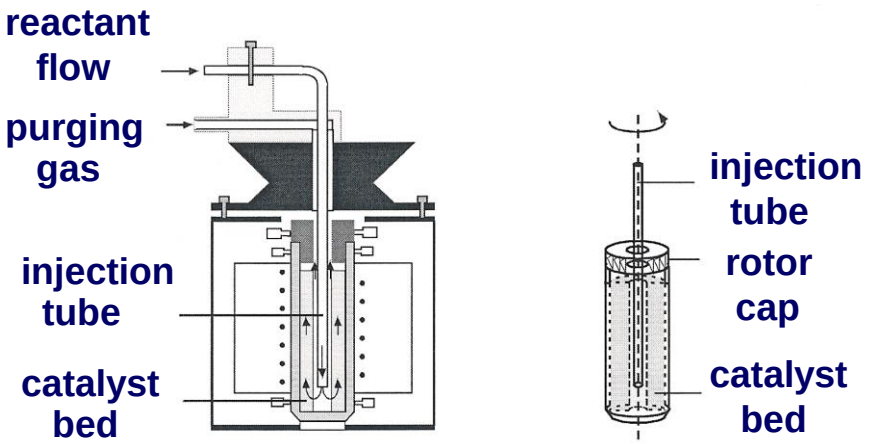
Approach for batch and continuous-flow experiments in an external reactor

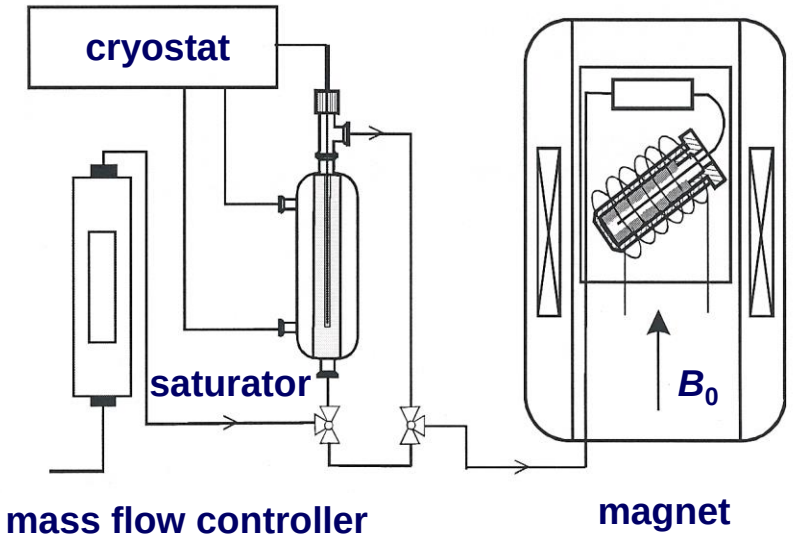
- apparatus for evacuation, loading and catalysis on solid materials in an external reactor
- no contact to air during the transfer of the catalyst material into an MAS NMR rotor
- sealing of the MAS NMR rotor inside the apparatus



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

Continuous-flow (CF) MAS NMR technique

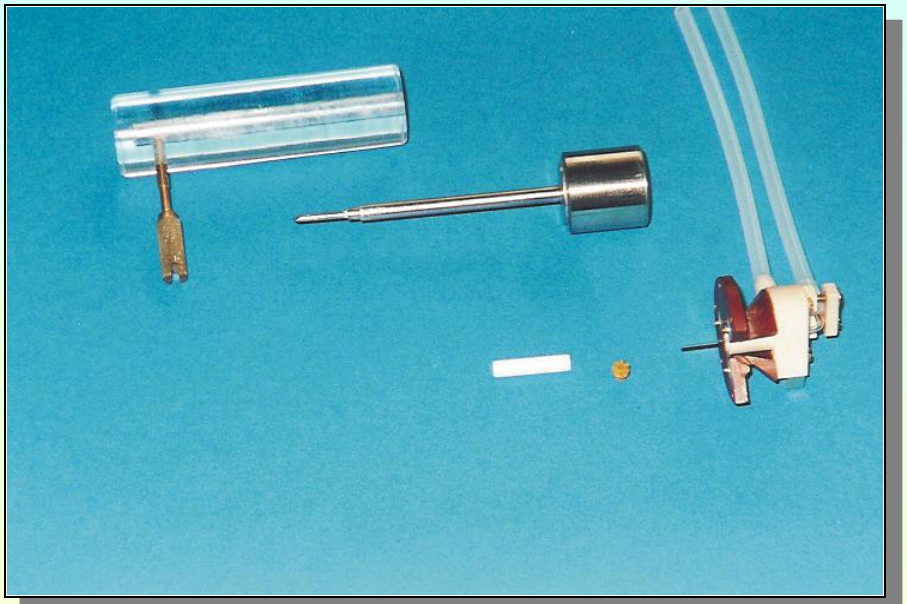


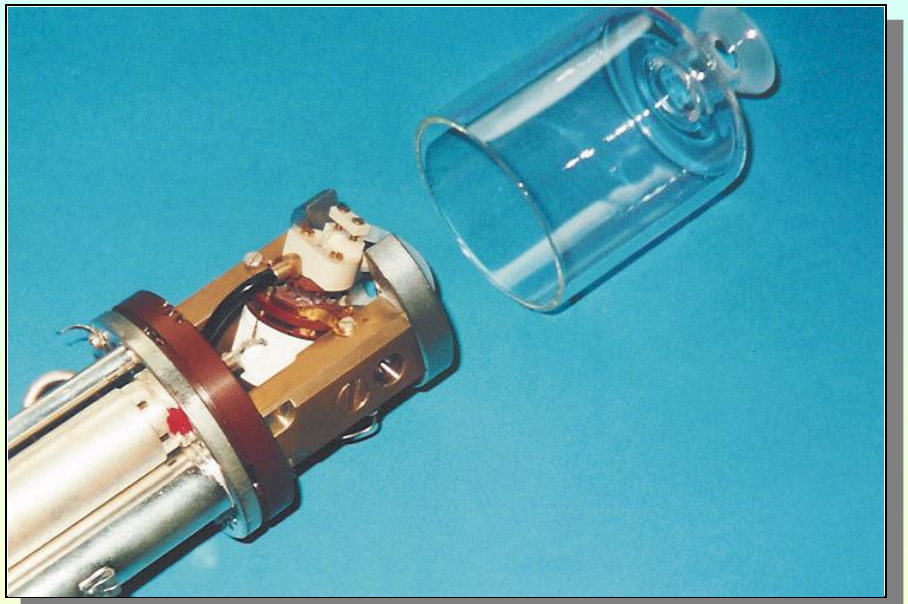


- **continuous injection of reactants into a spinning MAS NMR rotor reactor (*T* < 923 K)**

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 $Pb(NO_3)_2$:**

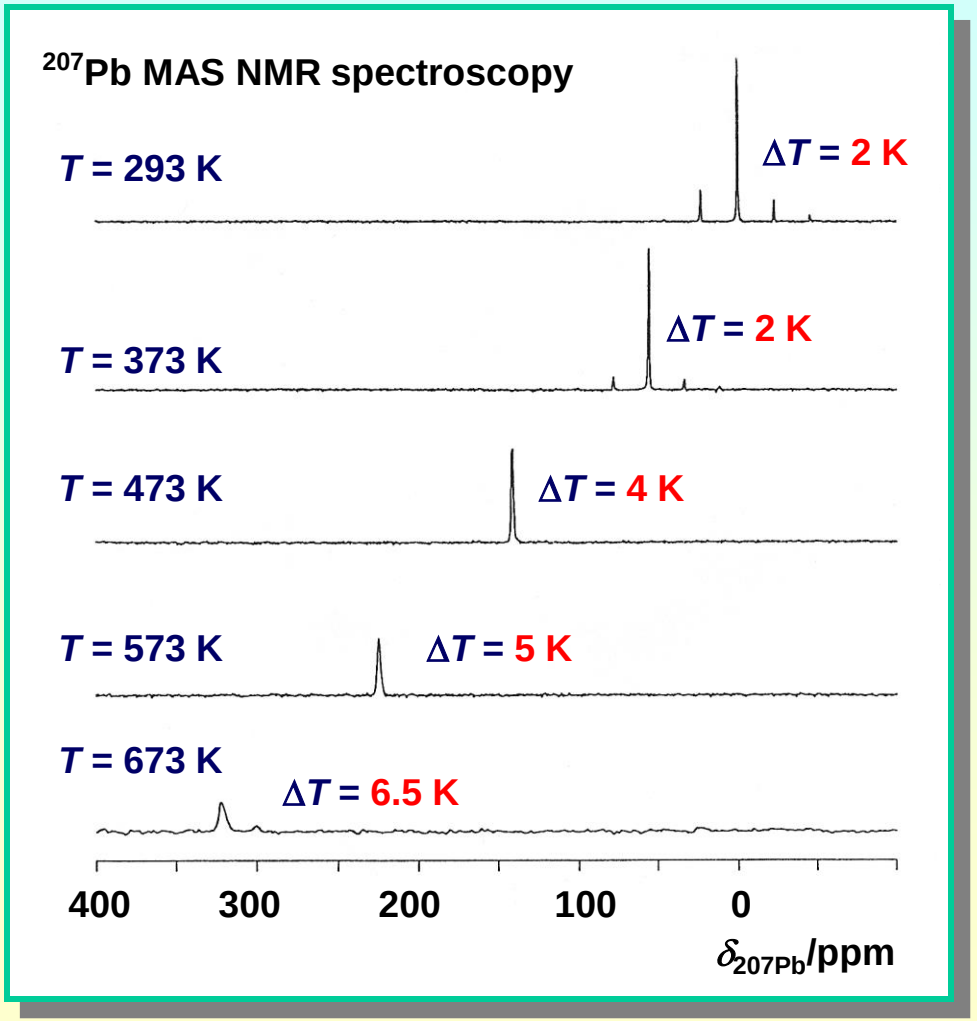
  $\Delta T / \Delta\delta$ = 1.29 K / ppm *

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

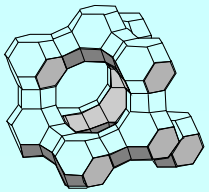
  ν_0 = 83.2 MHz

  ν_{rot} = 2.5 kHz

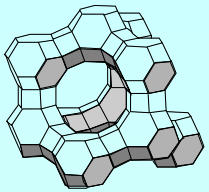
  F_{N2} = 15 ml/min



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

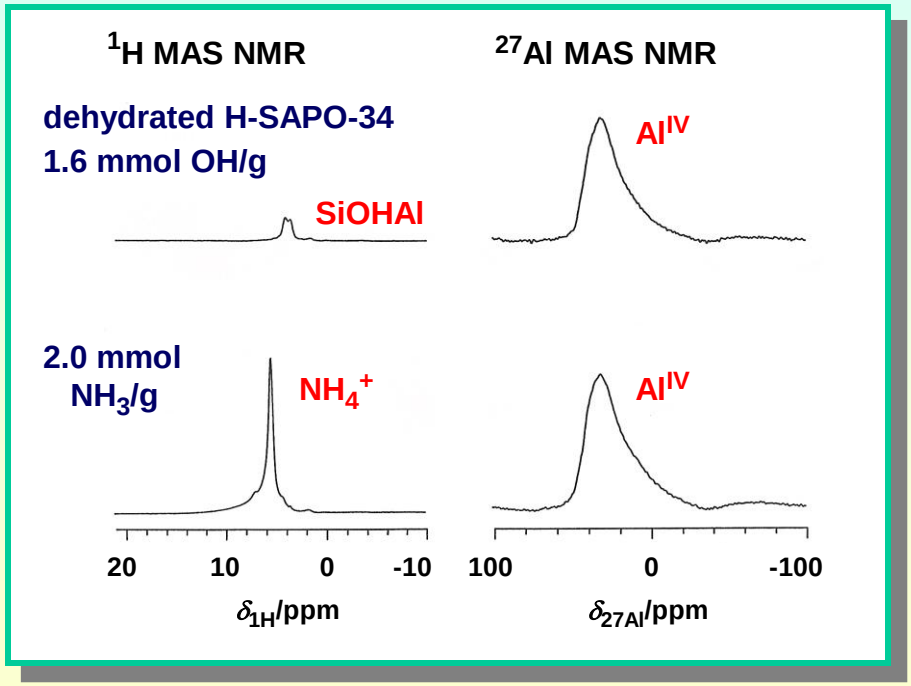


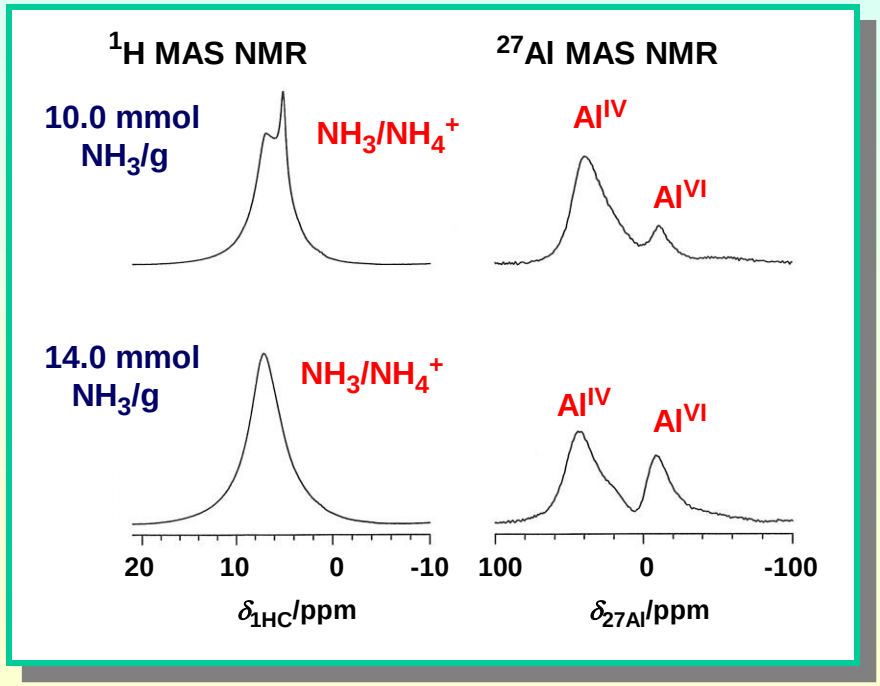
Investigation of the catalyst framework and of surface sites under in situ conditions



Ammoniation of H-SAPO-34

- **stabilizing effect of ammonia on H-SAPO-34 (Mees et al., Chem. Commun. (2003) 44)**

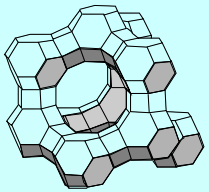




$$SiOHAl + NH_3^{gas} \rightarrow SiOAl^-(NH_4)^+$$

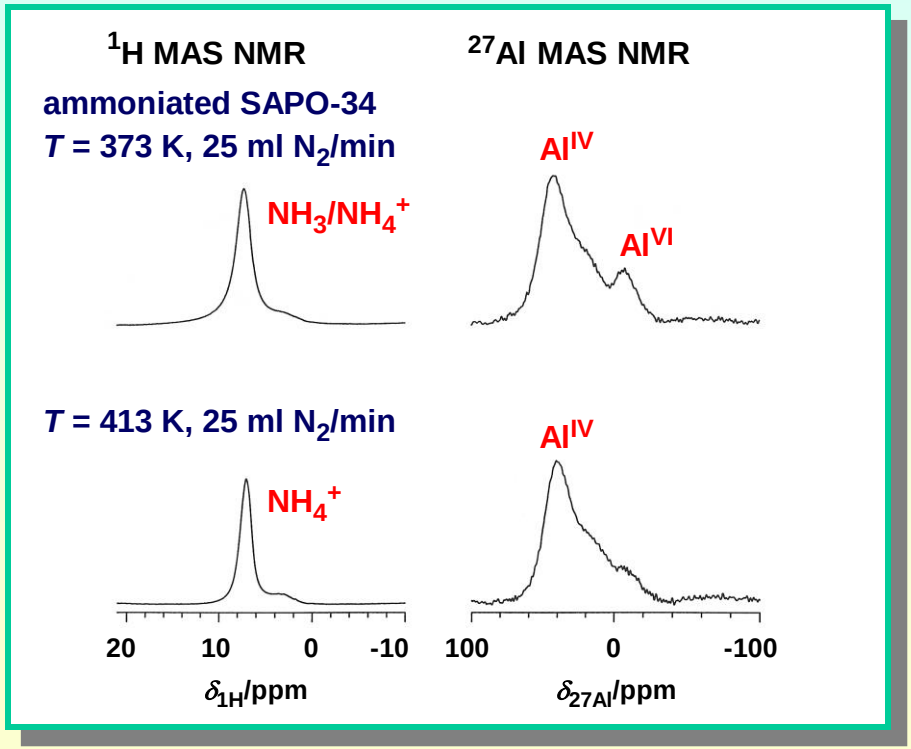
$$Al^{IV} + n\ NH_3^{gas} \rightarrow Al^{VI}(n\ NH_3^{coord})$$

A. Buchholz et al., J. Phys. Chem. B, submitted.

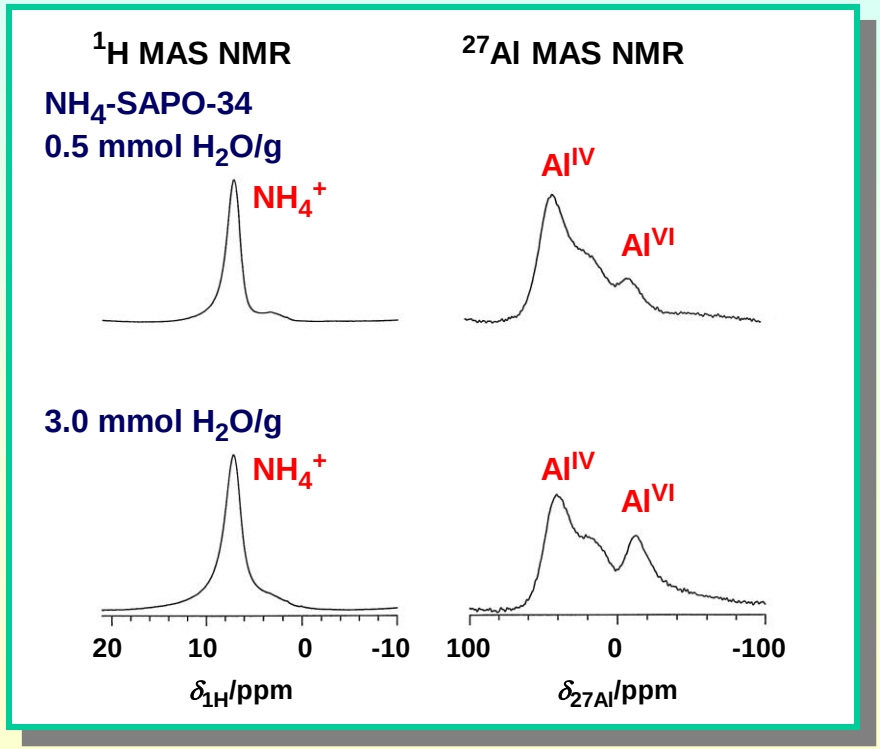


Ammoniation of H-SAPO-34

- **reversibility of framework ammoniation**



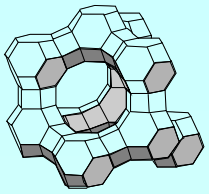
- **influence on the hydration behavior**



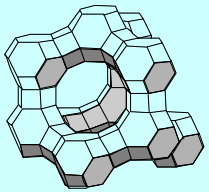
$Al^{VI}(n\ NH_3^{coord}) \rightarrow Al^{IV} + n\ NH_3^{gas}$

$Al^{IV} + n\ H_2O^{gas} \rightarrow Al^{VI}(n\ H_2O^{coord})$

A. Buchholz et al., J. Phys. Chem. B, submitted.

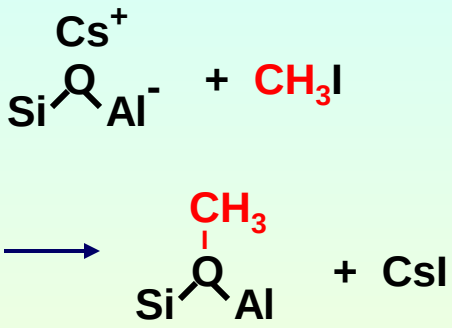


Investigation of base sites and of reactions catalyzed by basic zeolites



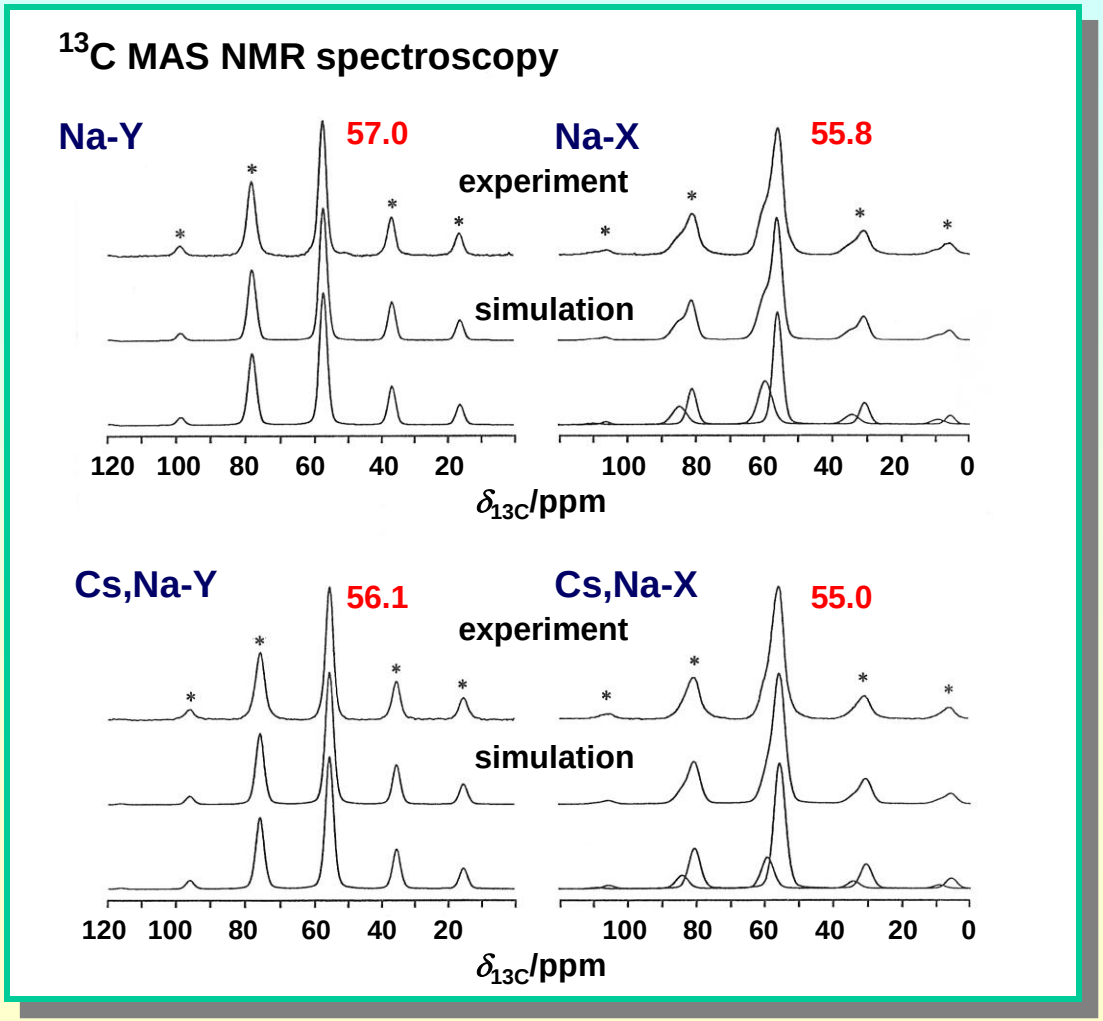
Characterization of basic zeolites under reaction conditions

- 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



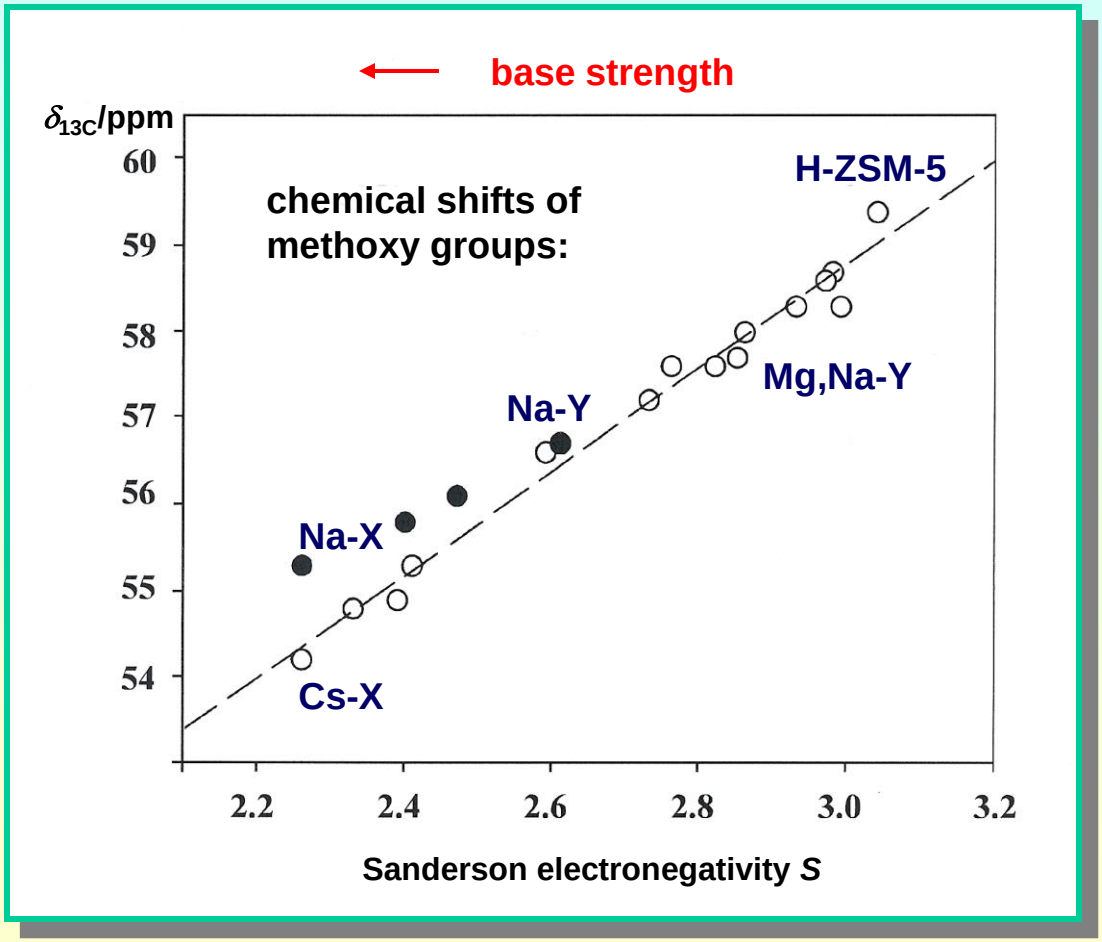
U. Schenk, PhD thesis, University of Stuttgart, 2001.

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**

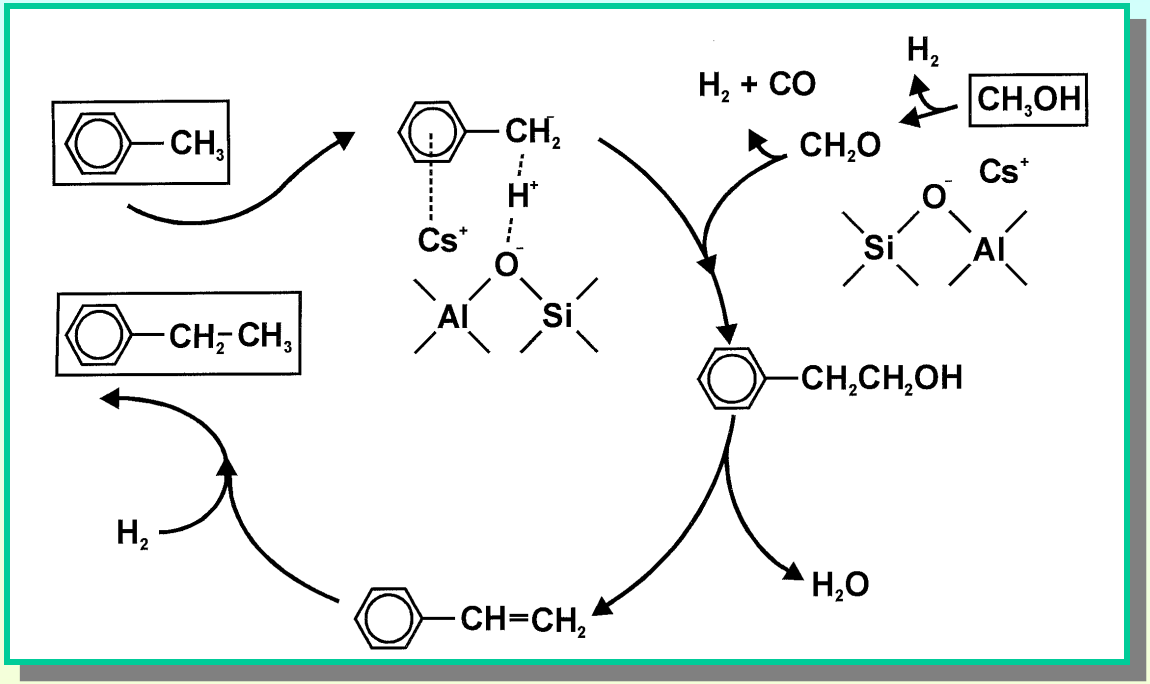


V. Bosacek et al., Z. Phys. Chem. 189 (1995) 241.

Side-chain alkylation of toluene with methanol on basic zeolites

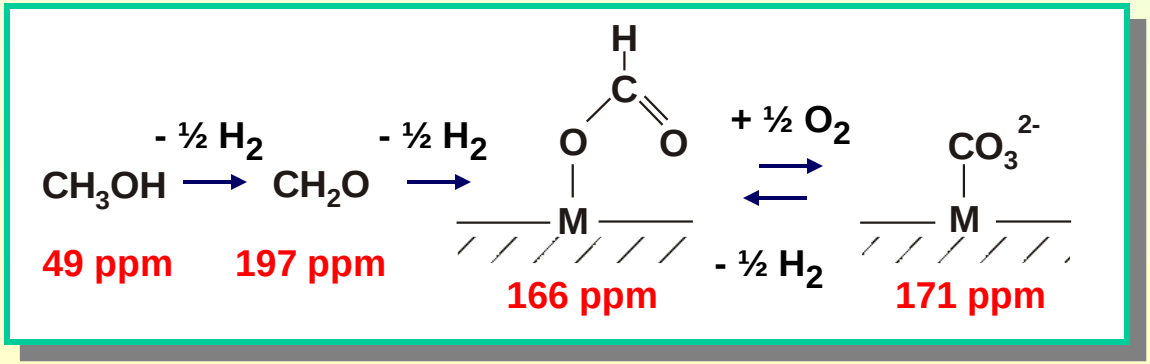
- **reaction scheme proposed by Yashima et al. , J. Catal. 26 (1972) 303:**

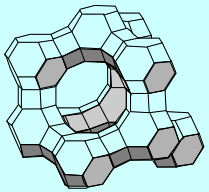
  - activation of toluene by adsorption on the zeolite
  - conversion of methanol to formaldehyde catalyzed by base sites



- **proposed surface species:**

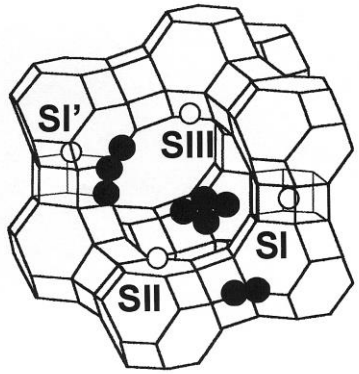
  - formate (δ_{13C} = 166 ppm)
  - carbonate (δ_{13C} = 171 ppm)





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

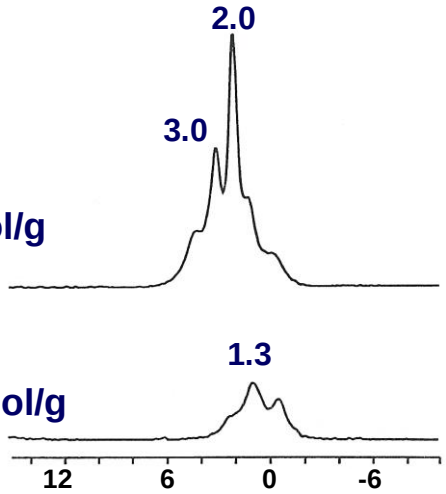
- **zeolite Na-X (n_{Si}/n_{Al} = 1.4) exchanged with cesium cations (55 %) and impregnated with cesium hydroxide (24 CsOH/u.c.)**



cations

guest species

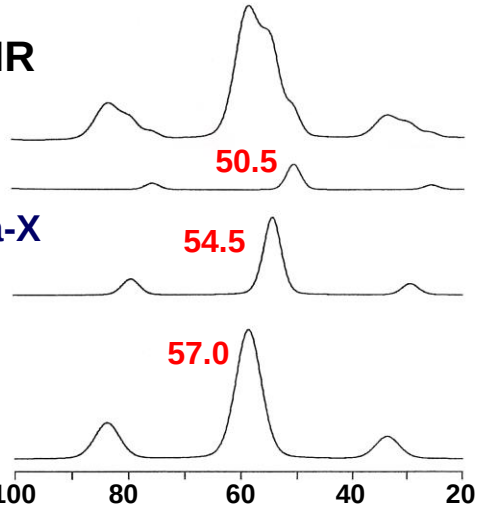
^{1}H MAS NMR



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

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

^{13}C MAS NMR



spectrum

methoxy 1

CsOH/Cs,Na-X
+ CH_3I

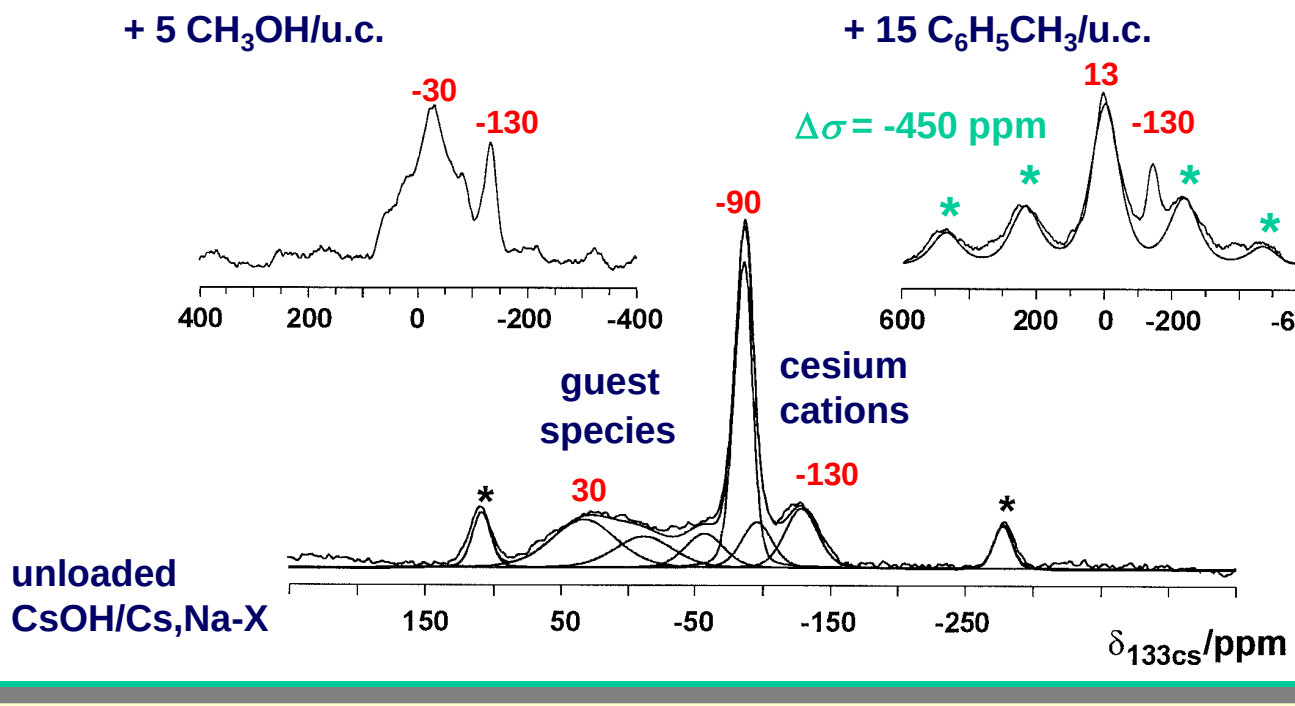
methoxy 2

methoxy 3

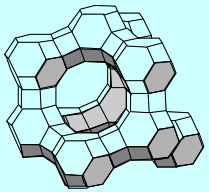
U. Schenk, PhD thesis, University of Stuttgart, 2001.

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**

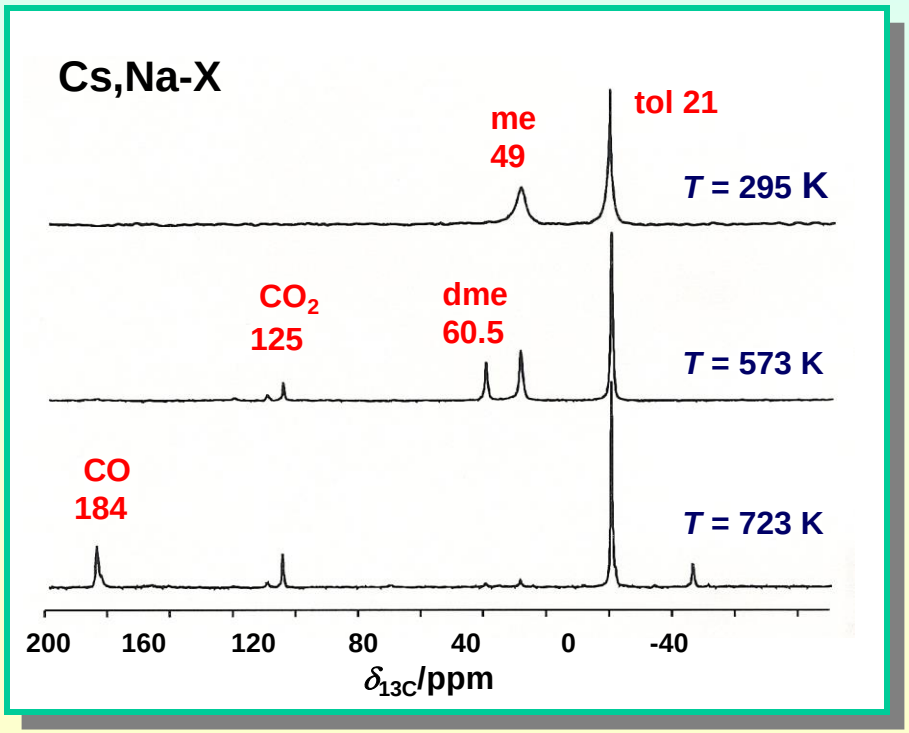


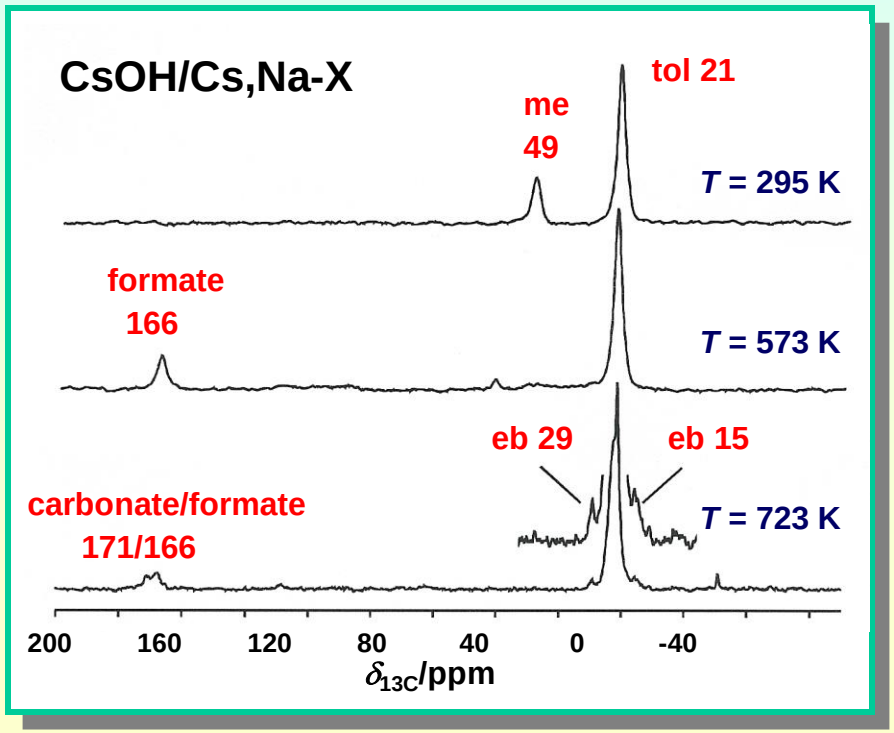
M. Hunger et al., J. Mol. Catal. A: Chem. 136 (2000) 123



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. 158 (2000) 123

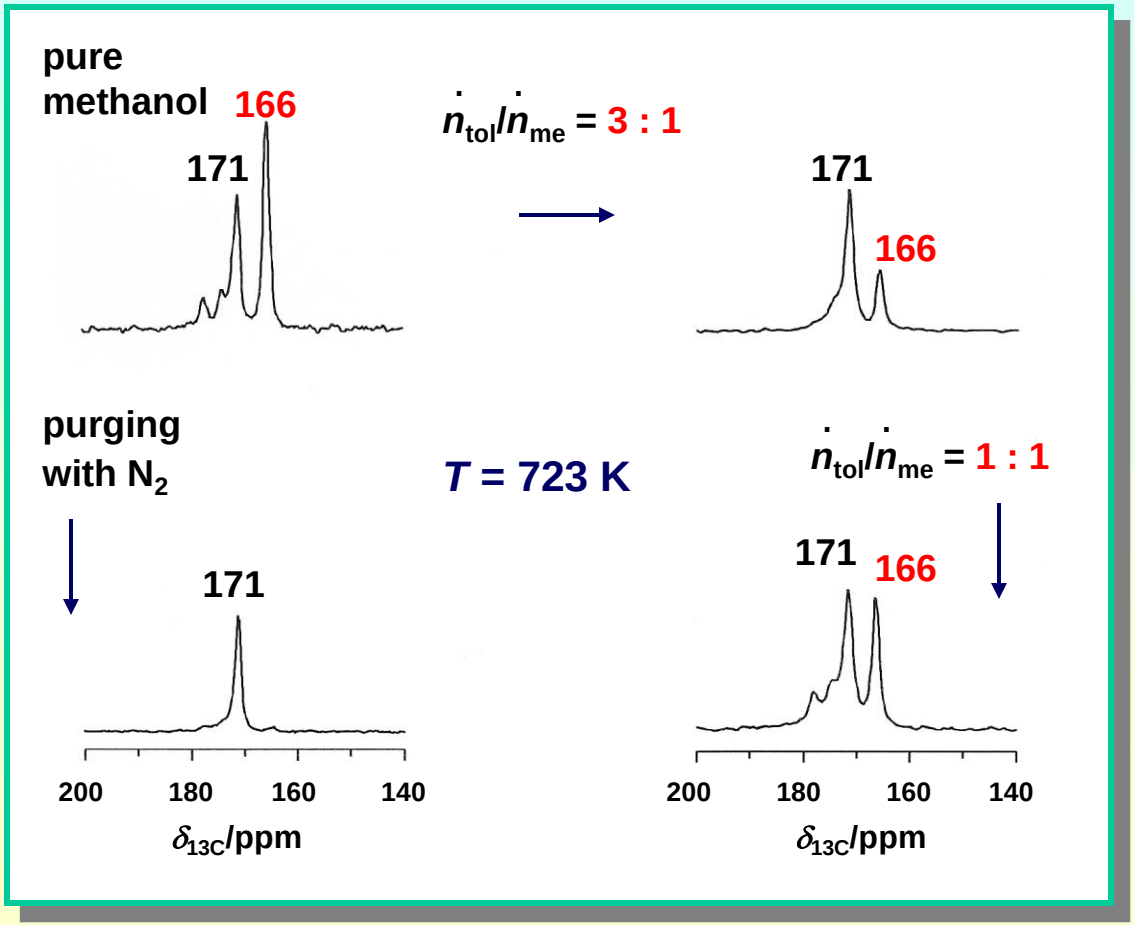
Reactivity of formate species on zeolite CsOH/Cs,Na-X under flow conditions

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

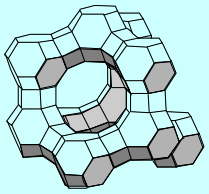
  W_{cat}/F_{me} = 60 gh/mol

  → **carbonate species are chemically stable**

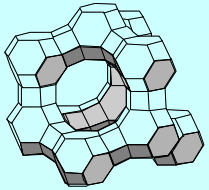
  → **formate species are consumed by toluene which indicates a high reactivity**



M. Hunger et al., J. Mol. Catal. A: Chem. 158 (2000) 233

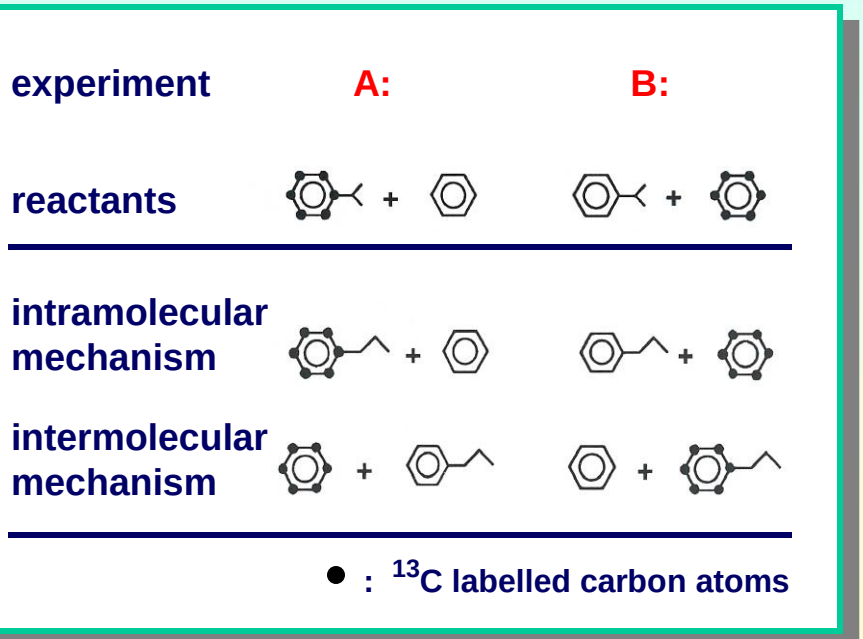


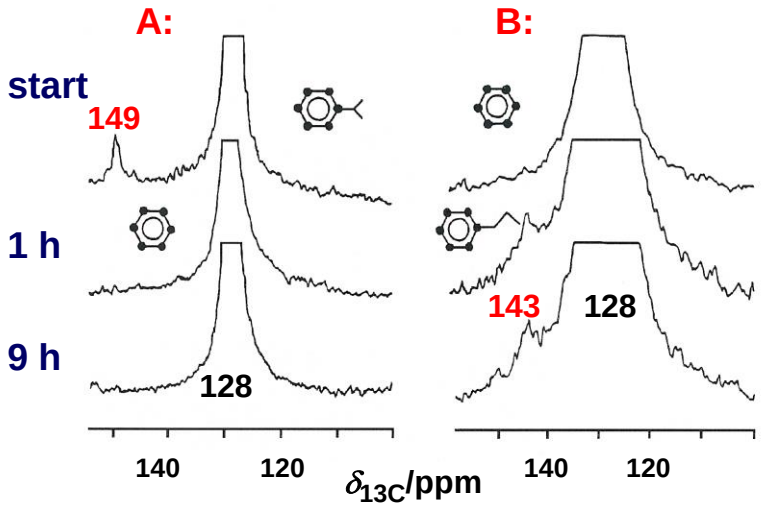
Investigation of reactions catalyzed by acidic zeolites



Investigation of reaction pathways by selectively labelled reactants

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



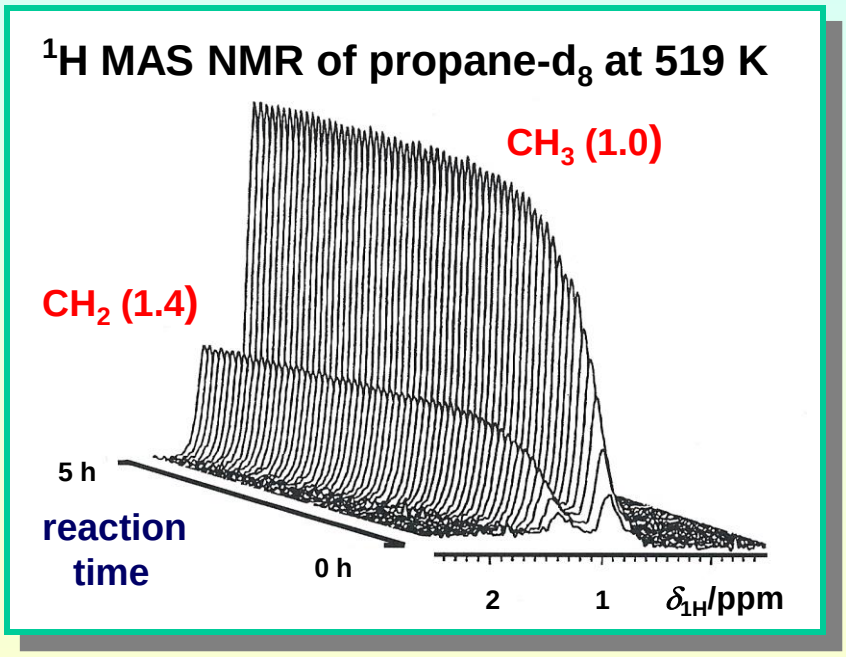


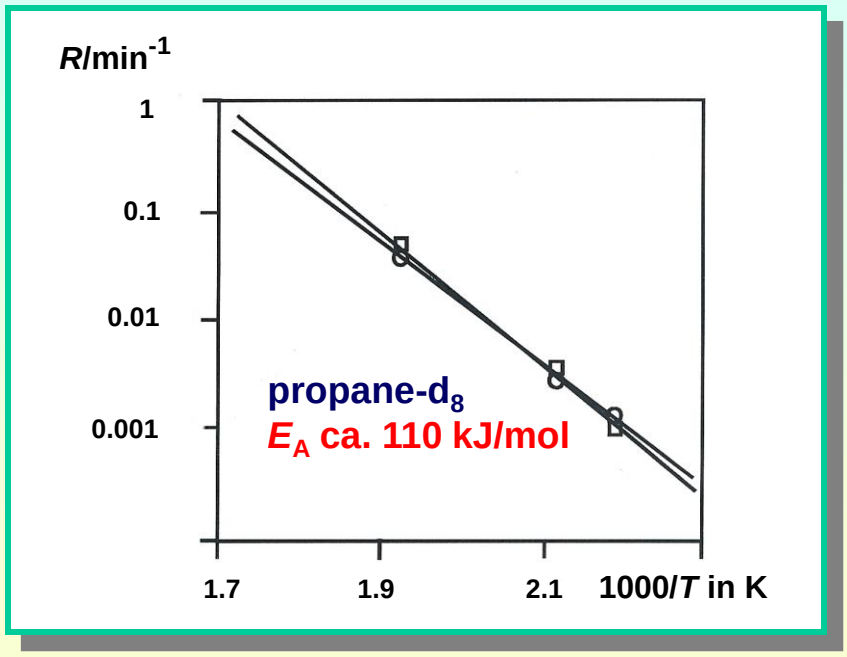
→ experiments A and B indicate an intermolecular reaction mechanism

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





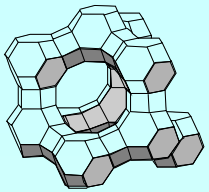
A:
- no regiospecific H/D exchange
- E_A of ca. 110 kJ/mol

→ no formation carbenium ions

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

→ formation carbenium ions

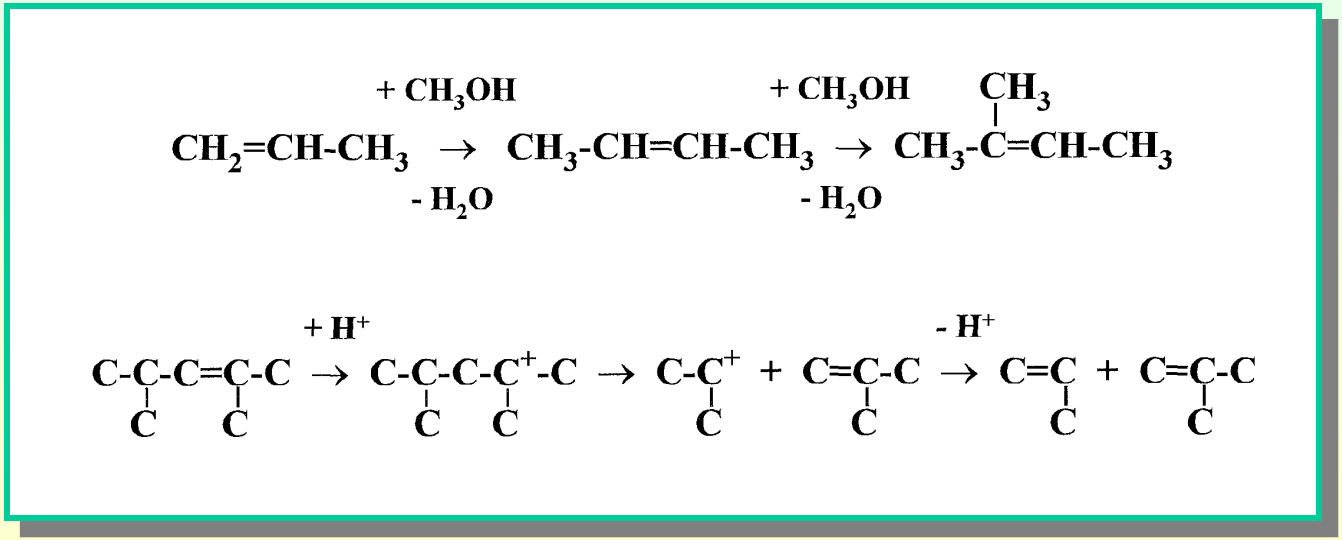
A.G. Stepanov et al., Catal. Lett. 54 (1998) 1; J. Sommer et al., J. Catal. 181 (1999) 265.



Methanol to olefin (MTO) conversion on acidic zeolites

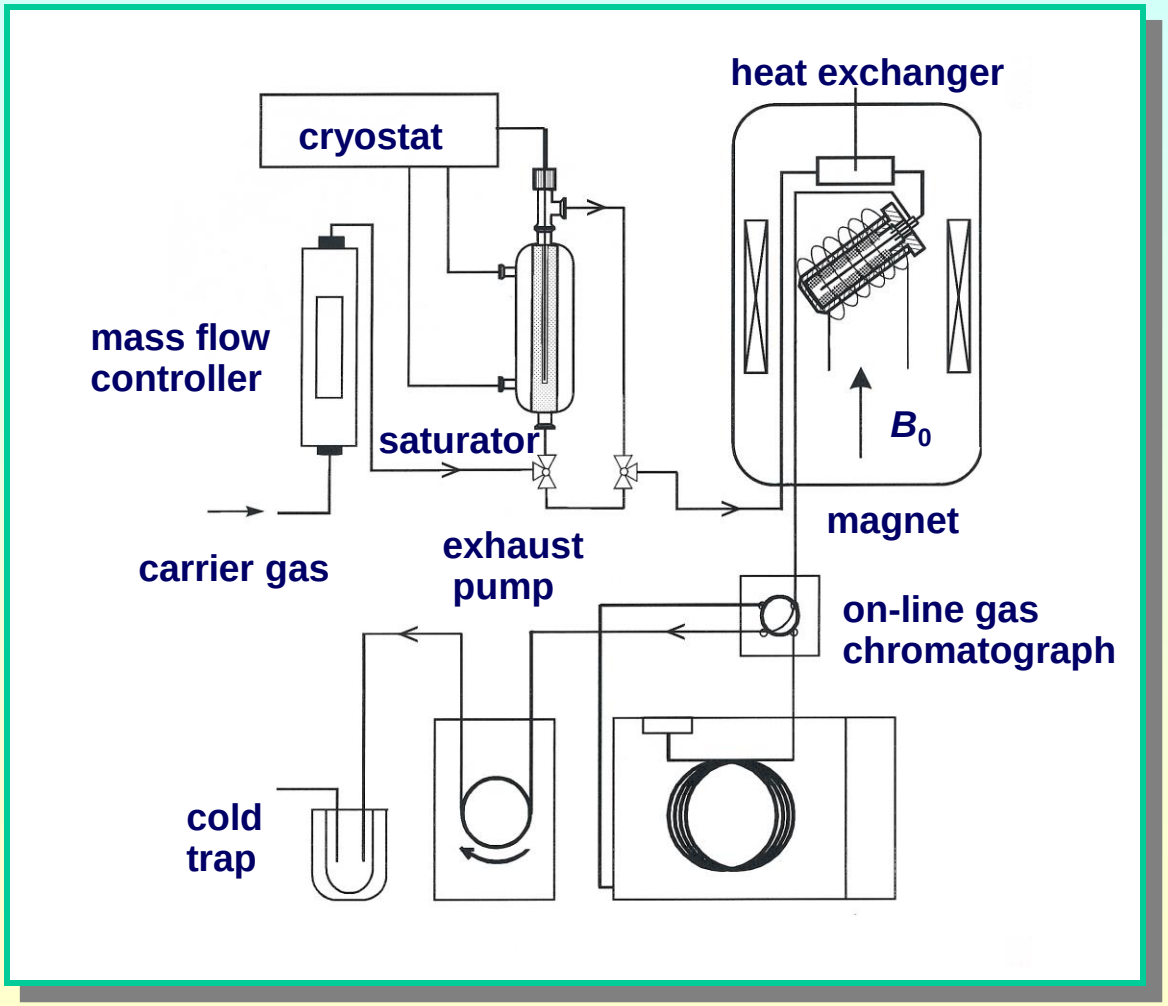
reaction mechanisms proposed in the literature:

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



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

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

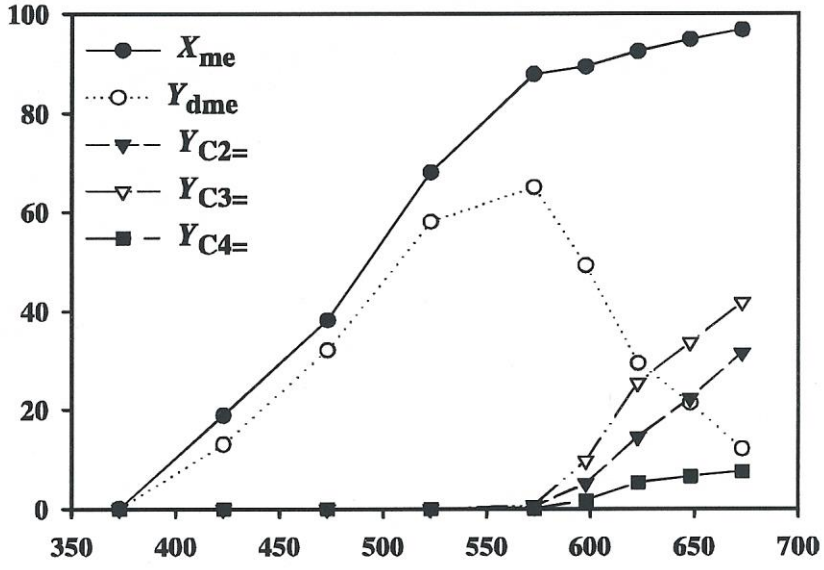


M. Hunger et al., Catal. Lett. 57 (1999) 199.

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

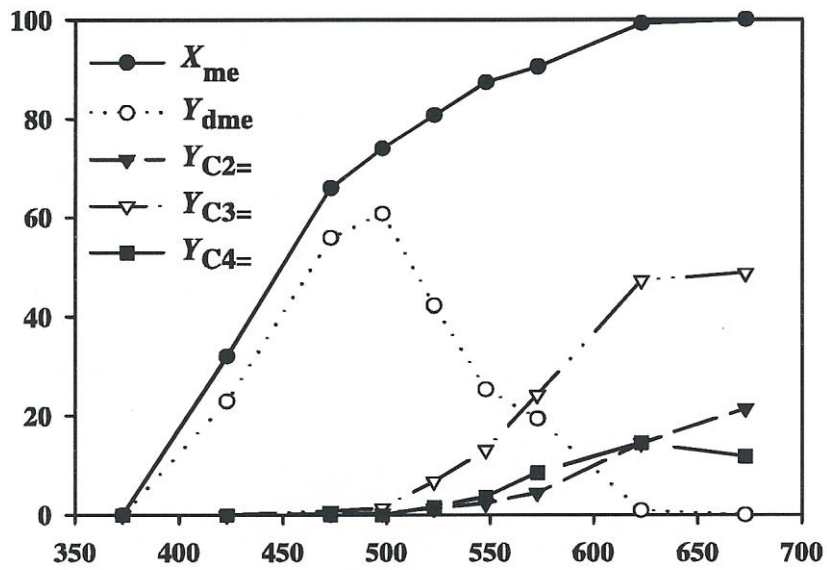
fixed-bed reactor

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

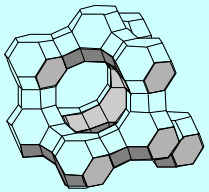


spinning (2 kHz) MAS NMR rotor reactor

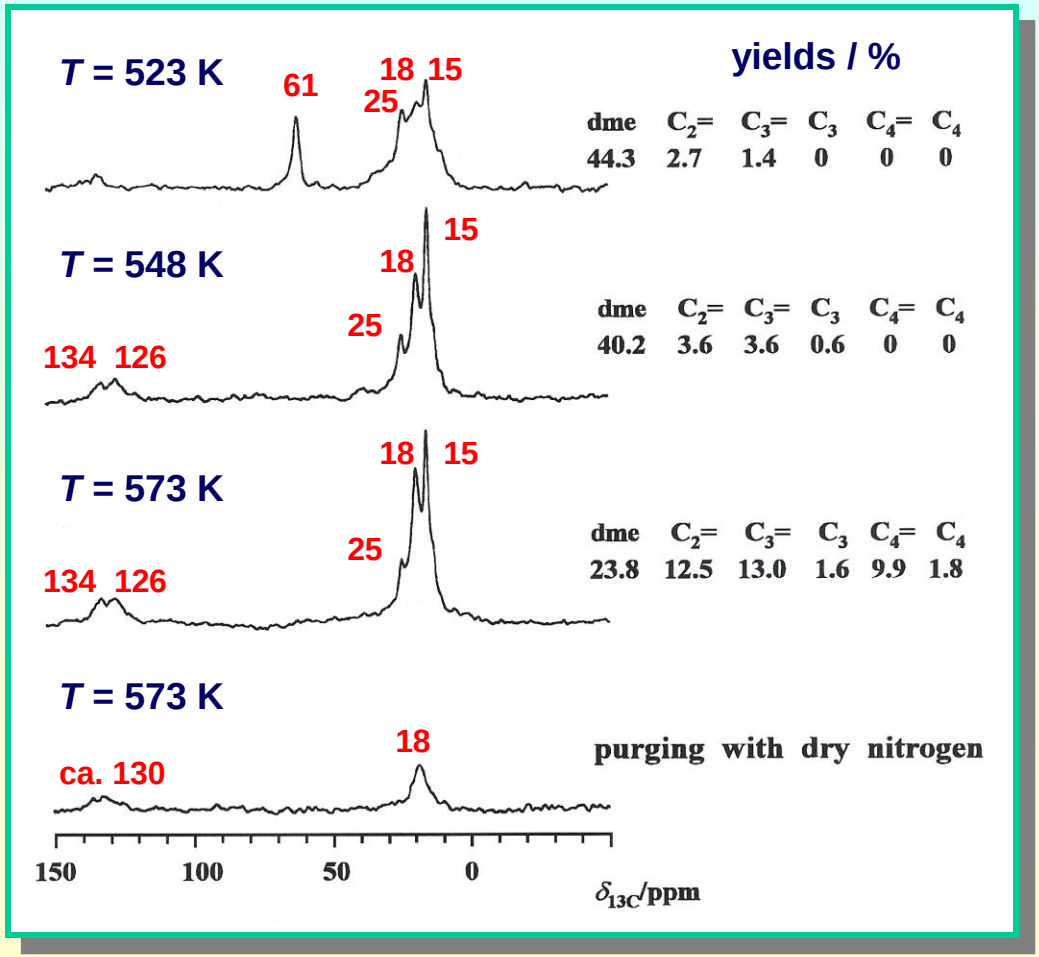
W_{cat}/F_{me} = 25 gh/mol



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



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



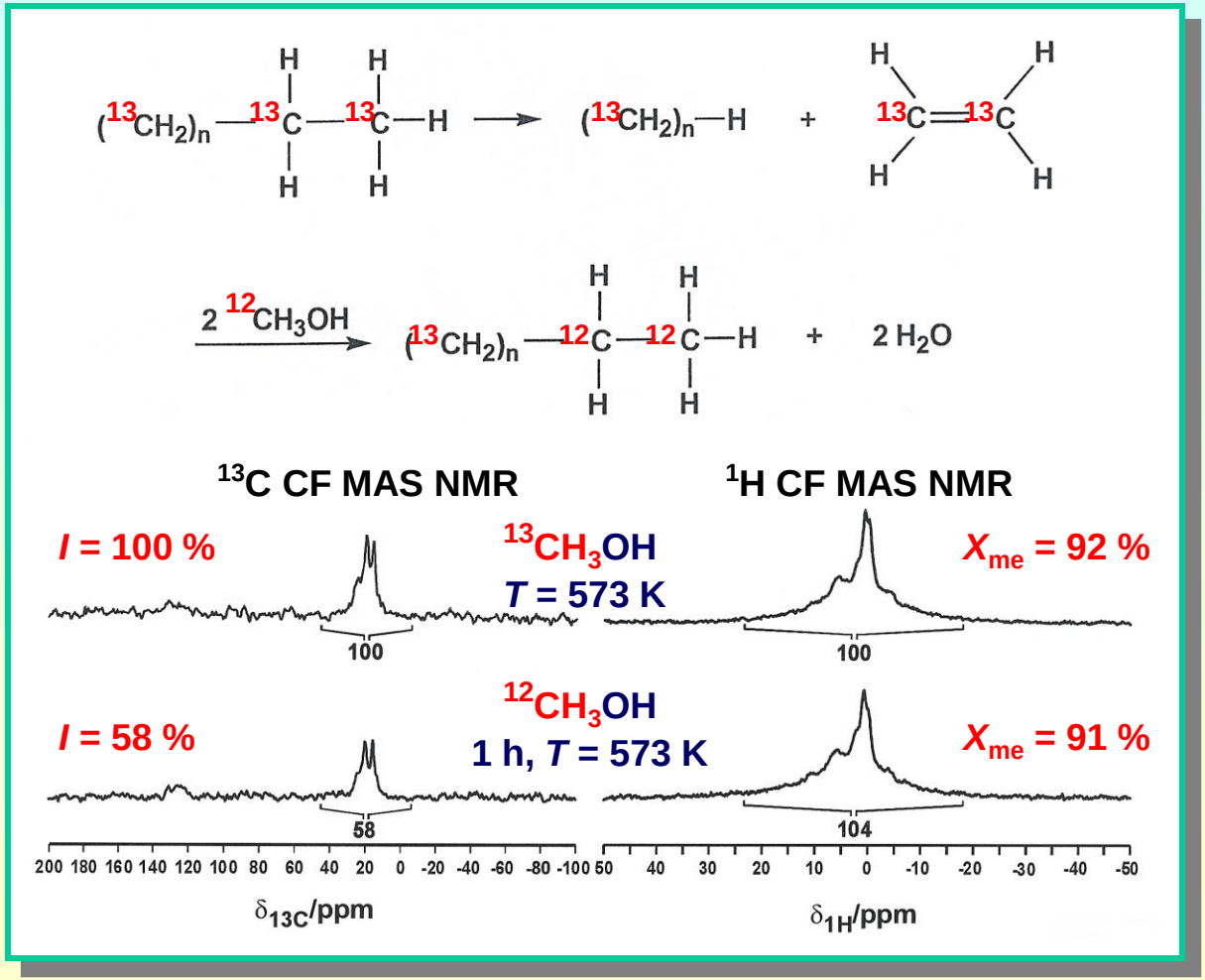
→ **aliphatic intermediates, e.g.:**
- 3-hexene (14.4, 25.9, 131.2 ppm)
- 2,3-hexadiene (17.5, 126.2, 132.5 ppm)
- ....

→ **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.

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

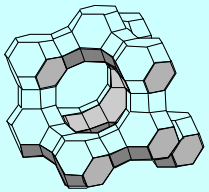


switching of the reactant flow induces a decrease of the ^{13}C-isotopes in the alkyl groups:

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

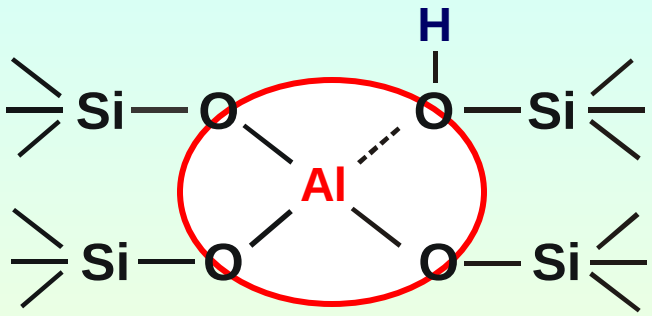
→ **carbon pool plays an active role in the MTO process**

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



State of SiOHAl groups in H-ZSM-5 during the MTO process

reactant / adsorbat



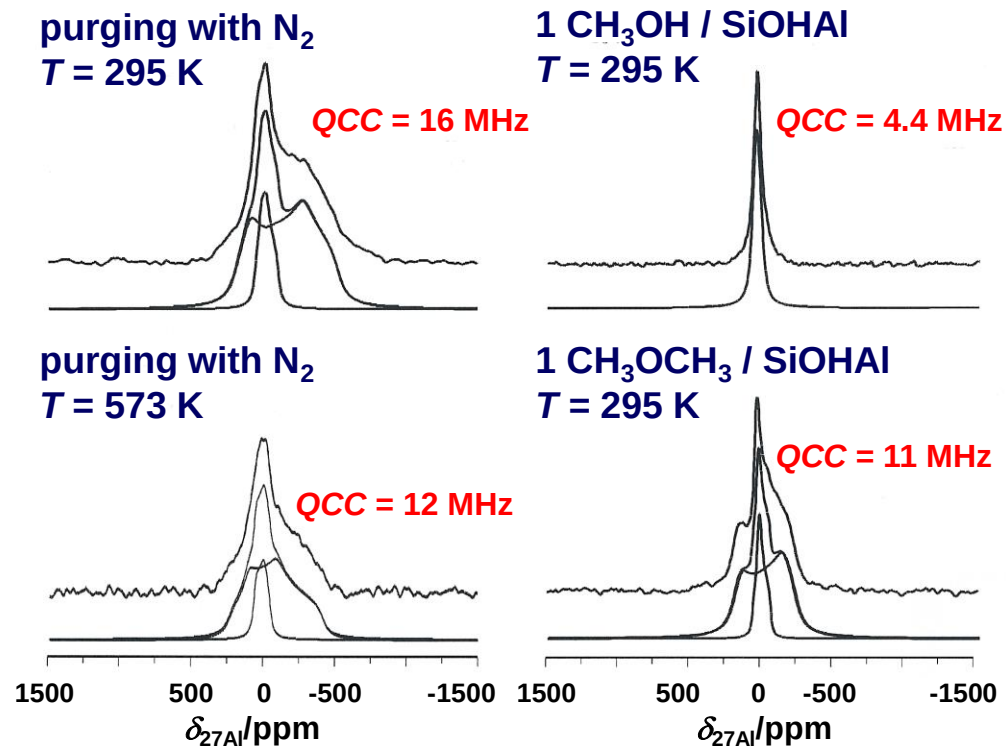
- electric field gradient :

$$V_{zz} = eq$$

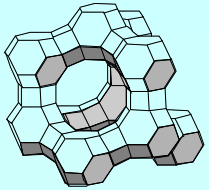
- quadrupole coupling constant:

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

^{27}Al spin-echo NMR experiments



M. Seiler et al., J. Phys. Chem. B 105 (2001) 8143.



NMR parameters of ^{27}Al nuclei during the MTO process

reactant / adsorbate	*QCC*	$\Delta\nu_{1/2}^{MAS}$*
calcined H-ZSM-5	16 MHz	36 kHz / 350 ppm
methoxy/H-ZSM-5	13 MHz	25 kHz / 235 ppm
1 CH_3OCH_3/SiOHAl	11 MHz	17 kHz / 165 ppm
1 CH_3OH/SiOHAl	4.4 MHz	2.8 kHz / 26.5 ppm
n H_2O/H-ZSM-5	2.0 MHz	0.6 kHz / 5.5 ppm

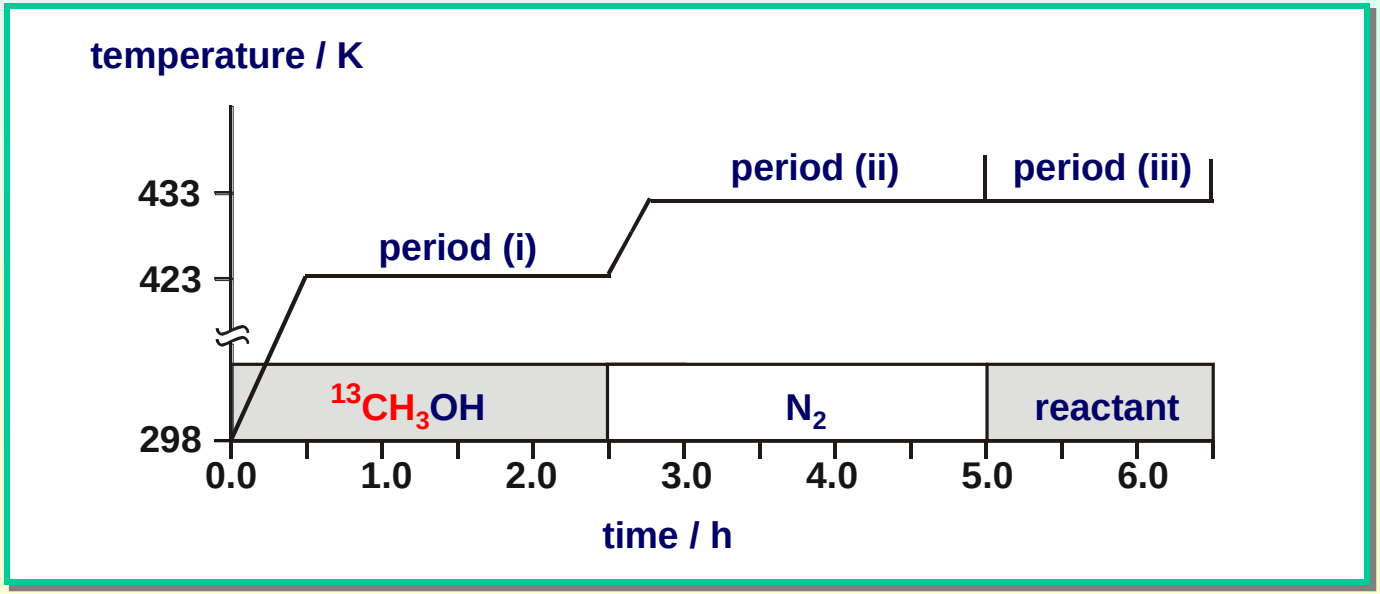
*: B_0 = 9.4 T

→ absence of narrow ^{27}Al MAS NMR signals indicates that no adsorption of CH_3OH and H_2O occurs at SiOHAl groups under reaction conditions

M. Seiler et al., J. Phys. Chem. B 105 (2001) 8143;
Wang et al., Chem. Phys. Lett. 370 (2003) 88.

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)**

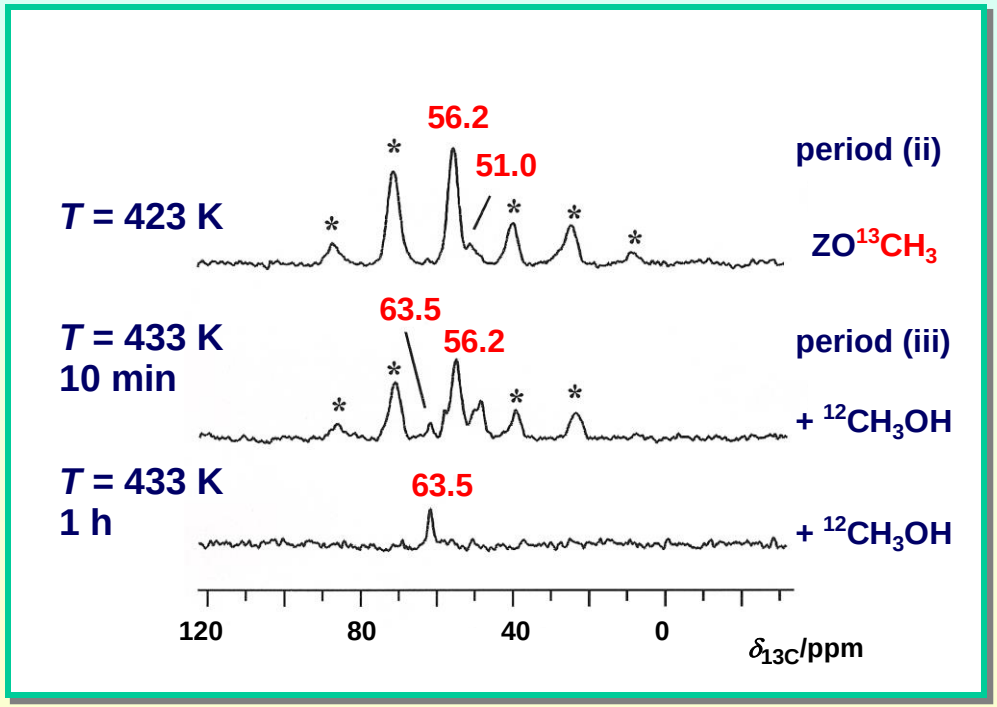


→ **investigation of the reactivity of intermediates**

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



$^{13}CH_3OH + ZOH$

49.0 ppm

$- H_2O$ →

$ZO^{13}CH_3$

56.2 ppm

$+ {}^{12}CH_3OH$ →

$- H_2O$

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

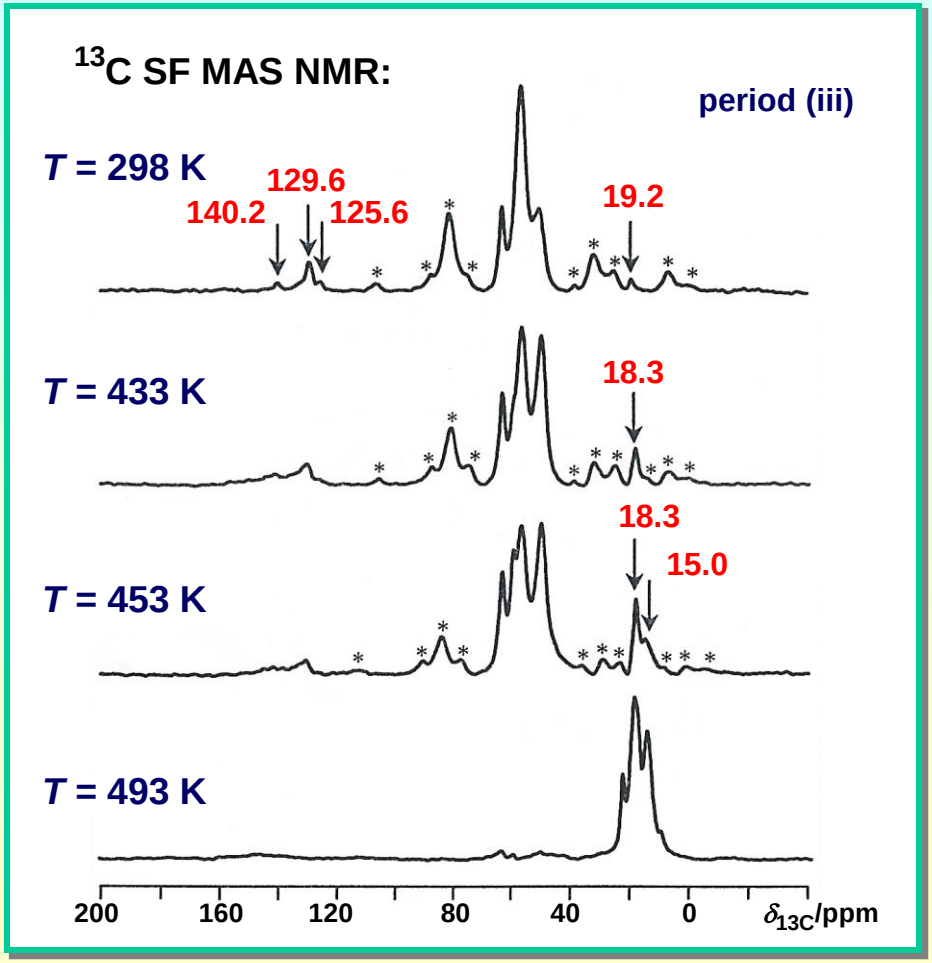
63.5 ppm

→ ^{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



56.2 ppm toluene

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

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

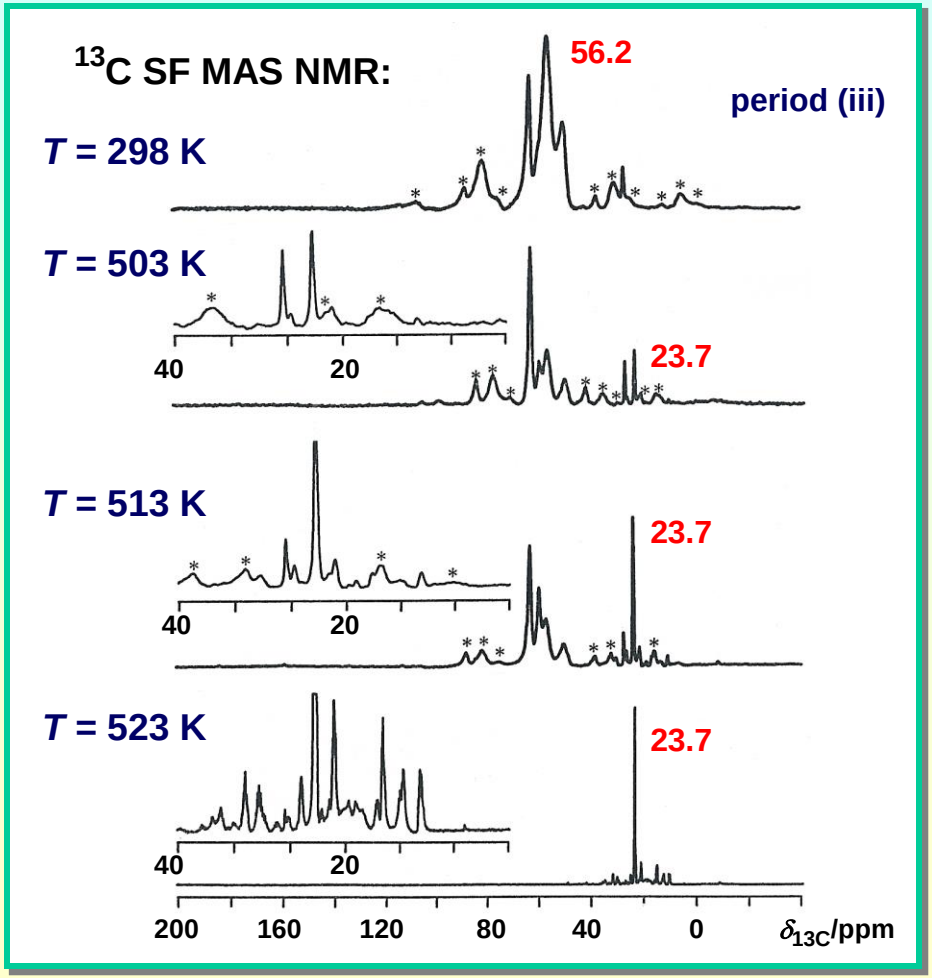
18.3 ppm

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

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

Methylation of alkanes by surface methoxy groups

- reaction of methoxy groups with cyclohexane on zeolite H-Y



56.2 ppm cyclohexane

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

$\rightarrow SiOHAl + {}^{13}CH_3C_6H_{11}$

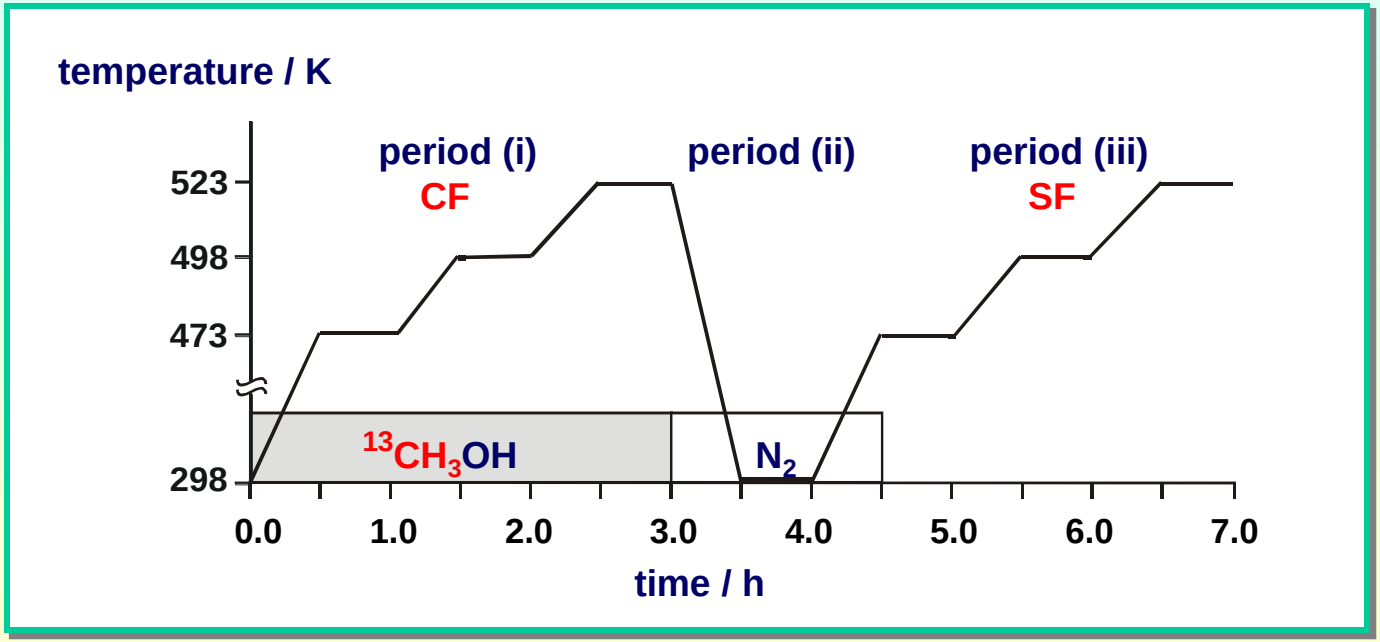
23.7 ppm

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

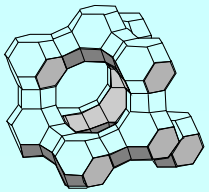
W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc., in press.

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

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

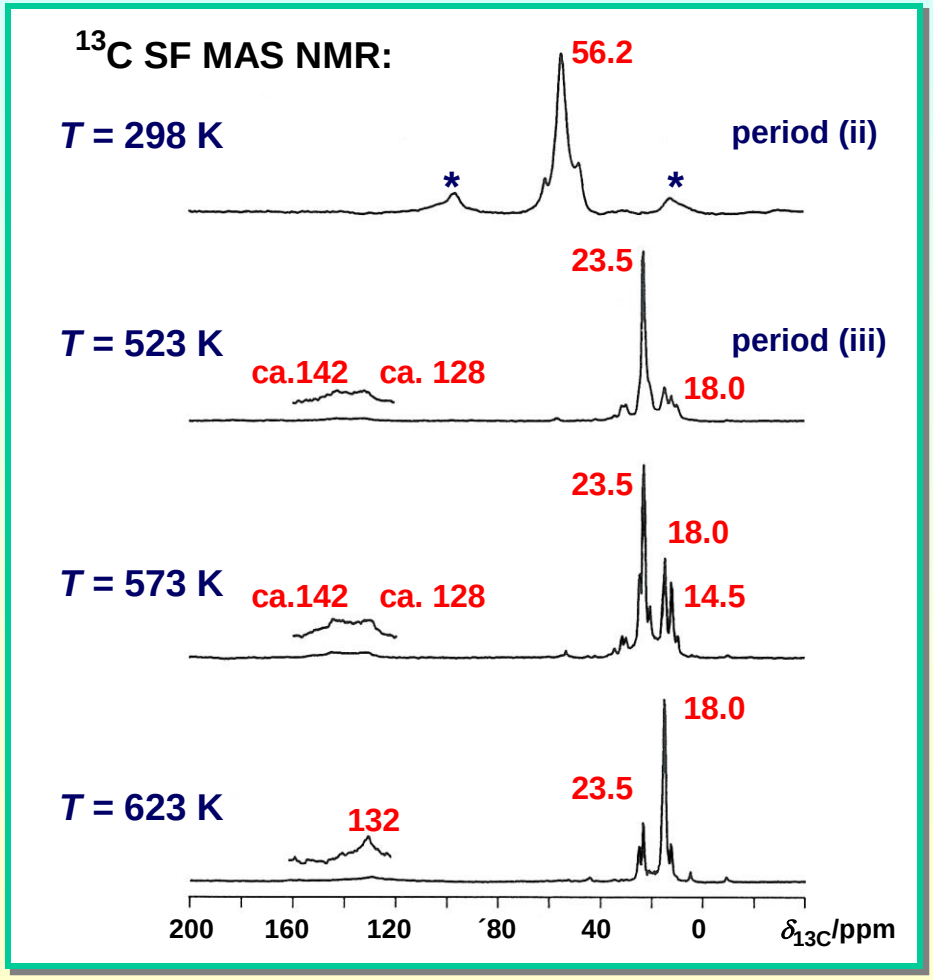


W. Wang, A. Buchholz, M. Seiler, M. Hunger, J. Am. Chem. Soc., in press.



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)
....

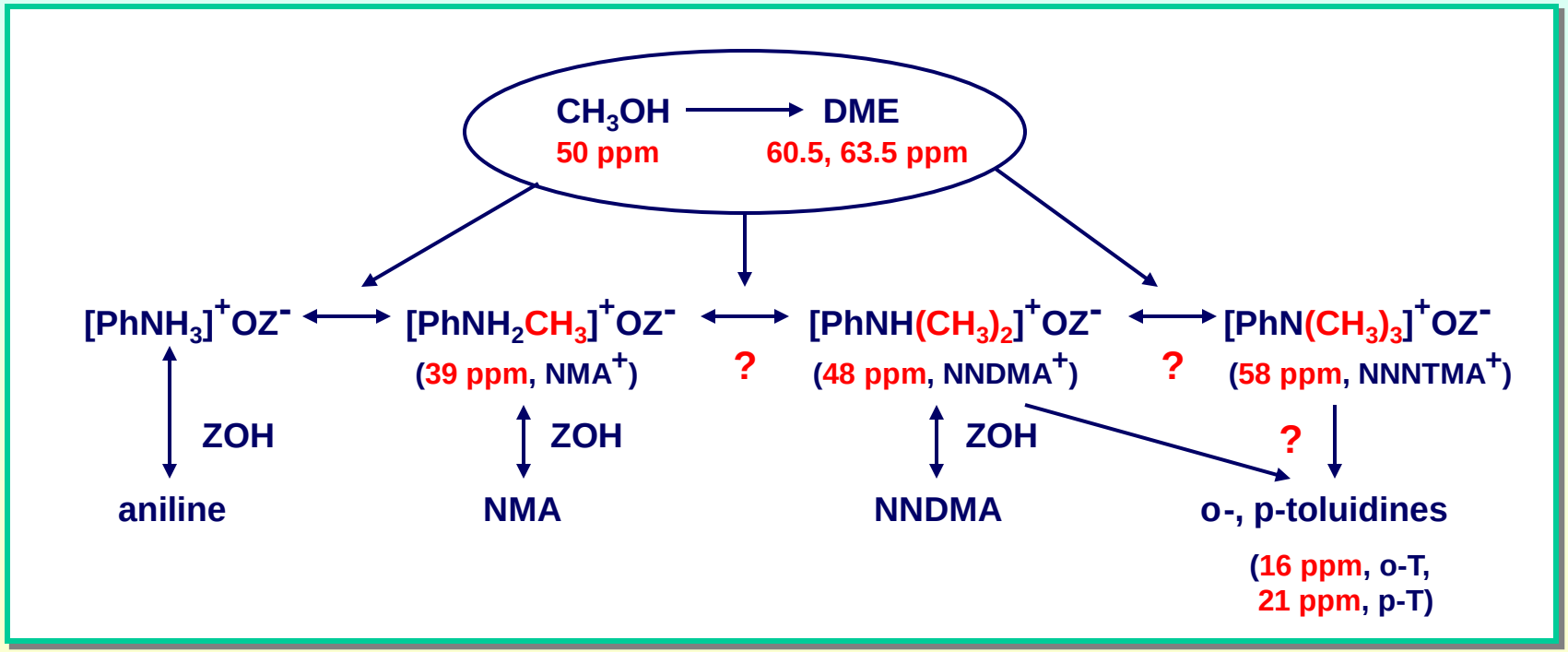
and aromatic compounds:

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

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

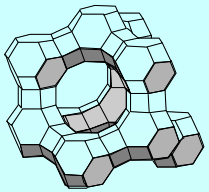
Methylation of anilin by methanol on acidic zeolites

- **protonation of methylated anilines by strong acid sites (SiOHAl) in zeolite H-Y**



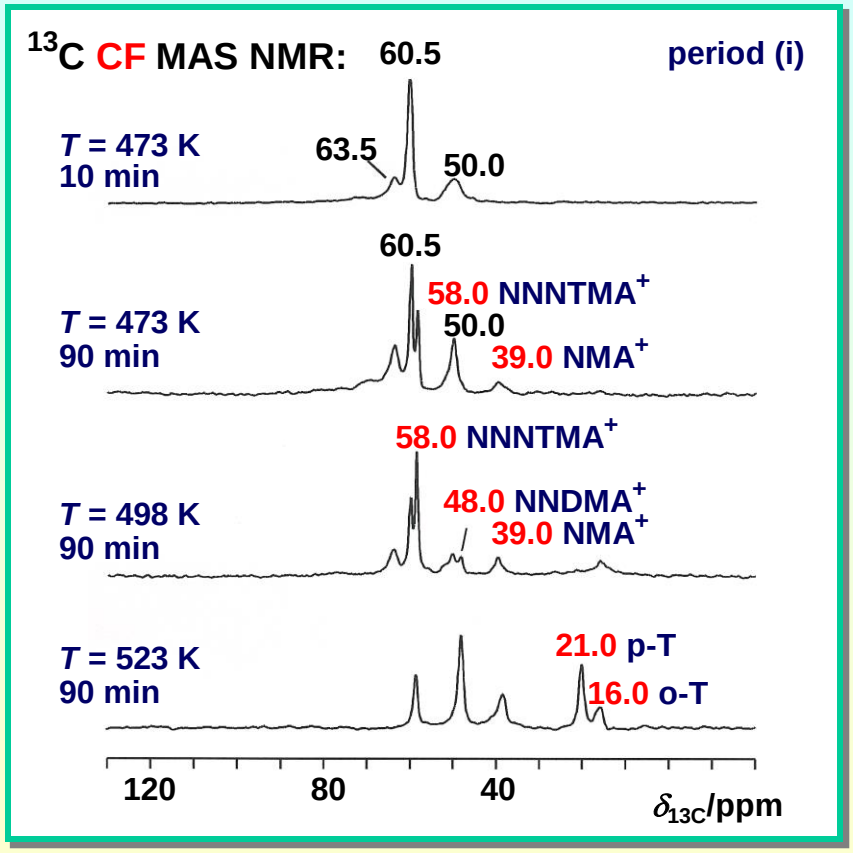
→ **are the N,N,N-trimethylanilinium cations non-reactive spectators ?**

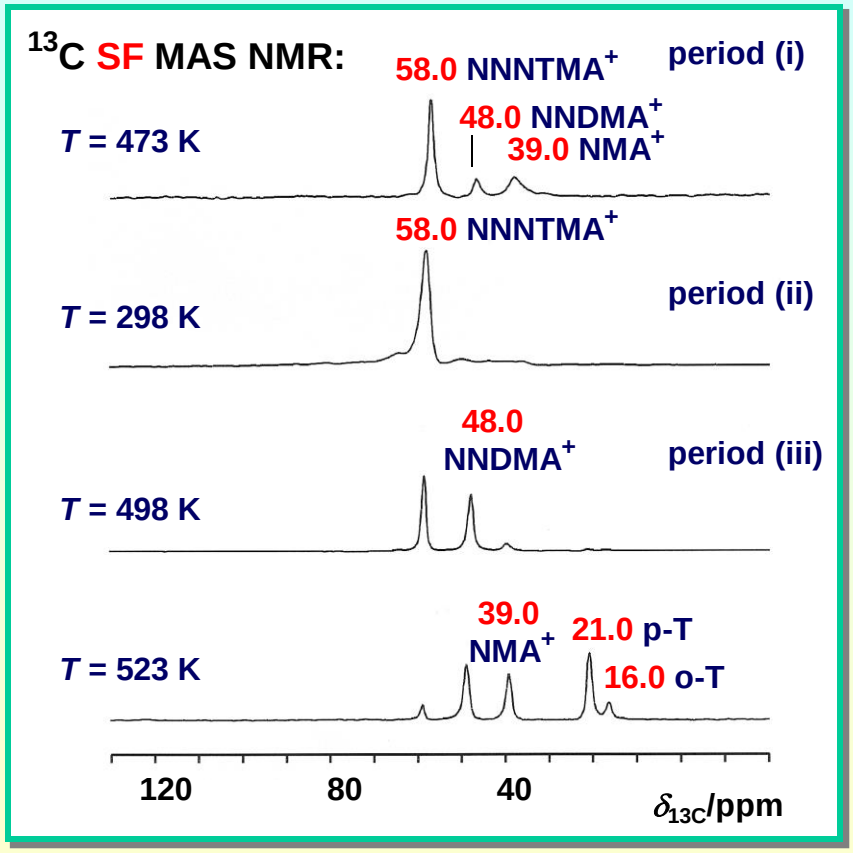
W. Wang et al., J. Am. Chem. Soc. 124 (2002) 7548.



Reactivity of anilinium cations on zeolite H-Y

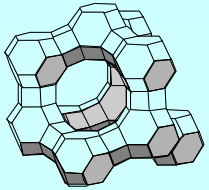
W_{cat}/F_{me} = 40 gh/mol, $^{13}CH_3OH$ / aniline = 2 : 1





all reaction products can be formed by a decomposion of NNNTMA$^+$ → chemical equilibrium

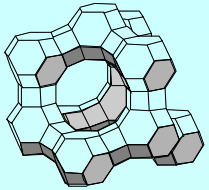
W. Wang et al., J. Am. Chem. Soc. 124 (2002) 7548.



Summary I

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

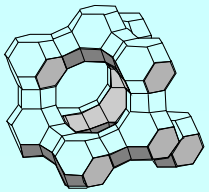
- **chemical behavior and local structure of active sites under reaction conditions**
- **origin of the catalyst deactivation under steady state conditions**
- **reaction pathways using labelled reactants**
- **activation energies of reaction steps**
- **reactivity of surface complexes and intermediates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



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