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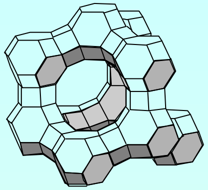

In situ spectroscopy in heterogeneous catalysis

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Components of heterogeneous reaction systems

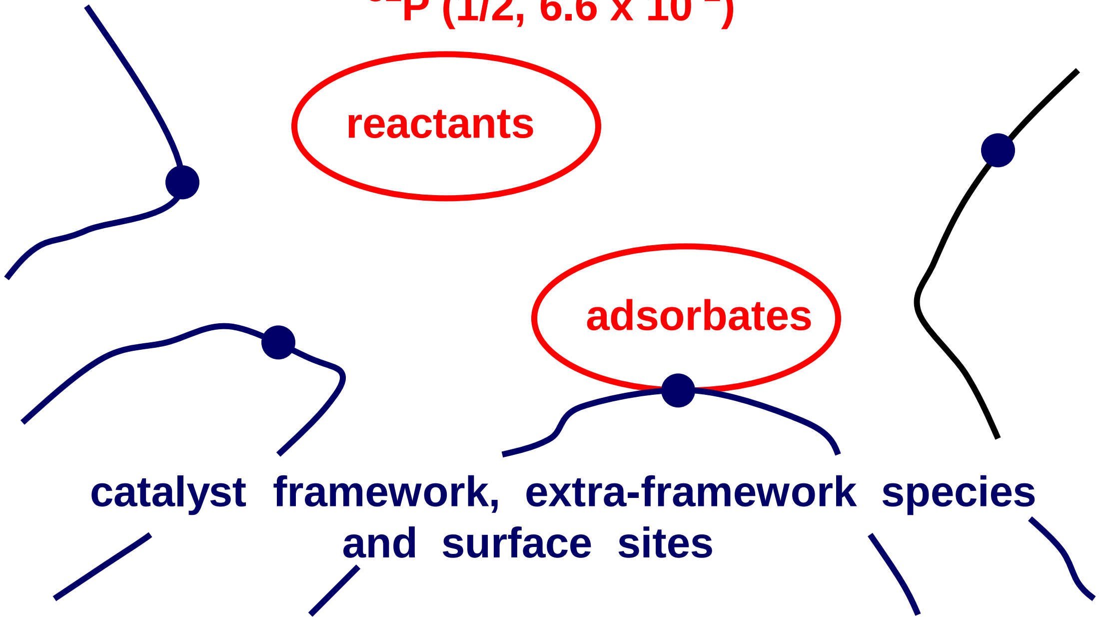
spectroscopically sensitive behaviors:

- **vibration modes of surface sites and adsorbates**
- **electron transitions of adsorbates and framework atoms**
- **unpaired electrons of adsorbates and framework atoms**
- **nuclear spins in all compounds contributing to the reaction systems**

^{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})



catalyst framework, extra-framework species and surface sites

^{11}B (3/2, 0.13), ^{17}O (5/2, 1.1 x 10^{-6}), ^{27}Al (5/2, 0.21),

^{29}Si (1/2, 3.7 x 10^{-4}), ^{71}Ga (3/2, 5.6 x 10^{-2})

Contents

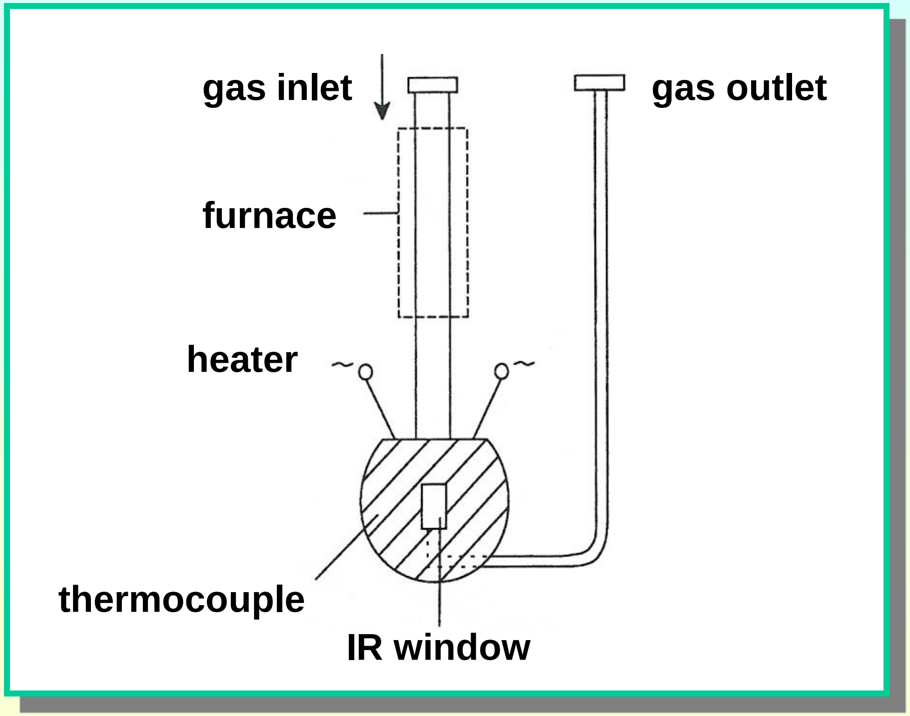
spectroscopic methods applied for studies of heterogeneous reaction systems under *in situ* conditions in the laboratory scale:

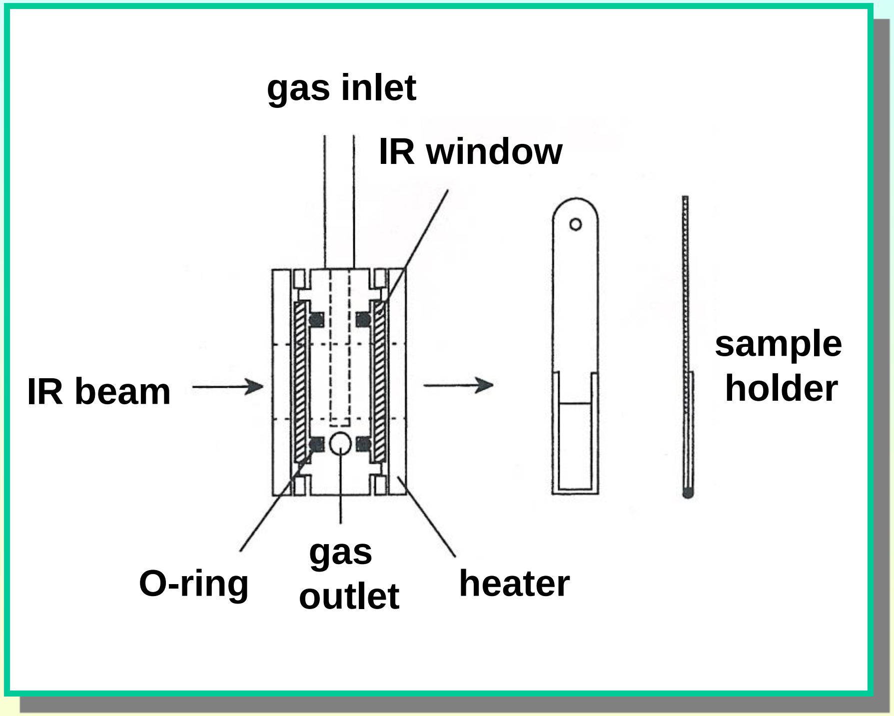
- **Fourier transform infrared (FTIR) spectroscopy**
  - **hydroxyl groups, reactants, adsorbates, coke**
- **UV-Vis spectroscopy**
  - **surface sites, conjugated double bonds, carbenium ions, coke**
- **electron spin resonance (ESR):**
  - **paramagnetic surface sites, adsorbates, coke**
- **solid-state nuclear magnetic resonance (NMR):**
  - **framework, surface sites, adsorbates, coke**

In situ FTIR spectroscopy in heterogeneous catalysis

FTIR spectroscopy

scheme of an *in situ* IR cell



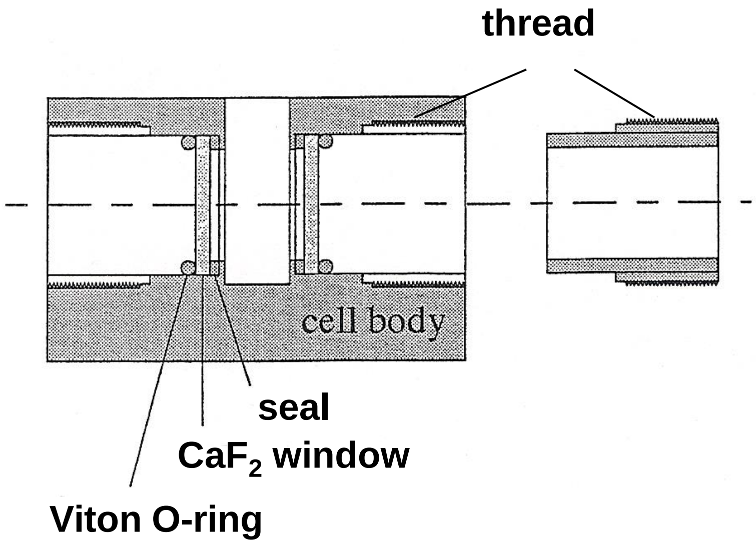


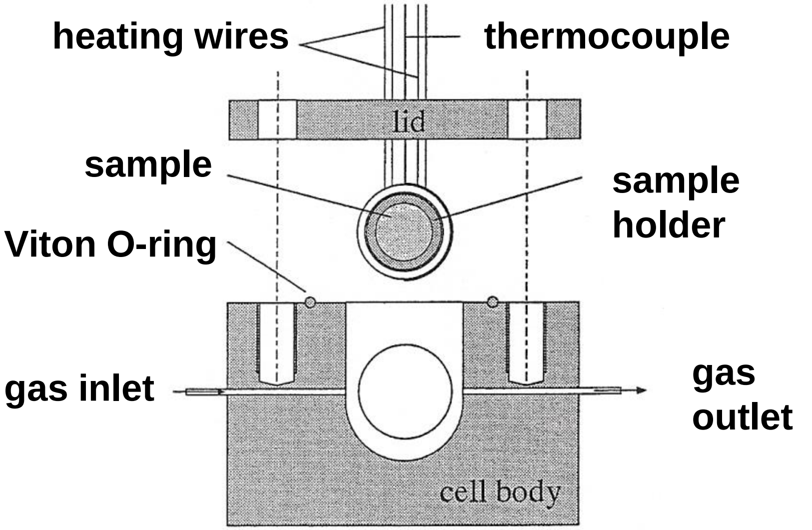
- up to 523 K under high-vacuum and up to 923 K at $p = 1$ bar

H.G. Karge et al., in: J. Weitkamp, L. Puppe (eds.), Catalysis and Zeolites, Springer-Verlag, Berlin, 1999, p. 198.

FTIR spectroscopy

scheme of an *in situ* IR cell



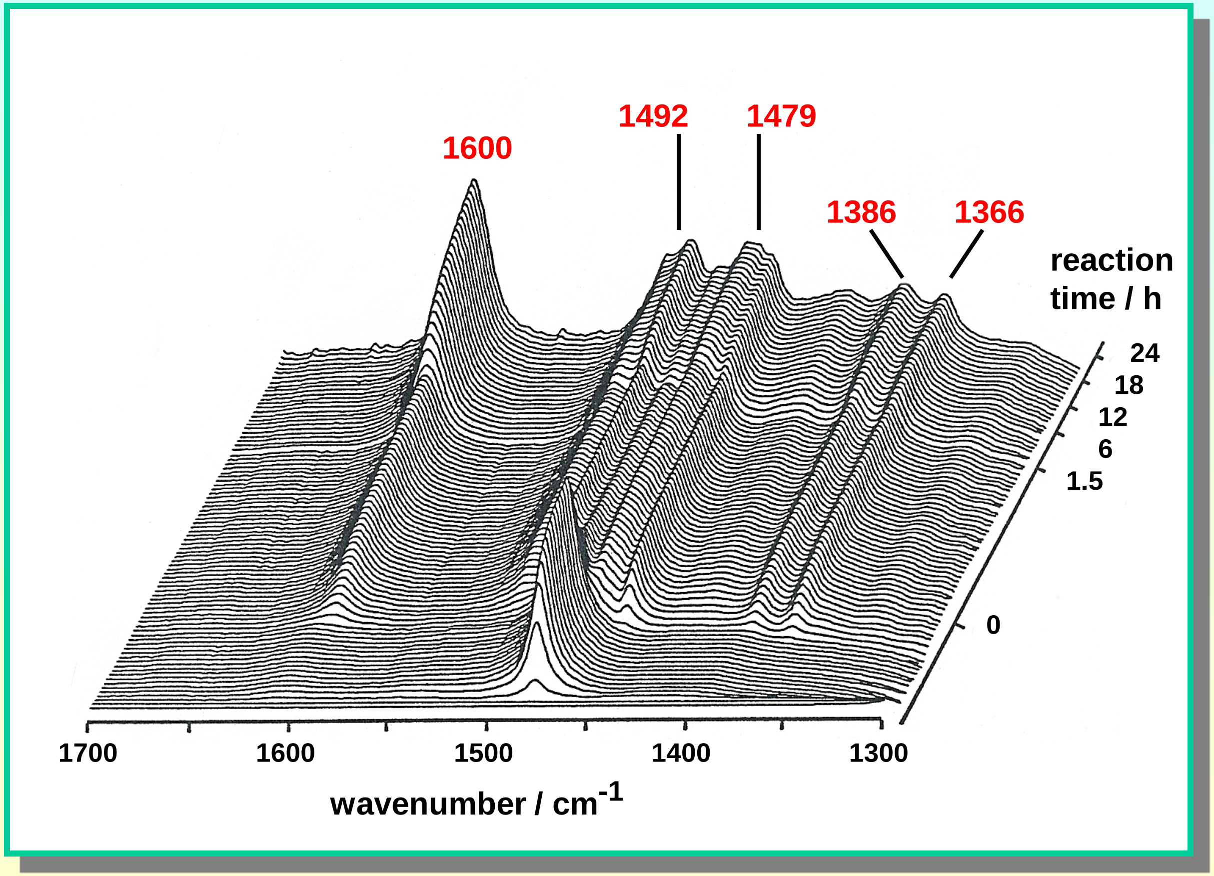


- maximum temperature of 870 K at up to p = 5 bar

G. Mirth et al., Applied Spectroscopy, 48 (1994) 194.

FTIR spectroscopy

synthesis of cumene by benzene and propene on zeolite H-EU-1 (n_{Si}/n_{Al} = 17) at 448 K



1366 cm^{-1}:
C-H vibration of diisopropylbenzene

1386 cm^{-1}:
C-H vibration of cumene

1479 cm^{-1}:
ring vibration of benzene

1492 cm^{-1}:
ring vibration of cumene

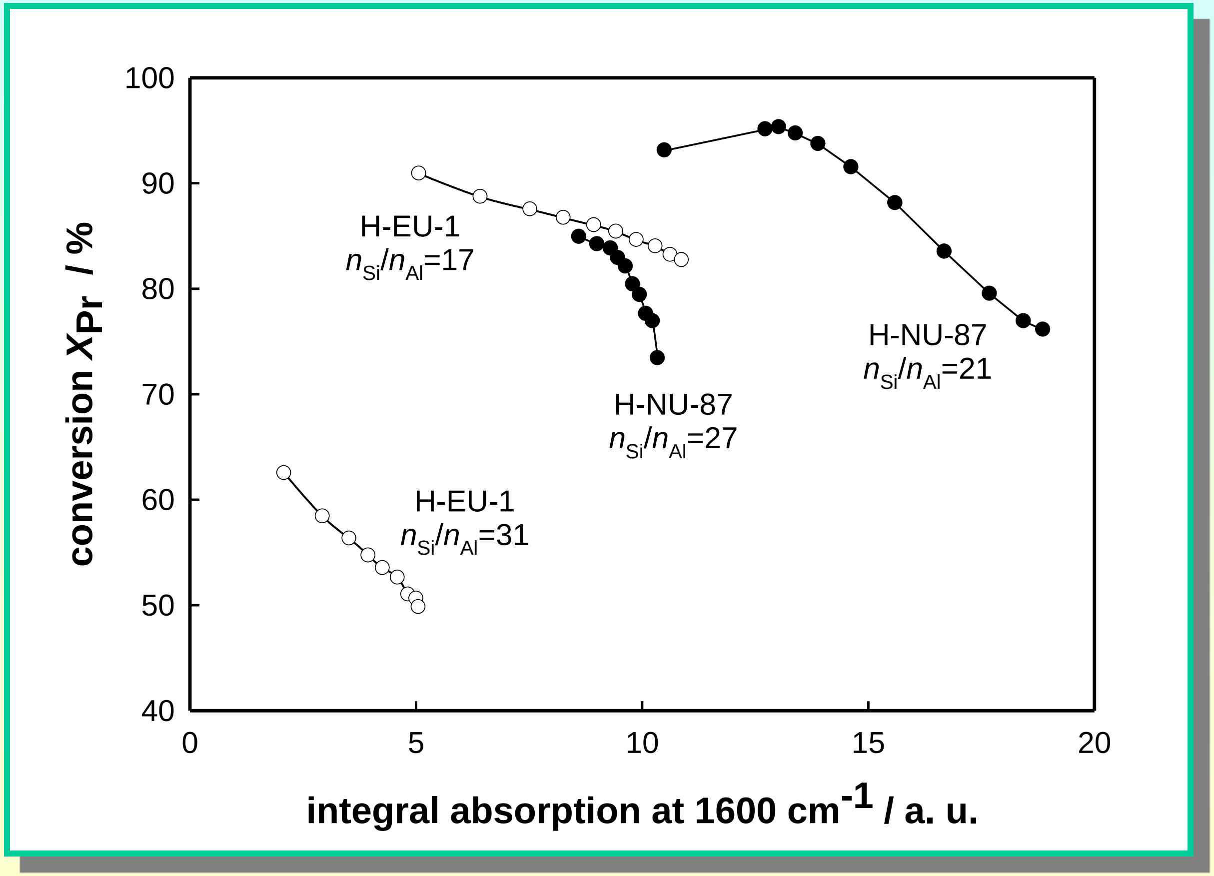
1600 cm^{-1}:
ring vibration of polyaromatics, conjugated polyene structures

→ **coke formation starts with injection of propene**

M. Breuninger et al., Chem. Ing. Tech. 73 (2001) 869.

FTIR spectroscopy

dependence of the catalytic activity on the formation of coke



M. Breuninger et al., Chem. Ing. Tech. 73 (2001) 869.

zeolite H-EU-1:

structure type EUO
10-ring pores [100]
0.41 x 0.54 nm
large side pockets

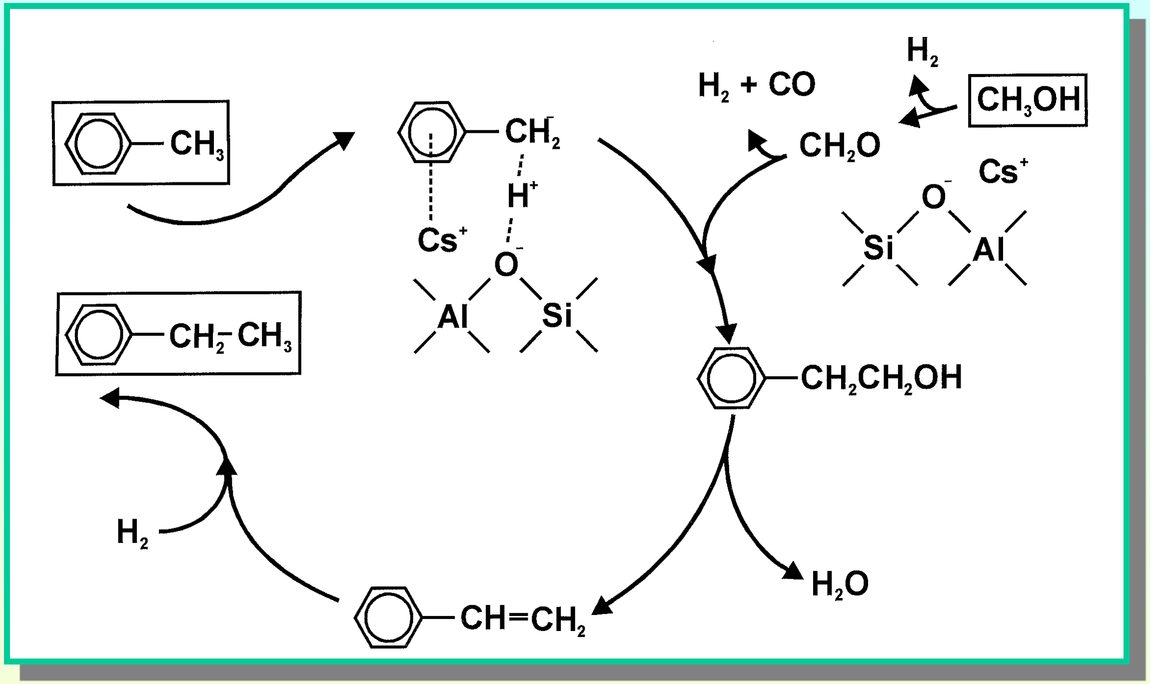
zeolite H-NU-87:

structure type NES
10-ring pores [100]
0.48 x 0.57 nm

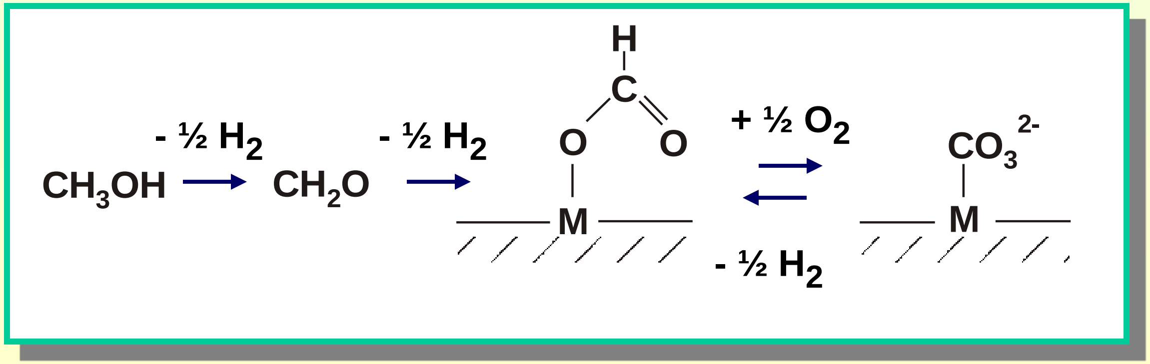
→ coke formation depends on the pore geometry as well as the aluminum content

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**

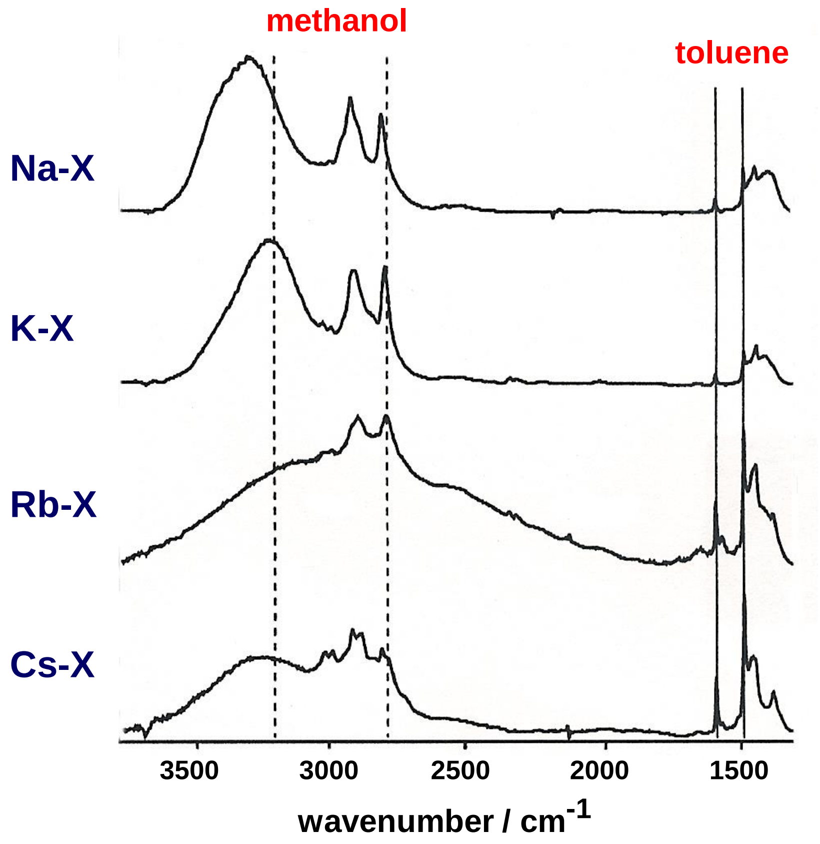


- **proposed surface species:**
  - **- surface formate species**
  - **- carbonates**



FTIR spectroscopy

co-adsorption of toluene and methanol on alkali-exchanged zeolites X at 308 K

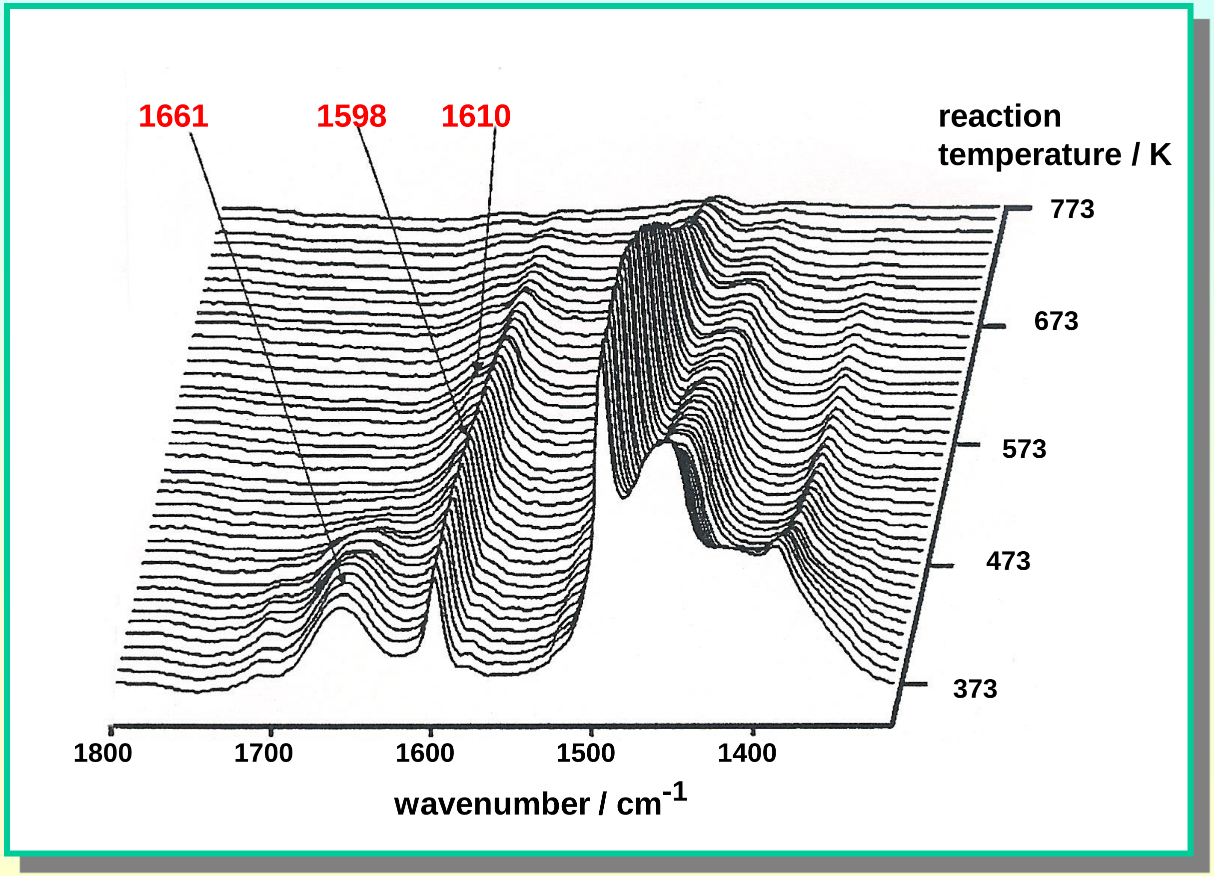


- co-adsorbed states of reactants don‘t dependent on the sequence of adsorption
- Cs-X: highest ratio (2:1) of adsorbed toluene in comparison with adsorbed methanol

A.E. Palomares et al., J. Catal. 168 (1997) 442.

FTIR spectroscopy

side-chain alkylation of toluene on zeolite Cs-X (100% Cs) at 373 to 773 K



1400 - 1500 cm^{-1}: ring vibration

1598 cm^{-1}: C-C vibration of toluene

1610 cm^{-1}: surface formate species

1661 cm^{-1}: adsorbed dimethyl ether

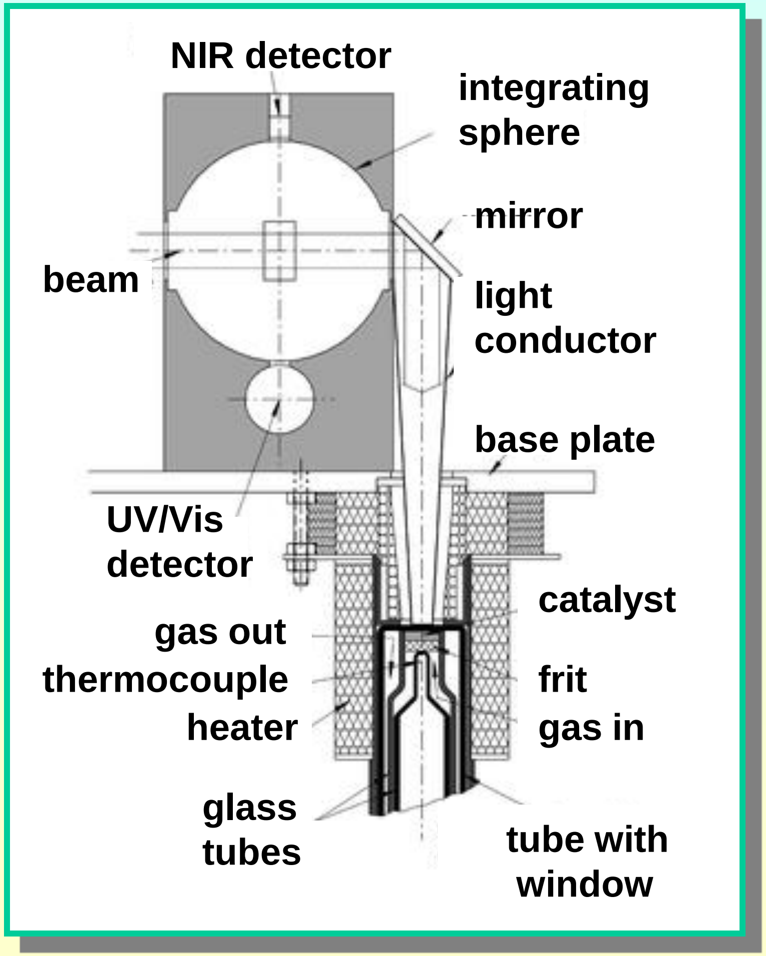
→ **surface formate species occur at reaction temperature**

A.E. Palomares et al., J. Catal. 180 (1998) 56.

In situ UV/Vis spectroscopy in heterogeneous catalysis

UV/Vis spectroscopy

scheme of an *in situ* UV/Vis-NIR setup

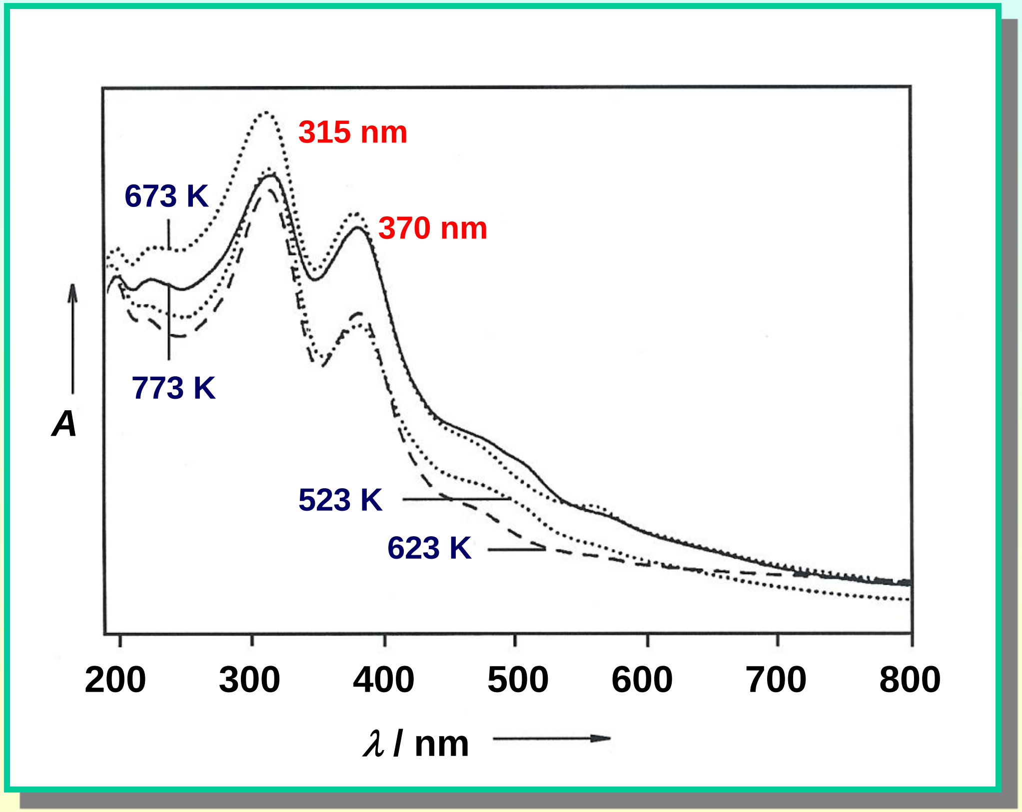


- suitable for *in situ* investigations at temperatures up to 723 K
- combination of UV/Vis and NIR spectroscopy
- increase of signal-to-noise ratio by 25% due to the light conductor
- horizontal arrangement of the powder material

J. Melsheimer et al., Phys. Chem. Chem. Phys. 5 (2003) 4366

UV/Vis spectroscopy

conversion of isobutane and 1-butene (9 : 1) on zeolite La,H-Y



sensitive for:

- **hydrocarbons with conjugated double bonds**
- **unsaturated carbenium ions**

→ **315 nm:**
monoenyl carbenium ions

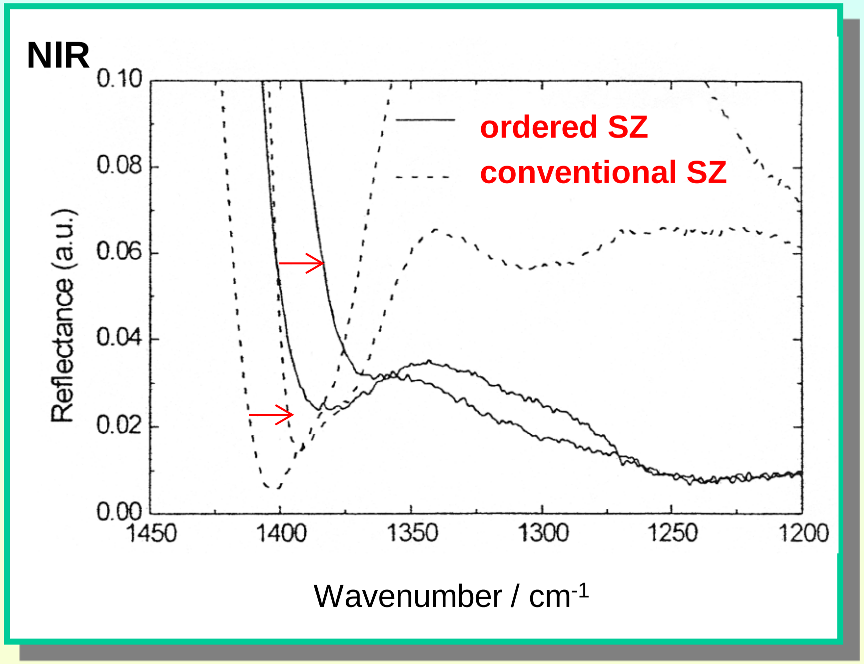
370 nm:
dienyl carbenium ions

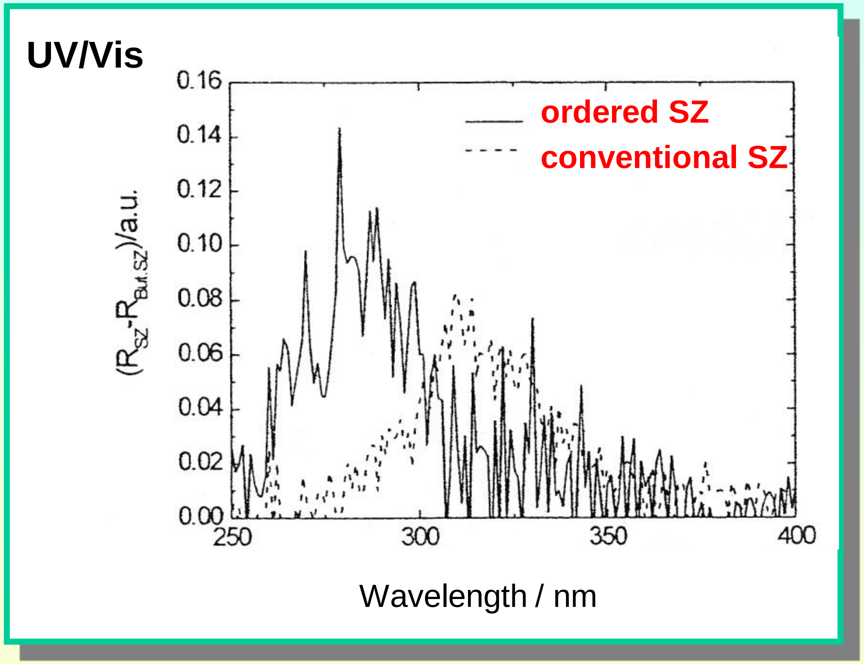
450 nm:
trienyl carbenium ions

I. Kiricsi et al., Chem. Rev. 99 (1999) 2085.

Simultaneous in situ NIR-UV/Vis and on-line GC

n-butane isomerization on conventional (MEL Chemicals) and mesoporous (ordered) sulfated zirconia (SZ)





- **different wavenumbers of the S-O stretching vibrations for ordered and conventional SZ indicate differences in the nature of surface sites; bands shift under reaction conditions**
- **preferred formation of cyclopentenyl cations (275 - 310 nm) on the ordered mesoporous SZ responsible for deactivation**

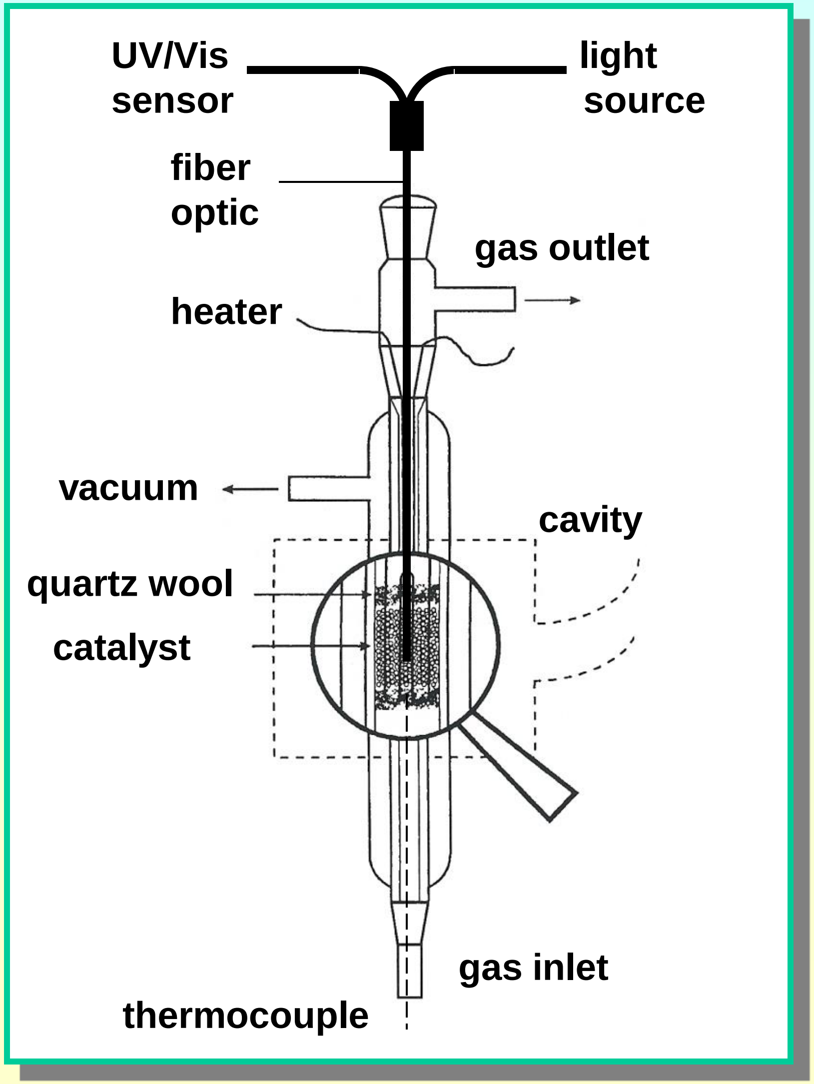
X. Yang et al., DGMK-Tagungsbericht 2002-4, ISBN 3-932850-98-6, p. 217.

In situ ESR spectroscopy in heterogeneous catalysis

ESR spectroscopy

scheme of an *in situ* ESR cell

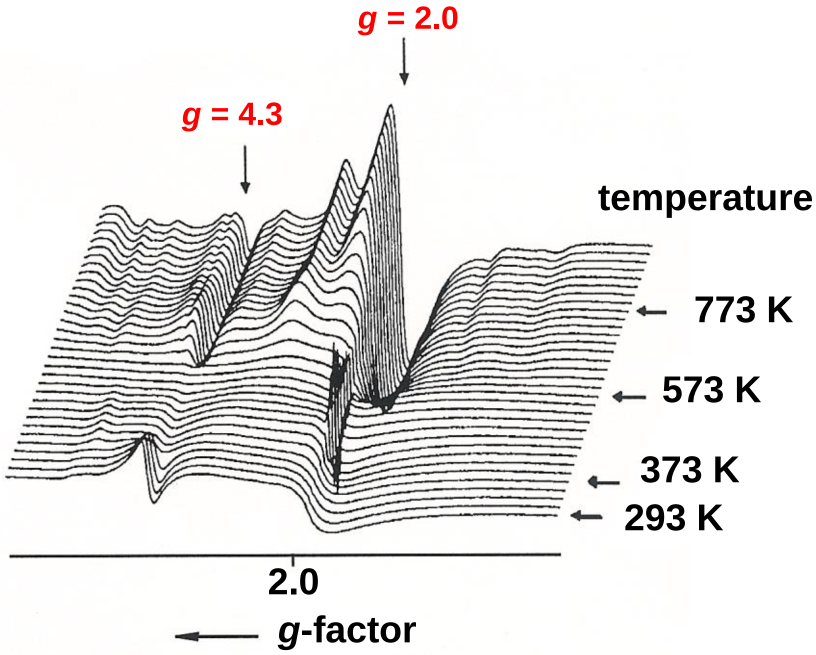
- ESR flow reactor for X-band (B_o = 0.35 T, ν = 9.5 GHz)
- suitable for *in situ* investigations at temperatures of up to 780 K
- combination of ESR and UV/Vis spectroscopy



A. Brückner et al., Stud. Surf, Sci. Catal. 142 (2002) 1141.

ESR spectroscopy

X-band *in situ* ESR spectrum of Fe/AlPO$_4$-5 recorded during calcination



→ Fe^{3+} species with different local structures:

g = 2.0:
octahedrally coordinated Fe^{3+} bound to four lattice oxygen bridges and two extra-framework ligands in the pores

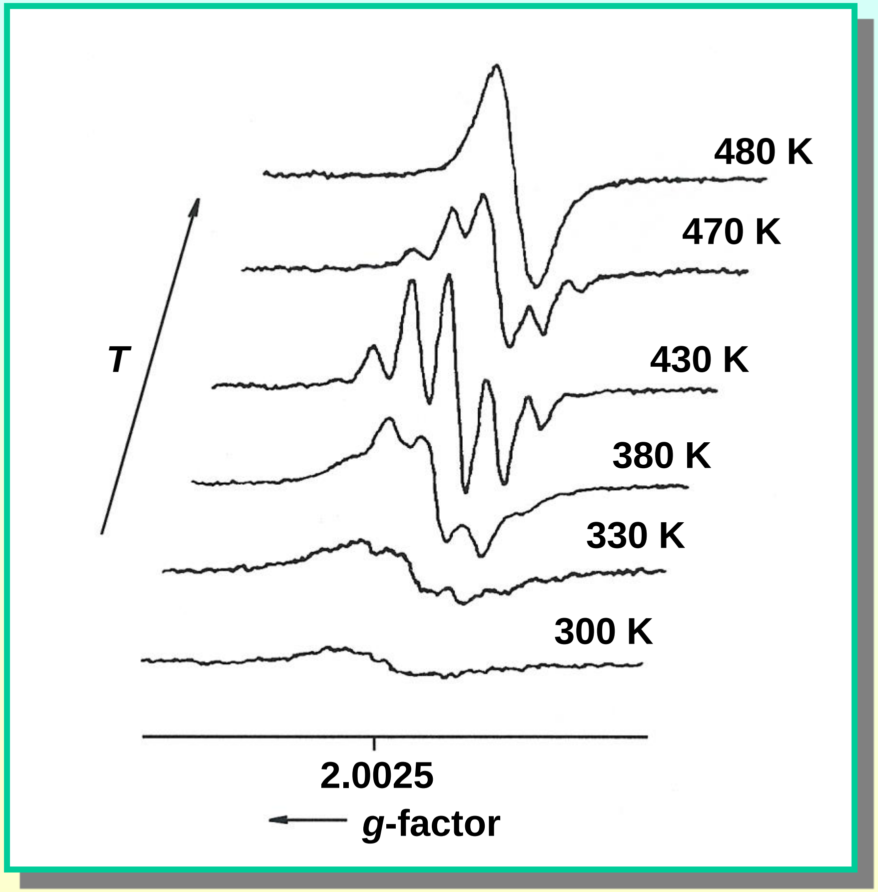
g = 4.3:
octahedrally coordinated Fe^{3+} in lattice defects bound to bridging oxygen and terminal oxygen

(also assigned to tetrahedrally coordinated Fe^{3+})

A. Brückner et al., Microporous Mesoporous Mater. 20 (1998) 207.

ESR spectroscopy

X-band *in situ* ESR spectrum recorded during conversion of ethene on H-MOR



→ **formation of coke:**

***T* = 380 – 470 K:**
olefinic and allyllic radicals
due to oligomerization of ethene,
hf-splitting due to coupling with Al,
low-temperature coke

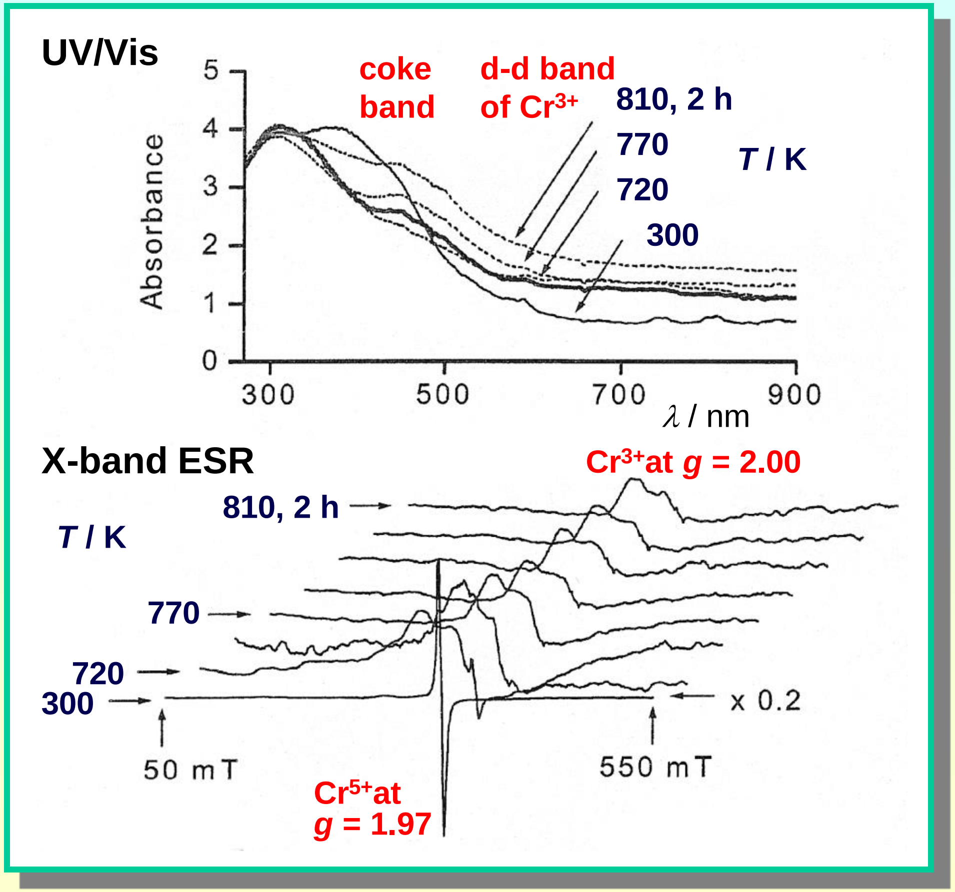
***T* > 470 K:**
polyaromatic radicals,
high-temperature coke

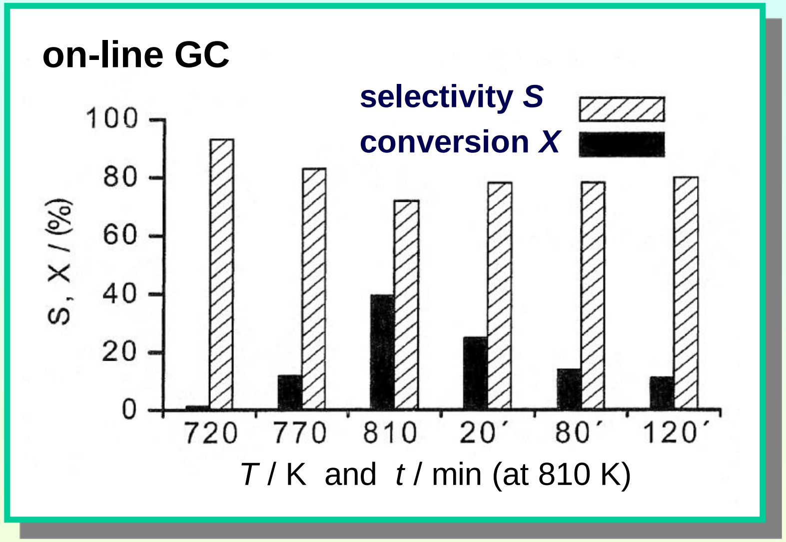
(1 radical per 1000 molcules)

H. Karge et al., J. Catal. 114 (1988) 144.

Simultaneous in situ ESR-UV/Vis and on-line GC

dehydrogenation of propane on La_2O_3/ZrO_2 (MEL Chemicals) impregnated with $(NH_4)_2CrO_4$





- dehydrogenation starts upon formation of Cr^{3+} species
- deactivation due to coke formation

A. Brückner, Chem. Commun. (2001) 2122.

In situ NMR spectroscopy in heterogeneous catalysis

Specific problems of NMR on working catalysts

magnetization:

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

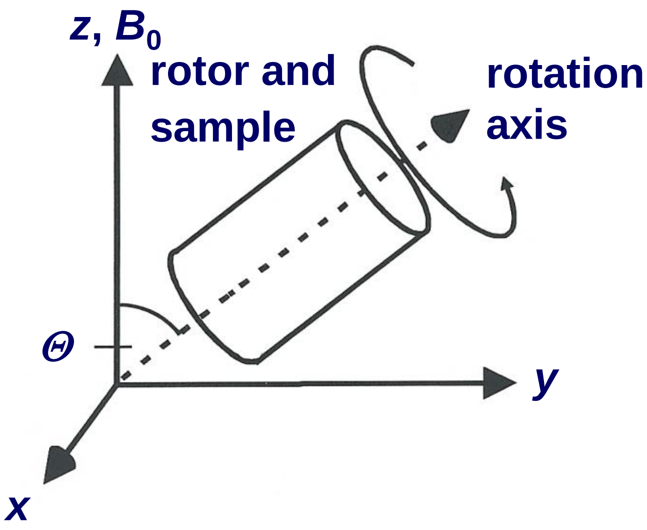
- **absolute number of spins of $N > 10^{19}$ per gram (^{1}H NMR)**
- **decrease of magnetization M_0 with increasing temperature T**
- **rapid chemical exchange of adsorbate complexes at elevated temperatures**
- **observation times of 10 ms (flow conditions) to hours (batch conditions)**
- **quenching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

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



spin *I* > ½ :

- **double oriented rotation (DOR)**

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

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

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

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:

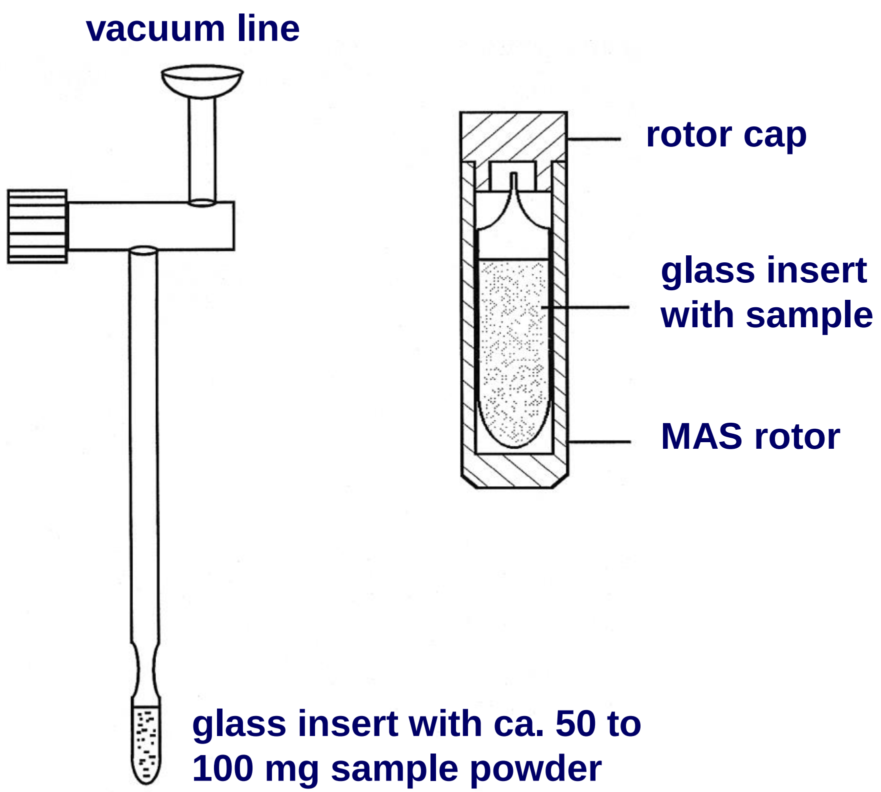
- self-made equipments
- study of reactions under staedy state conditions

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**

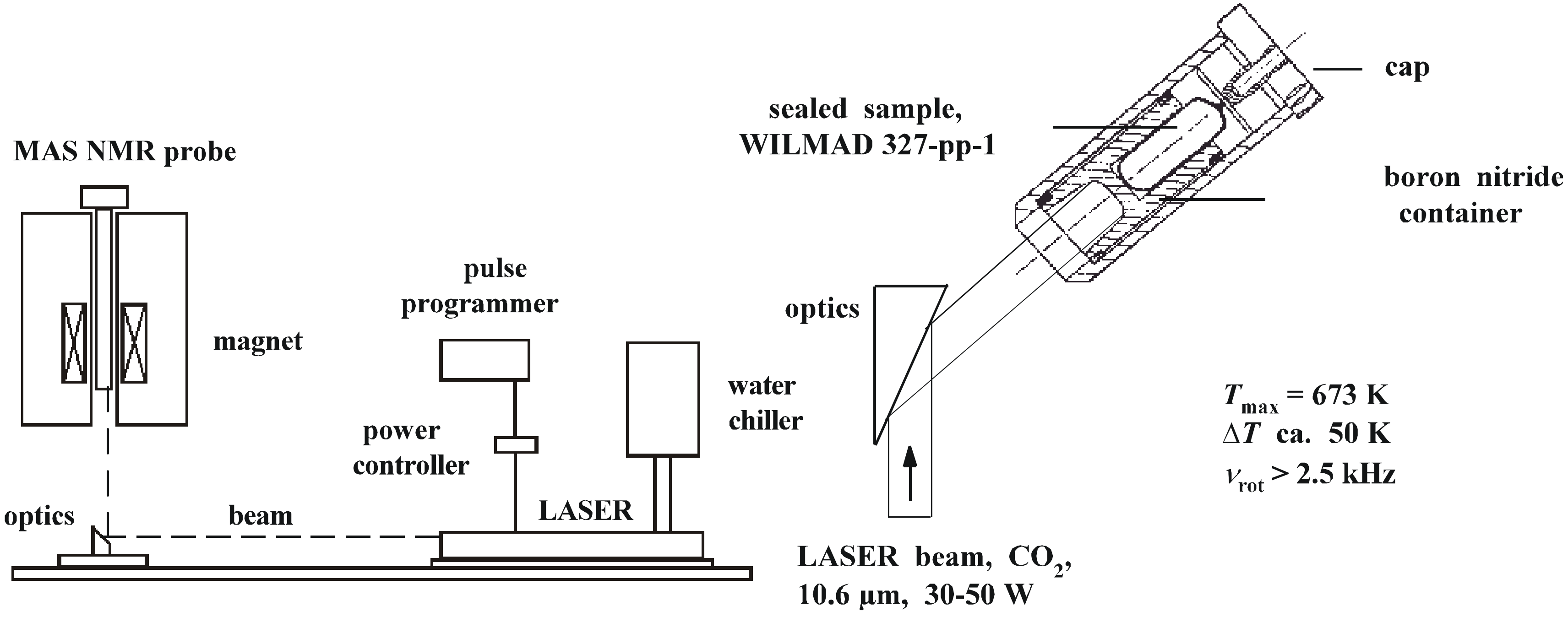
- **suitable for *ex situ* and *in situ* MAS NMR studies under batch conditions**



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

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

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

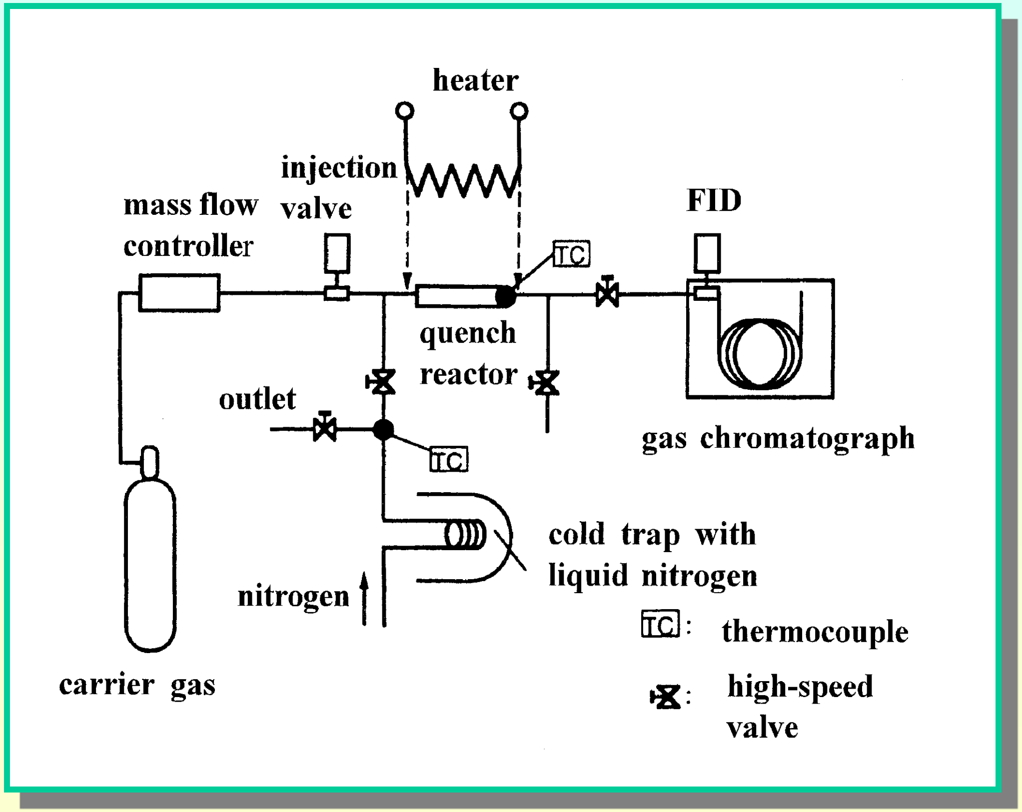


T_{max} = 673 K
ΔT ca. 50 K
ν_{rot} > 2.5 kHz

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

Go-and-stop experiments using an external reactor

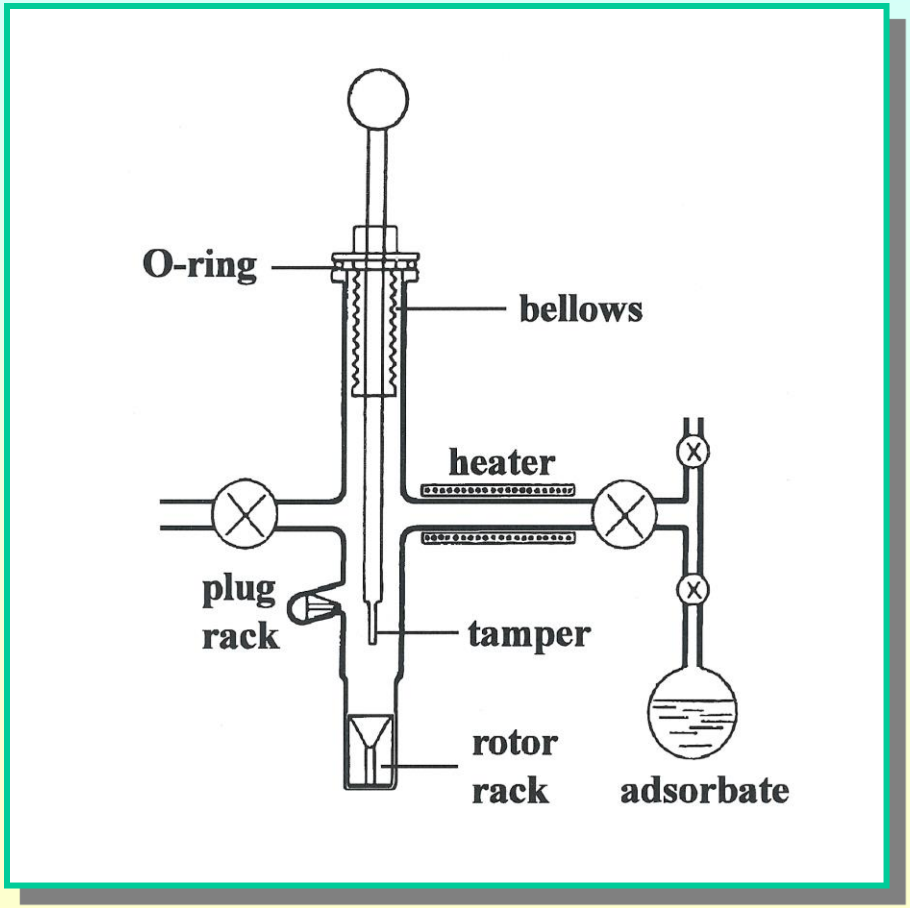
- **pulse-quench technique:**
  - **- conversion of reactants in an external fixed-bed reactor**
  - **- rapid stopping of the reaction by pre-cooled nitrogen gas**
- **NMR investigations:**
  - **- transfer of the catalyst loaded with reaction products into an MAS NMR rotor**
  - **- measurements performed at room temperature**



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

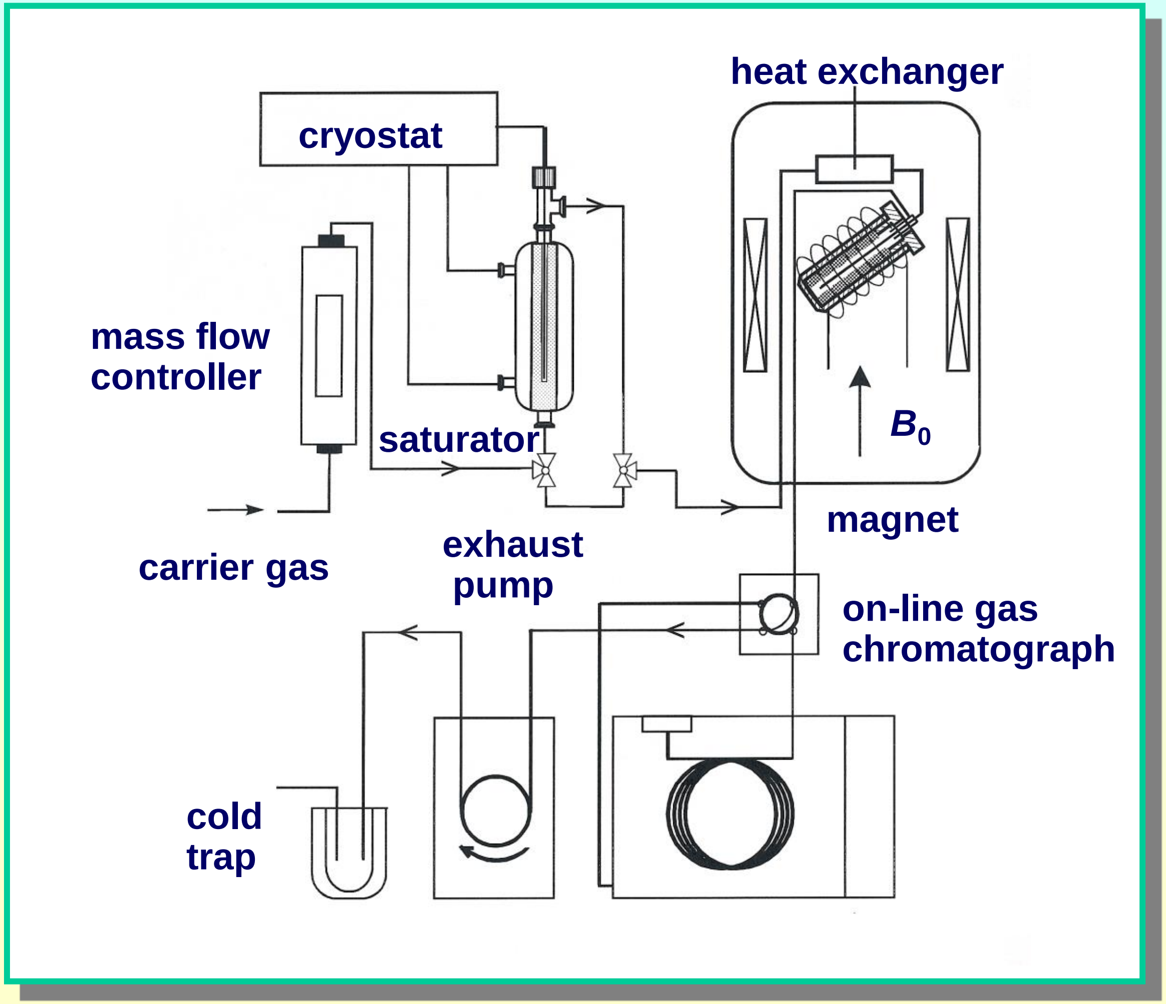
Approach for batch and continuous-flow experiments in an external reactor

- **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.

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



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

Behavior of the high-temperature CF MAS NMR probe

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

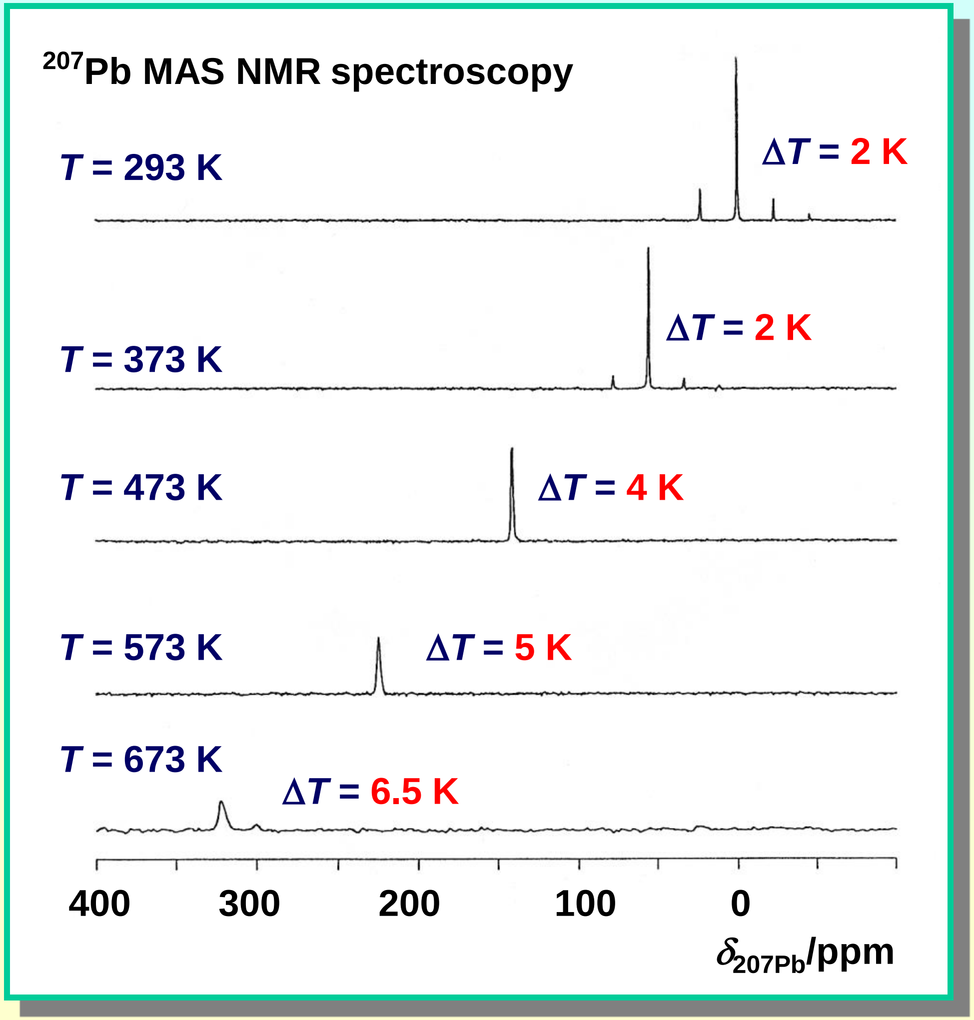
  $\Delta T / \Delta\delta = 1.29$ K / ppm *

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

  $\nu_0 = 83.2$ MHz

  $\nu_{rot} = 2.5$ kHz

  $F_{N2} = 15$ ml/min



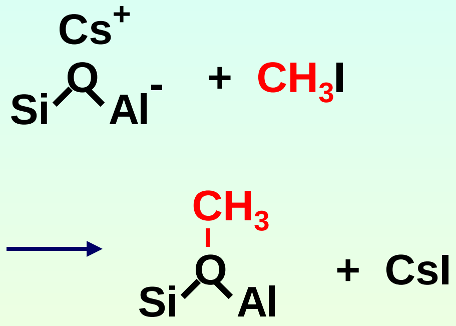
^{207}Pb MAS NMR spectroscopy

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

NMR investigations of base sites and reaction catalyzed by basic zeolites

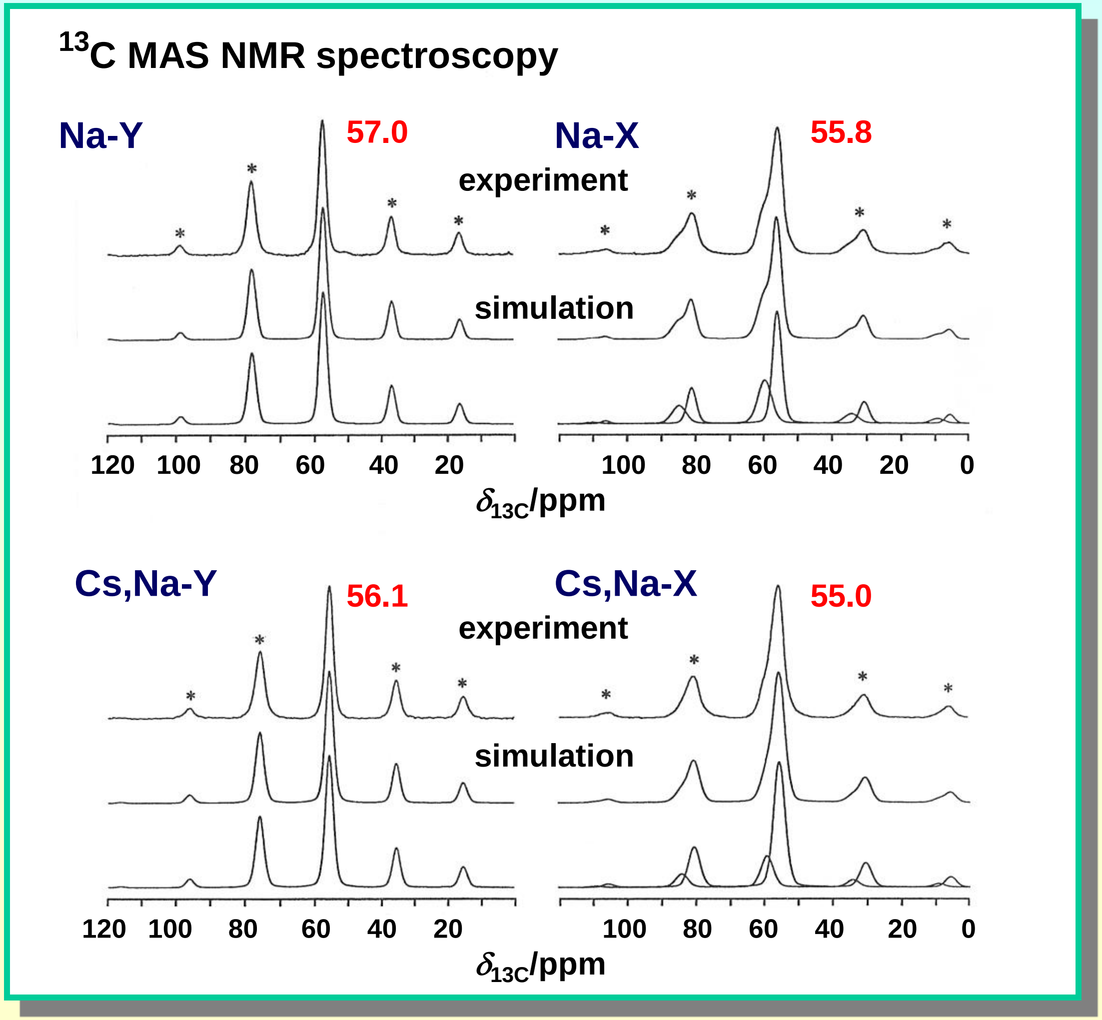
Characterization of basic zeolites under reaction conditions

- **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

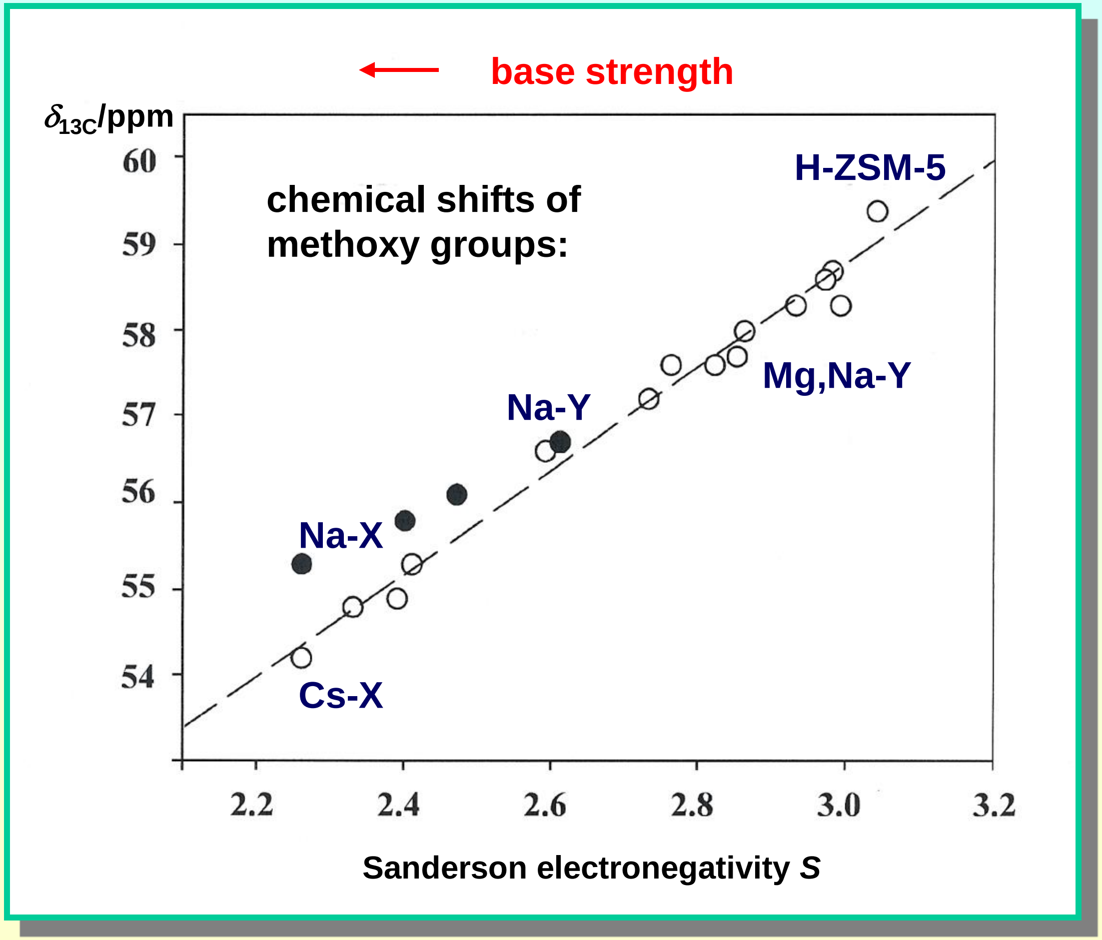
U. Schenk, PhD thesis, University of Stuttgart, 2001.

Characterization of basic zeolites under reaction conditions

- **mean Sanderson electronegativity:**

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

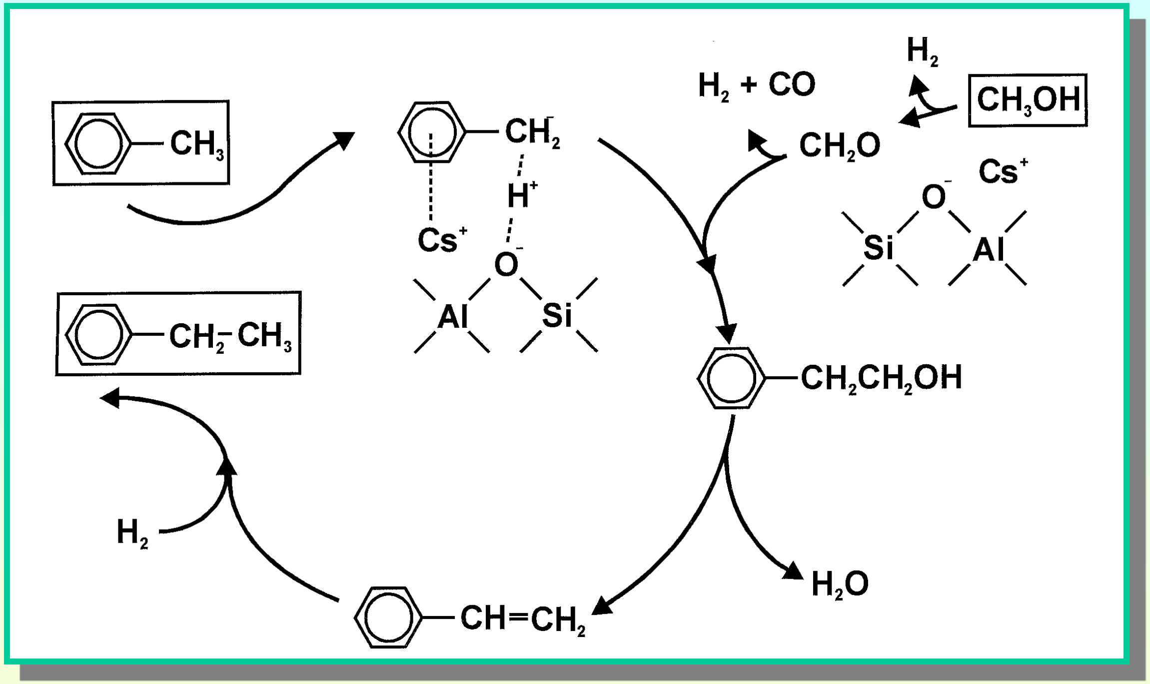
→ **decreasing ^{13}C NMR shift of surface methoxy groups with increasing base strength of the framework oxygen atoms**



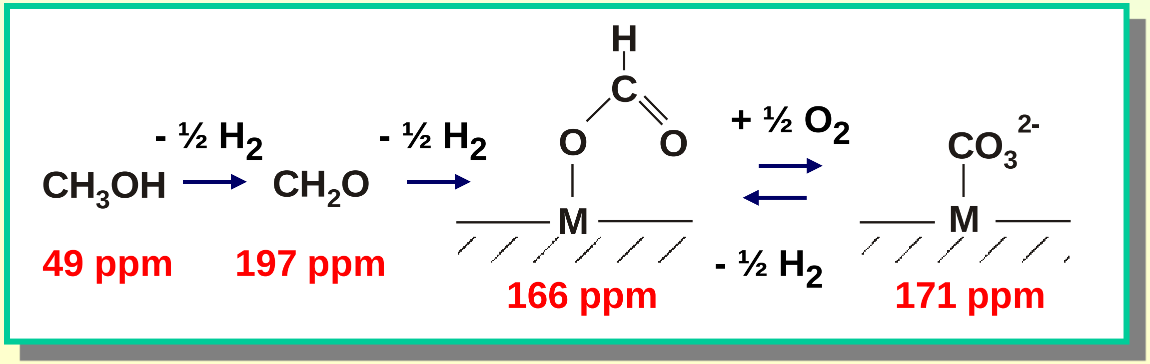
V. Bosacek et al., Z. Phys. Chem. 189 (1995) 241.

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

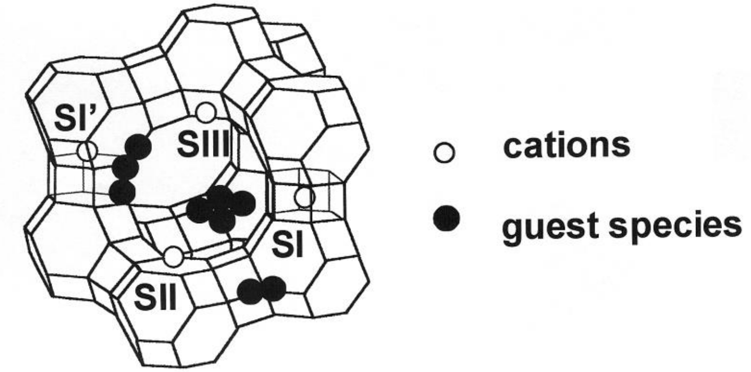


- proposed surface species:
  - formate (δ_{13C} = 166 ppm)
  - carbonate (δ_{13C} = 171 ppm)



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

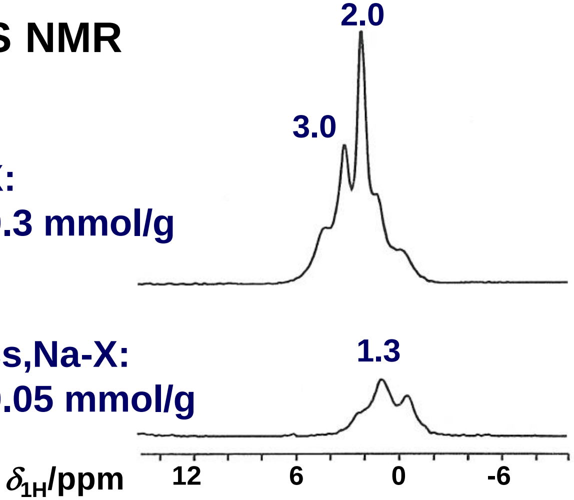
- **zeolite Na-X (n_{Si}/n_{Al} = 1.4) exchanged with cesium cations (55 %) and impregnated with cesium hydroxide (24 CsOH/u.c.)**



^{1}H MAS NMR

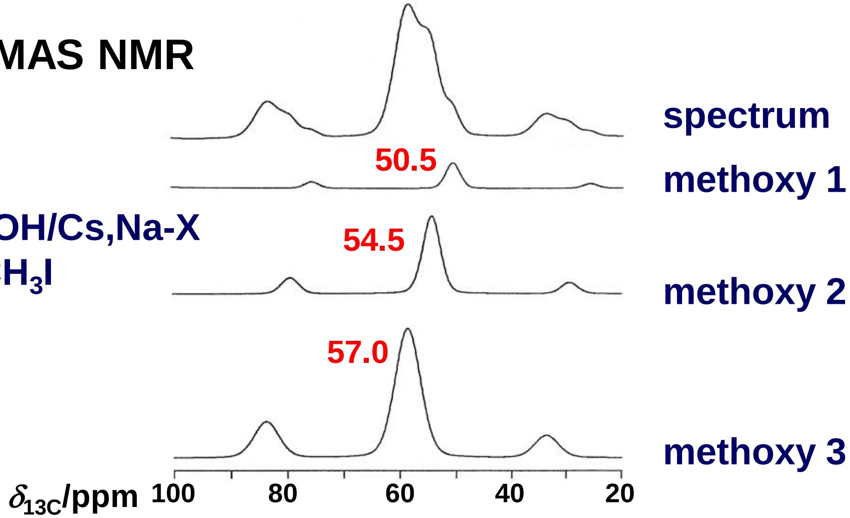
Cs,Na-X:
c_{OH} = 0.3 mmol/g

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



^{13}C MAS NMR

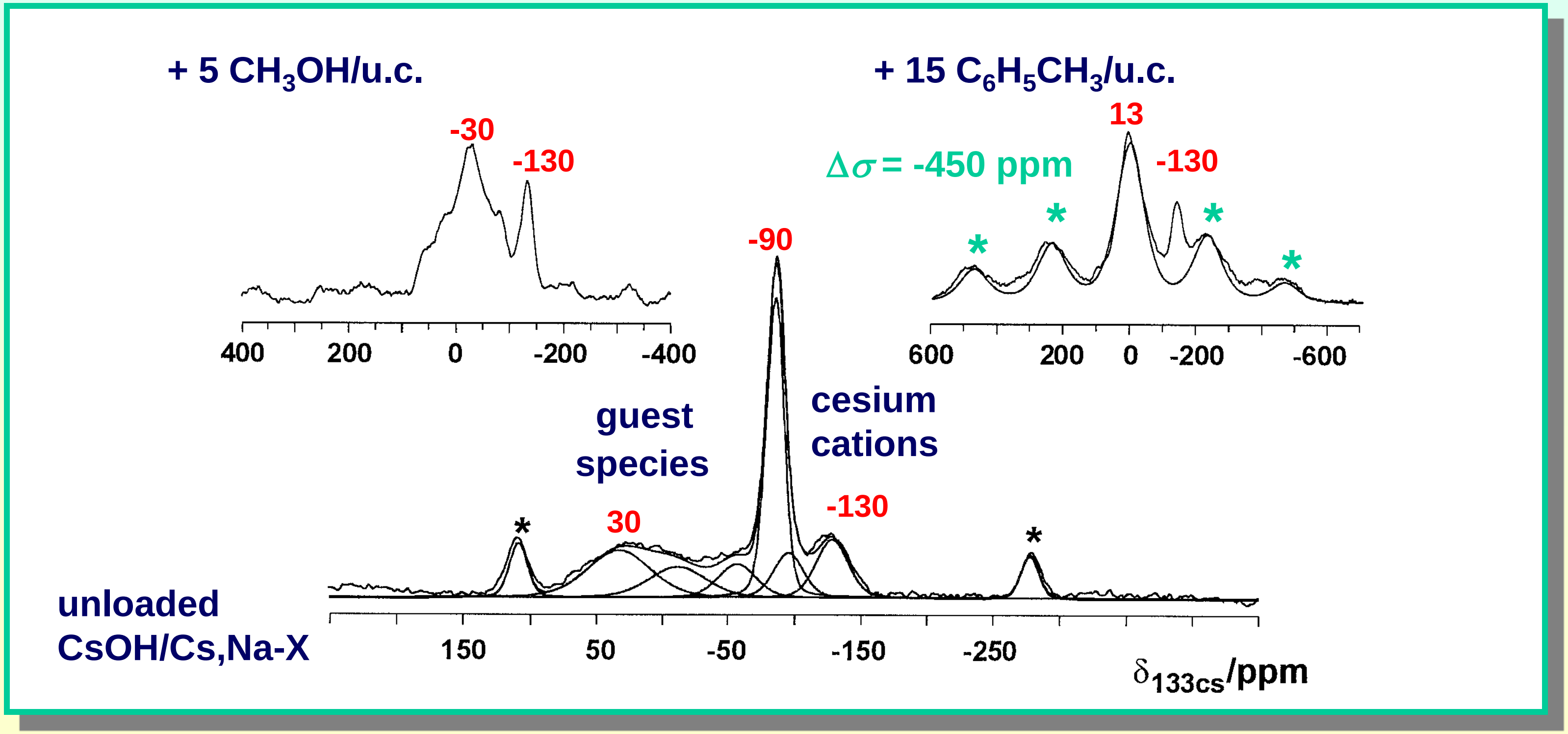
CsOH/Cs,Na-X + CH_3I



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

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

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

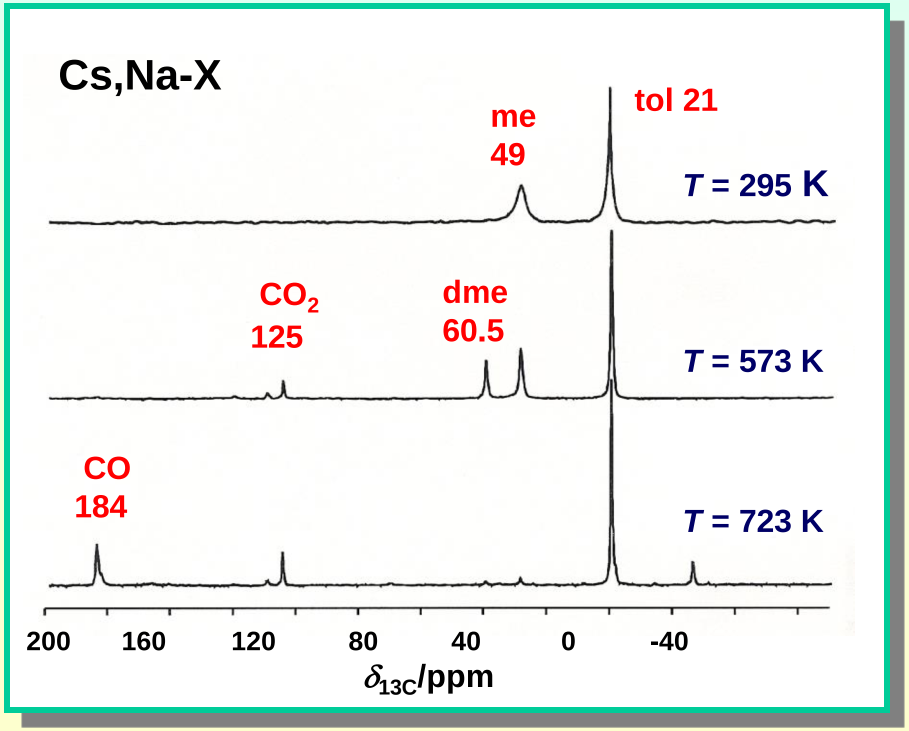


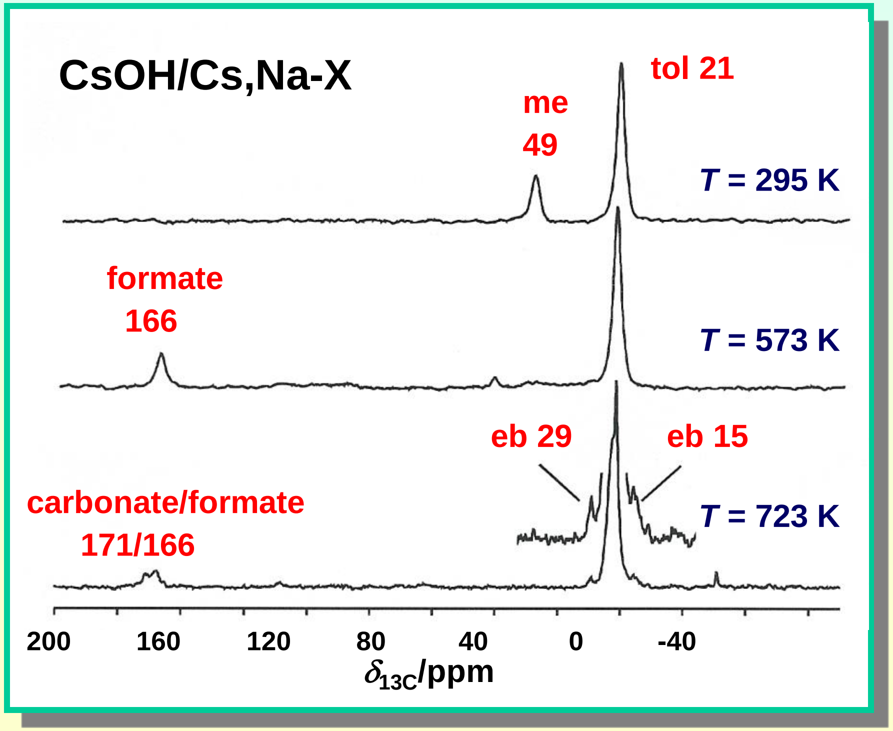
M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

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

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

5 $^{13}CH_3OH$/u.c.





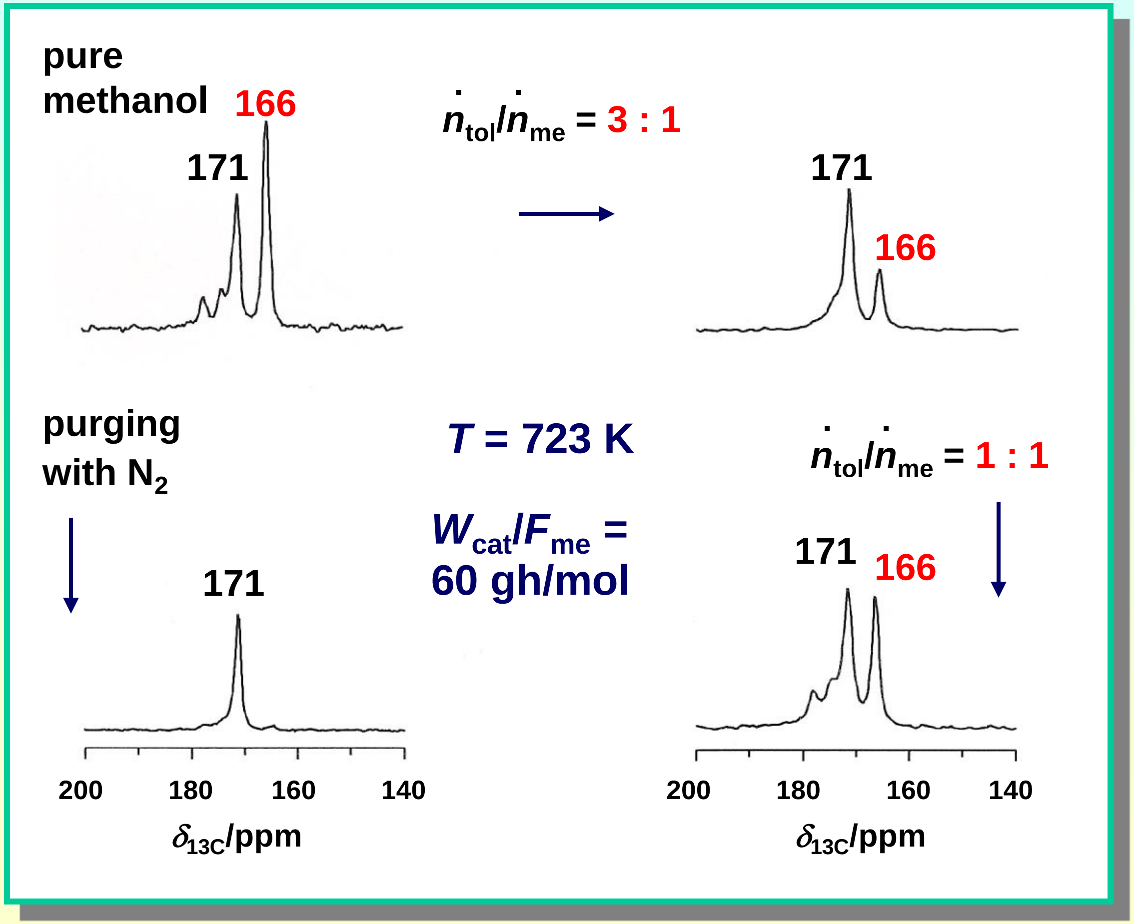
M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

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

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

→ **carbonate species (171 ppm) are chemically stable**

→ **formate species (166 ppm) are consumed by toluene which indicates a high reactivity**

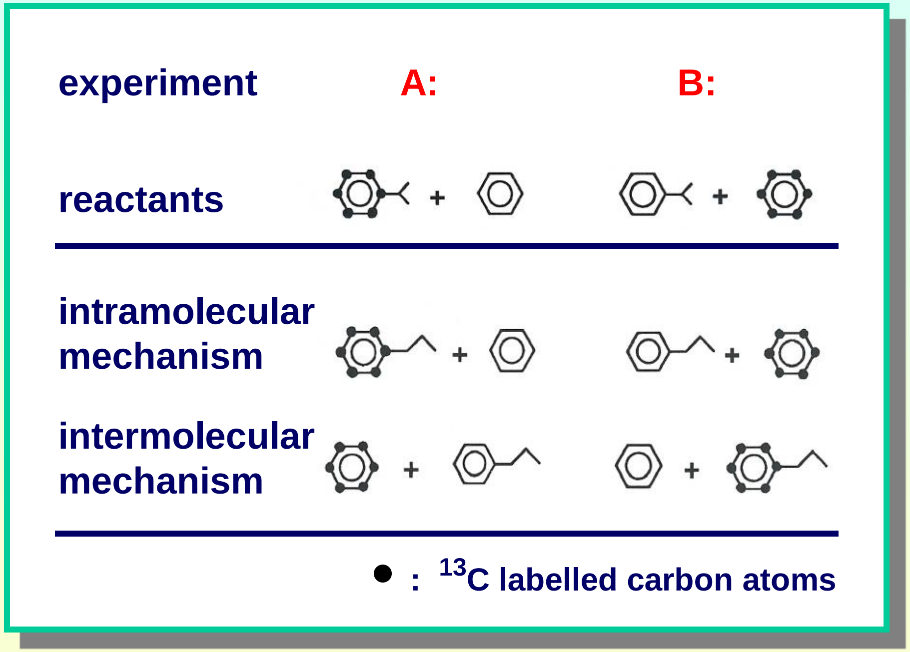


M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

NMR investigations of reactions catalyzed by acidic zeolites

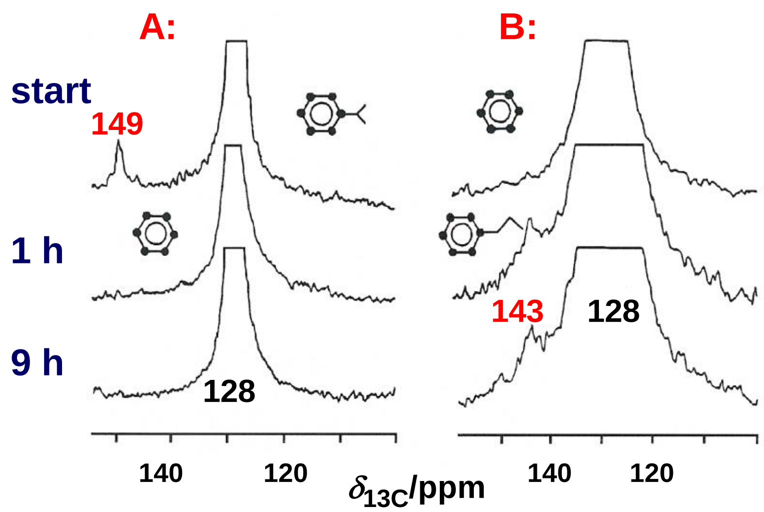
Investigation of reaction pathways by selectively labelled reactants

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



● : ^{13}C labelled carbon atoms

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

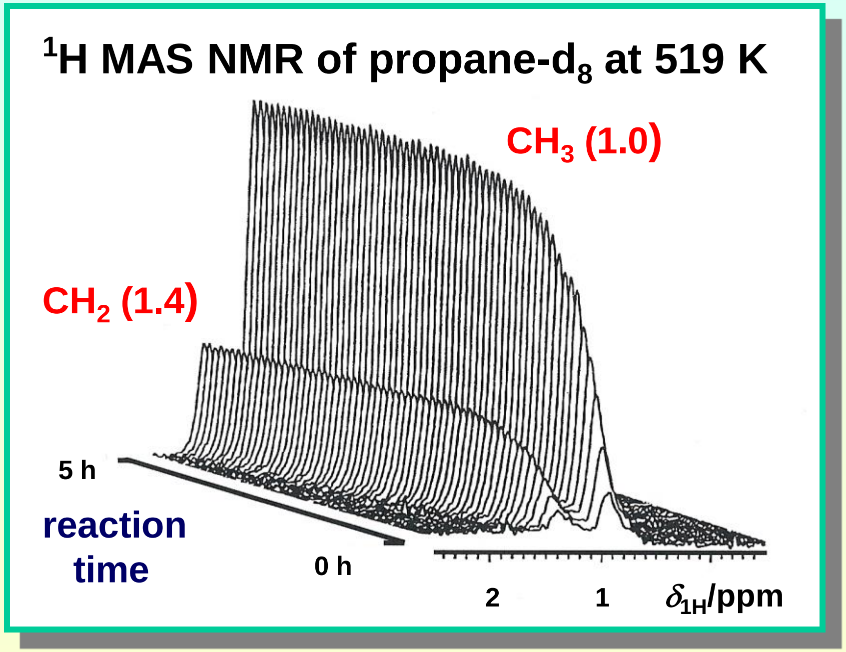


→ **experiments A and B indicate an intermolecular reaction mechanism**

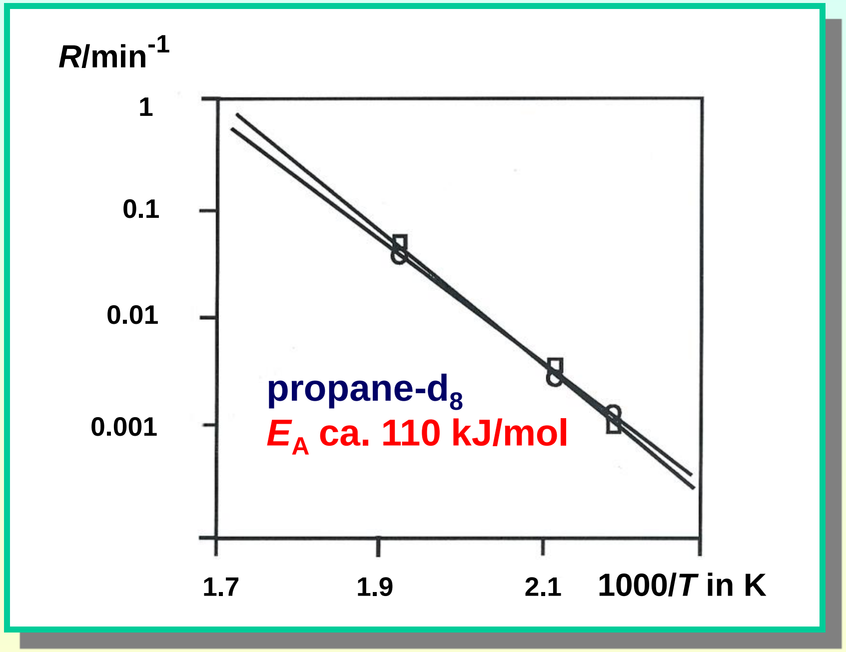
E. Derouane et al., Catal. Lett. 58 (1999) 1.

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**



^{1}H MAS NMR of propane-d_8 at 519 K



A:

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

→ no formation carbenium ions

B:

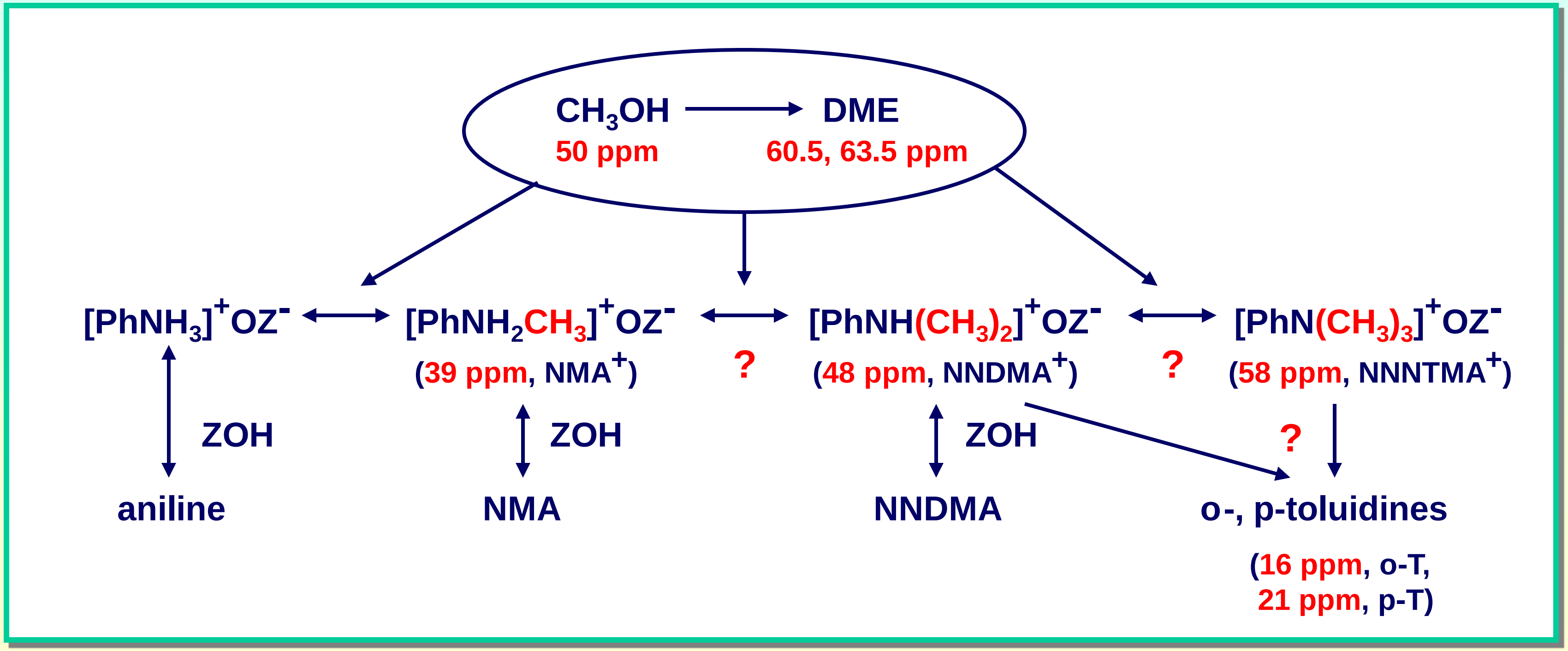
- **regiospecific H/D exchange**
- **E_A of ca. 50 kJ/mol**

→ formation carbenium ions

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

Methylation of anilin by methanol on acidic zeolites

- **different types of methylanilinium cations formed on acidic zeolite H-Y**



CH_3OH → DME

50 ppm **60.5, 63.5 ppm**

$[PhNH_3]^+OZ^-$ ↔ $[PhNH_2CH_3]^+OZ^-$ ↔ $[PhNH(CH_3)_2]^+OZ^-$ ↔ $[PhN(CH_3)_3]^+OZ^-$

(39 ppm, NMA^+) **?** **(48 ppm, $NNDMA^+$)** **?** **(58 ppm, $NNNTMA^+$)**

ZOH **ZOH** **ZOH** **?**

aniline **NMA** **NNDMA** **o-, p-toluidines**

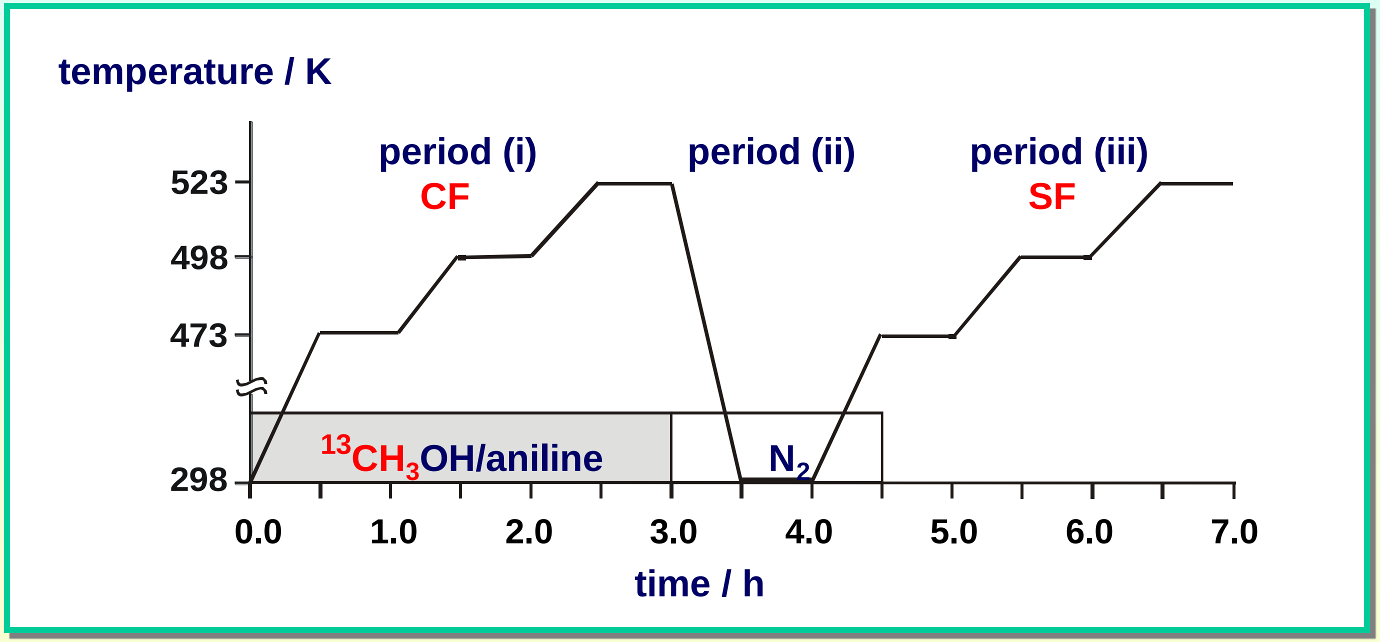
(16 ppm, o-T,
21 ppm, p-T)

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

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

Study of reaction intermediates by in situ SF (stopped-flow) MAS NMR

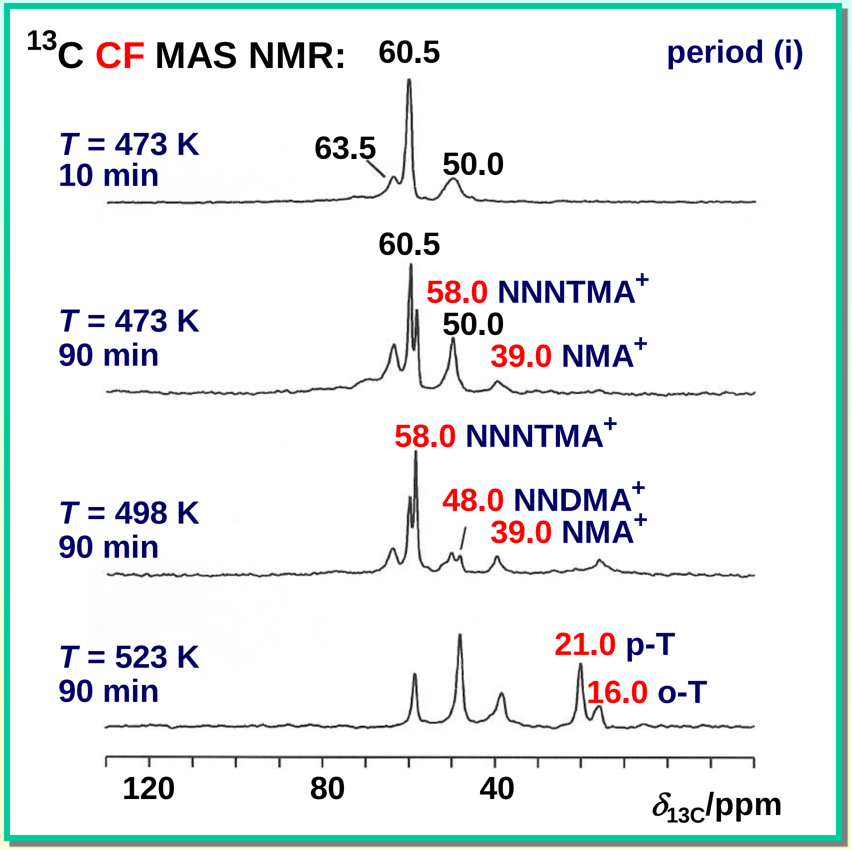
- **reaction of pure methoxy groups on zeolite H-Y at elevated temperatures**

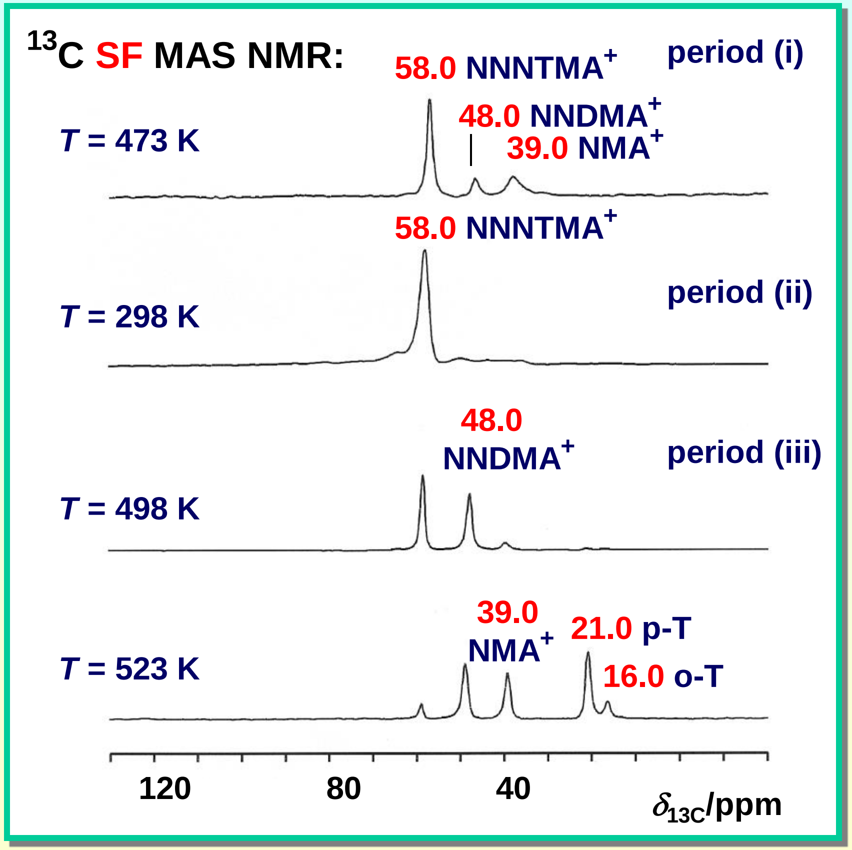


W. Wang et al., J. Am. Chem. Soc. 124 (2002) 7548.

Reactivity of anilinium cations on zeolite H-Y

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



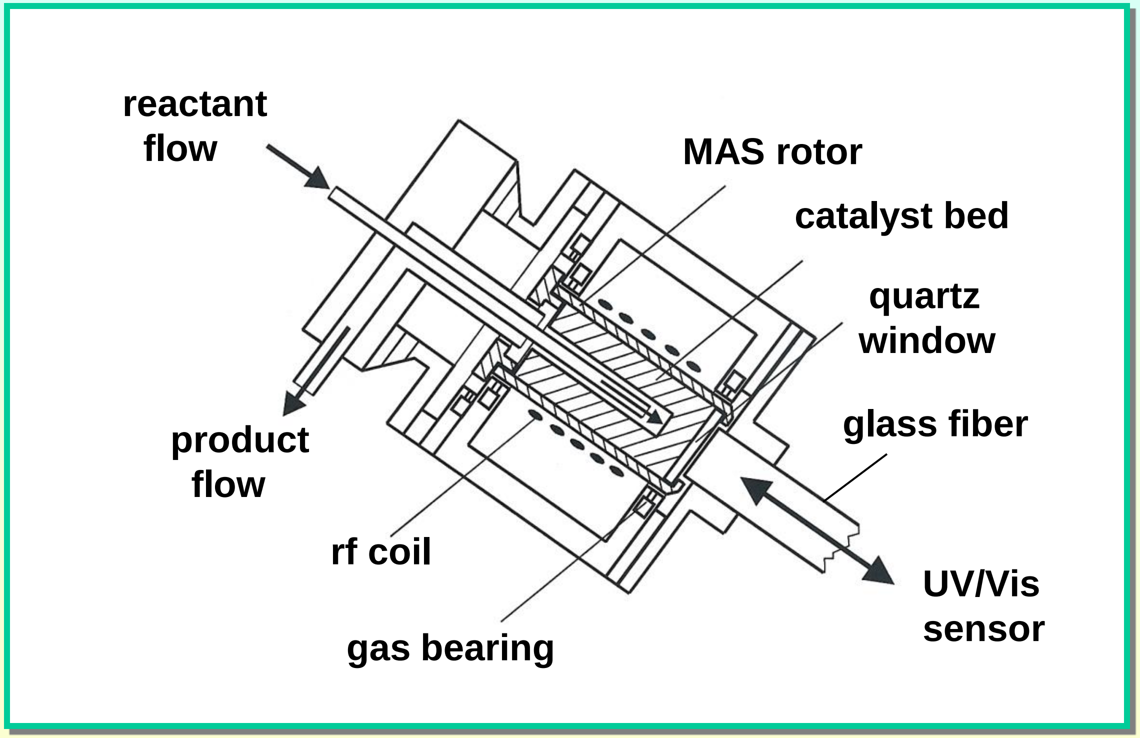


all reaction products can be formed by a decomposion of NNNTMA$^+$ → chemical equilibrium

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

MAS NMR-UV/Vis Coupling

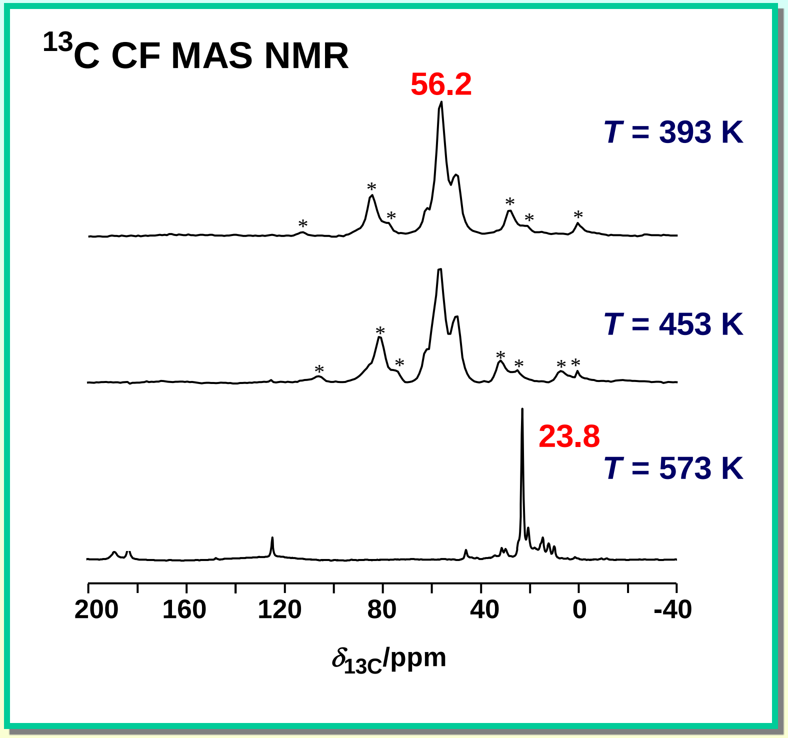
installation of a quartz fiber optic at the bottom of the CF MAS NMR stator

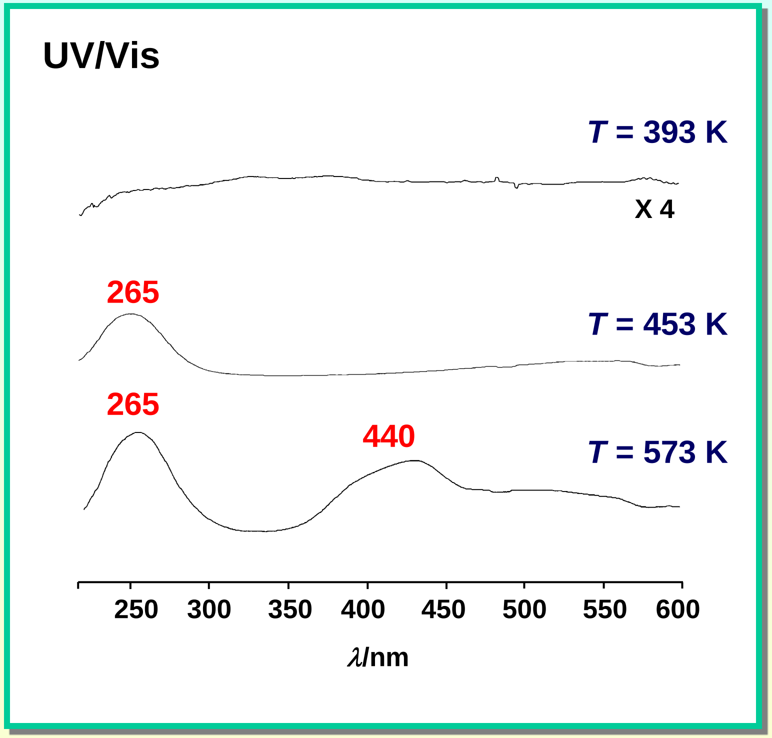


M. Hunger, W. Wang, Chem. Commun. (2004) 584.

Simultaneous in situ NMR-UV/Vis spectroscopy

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

advantages:

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

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

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

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

disadvantages:

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

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

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

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

Summary II

applications of *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**