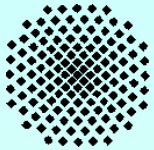
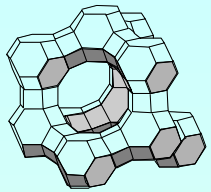




Applications of in situ spectroscopy in zeolite science

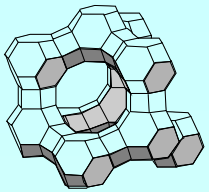
Michael Hunger

Institute of Chemical Technology

University of Stuttgart, Germany

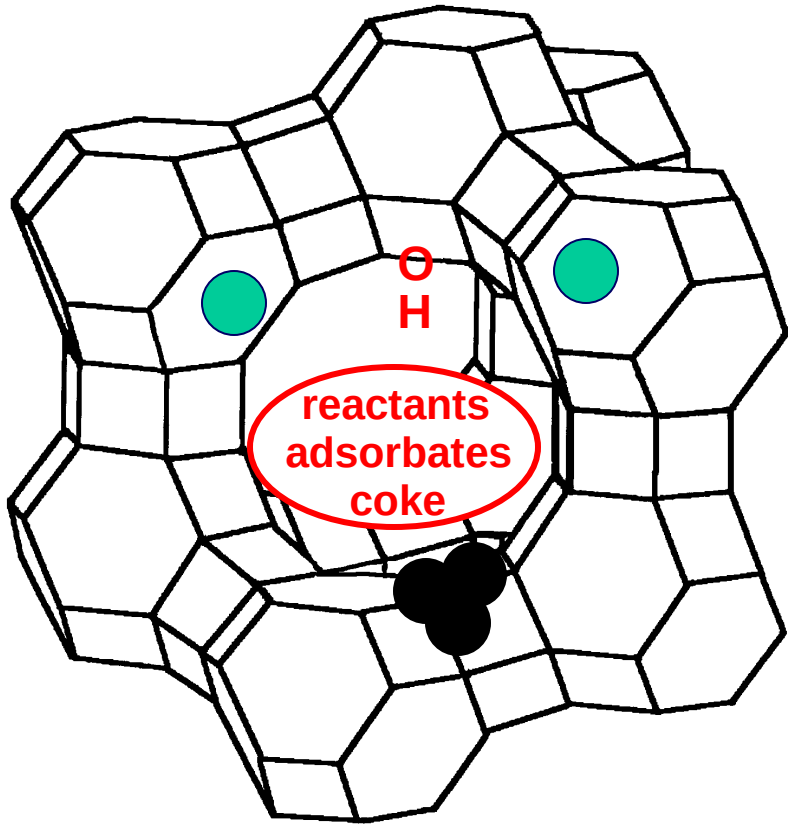
14th International Zeolite Pre-Conference School

23 – 25 April 2004, Stellenbosch, South Africa



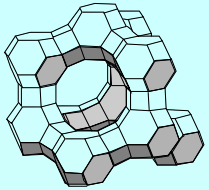
Components of heterogeneous reaction systems

catalyst framework, extra-framework species, and surface sites



spectroscopically sensitive behaviors:

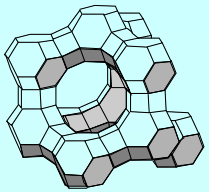
- **various vibrations**
- **electron transitions**
- **unpaired electrons**
- **nuclear spins**



Contents

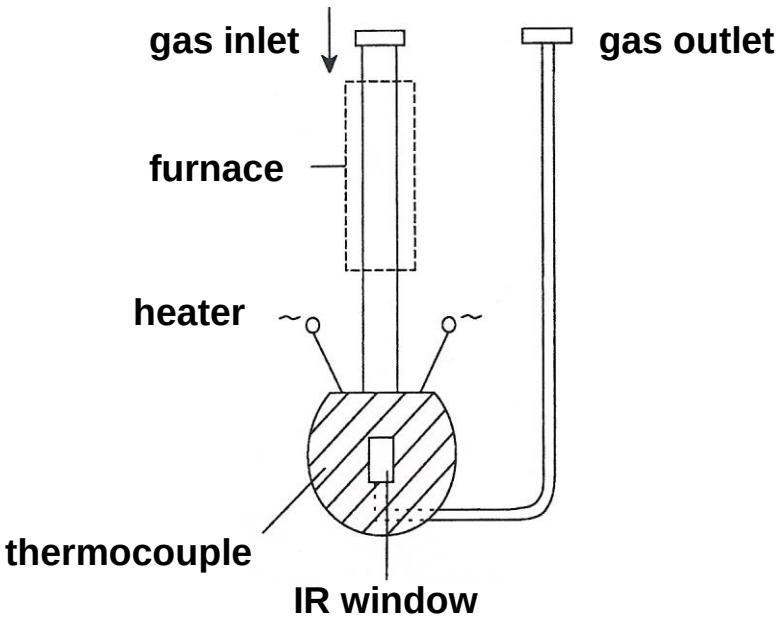
spectroscopic methods applied for studies of heterogeneous reaction systems under *in situ* conditions in the laboratory scale:

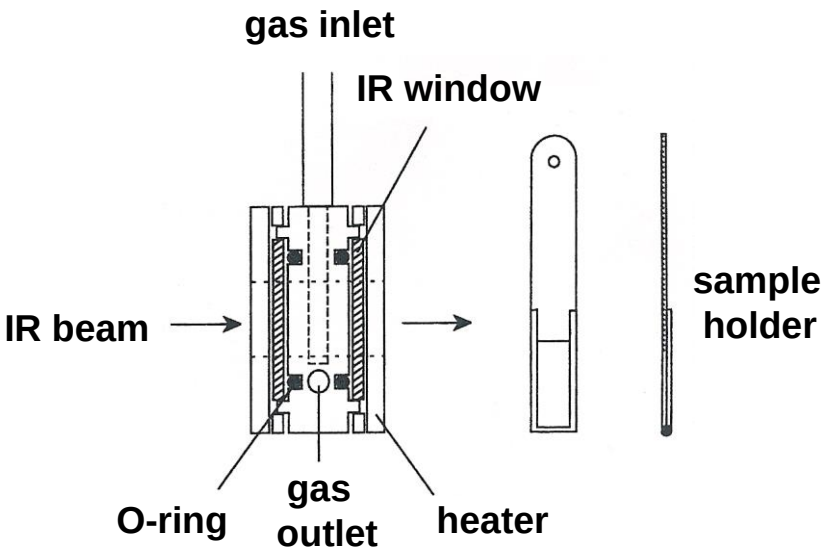
- **Fourier transform infrared (FTIR) spectroscopy**
  - **hydroxyl groups, reactants, adsorbates, coke**
- **UV-Vis spectroscopy**
  - **surface sites, conjugated double bonds, carbenium ions, coke**
- **electron spin resonance (ESR):**
  - **paramagnetic surface sites, adsorbates, coke**
- **solid-state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



In situ FTIR spectroscopy in zeolite science

scheme of an *in situ* IR cell

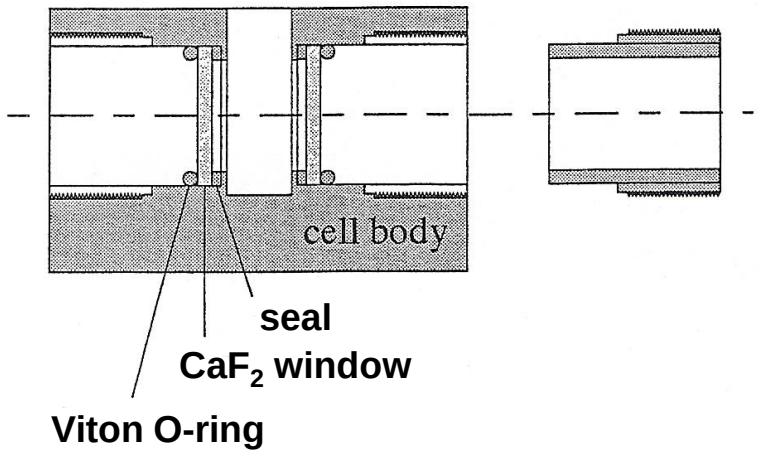


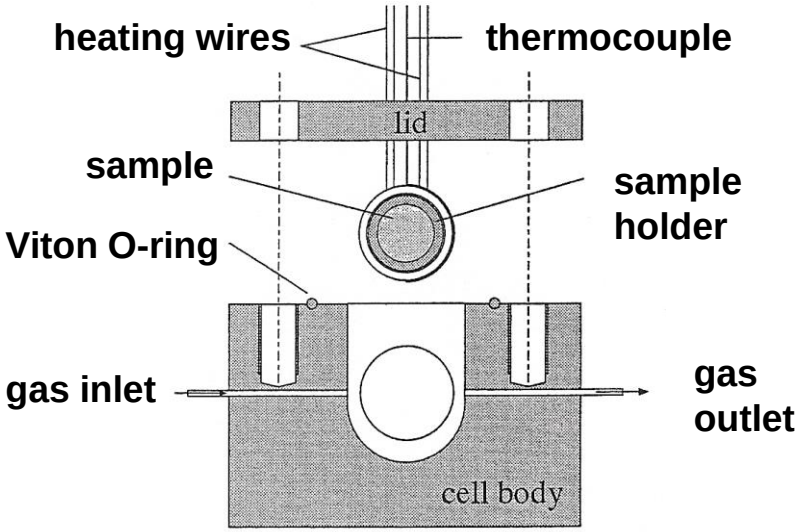


- **up to 523 K under high-vacuum and up to 923 K at *p* = 1 bar**

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

scheme of an *in situ* IR cell



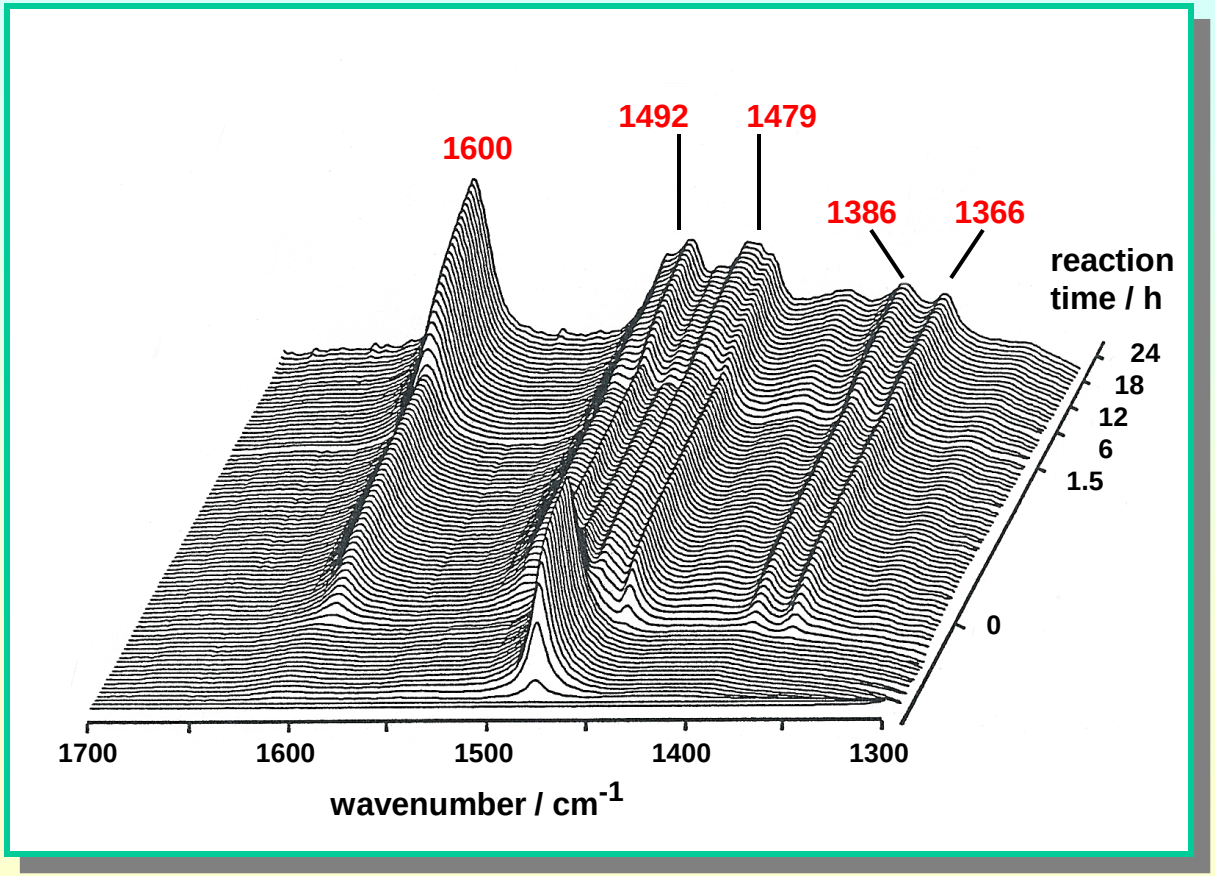


- **maximum temperature of 870 K at up to *p* = 5 bar**

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 deformation vibration of diisopropylbenzene

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

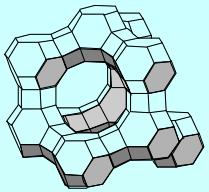
1479 cm^{-1}:
ring vibration of benzene

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

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

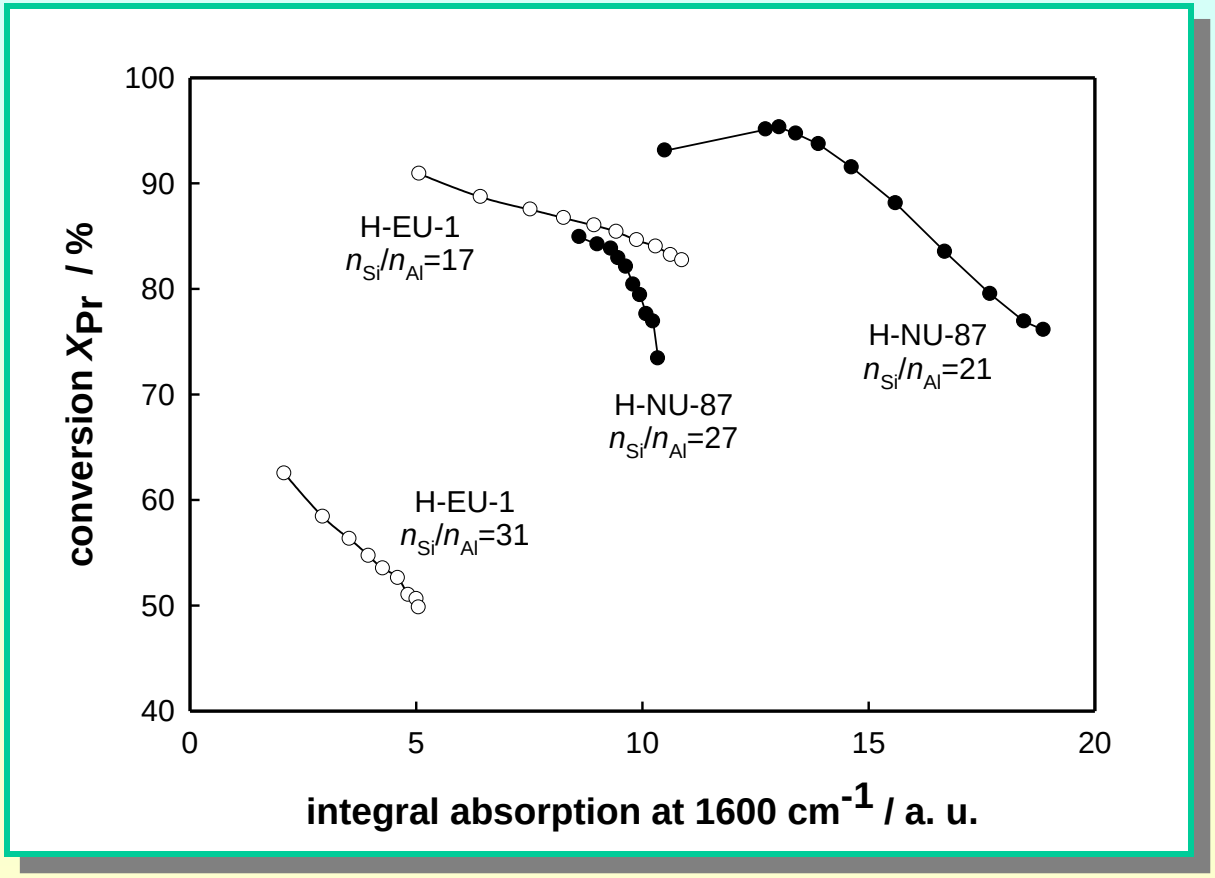
→ **coke formation starts with injection of propene**

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



FTIR spectroscopy

dependence of the catalytic activity on the formation of coke



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

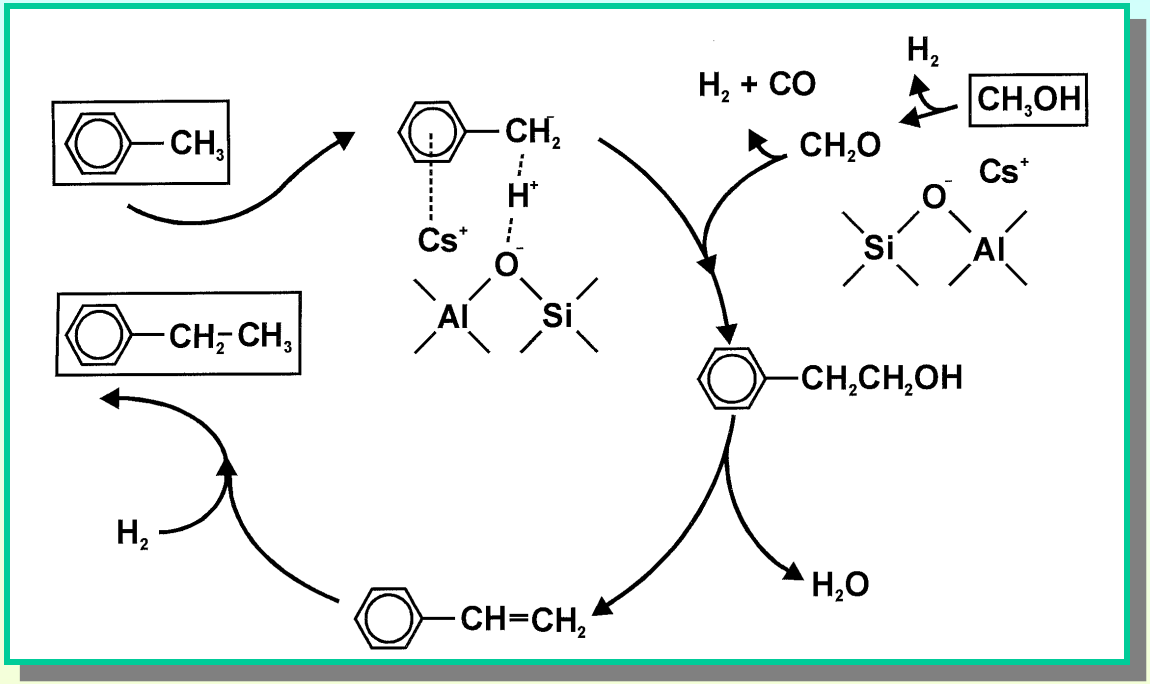
→ **depends on the aluminum content and pore geometry**

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

Side-chain alkylation of toluene with methanol on basic zeolites

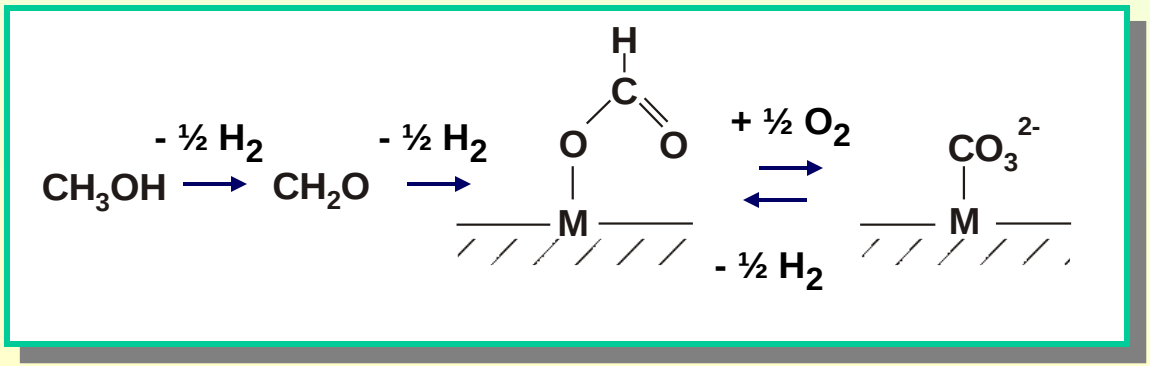
- **reaction scheme proposed by Yashima et al. , J. Catal. 26 (1972) 303:**

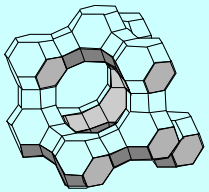
  - activation of toluene by adsorption on the zeolite
  - conversion of methanol to formaldehyde catalyzed by base sites



- **proposed surface species:**

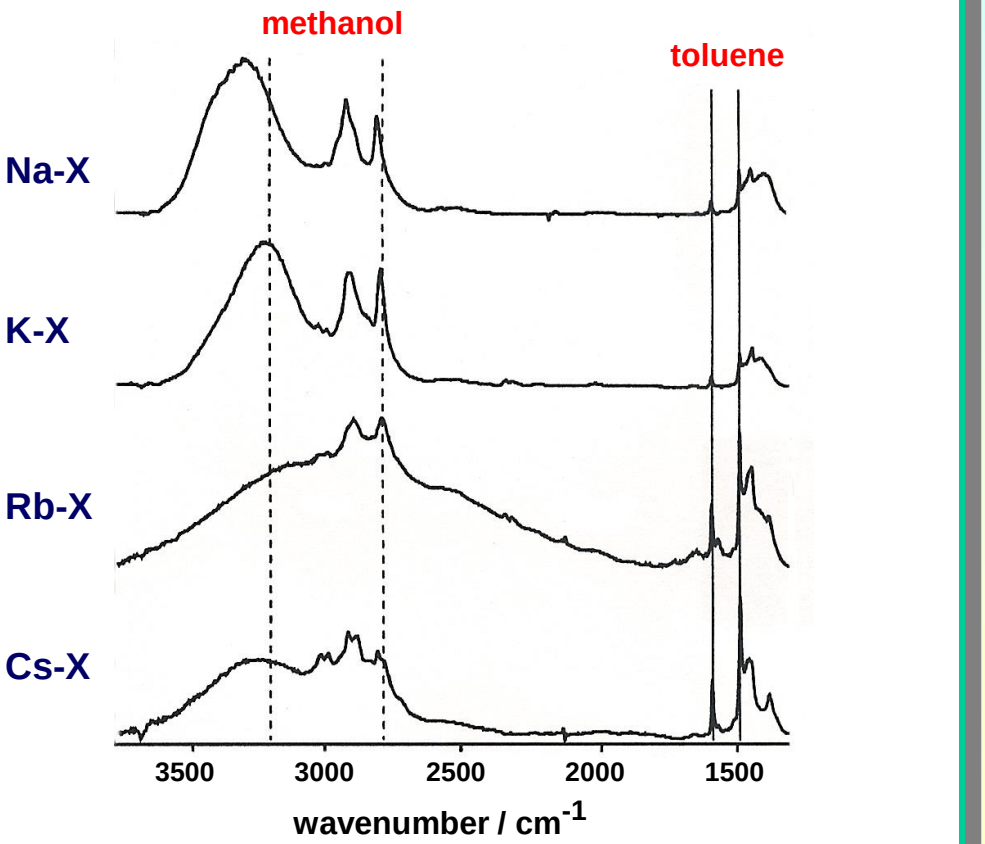
  - surface formate species
  - carbonates





FTIR spectroscopy

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



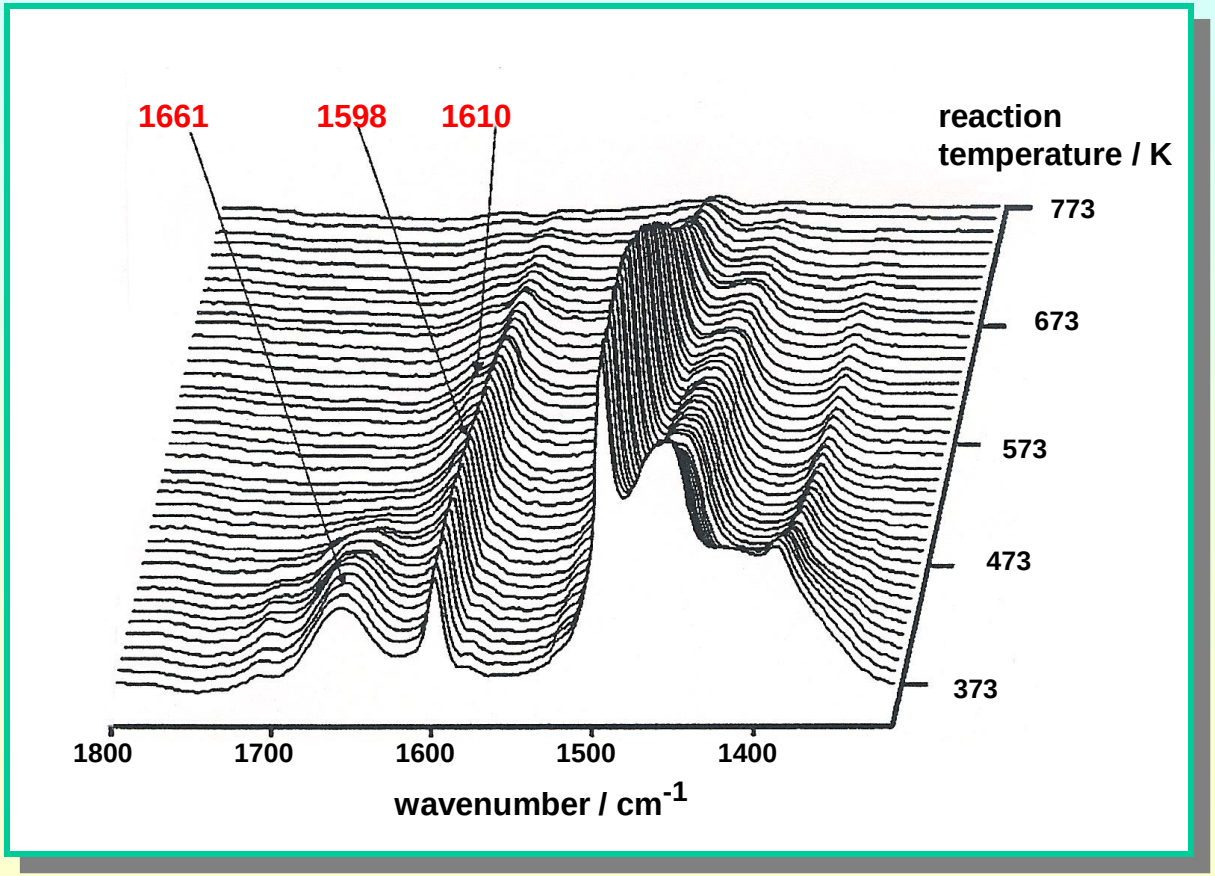
→ **same co-adsorbed states independent on the sequence of adsorption**

→ **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 deformation vibration

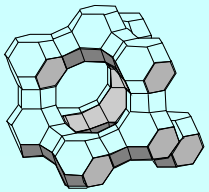
1598 cm^{-1}:
C-C vibration of toluene

1610 cm^{-1}:
surface formate species

1661 cm^{-1}:
adsorbed dimethyl ether

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

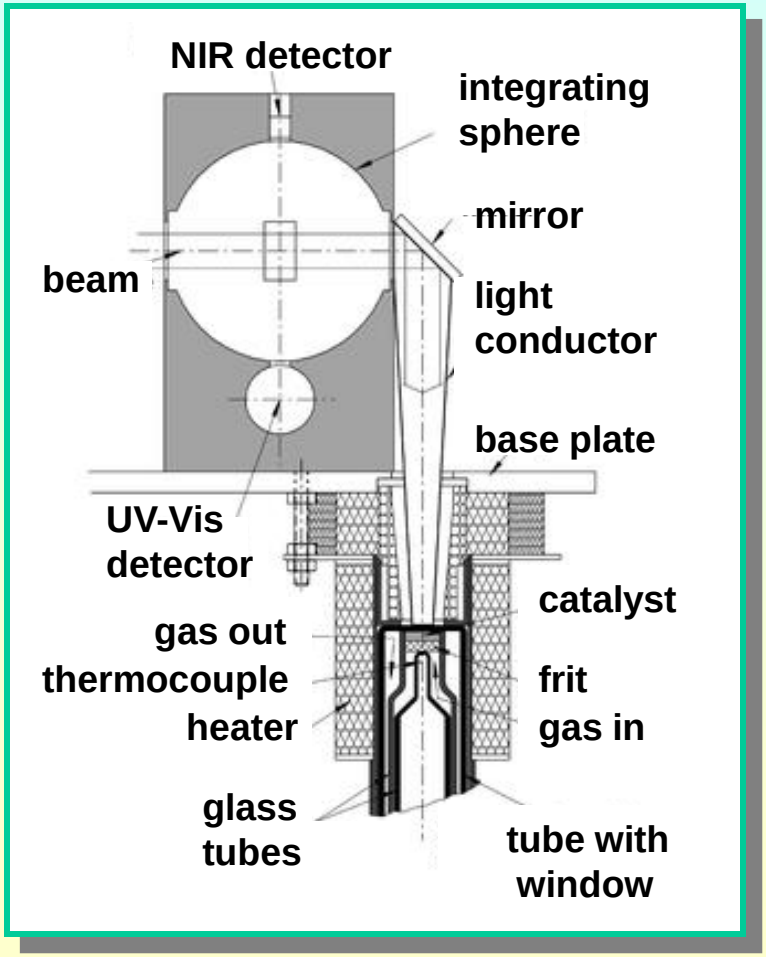
A.E. Palomares et al., J. Catal. 180 (1998) 56.



In situ UV-Vis spectroscopy in zeolite science

UV-Vis spectroscopy

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

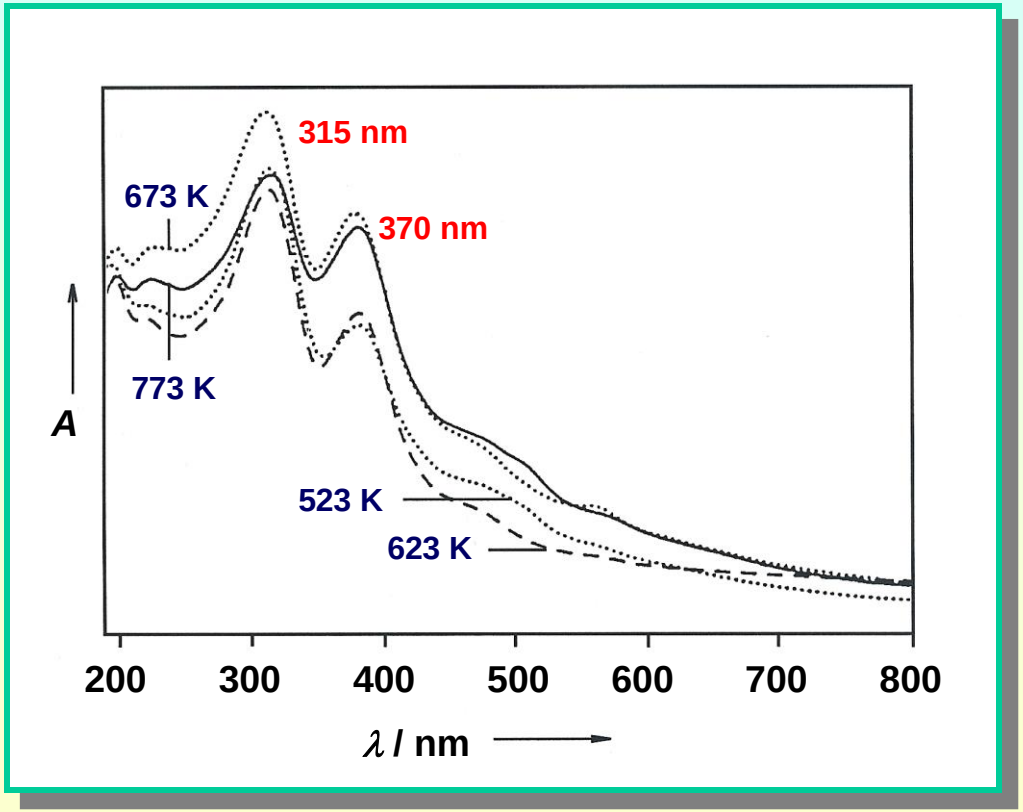


- suitable for *in situ* investigations at temperatures up to 723 K
- combination of UV-Vis and NIR spectroscopy
- increase of signal-to-noise ratio by 25% due to the light conductor
- horizontal arrangement of the powder material

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:

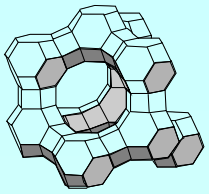
- **hydrocarbons with conjugated double bonds**
- **unsaturated carbenium ions**

→ **315 nm:**
monoenyl carbenium ions

370 nm:
dienyl carbenium ions

450 nm:
trienyl carbenium ions

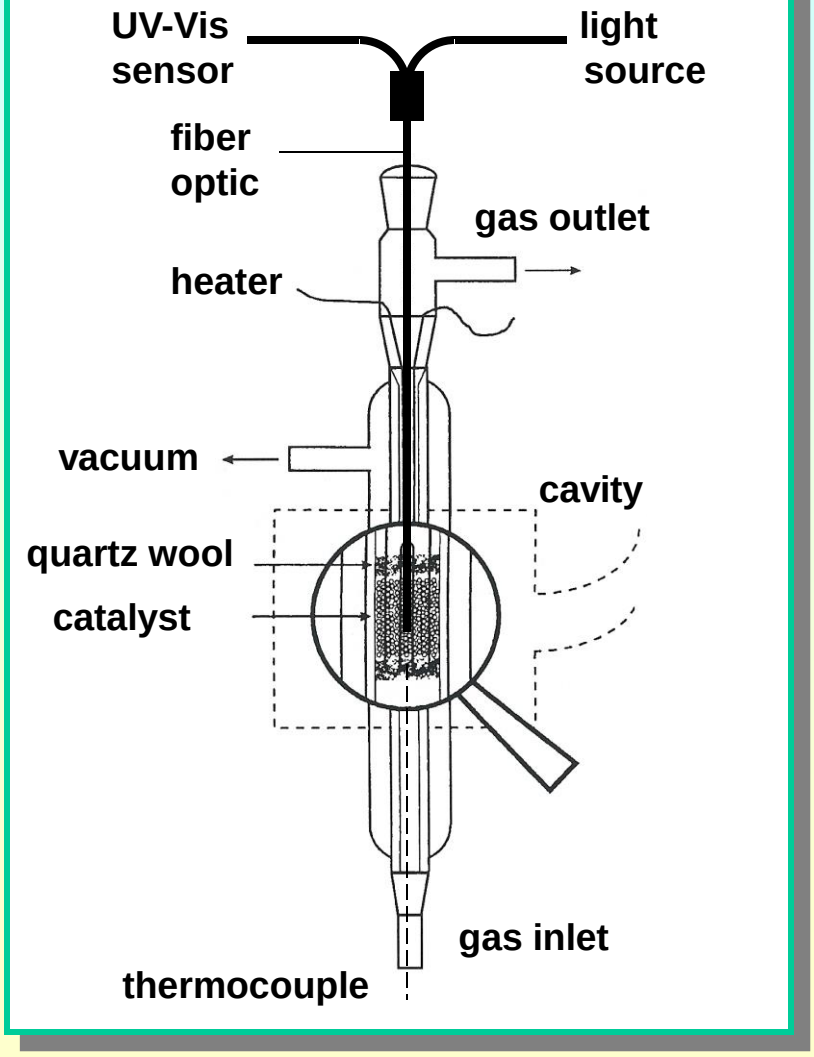
I. Kiricsi et al., Chem. Rev. 99 (1999) 2085.



In situ ESR spectroscopy in zeolite science

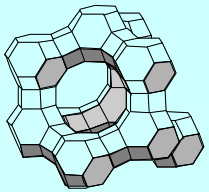
ESR spectroscopy

scheme of an *in situ* ESR cell



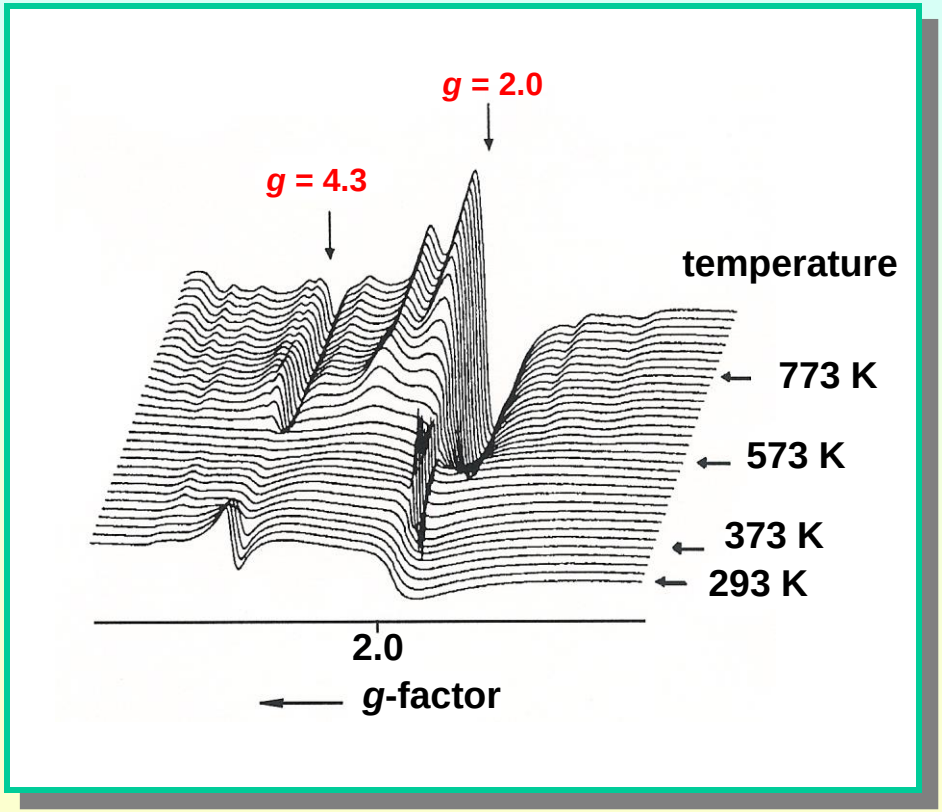
- **ESR flow reactor for X-band (B_o = 0.35 T, ν = 9.5 GHz)**
- **suitable for *in situ* investigations at temperatures of up to 780 K**
- **combination of ESR and UV-Vis spectroscopy**

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:**
octahedrical Fe^{3+} coordinated to four lattice oxygen bridges and two extra-framework ligands in the pores

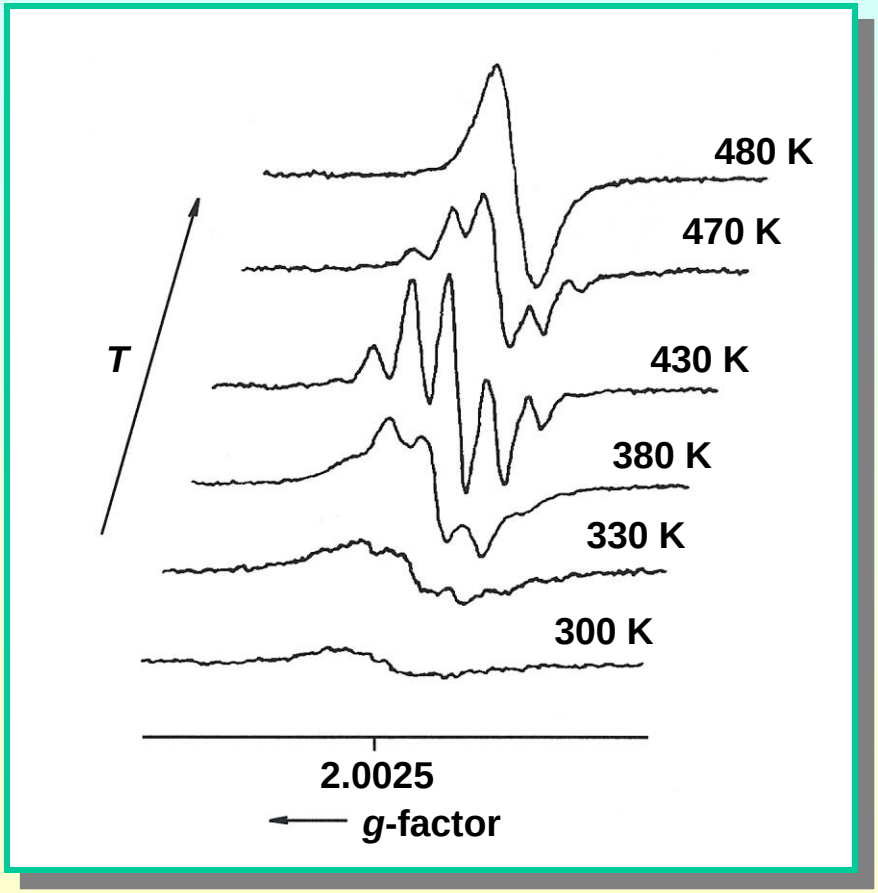
***g* = 4.3:**
octahedral Fe^{3+} in lattice defects coordinated to bridging oxygen and terminal oxygen

(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



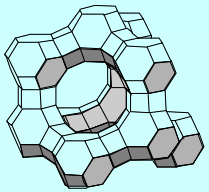
→ **formation of coke:**

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

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

(1 radical per 1000 molcules)

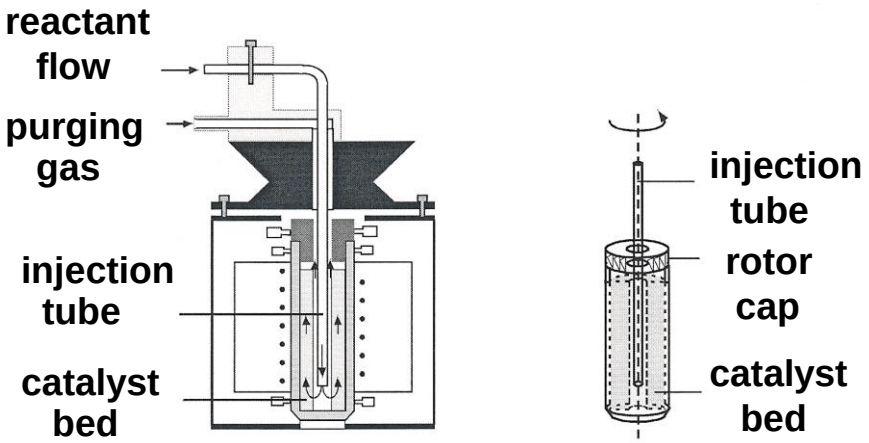
H. Karge et al., J. Catal. 114 (1988) 144.

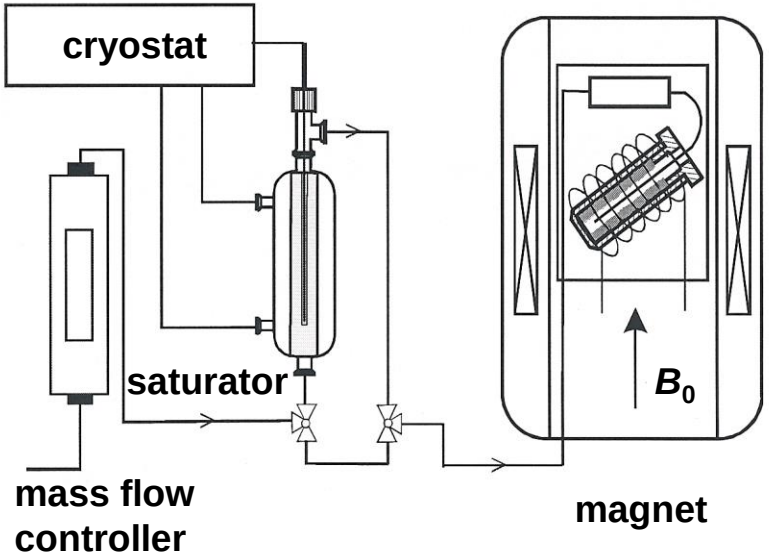


In situ solid-state NMR spectroscopy in zeolite science

Continuous-flow (CF) MAS NMR technique

scheme of an *in situ* MAS NMR probe

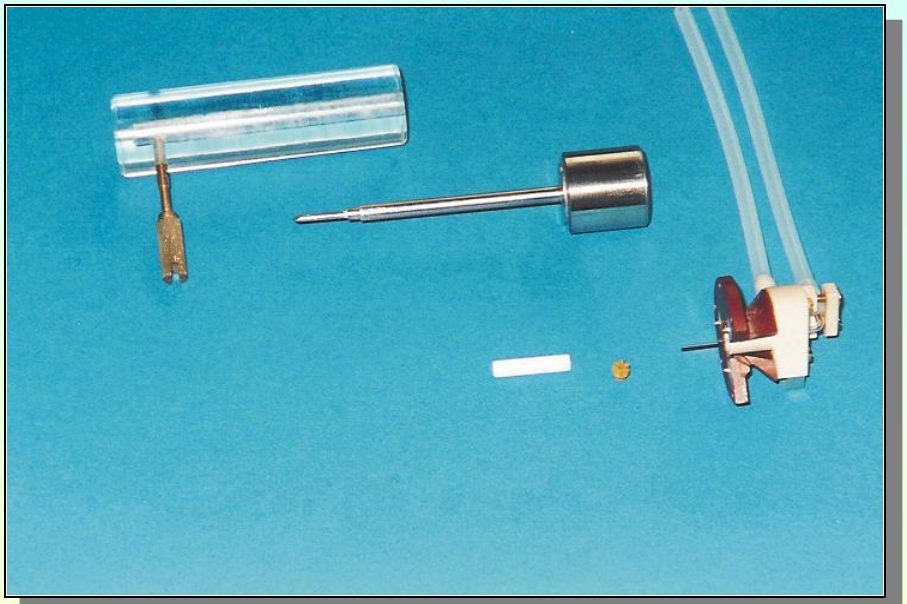


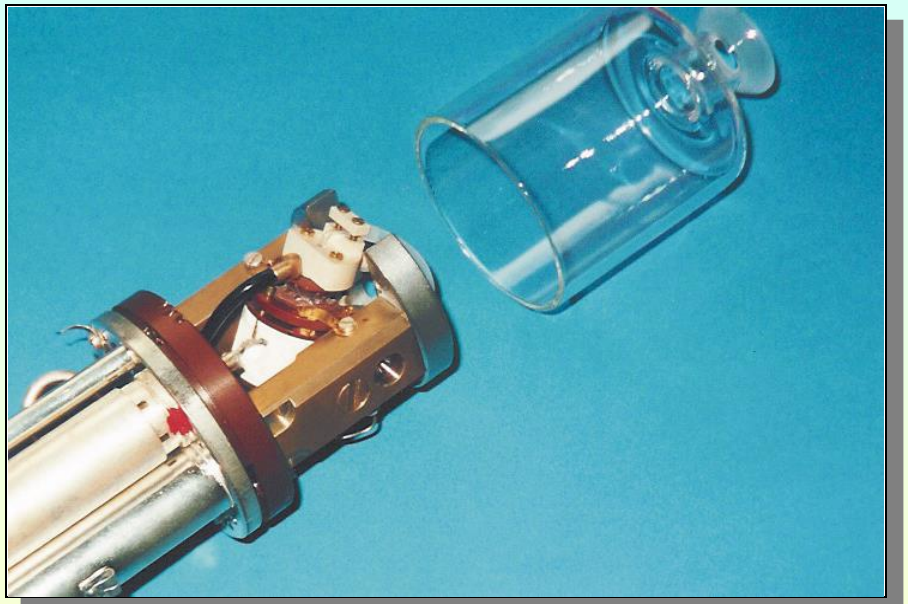


- **continuous injection of reactants into a spinning MAS NMR rotor reactor (T < 923 K)**

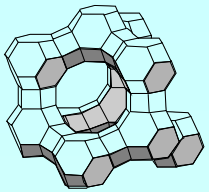
M. Hunger, T. Horvath, J. Chem. Soc., Chem. Commun. (1995) 1423.

Continuous-flow (CF) MAS NMR technique





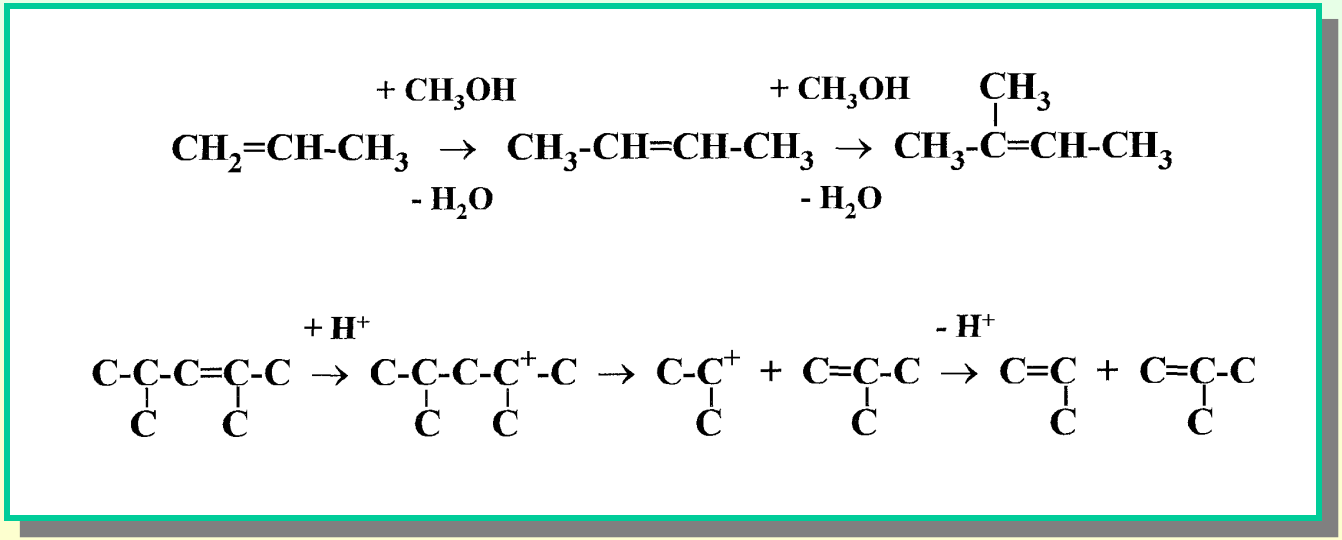
A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.



Methanol to olefin (MTO) conversion on acidic zeolites

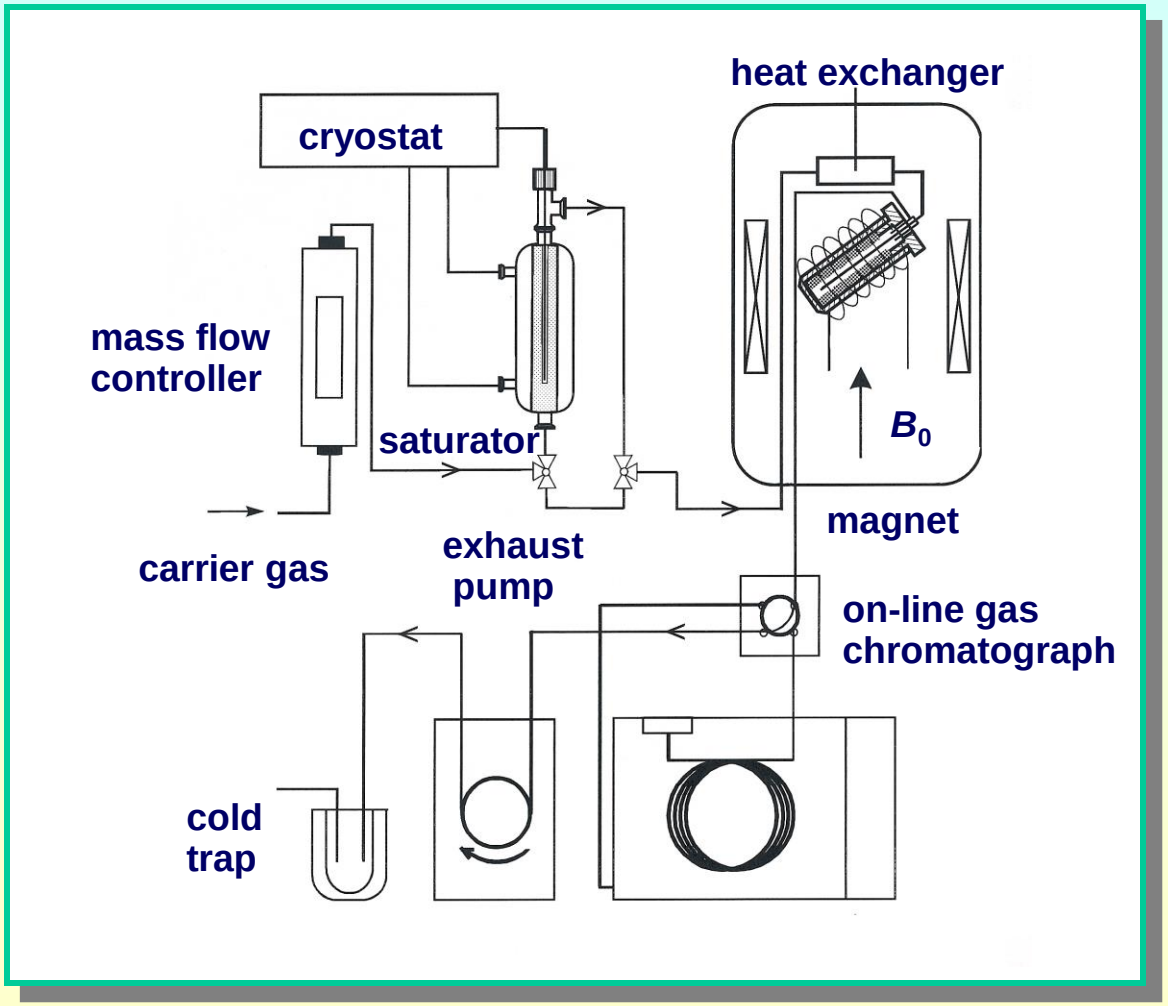
reaction mechanisms proposed in the literature:

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



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

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

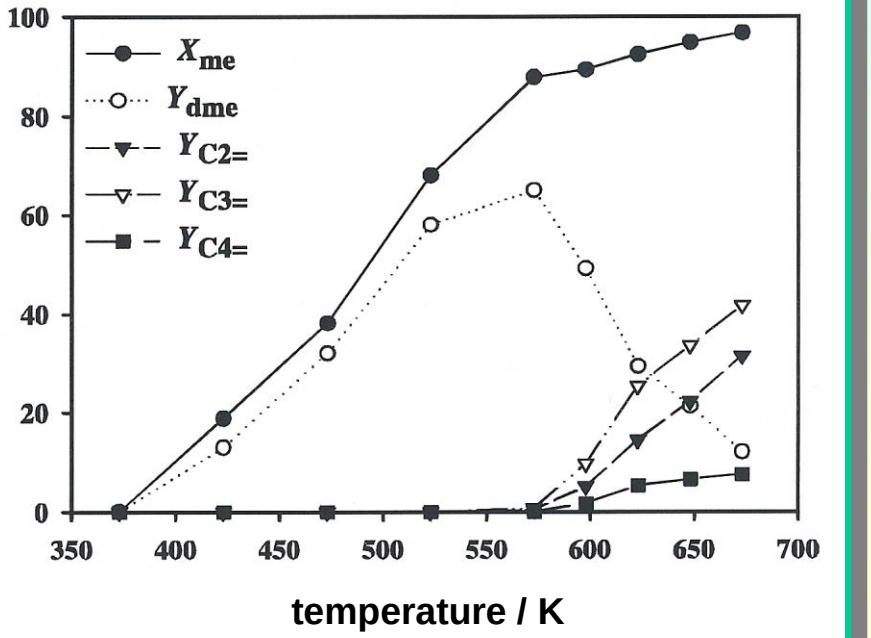


M. Hunger et al., Catal. Lett. 57 (1999) 199.

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

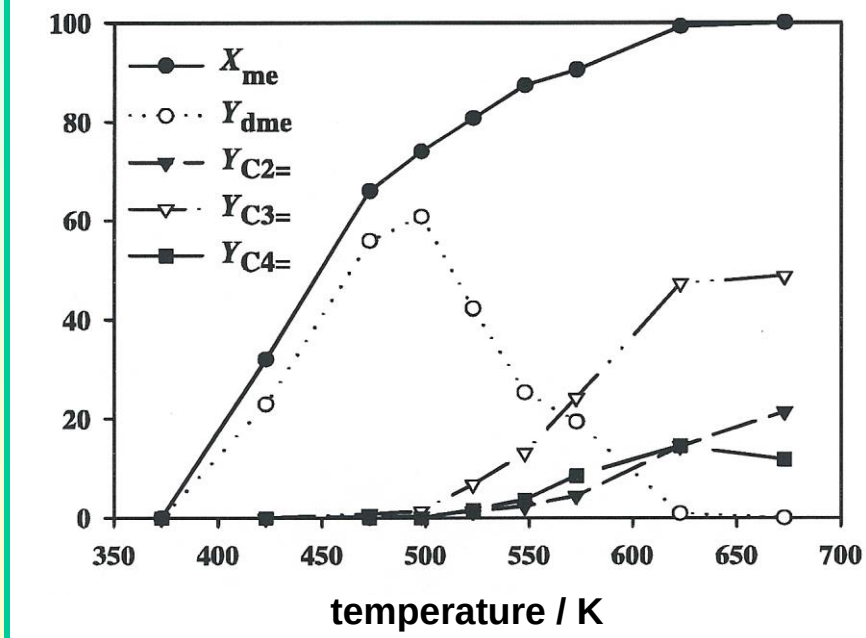
fixed-bed reactor

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



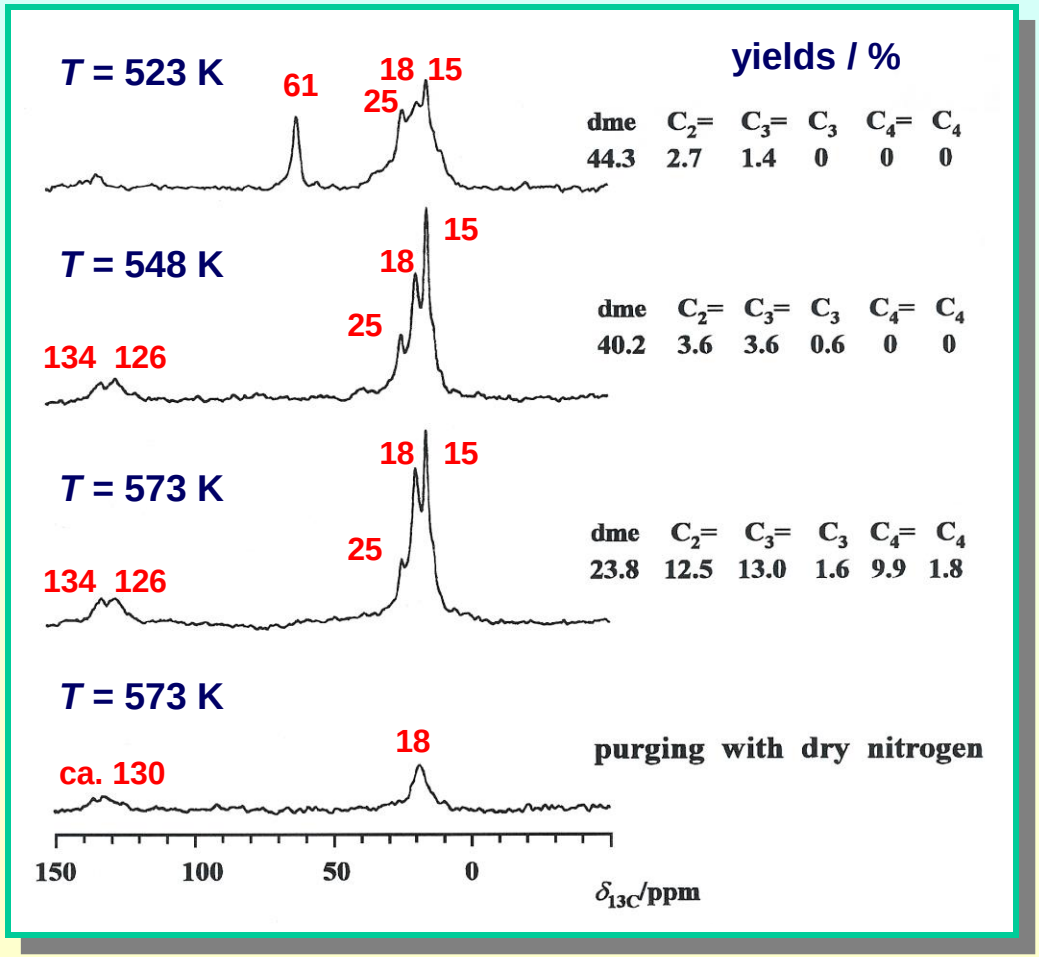
spinning (2 kHz) MAS NMR rotor reactor

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



→ **olefinic compounds, e.g.:**

3-hexene (14.4, 25.9, 131.2 ppm)

2,3-hexadiene (17.5, 126.2, 132.5 ppm)

....

and polymethylaromatics, e.g.:

toluene (20.3, 127-138 ppm)

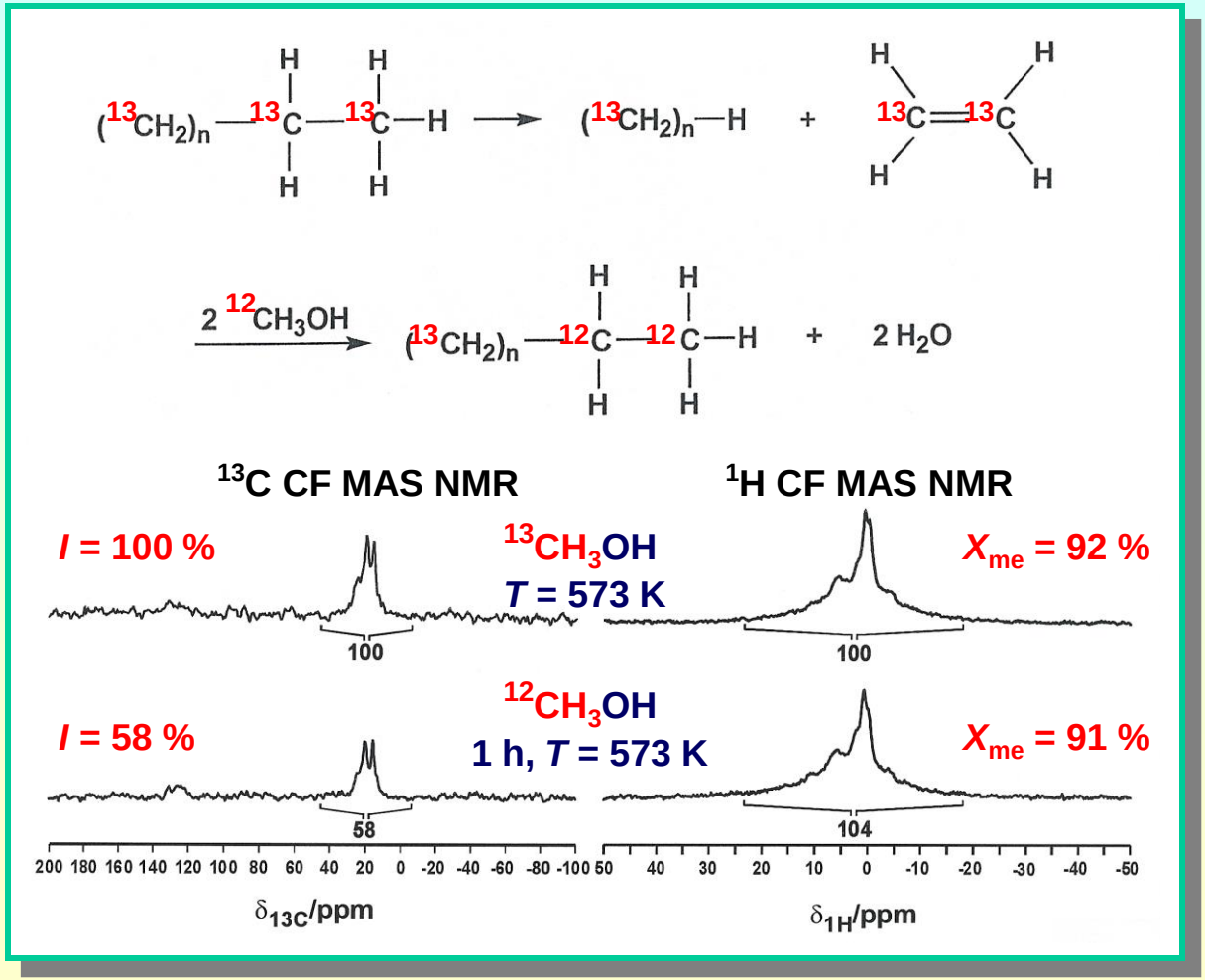
....

hexamethylbenzene (17.6, 132.1 ppm)

→ **aromatic compounds dominate after purging with pure carrier gas**

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

Role of the hydrocarbon 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:

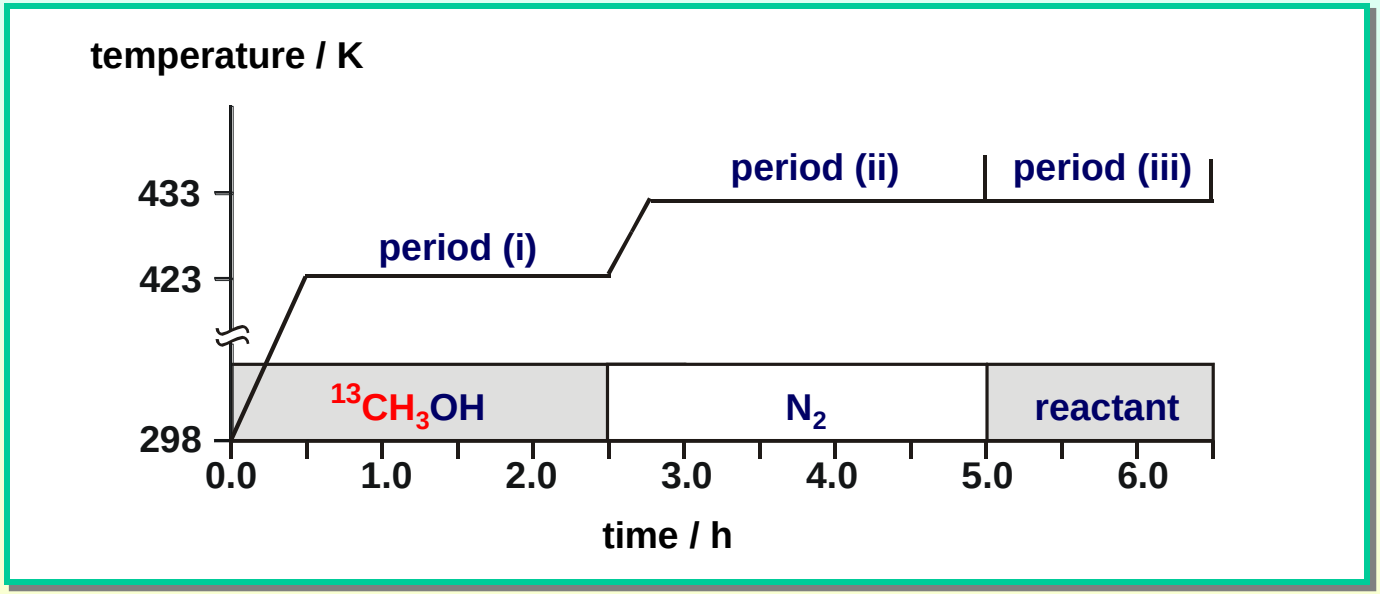
→ **alkyl groups are involved in the formation of olefins**

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

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

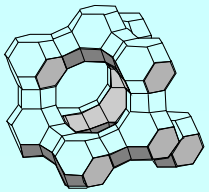
Study of surface methoxy groups by in situ SF (stopped-flow) MAS NMR

selective preparation of adsorbates by purging of volatile reactants in period (ii)



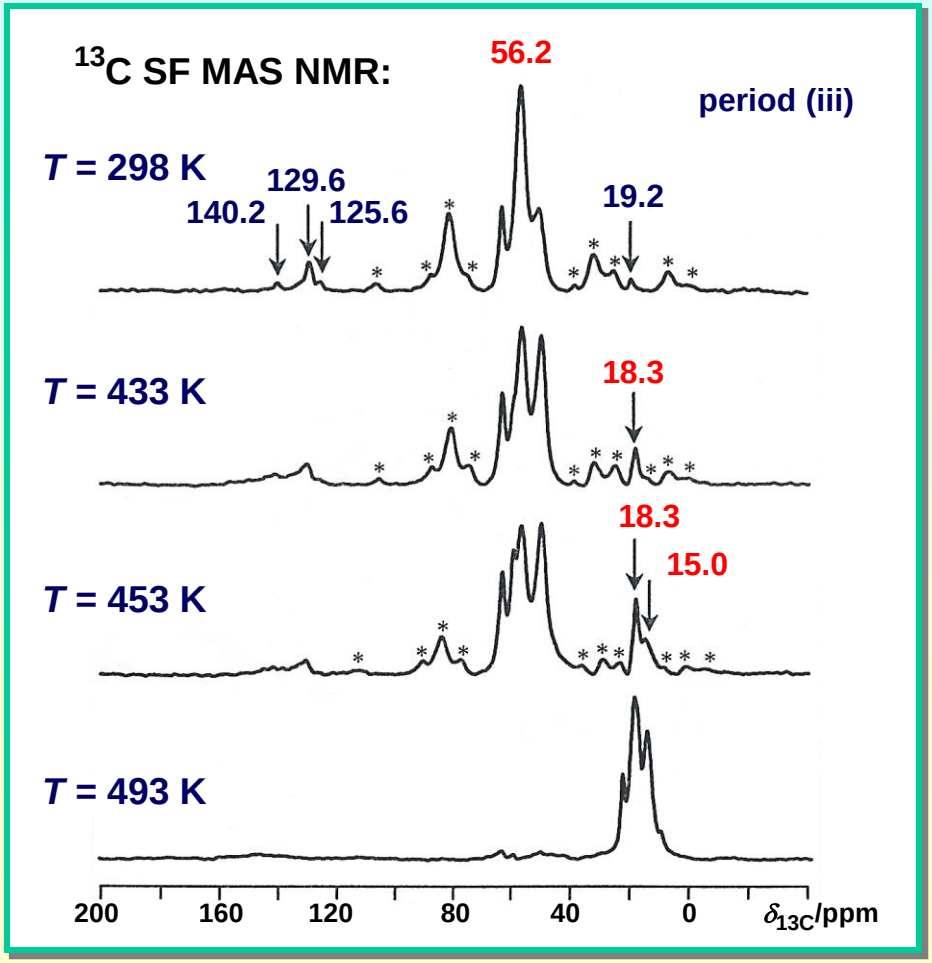
→ **investigation of the reactivity of intermediates**

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

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

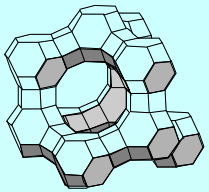
56.2 ppm 19.2 ppm

→ $SiOHAl + CH_3C_6H_4{}^{13}CH_3$

18.3 ppm

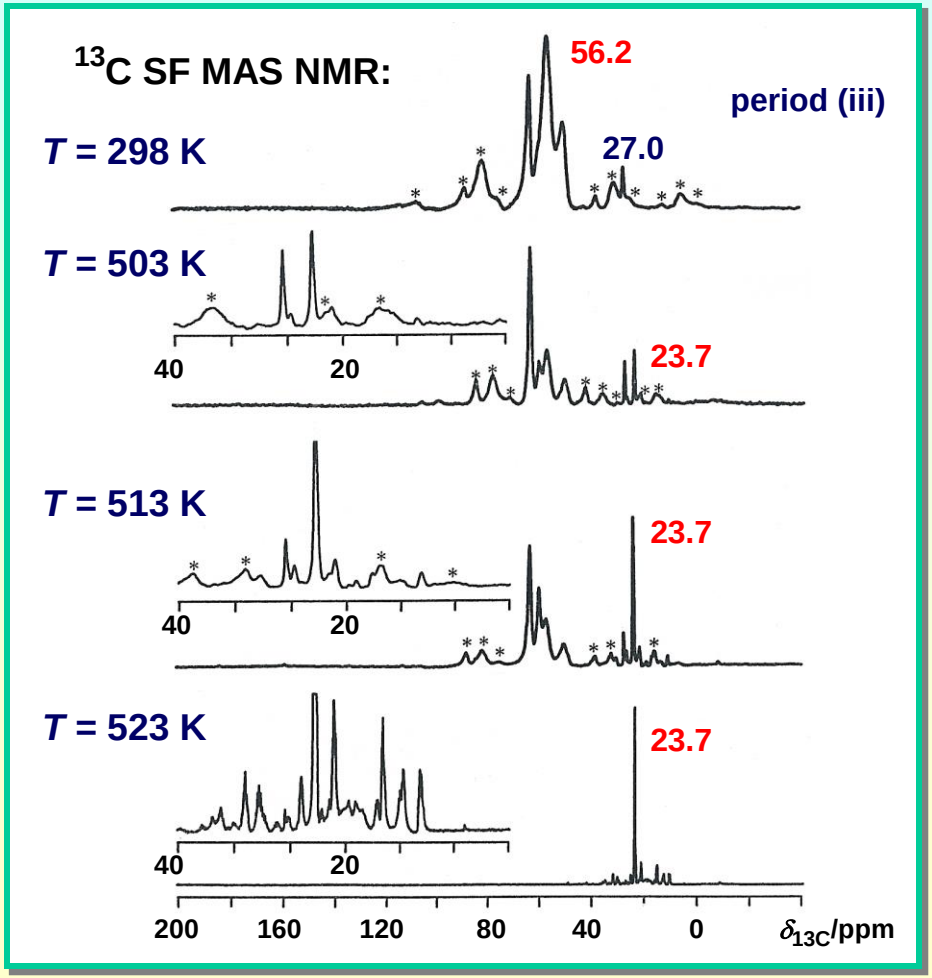
- methylation of aromatics by surface methoxy groups starts at *T* = 433 K

W. Wang, A. Buchholz, M. Seiler, M. Hunger, 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

→ $SiOHAl + {}^{13}CH_3C_6H_{11}$

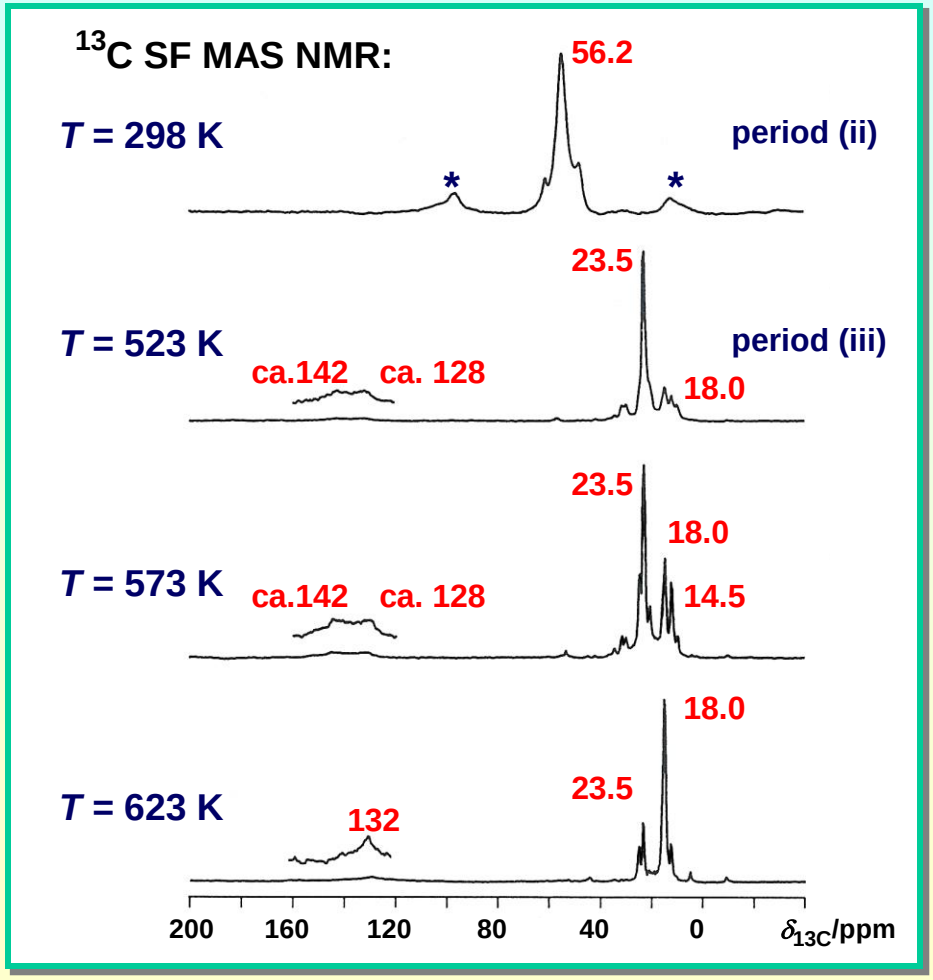
23.7 ppm

- 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. 125 (2003) 15260.

Role of surface methoxy groups in the MTO process

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)

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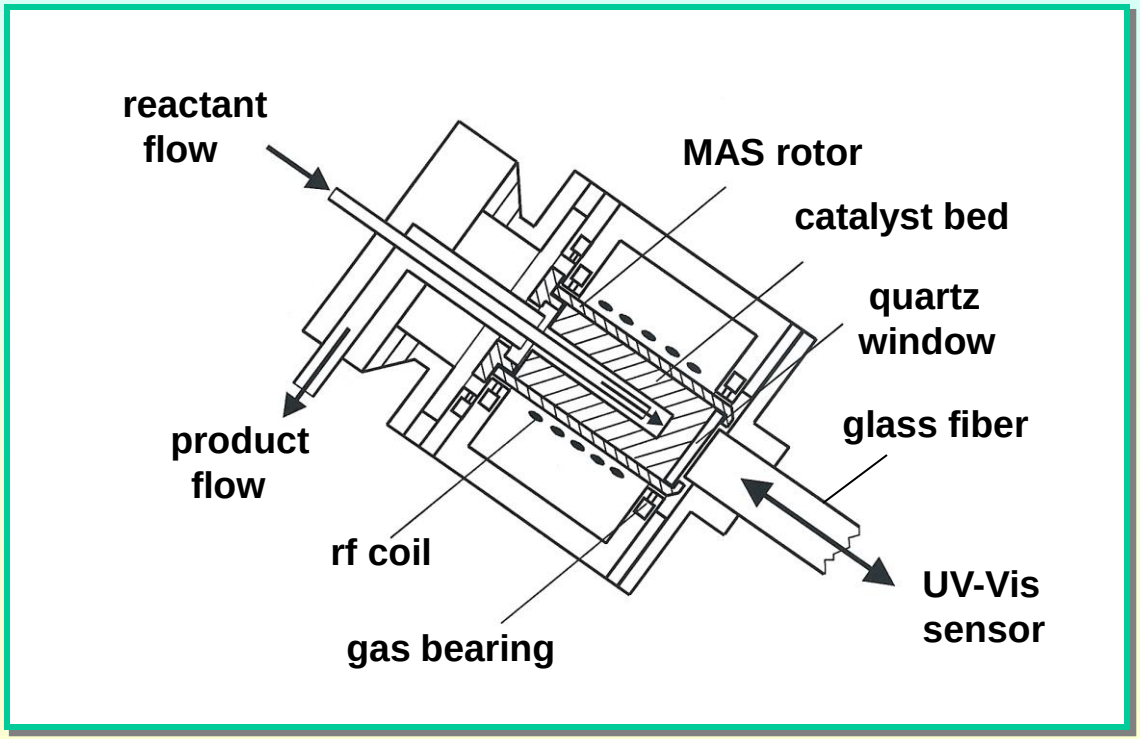
MAS NMR/UV-Vis coupling

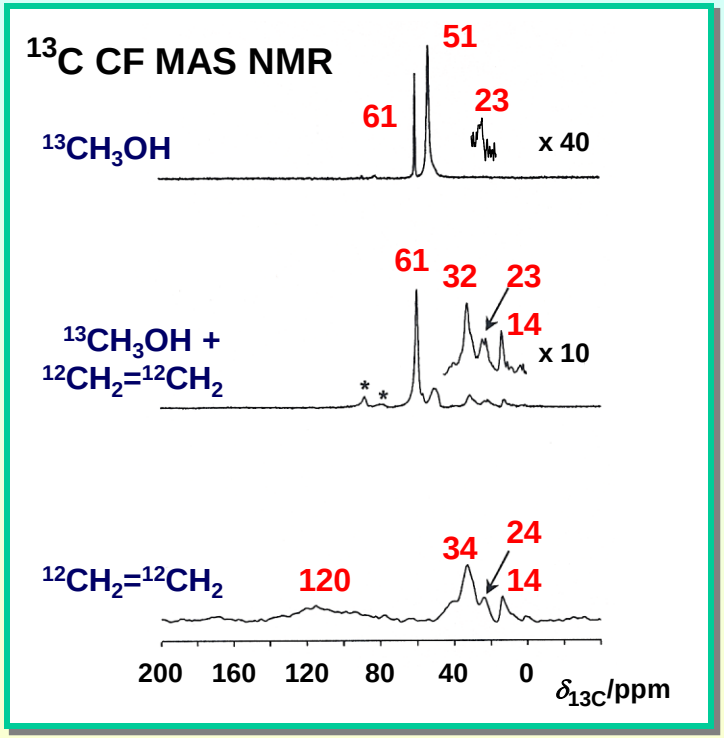
installation of a quartz fiber optic at the bottom of a CF MAS NMR turbine

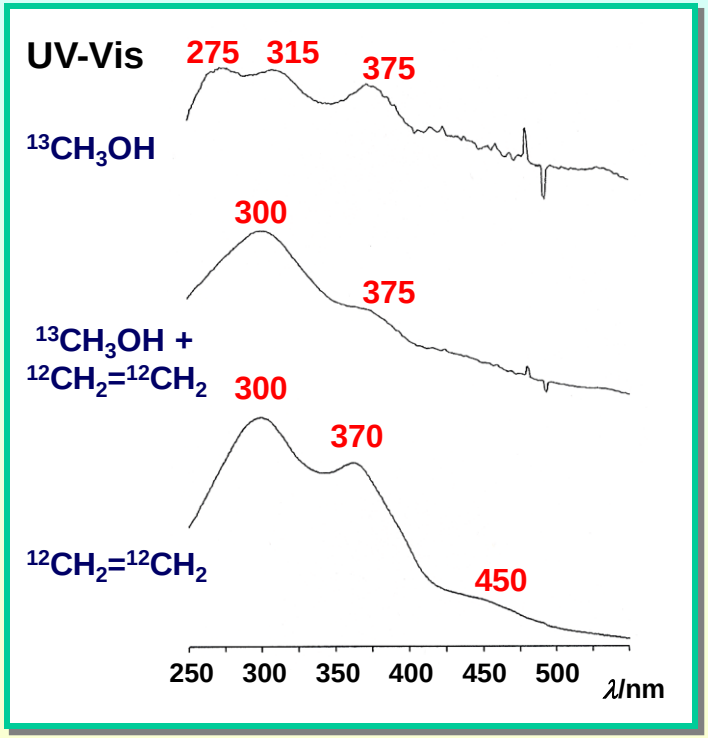


M. Hunger, W. Wang, Chem. Commun. (2004) 584.

MAS NMR/UV-Vis coupling

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





275 nm: neutral aromatic compounds
315 nm: monoenyl carbenium ions

375 nm: dienyl carbenium ions
450 nm: polyaromatic compounds

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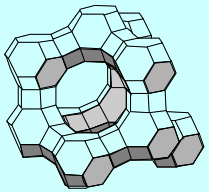


Comparison of Methods

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

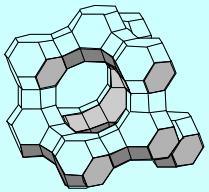
disadvantages:

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
- limited temperature range



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