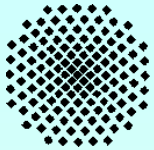
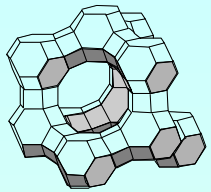
University of Stuttgart

Institute of
Chemical Technology





Operando spectroscopy in heterogeneous catalysis

Michael Hunger

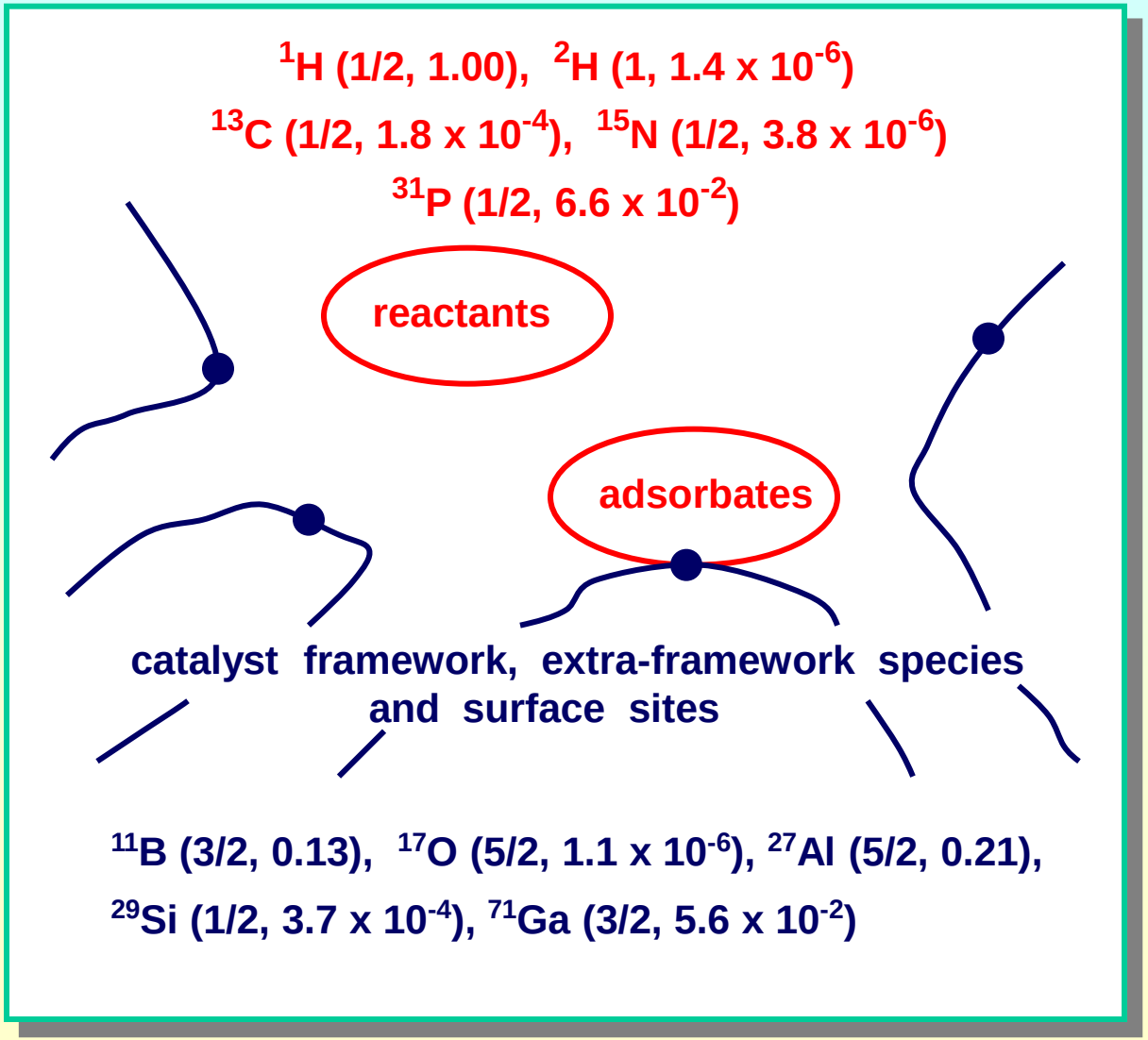
Institute of Chemical Technology

University of Stuttgart, Germany

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**



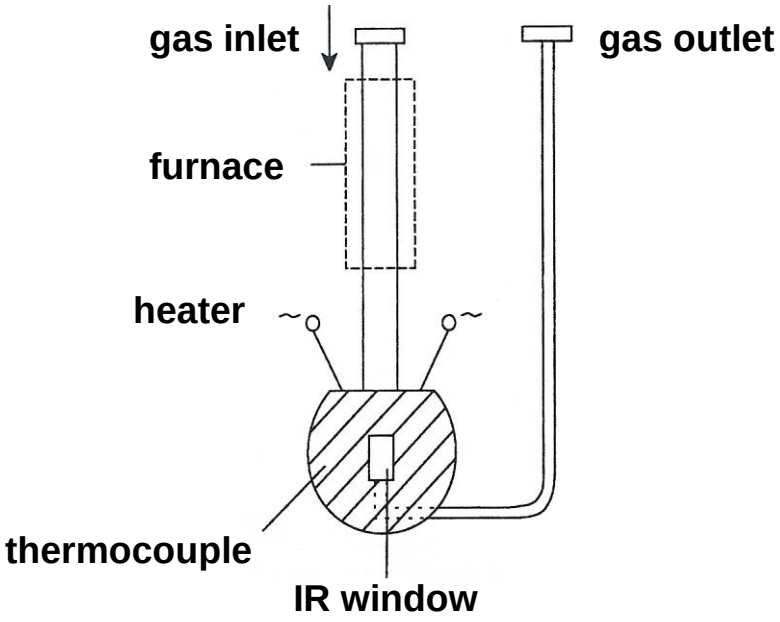
Contents

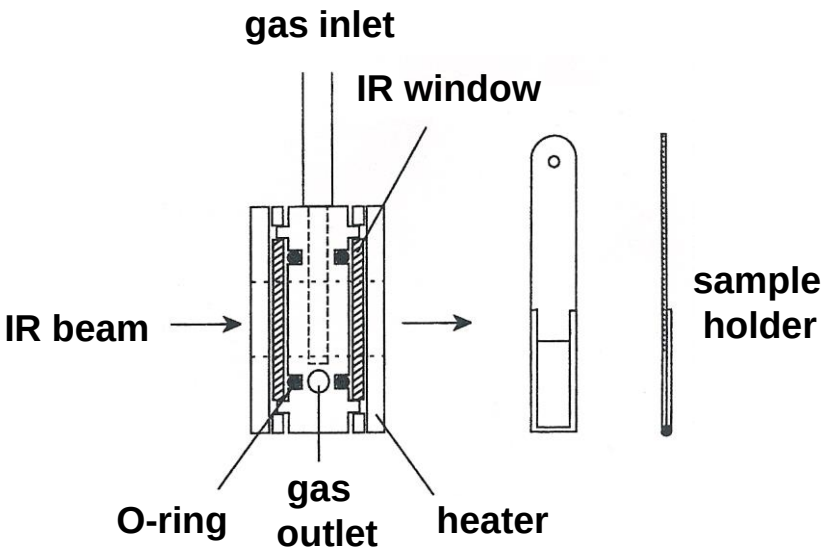
spectroscopic methods applied for studies of heterogeneous reaction systems under *in situ* conditions in the laboratory scale:

- **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

scheme of an *in situ* IR cell

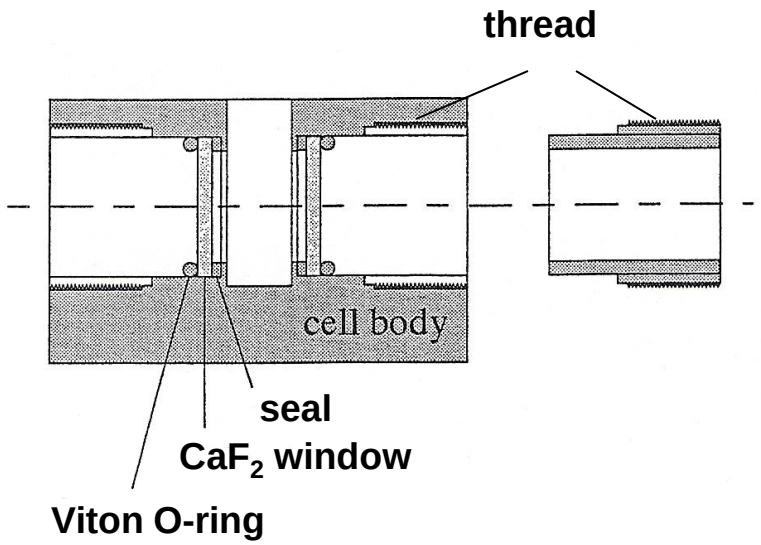


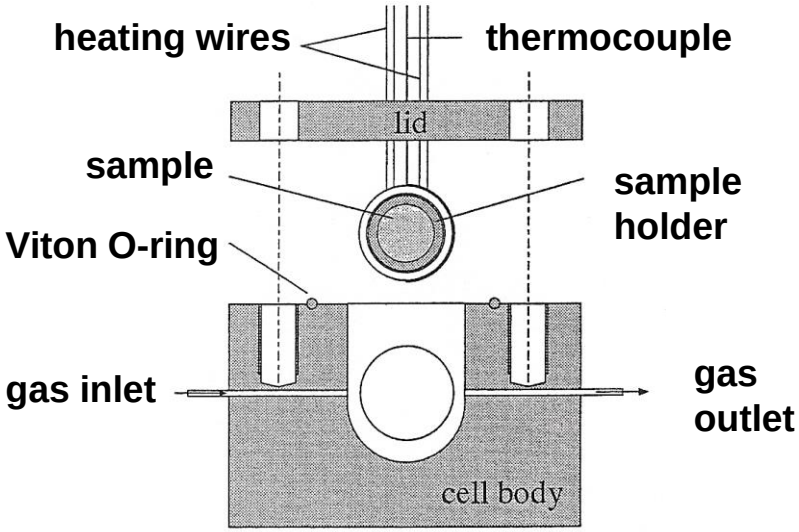


- **up to 523 K under high-vacuum and up to 923 K at *p* = 1 bar**

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



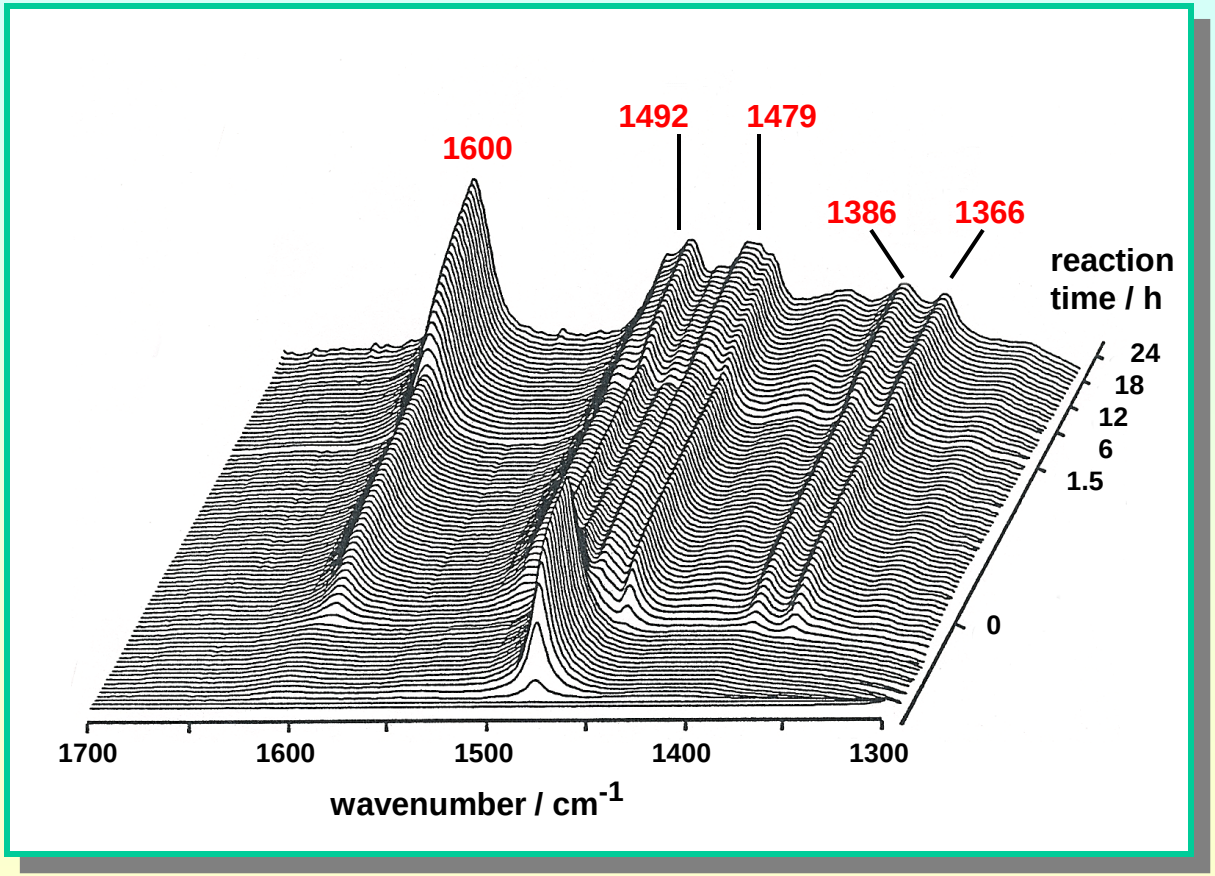


- **maximum temperature of 870 K at up to *p* = 5 bar**

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 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

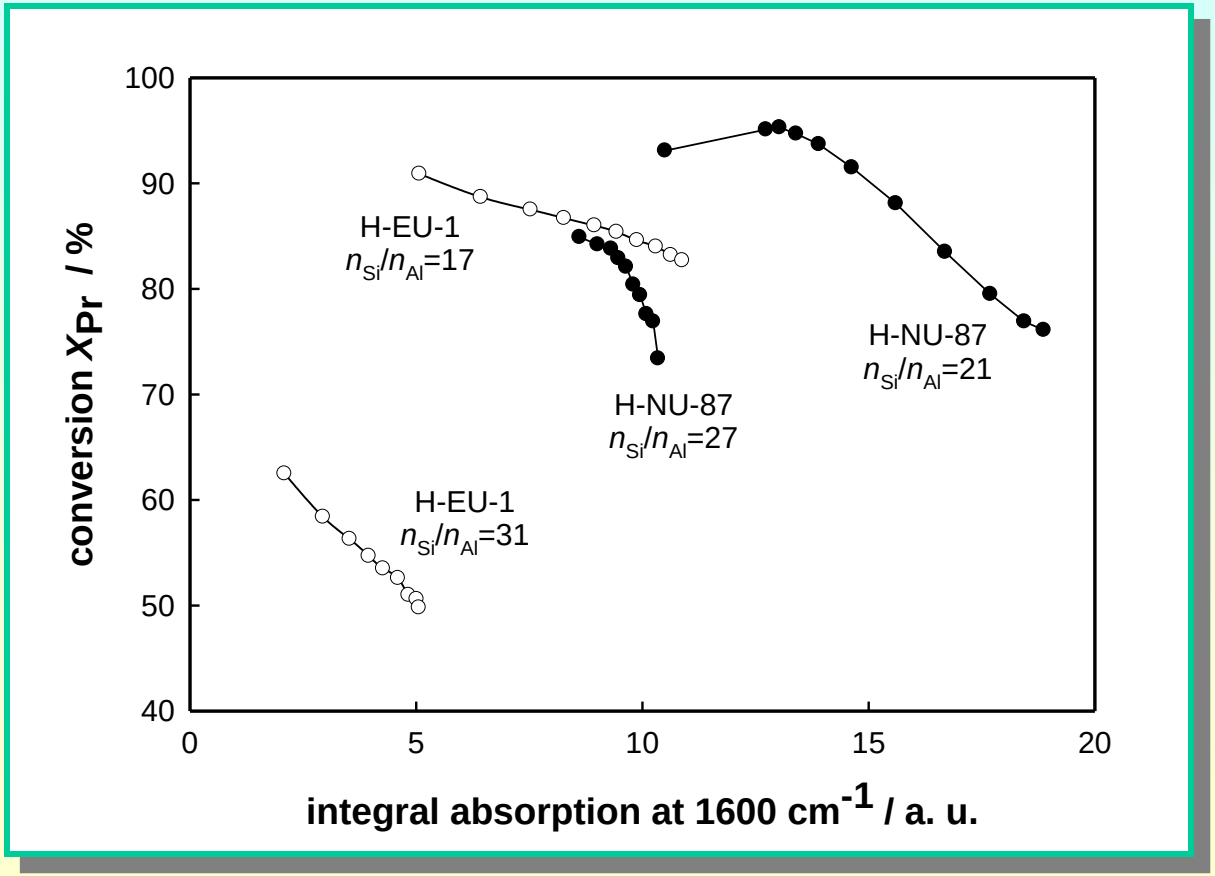
1600 cm^{-1}:
ring vibration of polyaromatics, conjugated polyene structures

→ **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



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

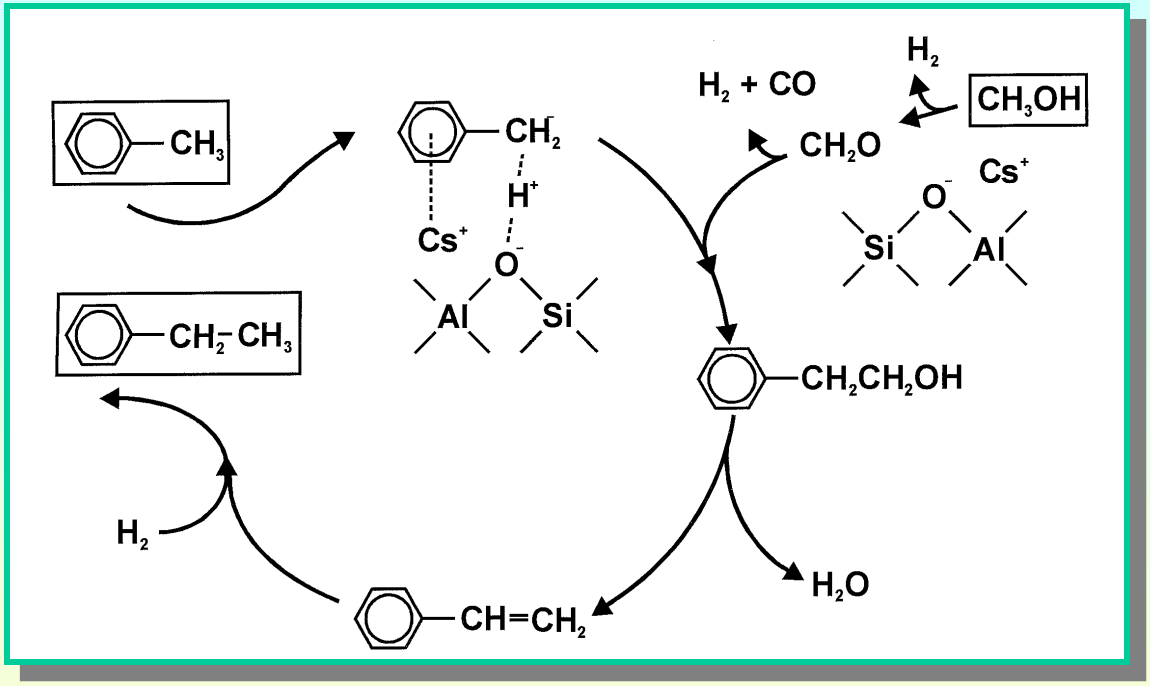
→ **coke formation depends on the pore geometry as well as the aluminum content**

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

Side-chain alkylation of toluene with methanol on basic zeolites

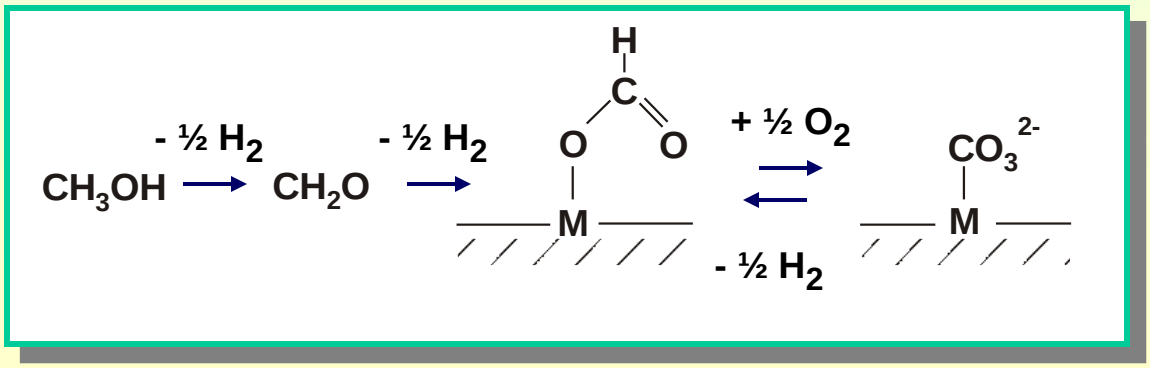
- reaction scheme proposed by Yashima et al. , J. Catal. 26 (1972) 303:

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



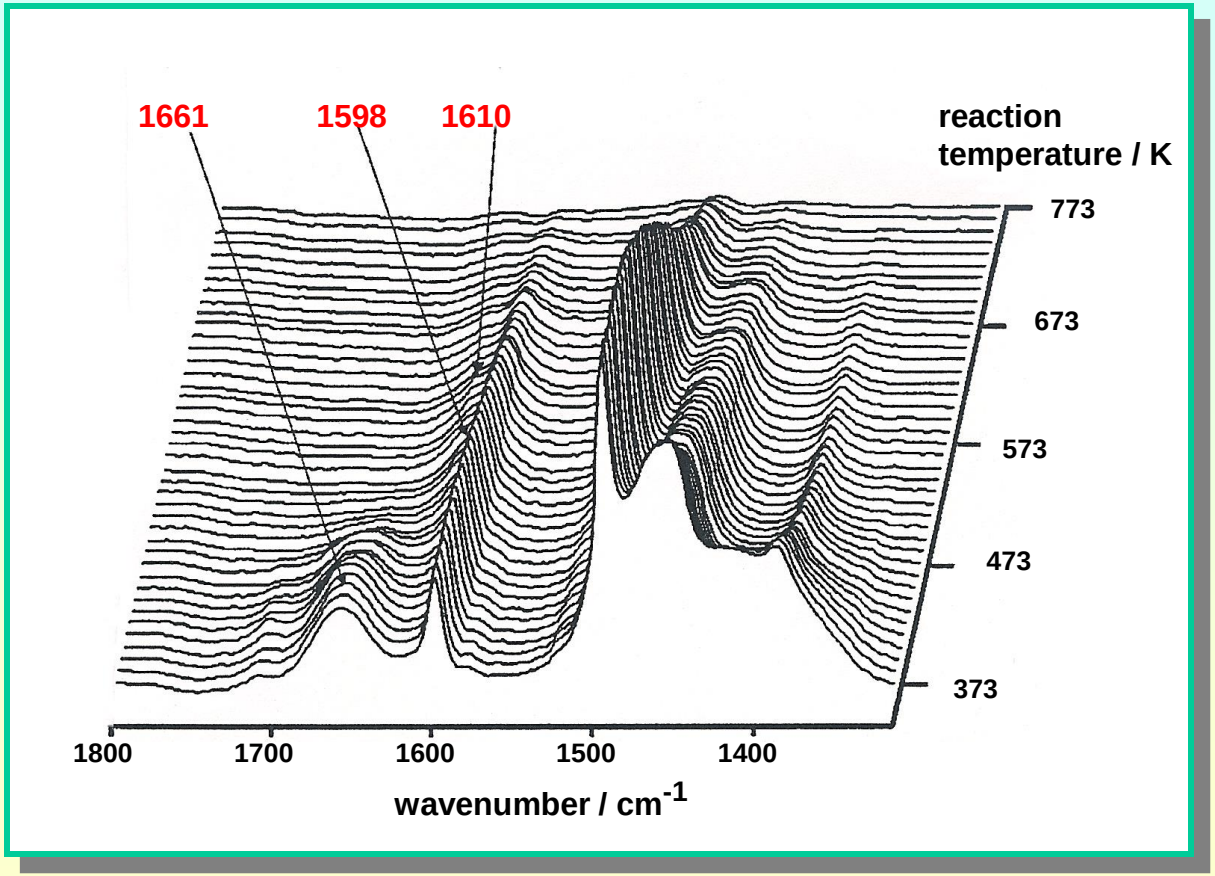
- proposed surface species:

  - surface formate species
  - carbonates



FTIR spectroscopy

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

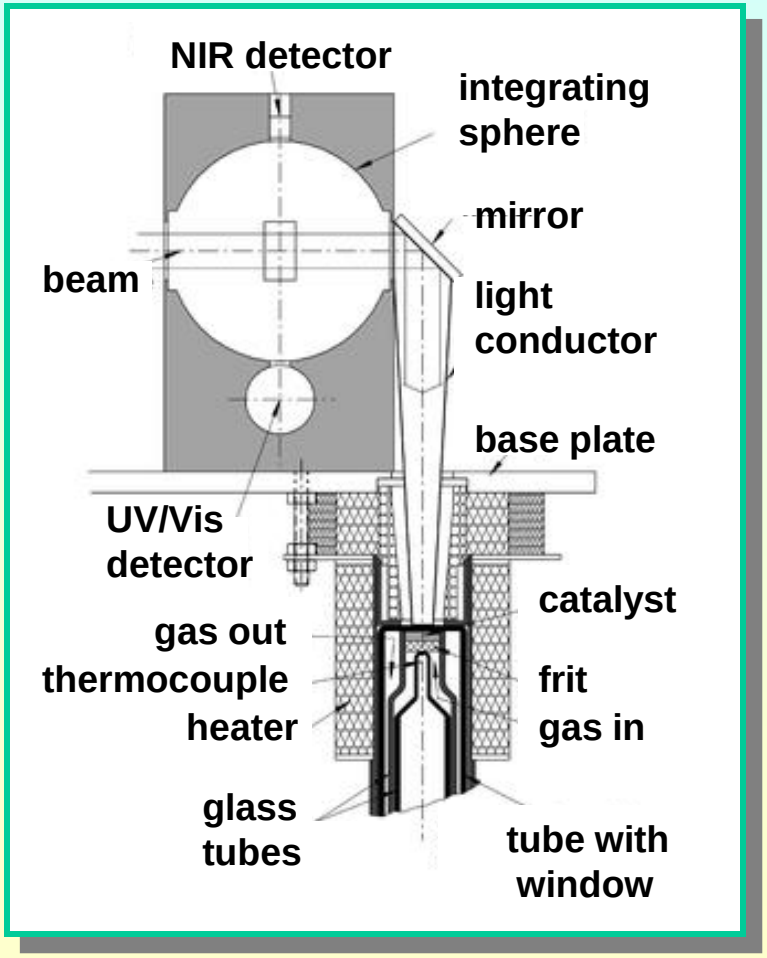
→ **surface formate species occur at reaction temperature**

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

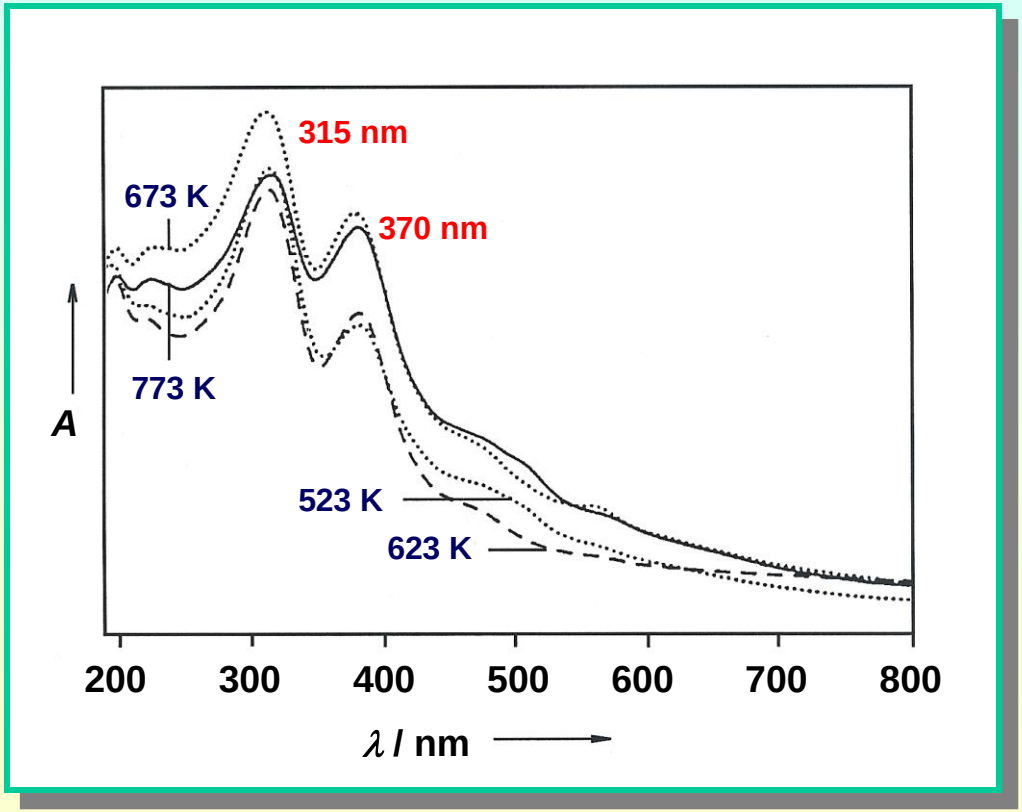


- suitable for *in situ* investigations at temperatures up to 723 K
- combination of UV/Vis and NIR spectroscopy
- increase of signal-to-noise ratio by 25% due to the light conductor
- horizontal arrangement of the powder material

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

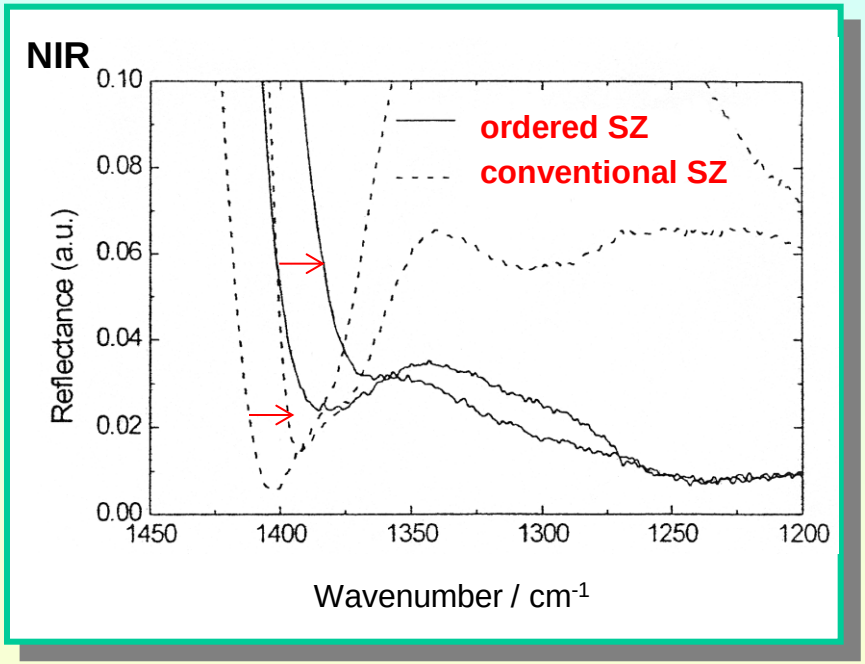
370 nm:
dienyl carbenium ions

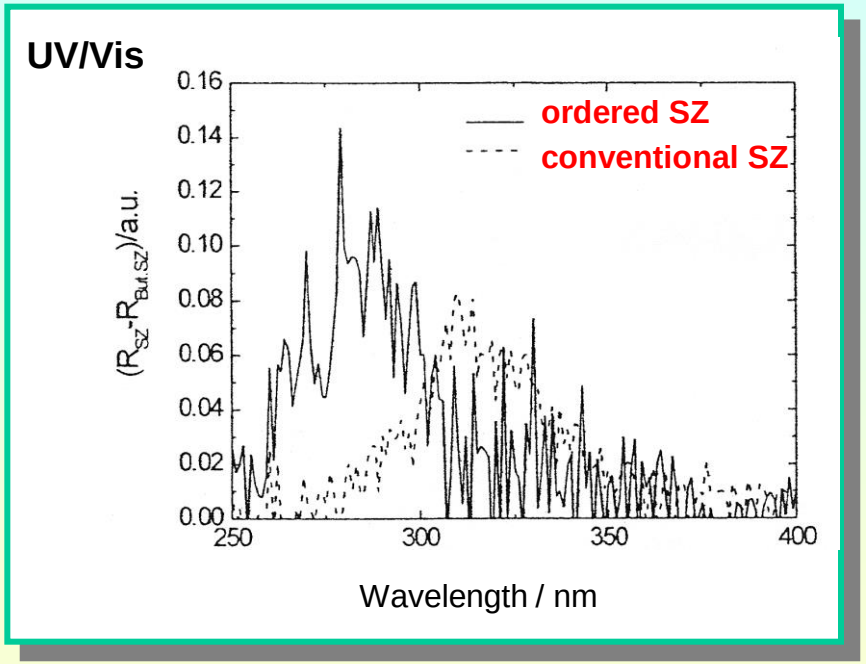
450 nm:
trienyl carbenium ions

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**

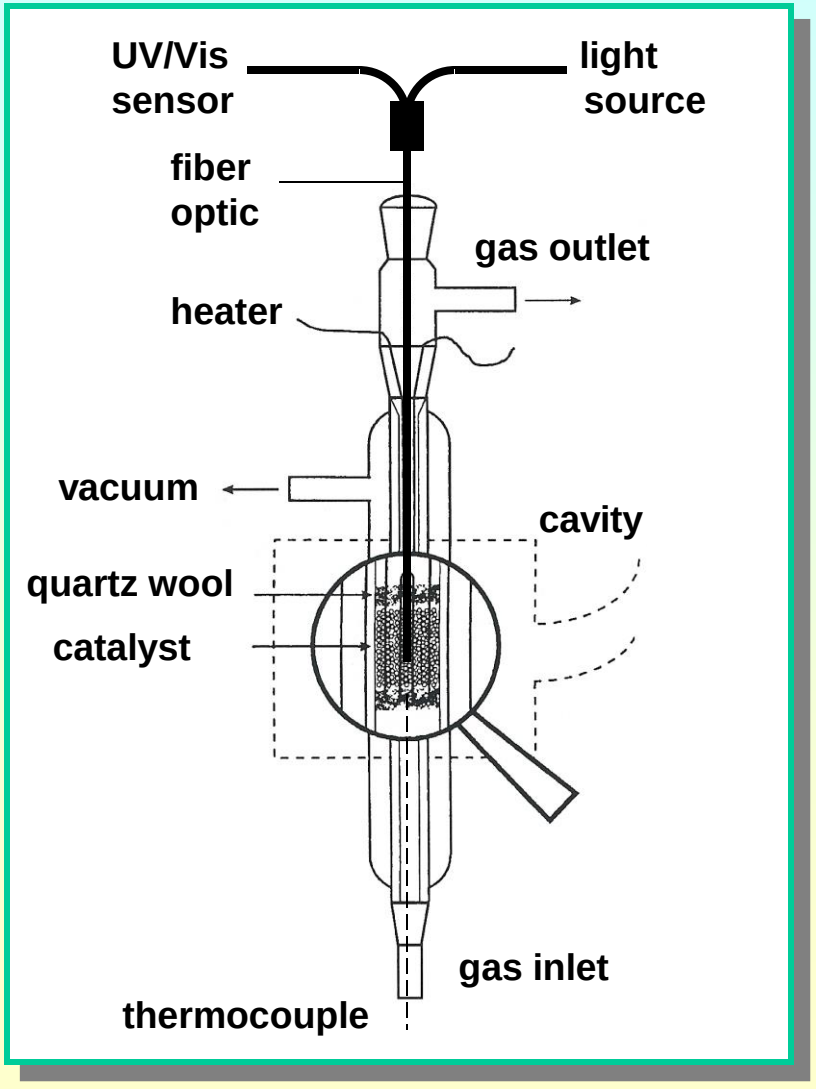
X. Yang et al., DGMK-Tagungsbericht 2002-4, ISBN 3-932850-98-6, p. 217.

In situ ESR spectroscopy in heterogeneous catalysis

ESR spectroscopy

scheme of an *in situ* ESR cell

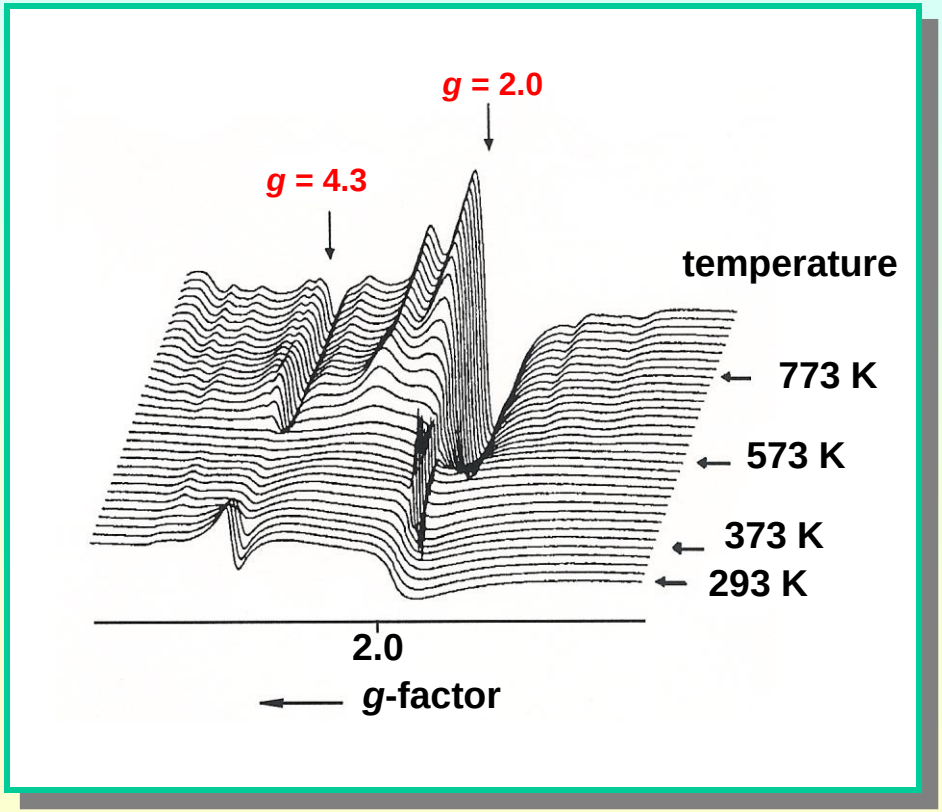
- **ESR flow reactor for X-band (B_0 = 0.35 T, ν = 9.5 GHz)**
- **suitable for *in situ* investigations at temperatures of up to 780 K**
- **combination of ESR and UV/Vis spectroscopy**



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

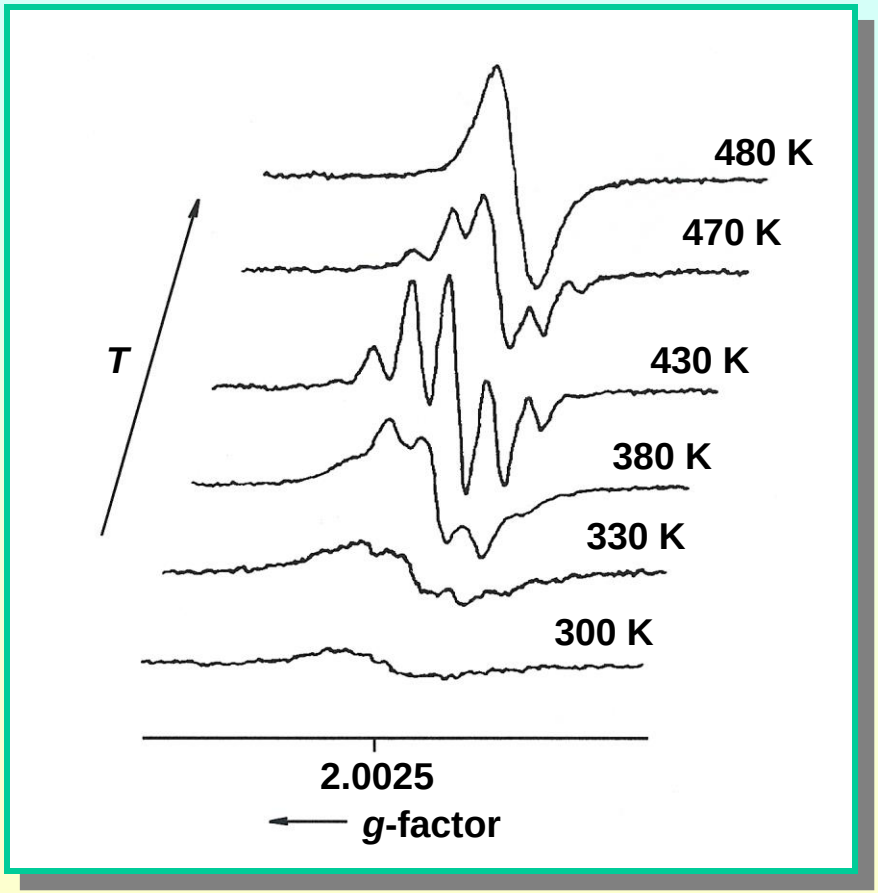
***g* = 4.3:**
octahedrally coordinated Fe^{3+} in lattice defects bound to bridging oxygen and terminal oxygen

(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

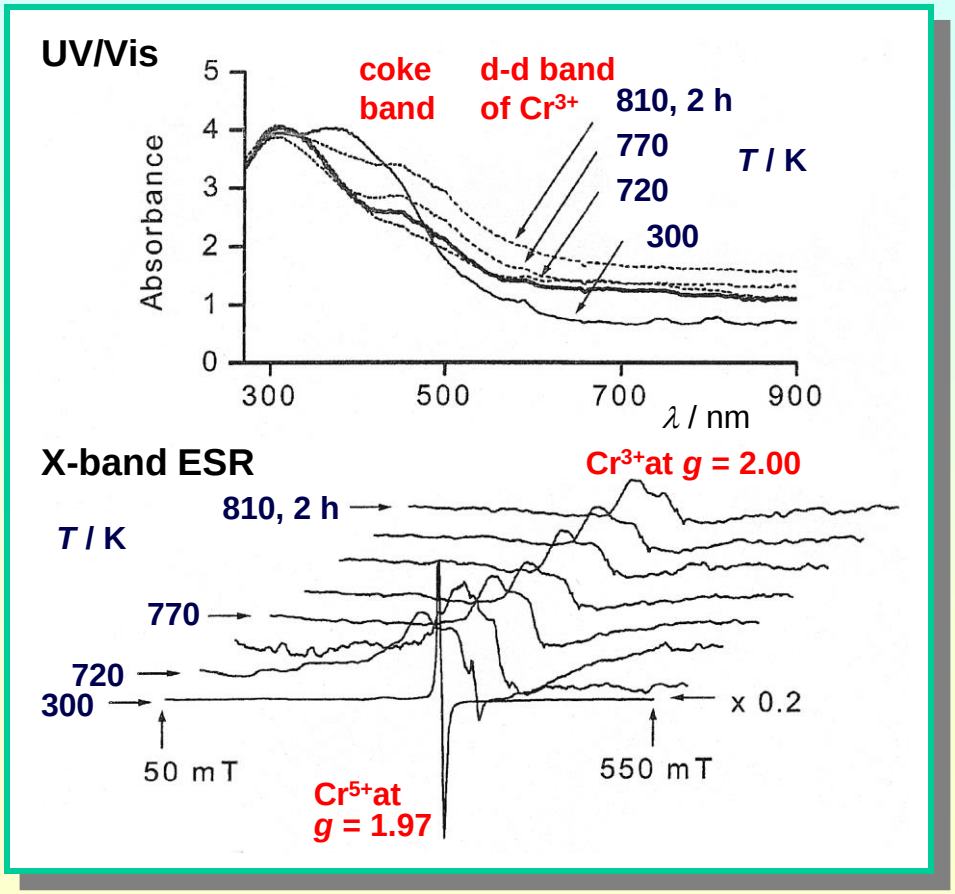
***T* > 470 K:**
polyaromatic radicals,
high-temperature coke

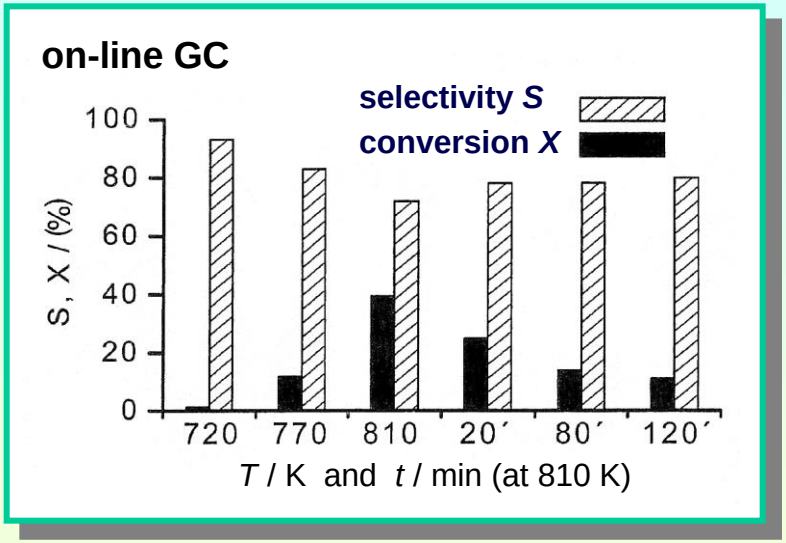
(1 radical per 1000 molcules)

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.

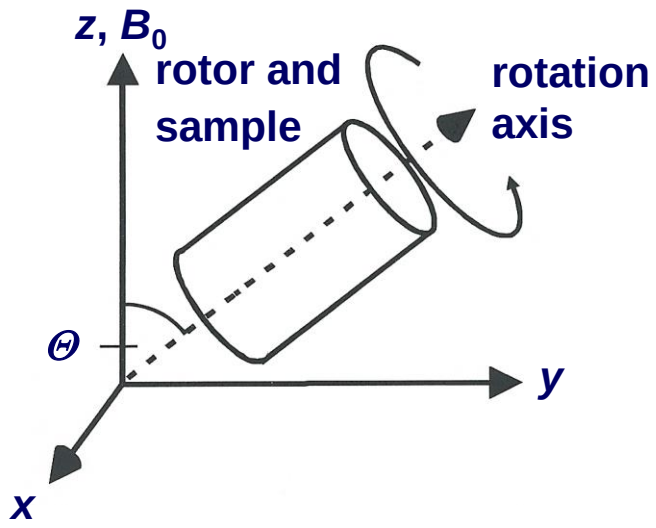
In situ NMR spectroscopy in heterogeneous catalysis

Solid-state NMR techniques

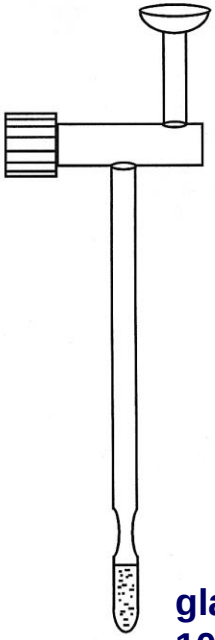
narrowing of solid-state NMR signals

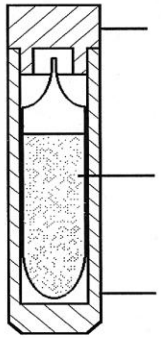
- magic angle spinning (MAS)

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

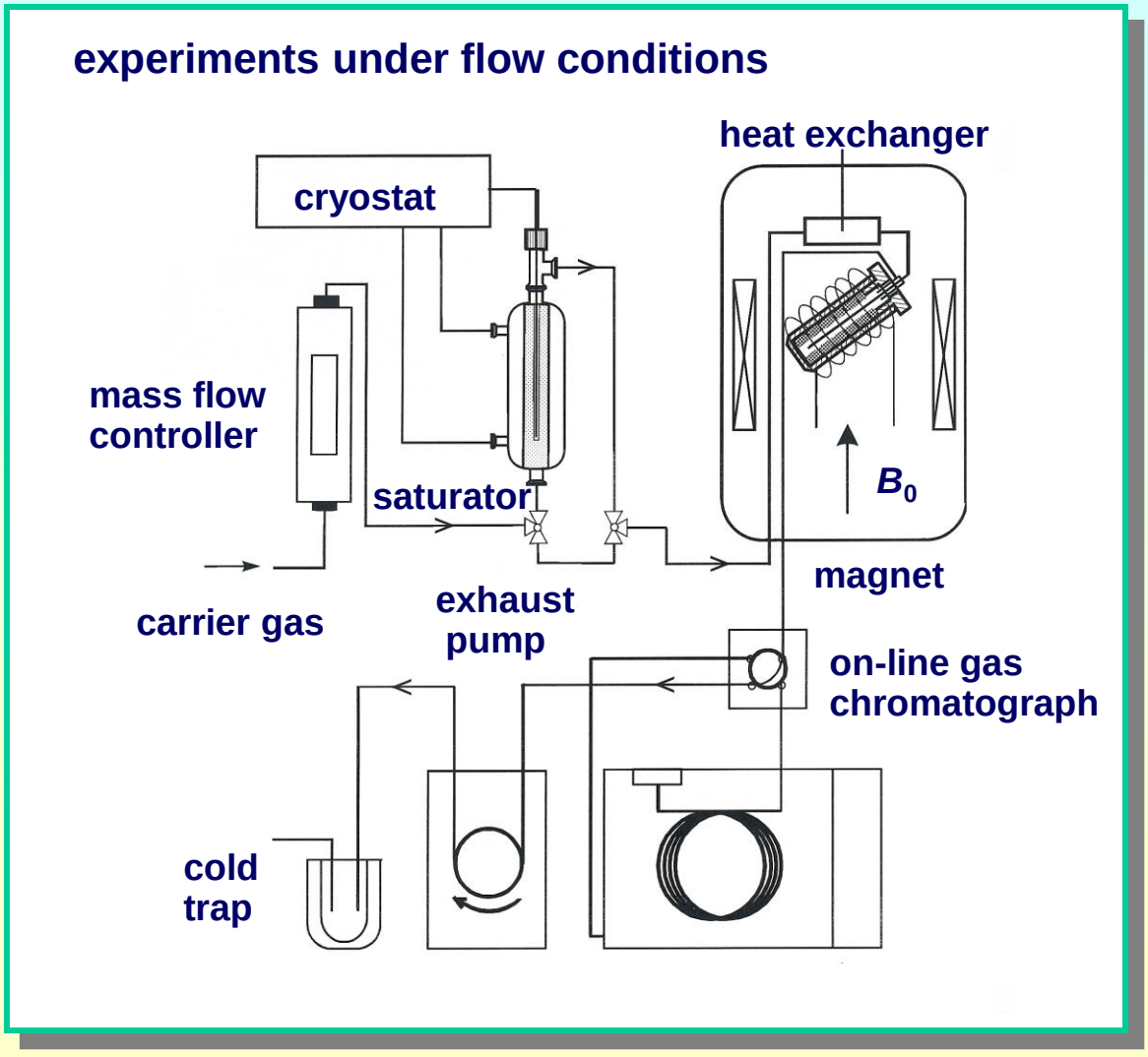


experiments under batch conditions



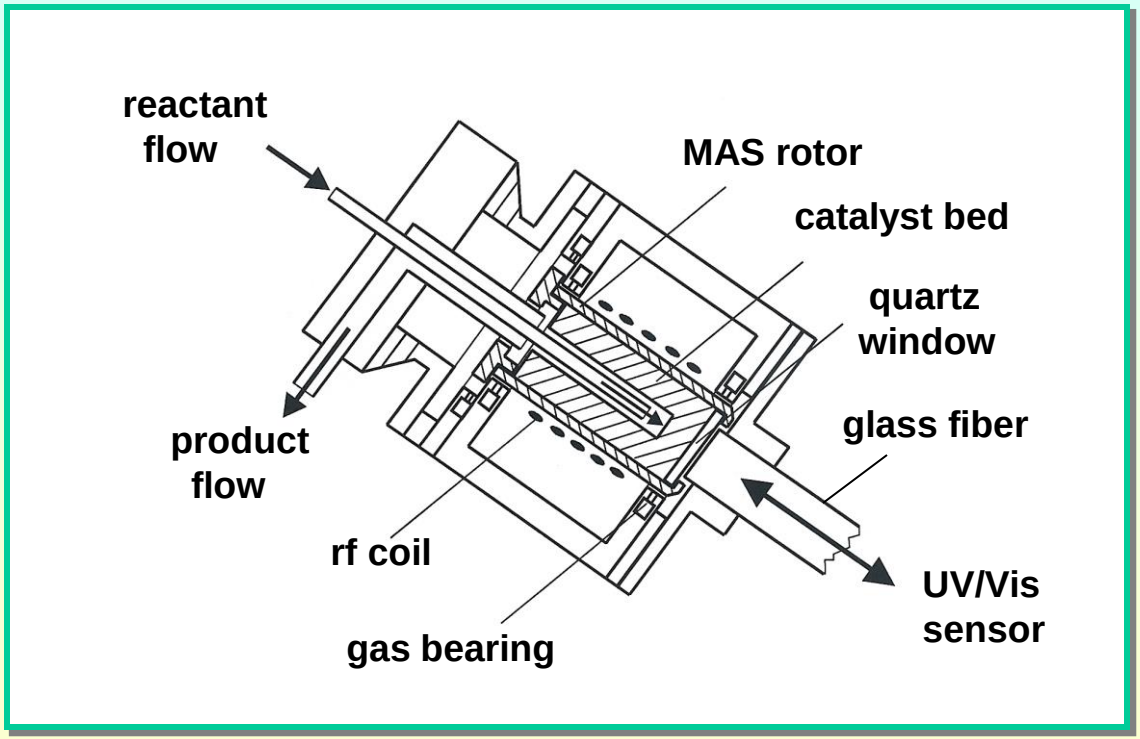


glass insert with ca. 50 to 100 mg sample powder



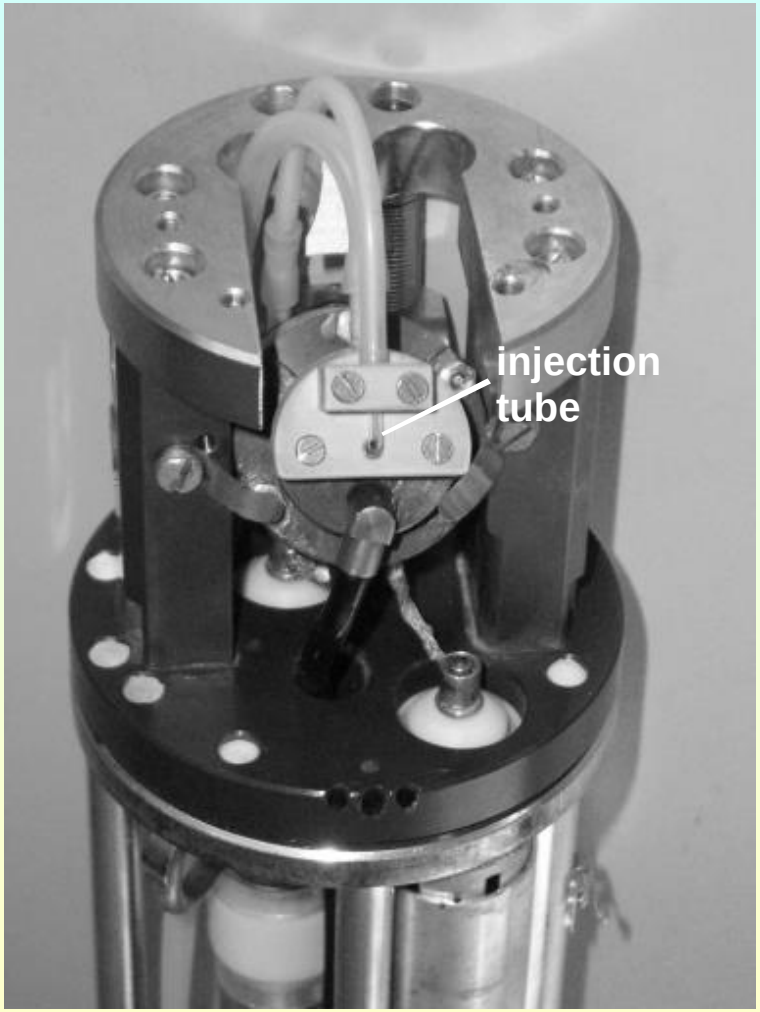
M. Hunger et al., Catal. Lett. 57 (1999) 199.

coupling of MAS NMR and UV/Vis spectroscopy by installation of a quartz fiber at the bottom of the MAS NMR stator

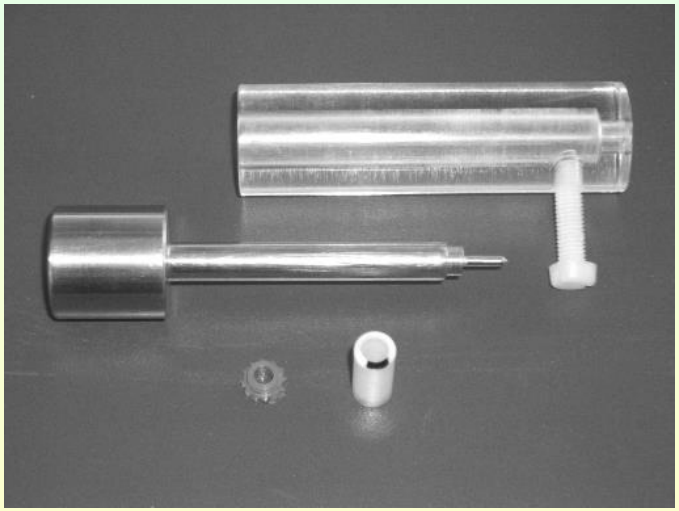


M. Hunger, W. Wang, Chem. Commun. (2004) 584.

Solid-state NMR techniques



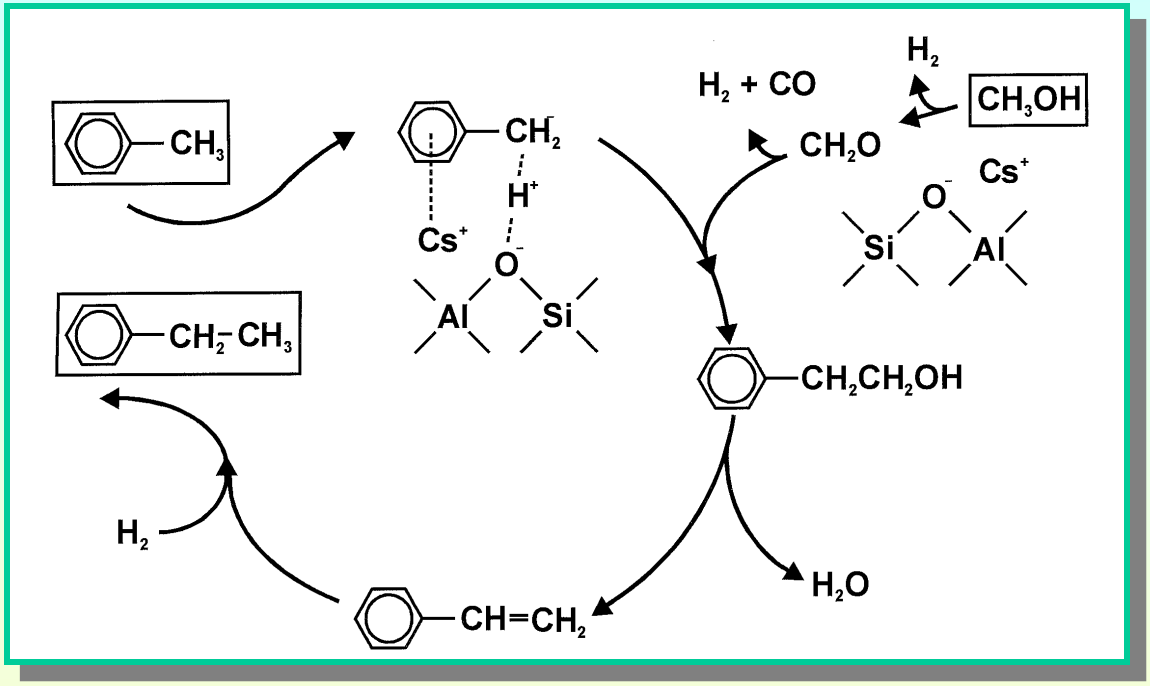
Bruker 7 mm MAS NMR probe modified for experiments under flow conditions (left) and special tools for shaping the catalyst to a hollow cylinder (bottom)



Side-chain alkylation of toluene with methanol on basic zeolites

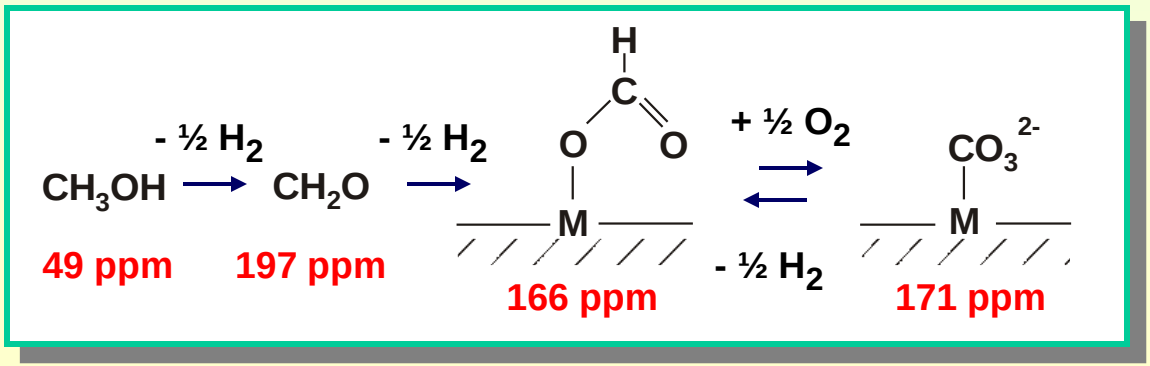
- reaction scheme proposed by Yashima et al. , J. Catal. 26 (1972) 303:

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



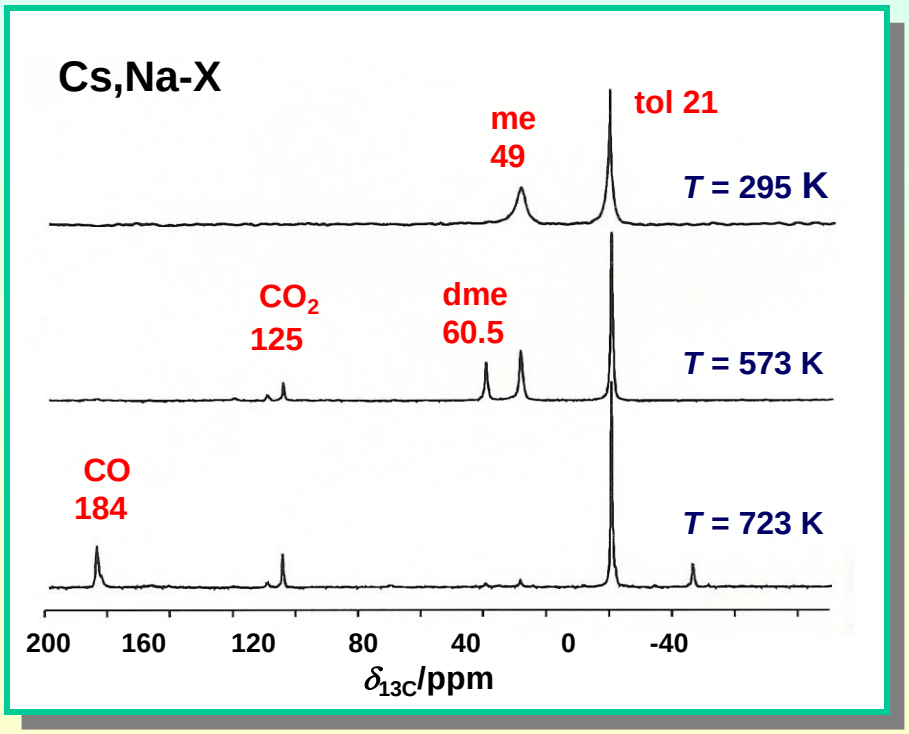
- proposed surface species:

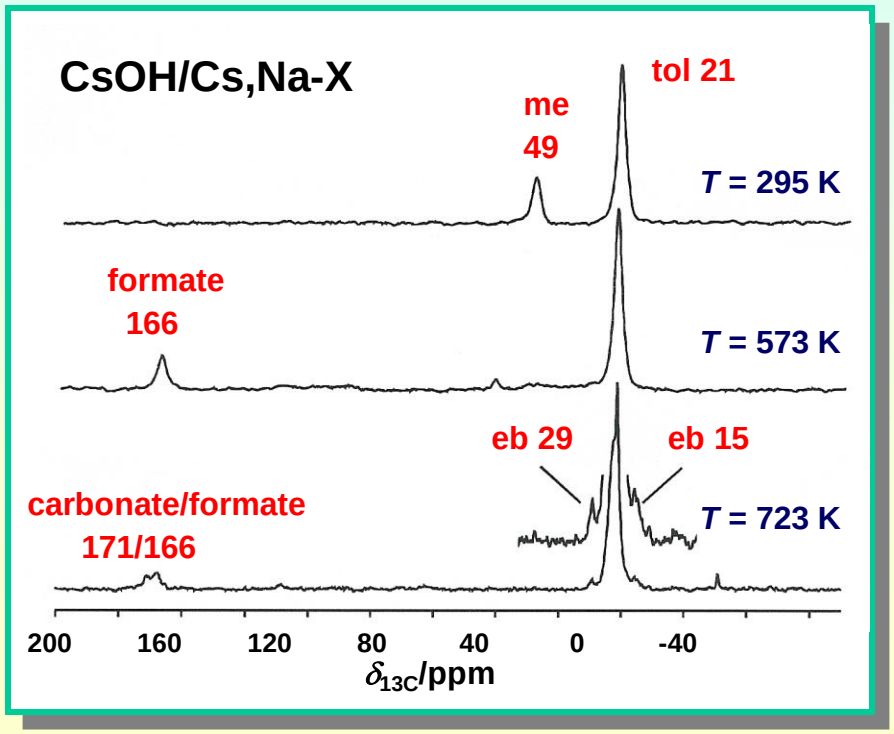
  - formate (δ_{13C} = 166 ppm)
  - carbonate (δ_{13C} = 171 ppm)



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.





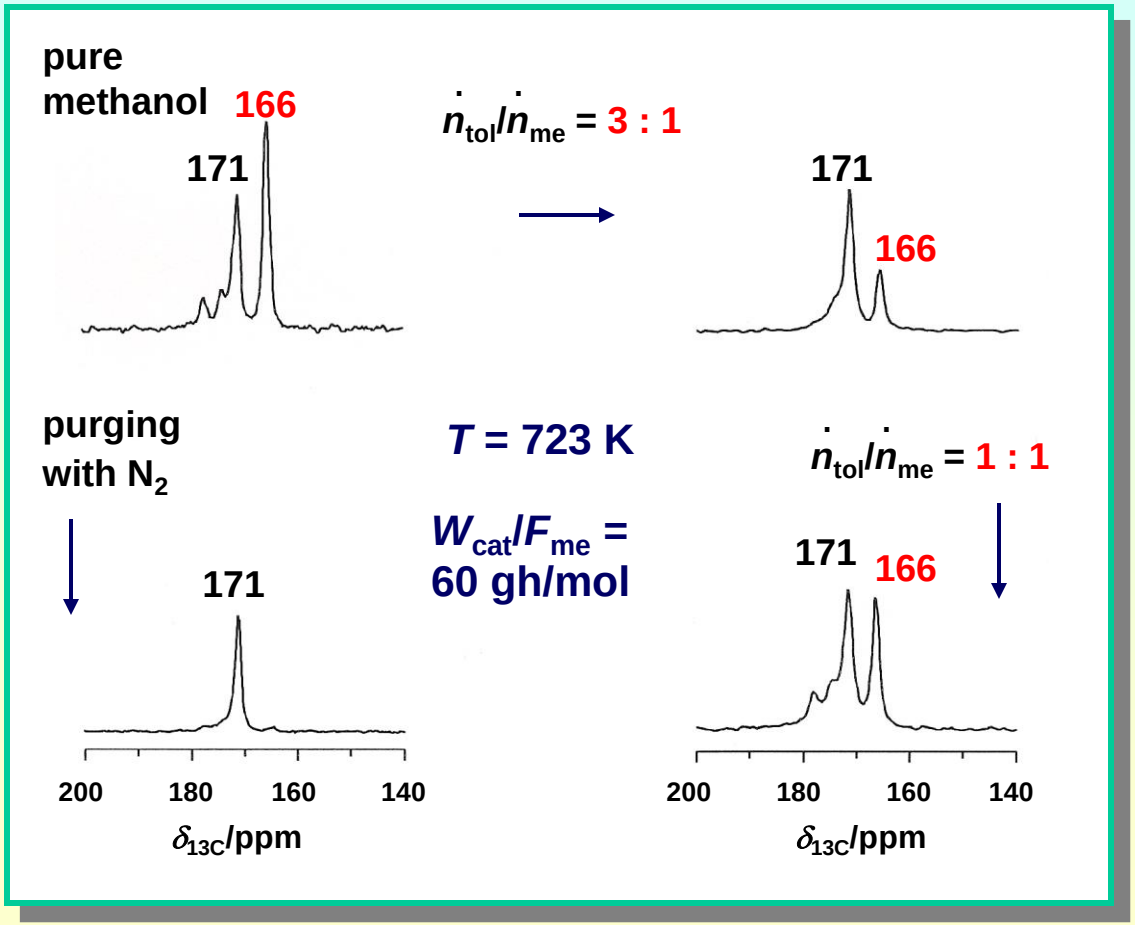
M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

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**

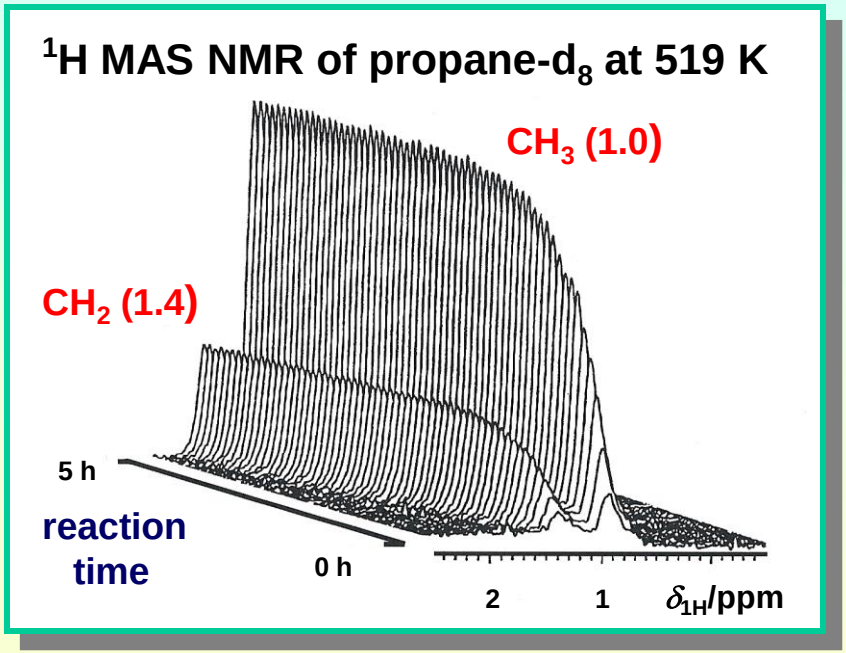
→ **formate species (166 ppm) are consumed by toluene which indicates a high reactivity**

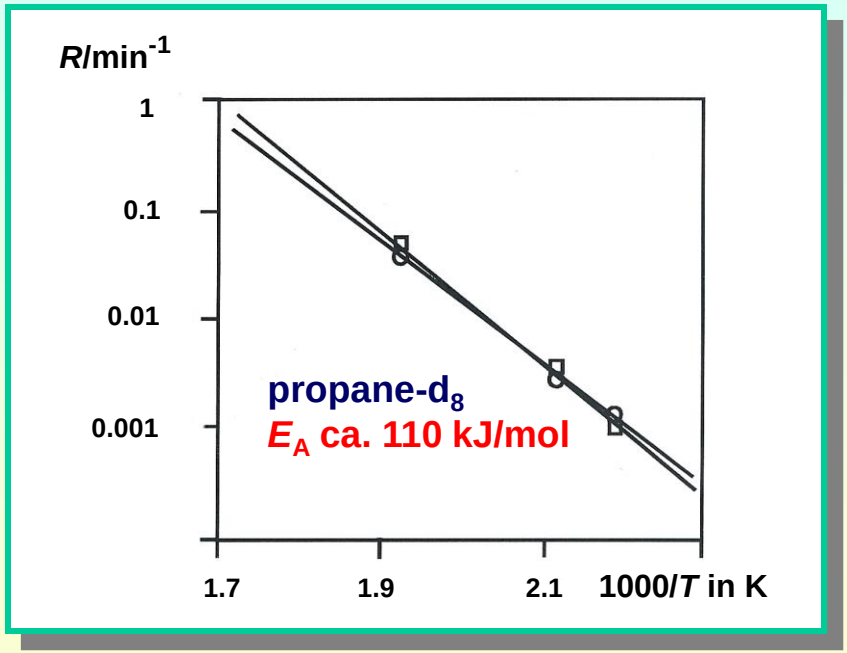


M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

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

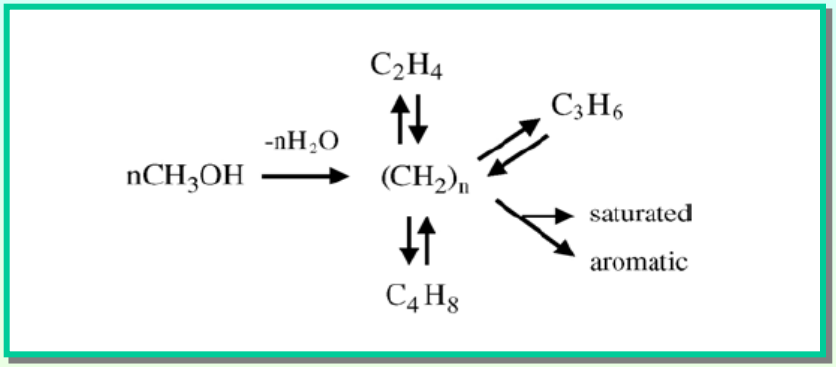
→ no formation carbenium ions

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

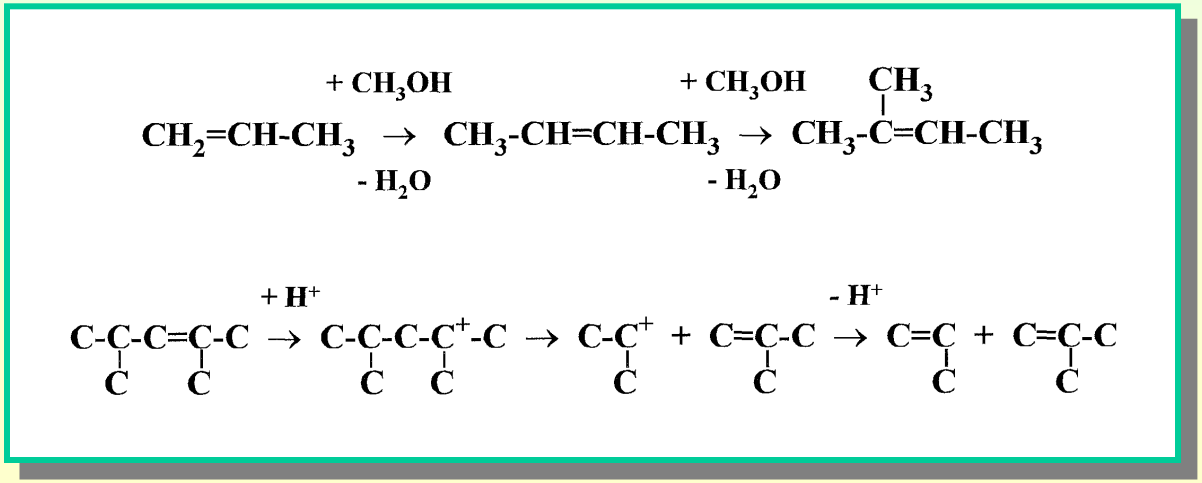
→ formation carbenium ions

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

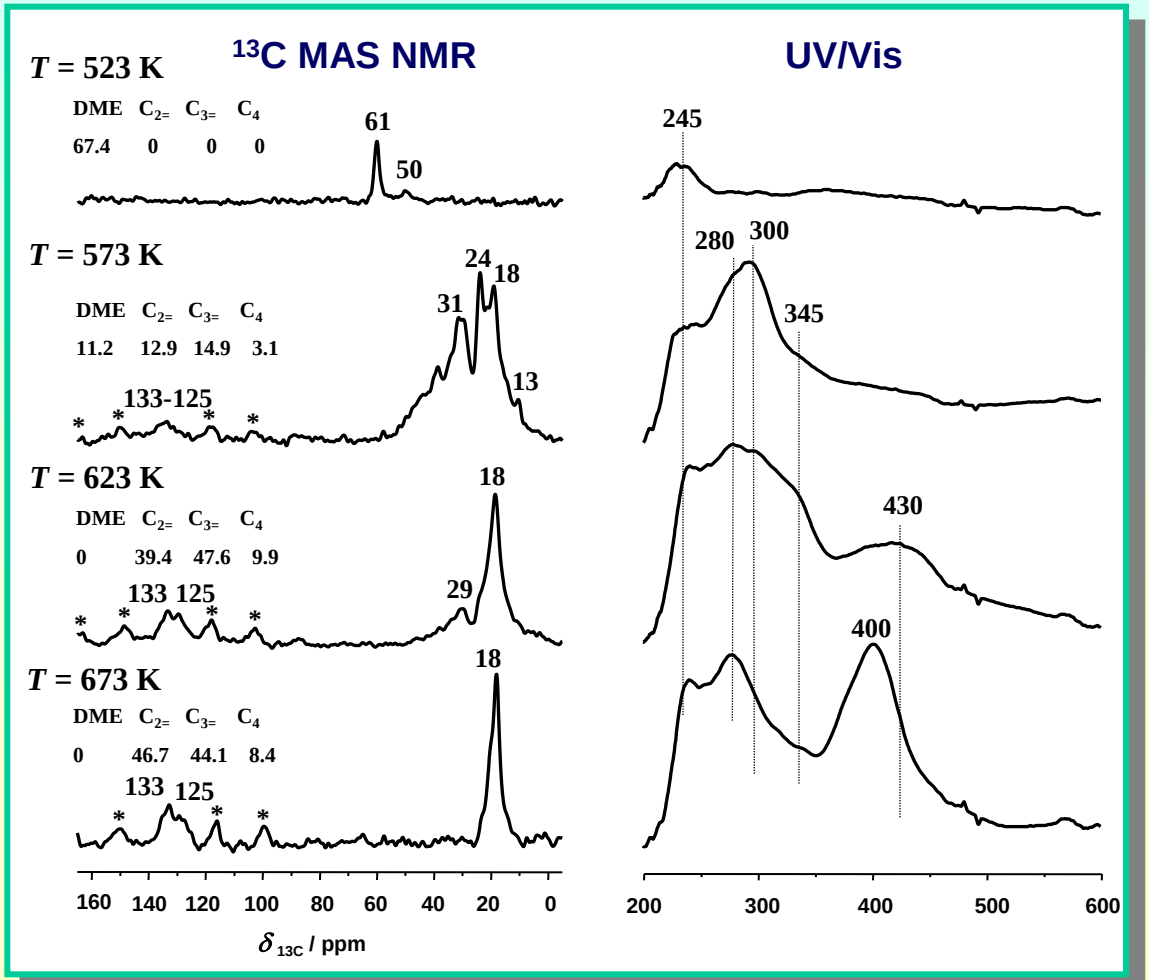
Most favored mechanism is the hydrocarbon pool mechanism, L.M. Dahl, S. Kolboe, J. Catal. 149 (1994) 458



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



In situ ^{13}C MAS NMR-UV/Vis study of the formation of organic deposits on H-SAPO-34 under continuous-flow conditions



NMR:

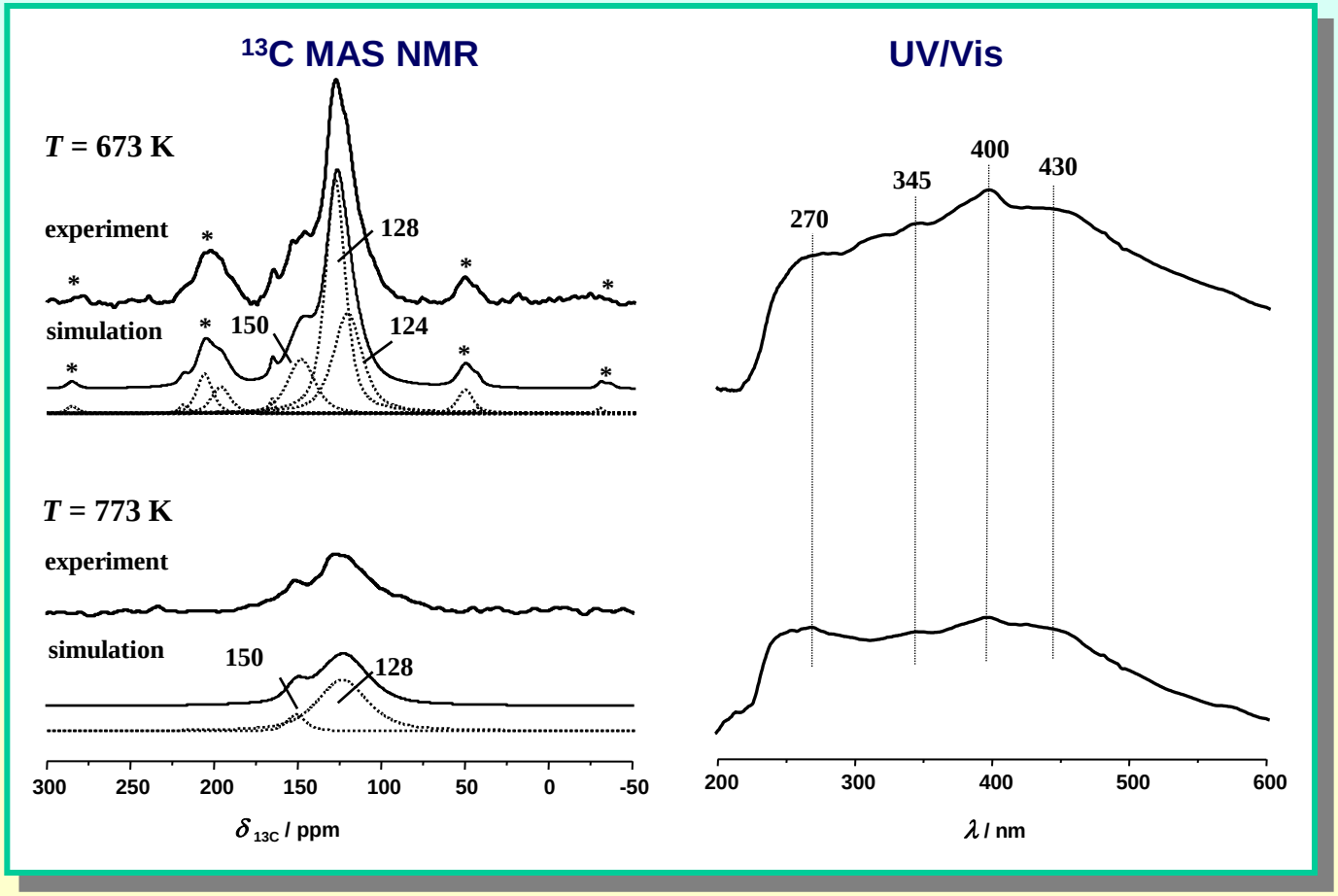
- quantitative evaluation
- separation of alkyl groups and aromatics
- rotor reactor comparable with fixed-bed reactor

UV/Vis:

- sensitive for carbenium cations
- separation of aromatics and polycyclic aromatics

Y. Jiang et al., Microporous Mesoporous Mater. (2007), in press.

Regeneration of used (673 K) H-SAPO-34 by purging with synthetic air (20 vol.-% O_2, 30 ml/min) at 673 and 773 K for 2 h



decrease of all aromatics including polycyclic coke (400 nm)

new band of phenolic species (270 nm)

Y. Jiang et al., Microporous Mesoporous Mater. (2007), in press.

Quantitative evaluation of the ^{13}C MAS NMR spectra of used H-SAPO-34 regenerated by purging with synthetic air for 2 h

Signal at δ_{13C} /ppm	Assignments	Number in mmol/g		
		reaction at 673 K	syn. air at 673 K	syn. air at 773 K
16-21	methyl groups bound to aromatics	0.53	-	-
14-15 and 22-29	ethyl groups bound to aromatics	0.08	-	-
125-137	alkylated and non-alkylated aromatic rings	0.56	0.17	0.05
145-155	carbon in aromatics bound to oxygen atoms	-	0.45	0.13

→ **strong decrease of aromatics (UV/Vis bands at 280 nm and 400 nm), but formation of oxygenated species (270 nm)**

Y. Jiang et al., Microporous Mesoporous Mater. (2007), in press.

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
- quantitative method

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* spectroscopy in heterogeneous 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**

for more details see:

M. Hunger, Microporous Mesoporous Mater. 82 (2005) 241-255.