State of the Art and Applications of In Situ Solid-State NMR Spectroscopy in Heterogeneous Catalysis

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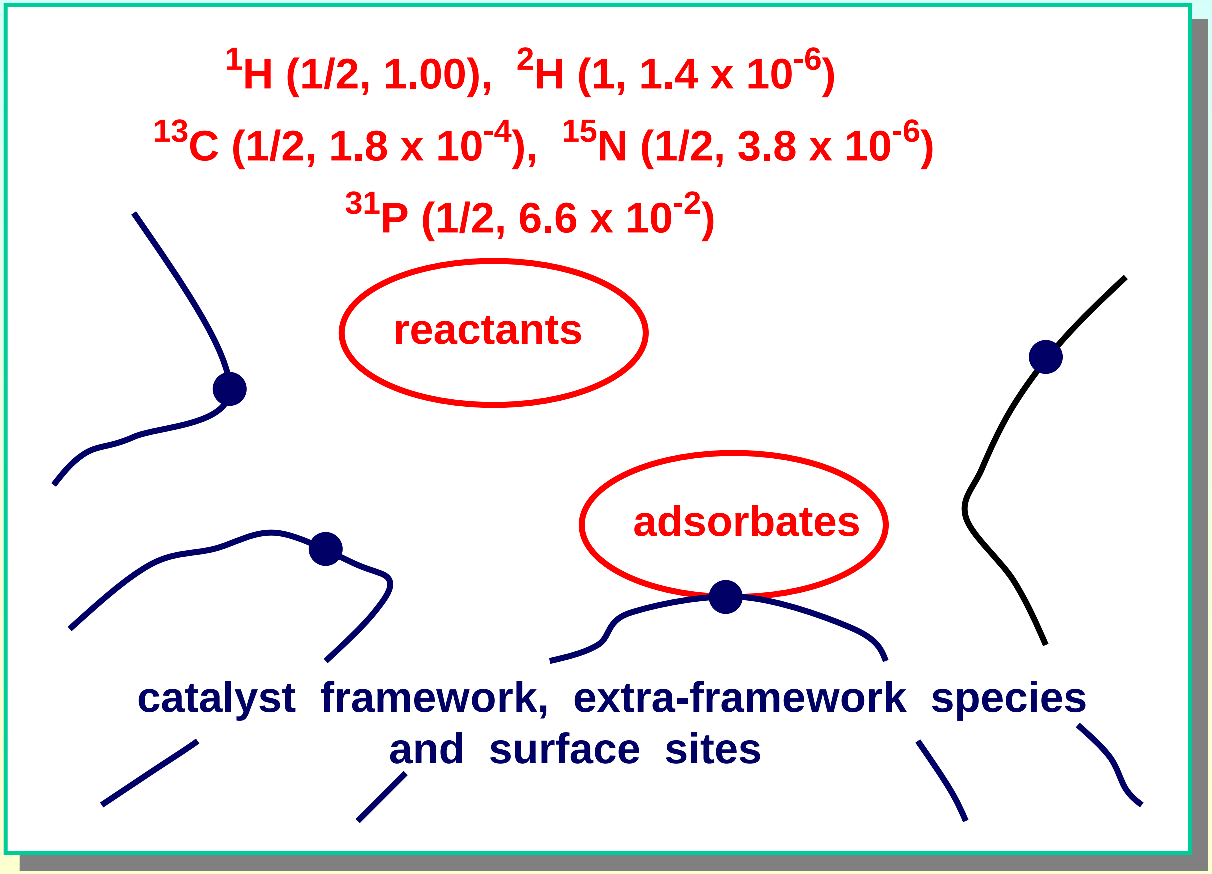
Examples of nuclei accessible for in situ NMR in heterogeneous catalysis



^{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})

reactants

adsorbates

catalyst framework, extra-framework species and surface sites

^{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)

Specific problems of NMR on working catalysts

magnetization:

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

- **minimum number of ca. 10^{18} spins for ^{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**

Signal broadening in solid-state NMR spectroscopy

- **Hamiltonians of the solid-state interactions of spins:**

$$H_{\mathrm{total}} = H_0 + H_{\mathrm{QI}} + H_{\mathrm{DI}} + H_{\mathrm{CS}} + H_{\mathrm{J}}$$

H_0 : Zeeman interaction $\gamma \cdot h \cdot I_z \cdot B_0$ of nuclear spins I in the external magnetic field B_0 $\nu_0 \leq 10^9\ \mathrm{s}^{-1}$

H_{QI} : interaction of the electric quadrupole moment of the resonating nuclei with the electric field gradient $\nu_{\mathrm{QI}} \leq 5 \times 10^6\ \mathrm{s}^{-1}$

H_{DI} : dipolar interaction with the magnetic dipole moments of nuclei in their vicinity $\nu_{\mathrm{DI}} \leq 5 \times 10^4\ \mathrm{s}^{-1}$

H_{CS} : shielding interaction caused by the electron shell around the resonating nuclei $\nu_{\mathrm{CS}} \leq 5 \times 10^3\ \mathrm{s}^{-1}$

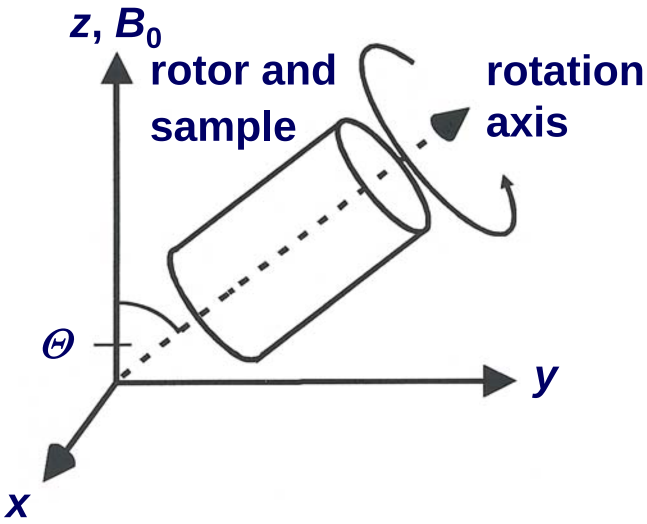
H_{J} : indirect or J-coupling of nuclei via their bond electrons $\nu_{\mathrm{J}} \leq 5 \times 10^2\ \mathrm{s}^{-1}$

Solid-state NMR techniques

spin $I = ½$:

- **magic angle spinning (MAS)**

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



spin $I > ½$:

- **double oriented rotation (DOR)**

$$\nu_{\mathrm{2QI}} = f\,\{35\cos^4\Theta - 30\cos^2\Theta + 3\} \rightarrow \begin{array}{l}\Theta = 30.6^{\circ}\\ \Theta = 70.1^{\circ}\end{array}$$

- **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

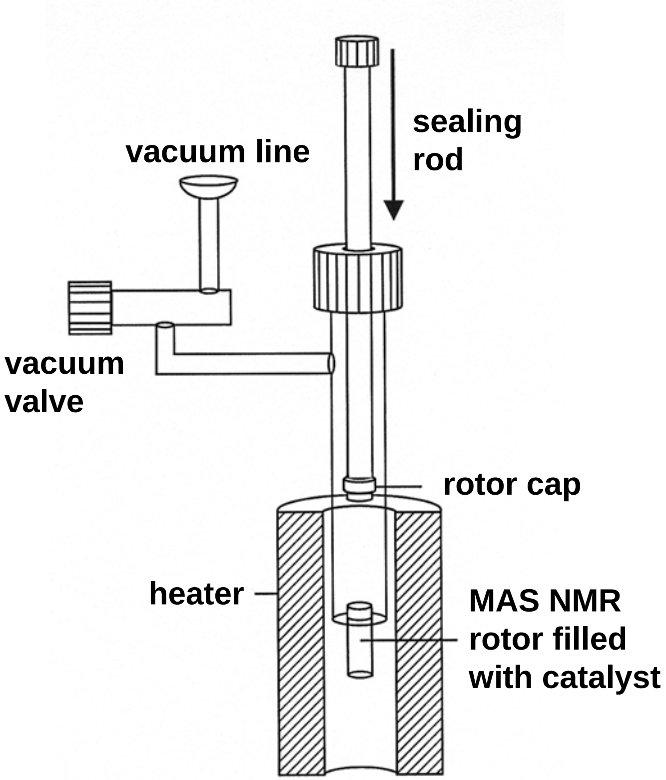
- flow experiments, *in situ* reaction
  - continuous injection of reactants into the MAS NMR rotor reactor
  - high-temperature solid-state NMR probes

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

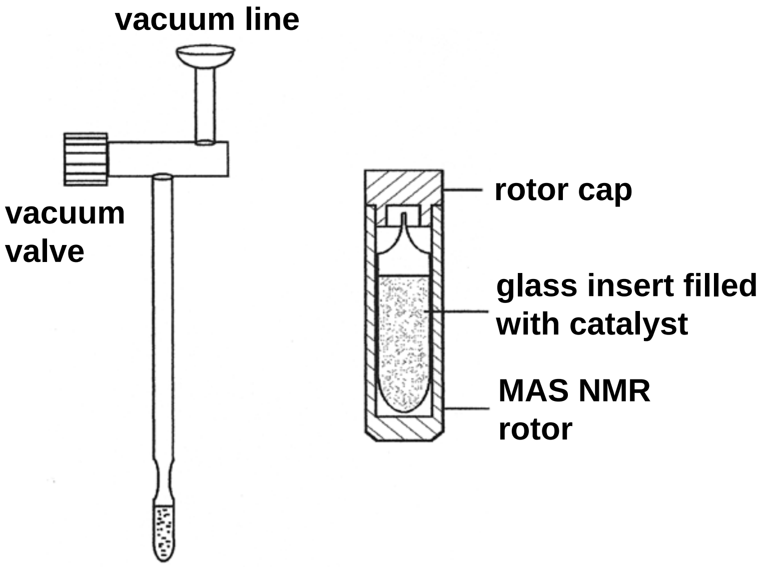
Experimental techniques applied for studies under batch and continuous-flow conditions

Handling of dehydrated catalysts under batch conditions

equipment for *in situ* dehydration and sealing of samples inside the MAS NMR rotor



dehydration of catalysts inside of glass inserts (e.g. commercial Wilmad MAS NMR inserts for 4 mm and 7 mm rotors)

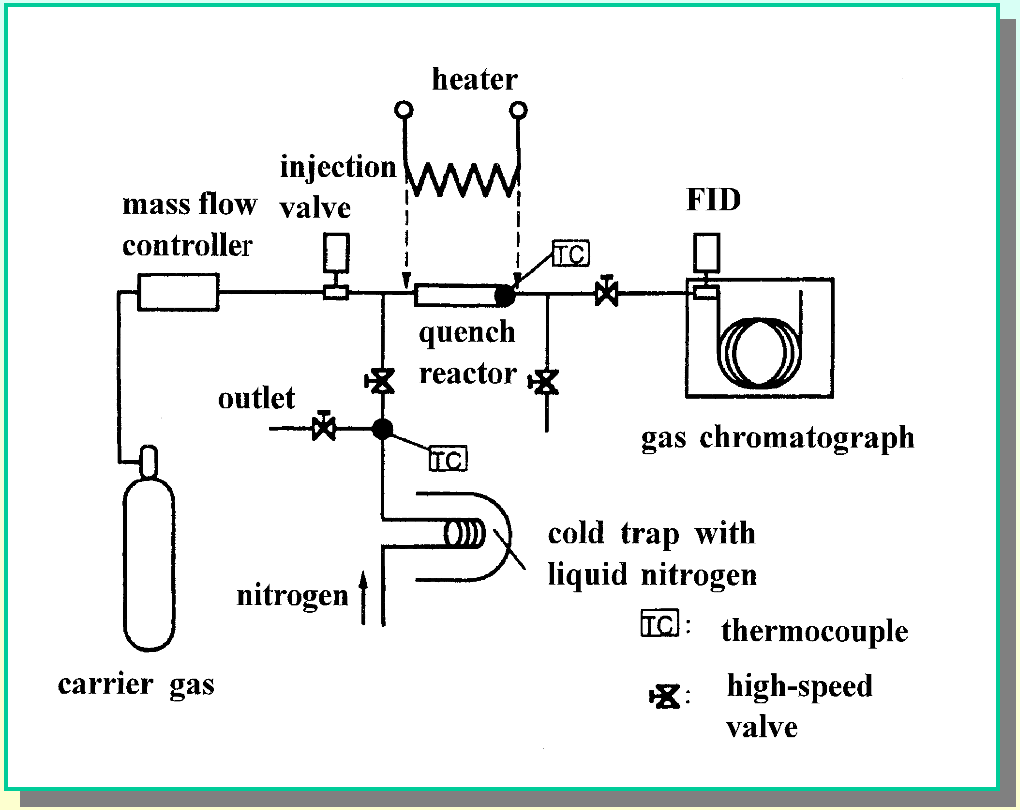


M. Hunger, J. Weitkamp, in: In-situ Spectroscopy of Catalysts, B.M. Weckhuysen (ed.), ASP, Stevenson R., 2004, p. 175.

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**



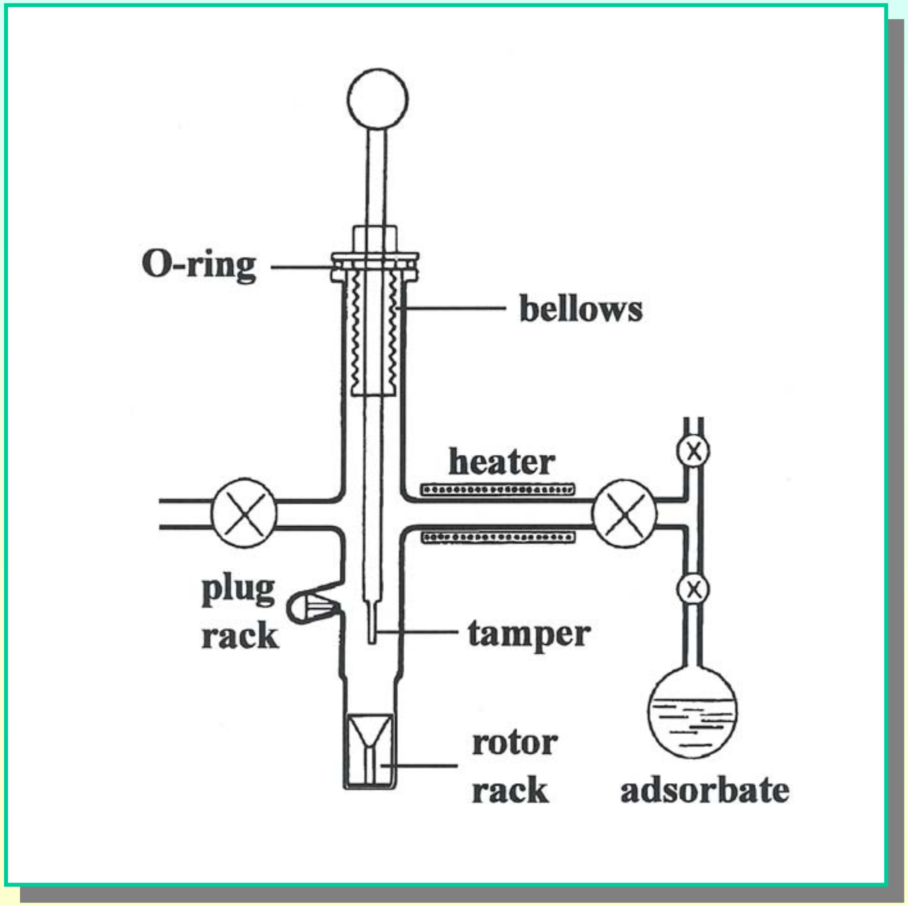
D.H. Barich et al., J. Phys. Chem. B 102 (1998) 7163.

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**

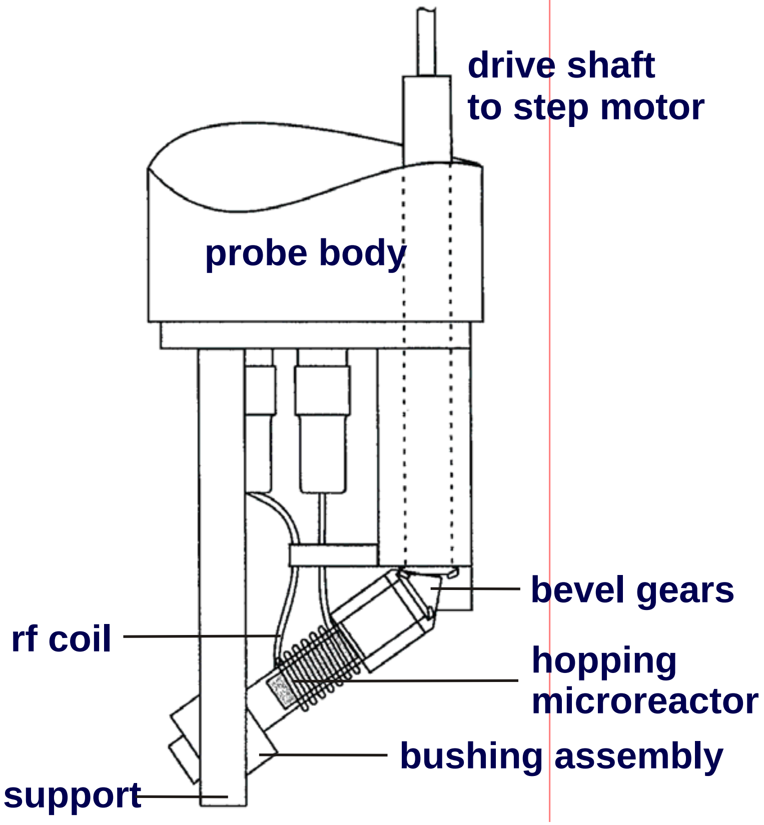
- **sealing of the MAS NMR rotor inside the apparatus**



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

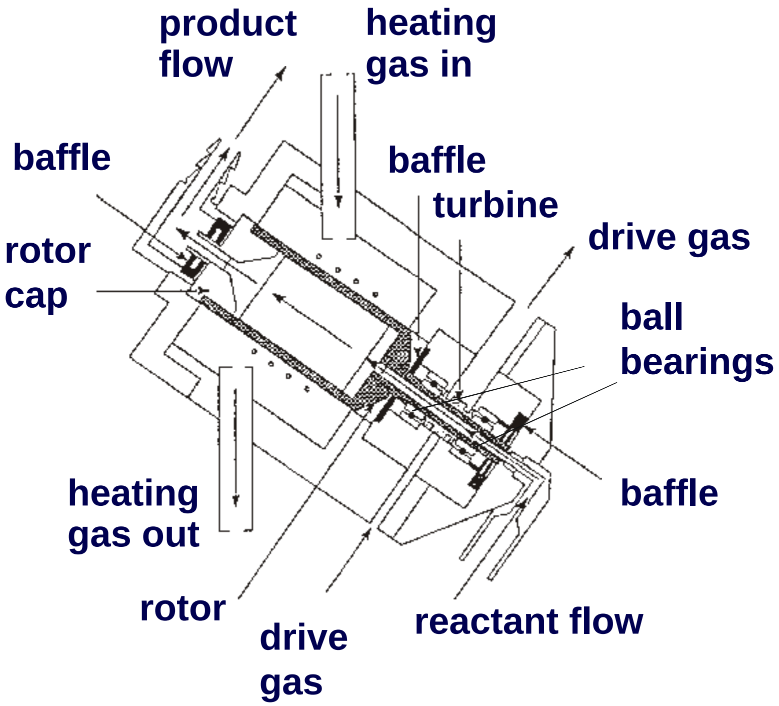
Approaches for in situ flow MAS NMR spectroscopy

flow MAS NMR probe with hopping microreactor (GRASSHopper II)



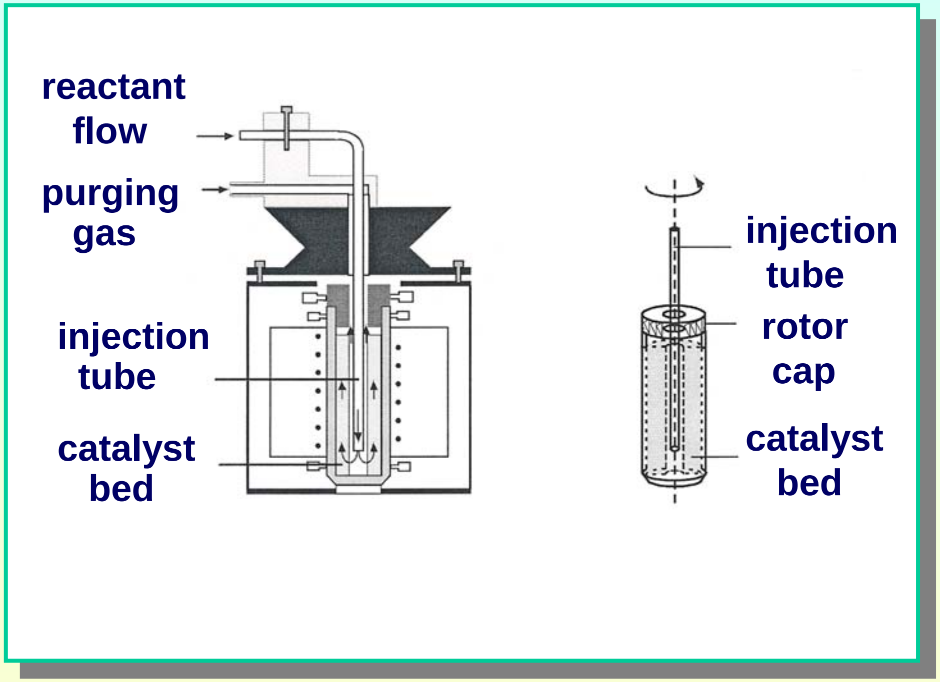
C. Keeler et al., Catal. Today 49 (1999) 377.

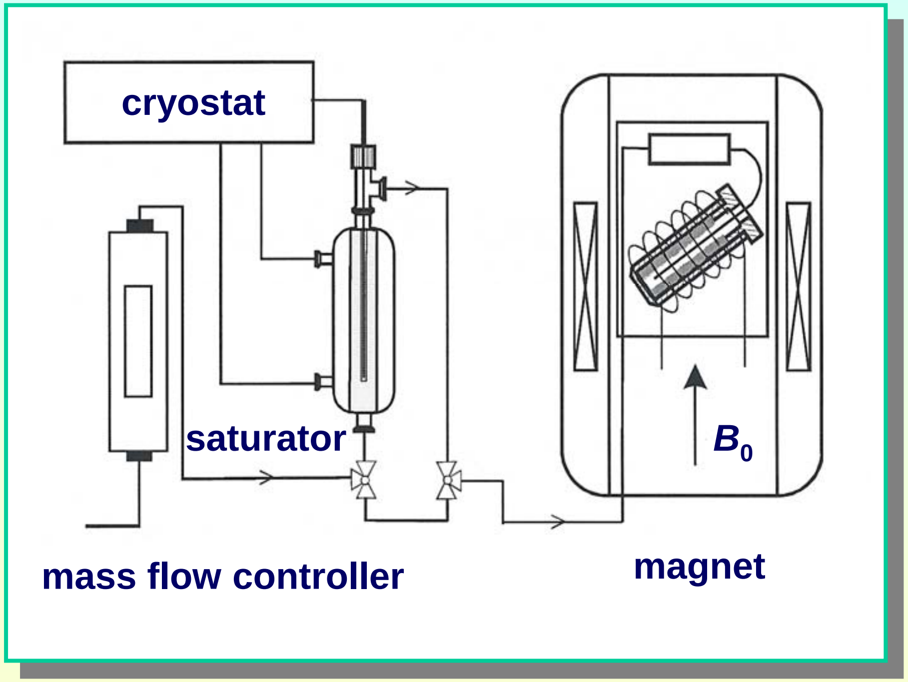
flow MAS NMR probe with ball bearings



P.K. Isbester et al., Catal. Today 49 (1999) 363.

Continuous-flow (CF) MAS NMR technique

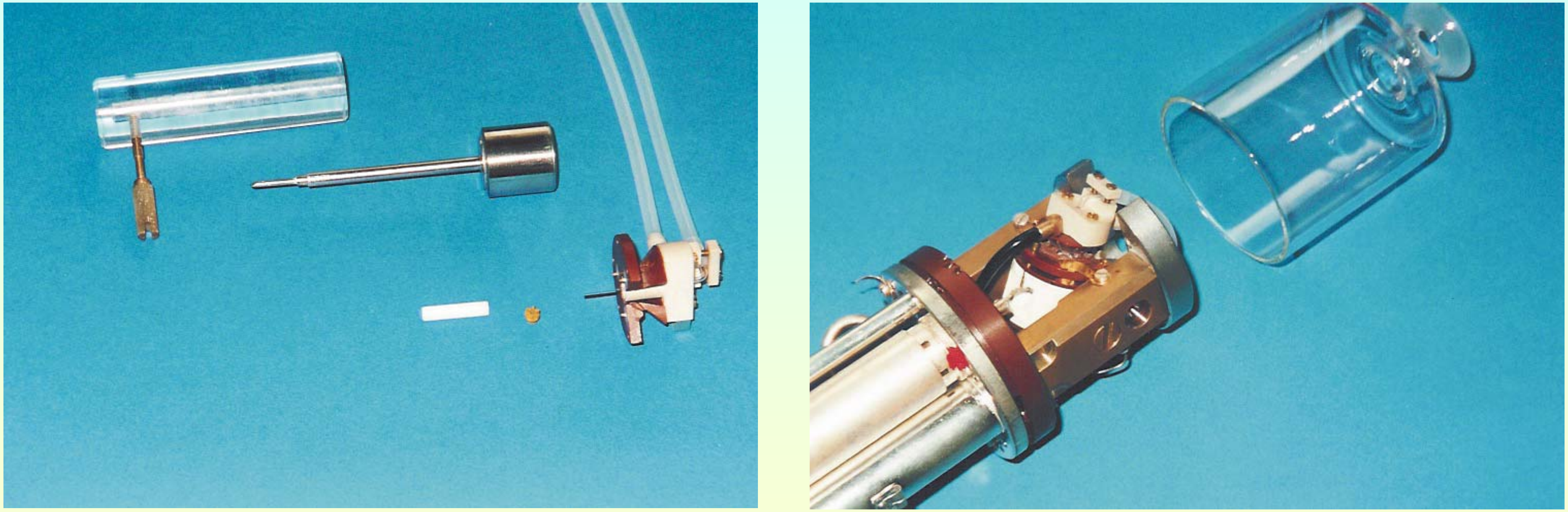




- **continuous injection of reactants into a spinning MAS NMR rotor reactor (*T* < 923 K)**

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

Continuous-flow (CF) MAS NMR technique

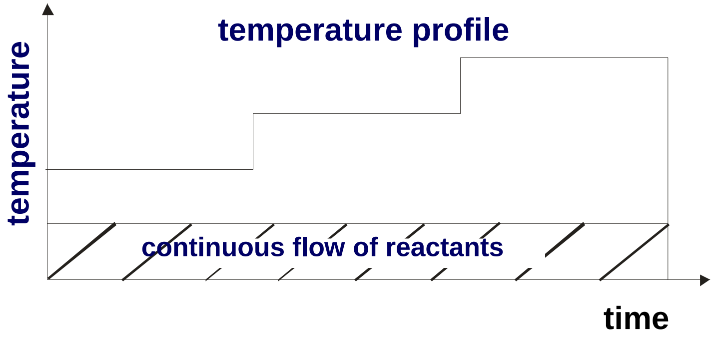


- **modified 4 mm Bruker MAS NMR probe equipped with an injection system**

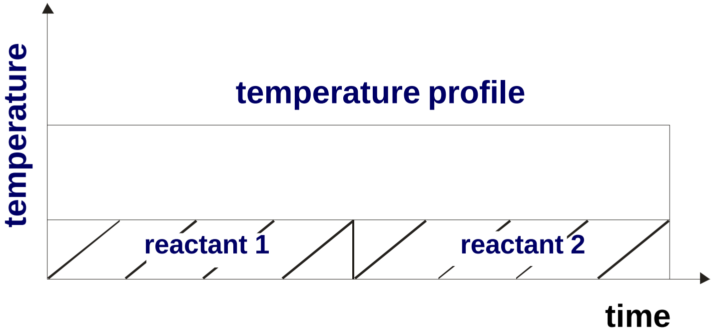
A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.

Types of flow experiments I

- **continuous-flow experiment**



- **switched-flow experiment**

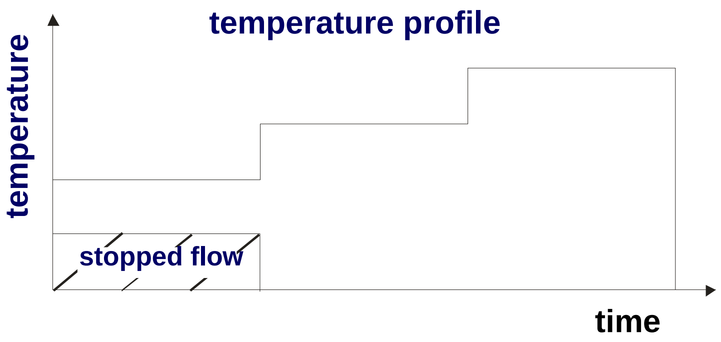


- **continuous-flow experiment:**
  - **study of adsorption or conversion of reactants at constant or different temperatures**
  - **study of formation of stable deposits of catalyst deactivatrion**

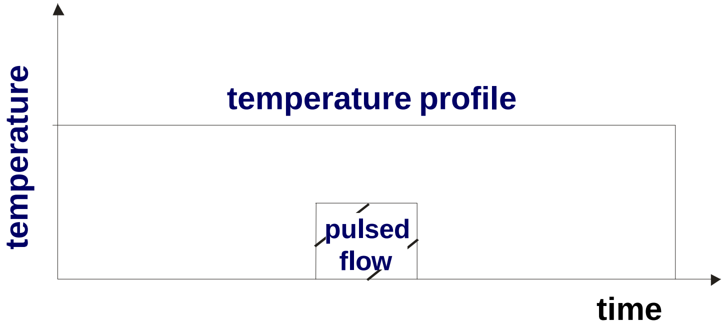
- **switched-flow experiment:**
  - **change of isotopic enrichment in reactants**
  - **study of the response of the composition of reaction products or deposits on the change of reactants**

Types of flow experiments II

- **stopped-flow experiment**



- **pulsed-flow experiment**



- **stopped-flow experiment:**

  - preparation of intermediates on the catalyst

  - study of the reactivity and conversion of intermediates at constant or different temperatures

- **pulsed-flow experiment:**

  - study of the time dependence of the conversion of reactants

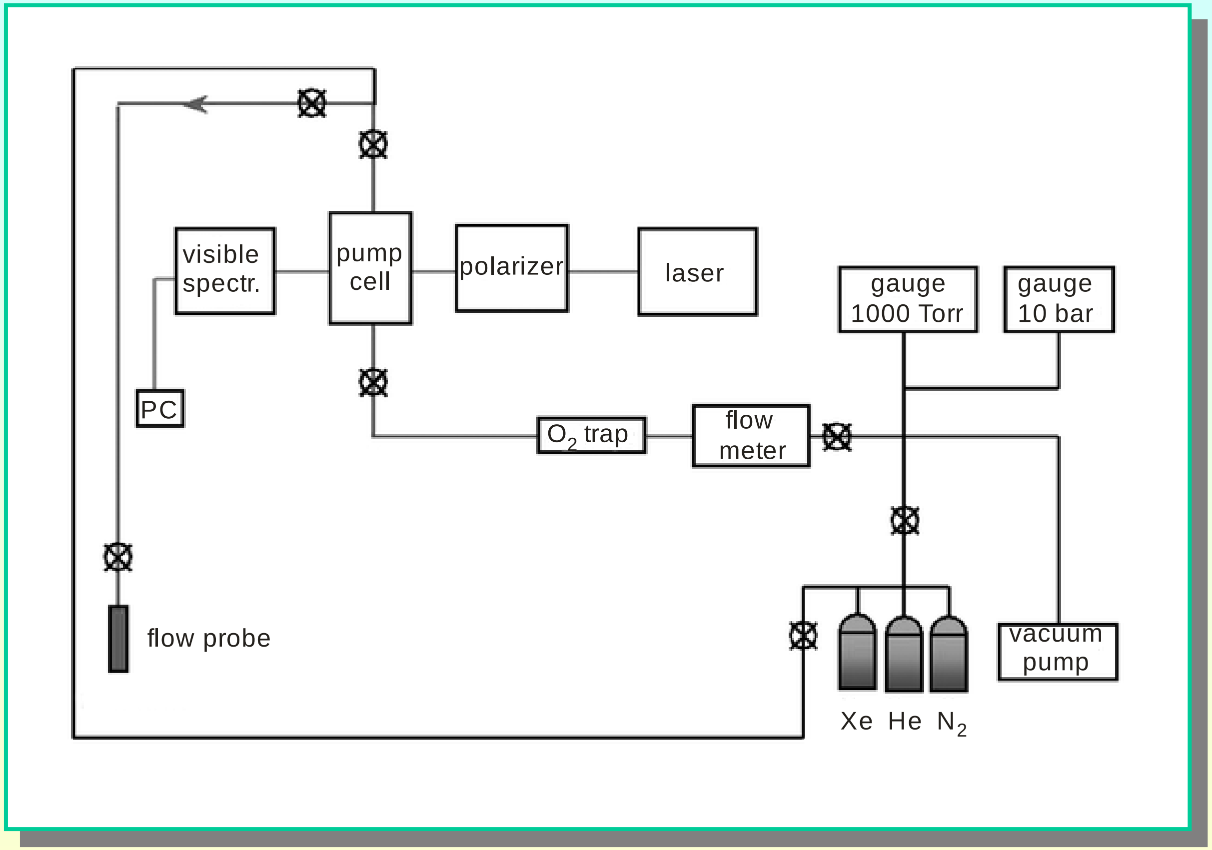
  - study of the isotopic exchange of reactants at high temperatures

Flow experiments with laser-polarized xenon

- **continuous injection of laser-polarized xenon:**

  - optical pumping of the D_1 transition (794.7 nm) of rubidium

  - spin exchange between excited rubidium atoms and the xenon atoms by gas phase collisions



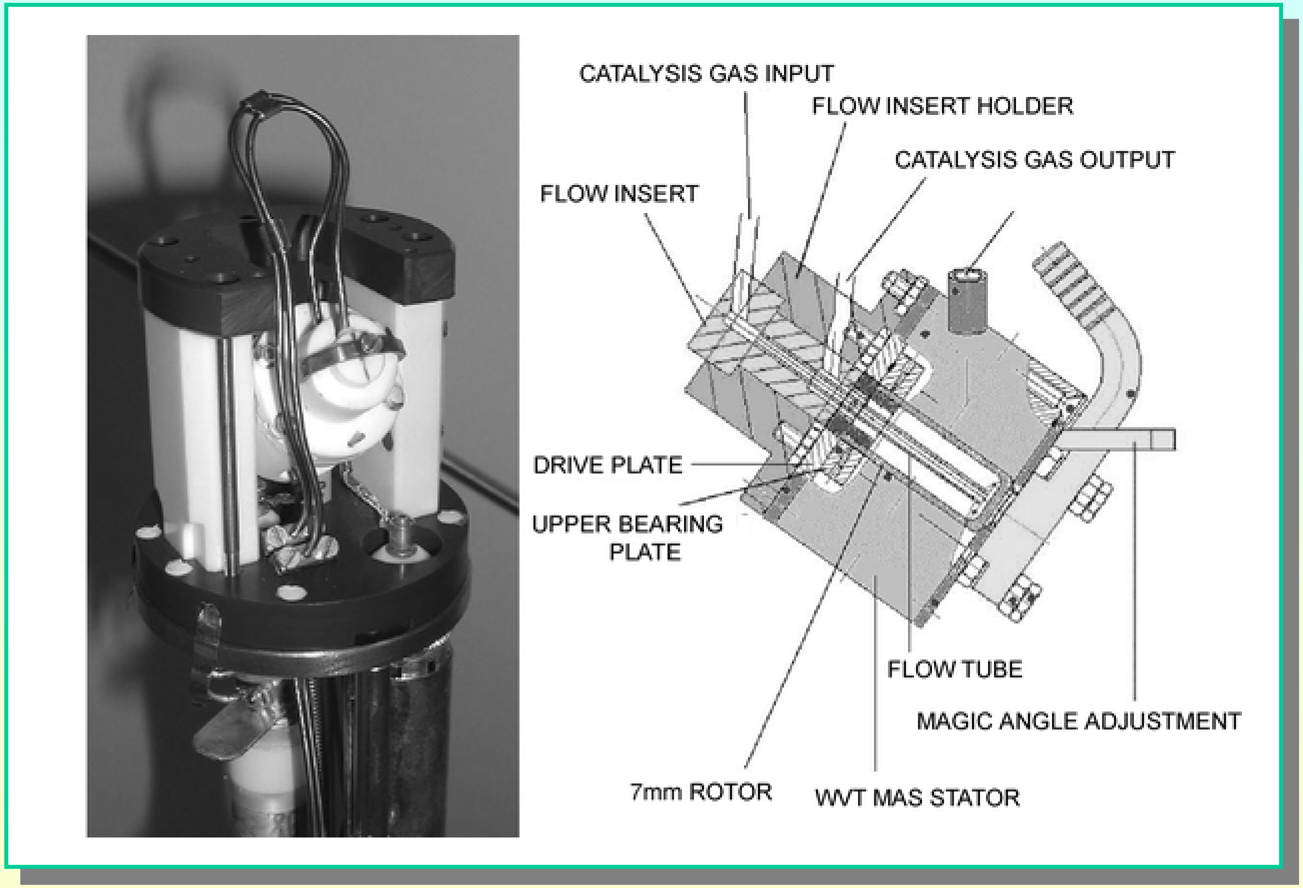
- **typical applications:**

  - study of the meso- and micropore systems of solid catalyst and adsorbents

  - study of the location of adsorbate complexes upon *in situ* adsorption of reactants

A. Nossov et al., Phys. Chem. Chem. Phys. 5 (2003) 4479.

CF MAS NMR probe of Bruker BioSpin



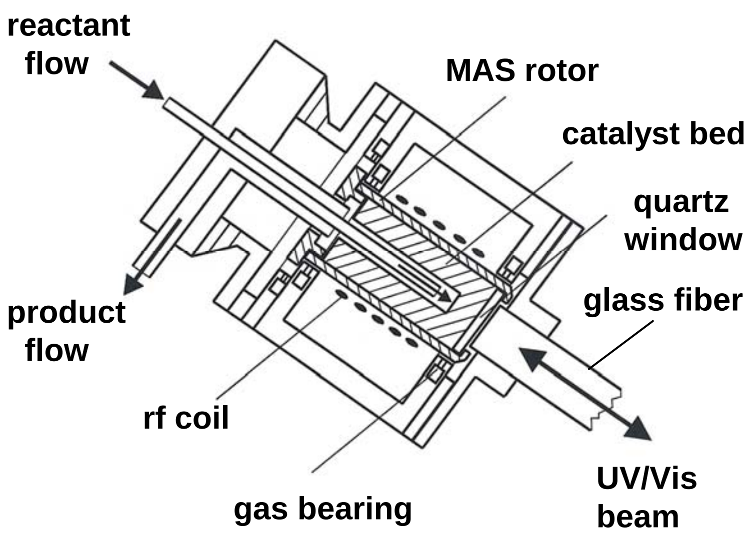
- **MASCAT probe design with 7 mm MAS NMR rotor and temperatures up to 623 K**

A. Nossov et al., Phys. Chem. Chem. Phys. 5 (2003) 4479.

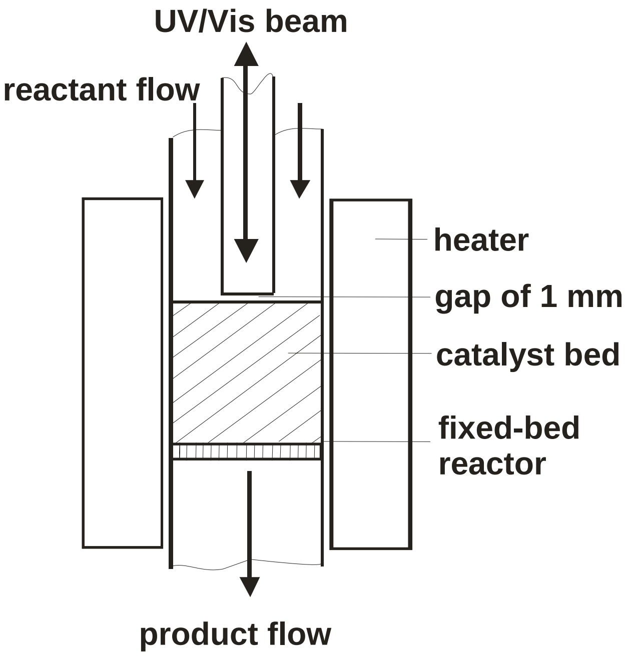
Technique of MAS NMR-UV/Vis spectroscopy

- **a flow MAS NMR probe (modified 7 mm MAS rotor with quartz glass window) was equipped with an UV/Vis glass fiber at the bottom of the MAS stator**

MAS NMR-UV/Vis probe



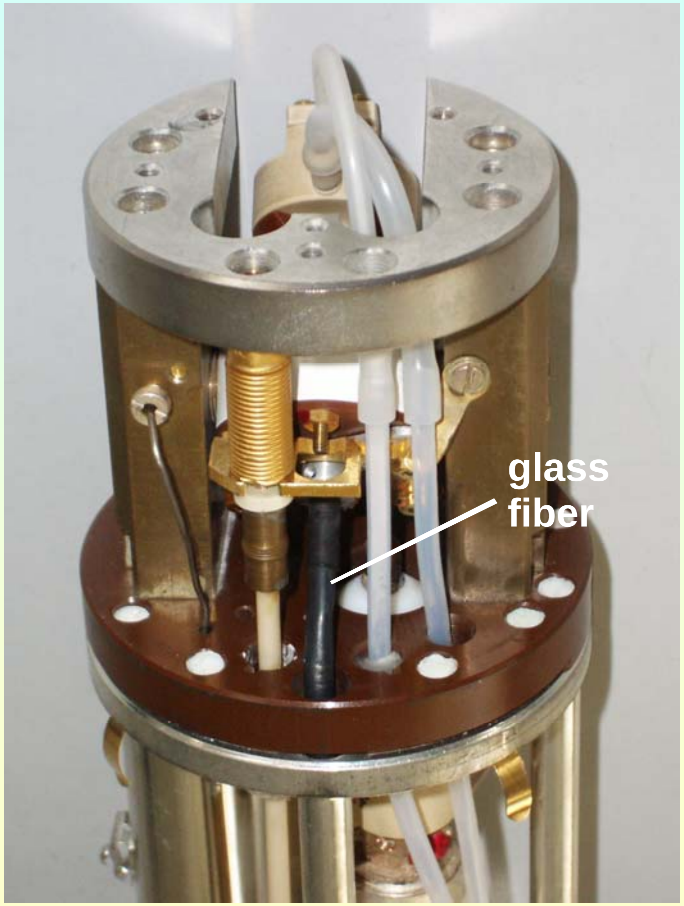
fixed-bed reactor



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

Y. Jiang et al., Stud. Surf. Sci. Catal. 105 (2007) 1137.

Technique of in situ flow MAS NMR



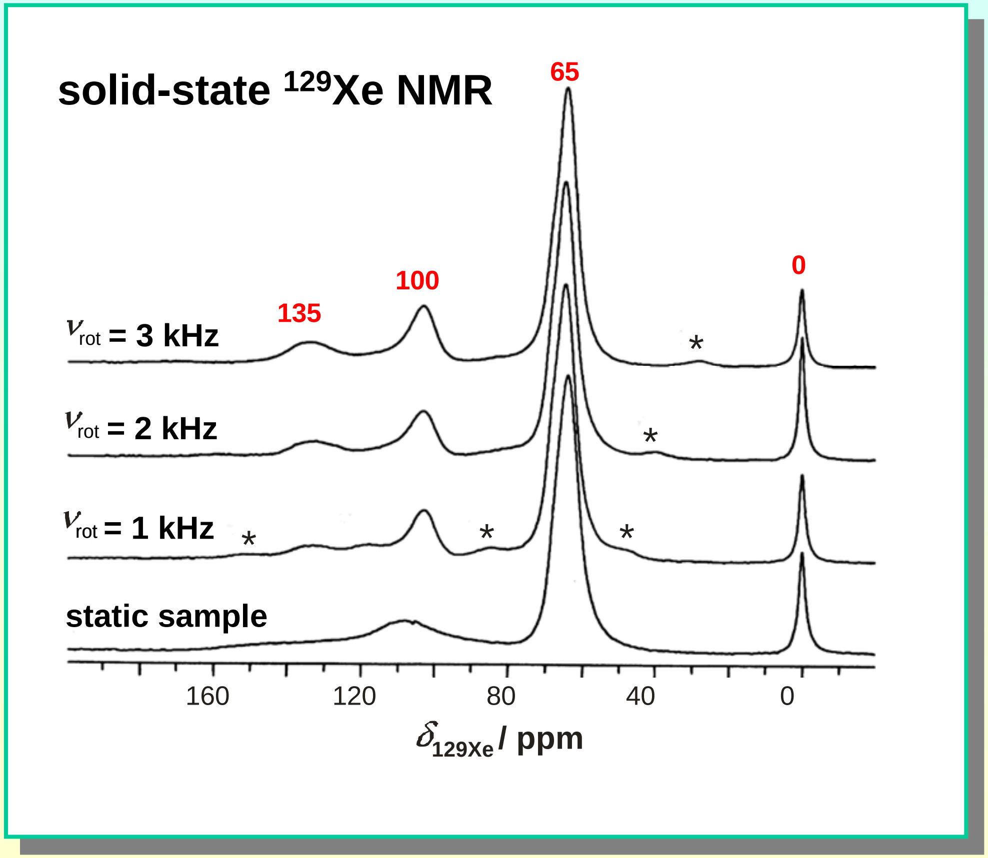
7 mm flow Bruker MAS NMR probe equipped with a glass fiber (left) and UV/Vis light source and spectrometer of Avantes (bottom)

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

Investigation of the pore system of solid catalysts

Advantage of MAS for NMR studies of laser-polarized xenon in porous solids

- **solid-state ^{129}Xe NMR spectroscopy of laser-poarized xenon adsorbed on zeolite ITQ-6:**
  - **- helium flow of 100 cm^3 min^{-1} with 1 % hyperpolarized xenon**
  - **- repetition time of 1 s in magnetic field of 7.0 T**
  - **- sufficient resolution requires application of MAS**



- **signal assignment:**
  - **- signal at 65 ppm is xenon in the interlamellar space**
  - **- signal at 100 ppm is xenon in cavities**
  - **- signal at 135 ppm corresponds to xenon in channels**

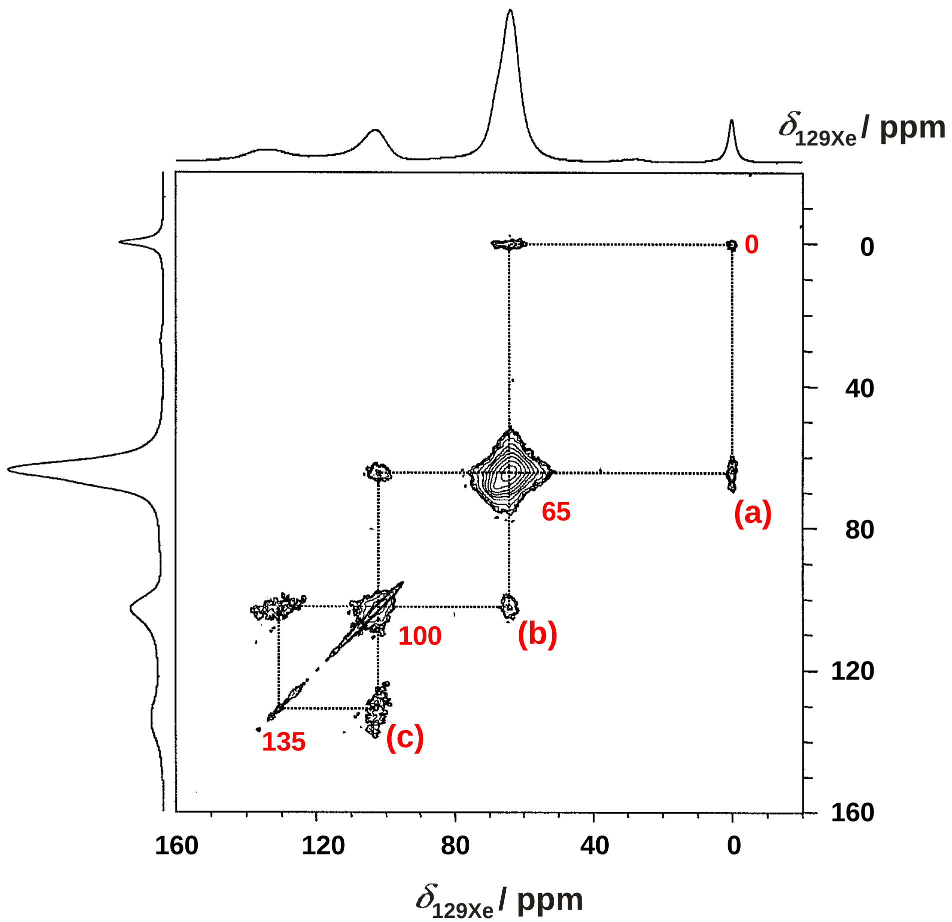
A. Nossov et al., Phys. Chem. Chem. Phys. 5 (2003) 4479.

Study of xenon exchange dynamics in zeolite ITQ-6

- **2D-exchange ^{129}Xe MAS NMR of laser-poarized xenon adsorbed on zeolite ITQ-6:**
  - **helium flow of 100 cm^3 min^{-1} with 1 % hyperpolarized xenon**
  - **magnetic field of 7.0 T**
  - **ν_{rot} = 3 kHz, repetition time of 2 s, and 8 scans per spectrum**
  - **mixing time of 50 ms**

- **cross peaks indicate xenon exchange between:**
  - **a) gas phase and the interlamellar space**
  - **b) cavities and the interlamellar space**
  - **c) channels and cavities**

2D-exchange ^{129}Xe MAS NMR

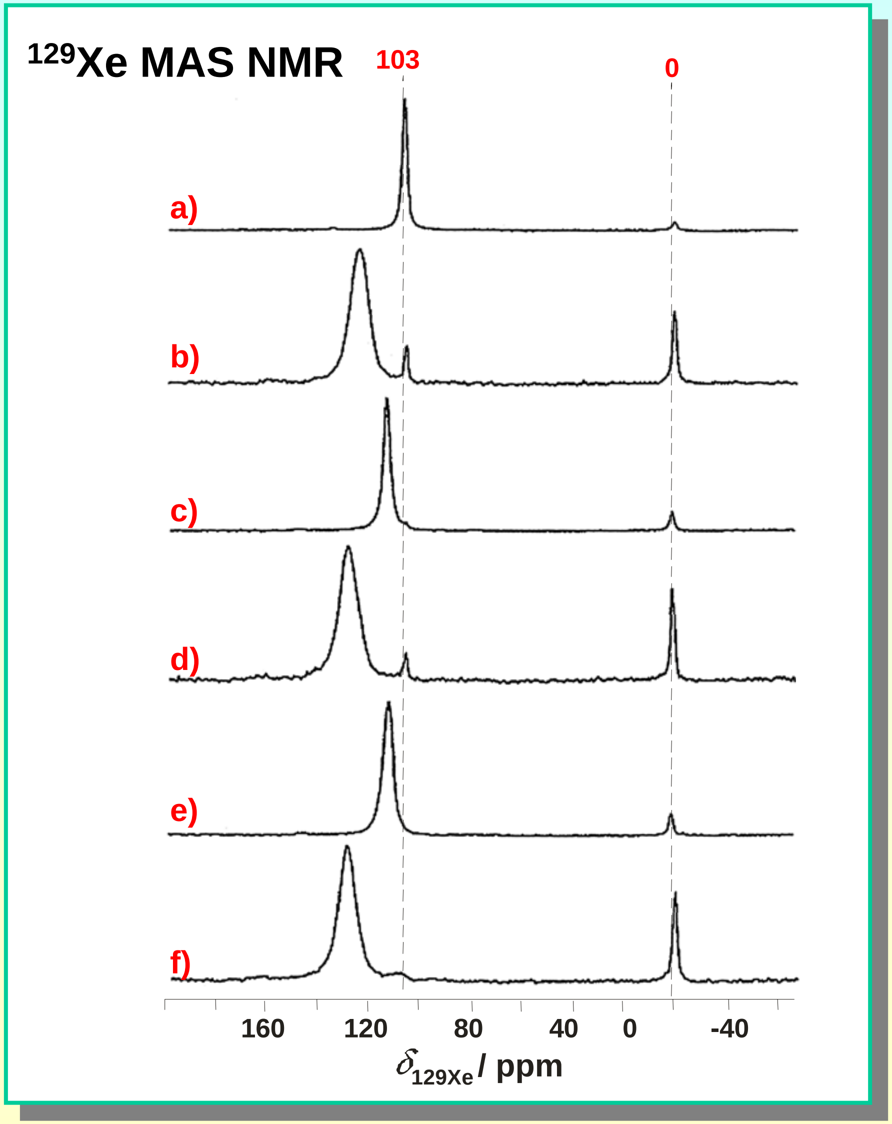


A. Nossov et al., Phys. Chem. Chem. Phys. 5 (2003) 4479.

Study of the location of reactant molecules in porous catalysts

- ^{129}Xe MAS NMR of laser-poarized xenon on silicalite-1:
  - helium flow with 1 % hyper-polarized xenon
  - magnetic field of 7.0 T
  - ν_{rot} = 3.5 kHz
  - signal at 103 ppm caused by xenon in empty 10-ring channels

- pulse-like addition of benzene (1.3 %):
  - resonance shift to left due to adsorption of benzene in 10-ring channels (b, d, f)
  - resonance shift to right due to desorption of benzene, i.e, 1.5 h later (c, e)

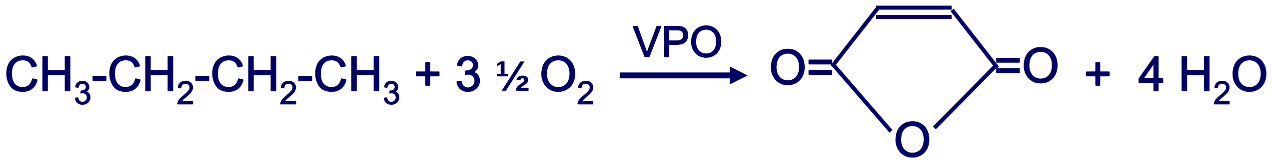


I.L. Moudrakovski et al., Chem. Mater. 12 (2000) 1181 .

Investigation of the selective oxidation of alkanes on VPO catalysts

Selective oxidation of n-butane to maleic anhydride (MA)

- **reaction:**



- possible intermediates are 1-butene, 1,3-butadiene, dihydrofuran, and furan [1]
- MA is an important step in the polyester resin production [1]

- **catalyst:**

- VPO catalysts are prepared by activation of vanadyl hydrogenphosphate hemihydrate $VOHPO_4 \cdot 0.5\ H_2O$ in n-butane/air flow [2]:

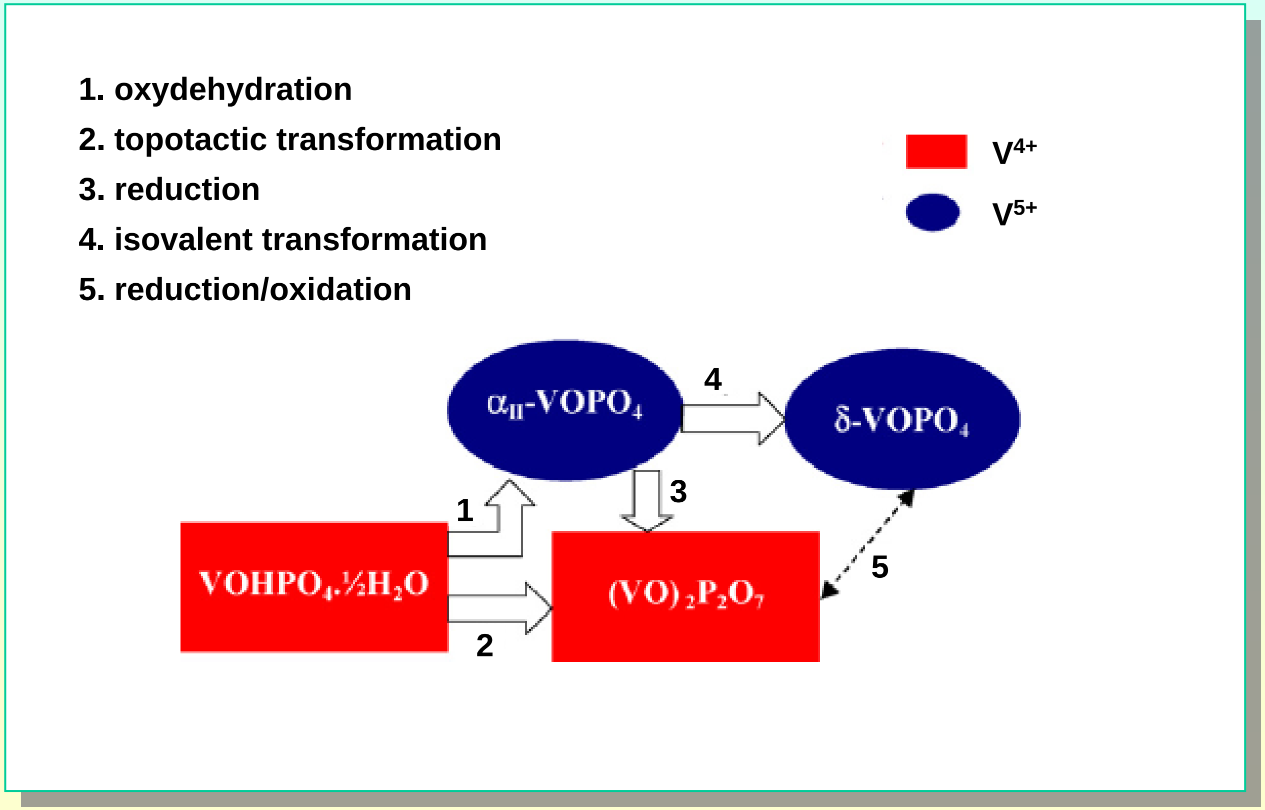
reducing atm. $\longrightarrow$ **$(VO)_2P_2O_7$ (vanadyl pyrophosphate)**
oxidizing atm. $\longrightarrow$ **$VOPO_4$ (vanadyl orthophosphate phases)**

- activity increases sharply for P / V ratio reaching > 1

[1] M. Hävecker et al., J. Phys. Chem. B, 107 (2003) 4587.
[2] R.A. van Santen, Handbook of Heterogeneous Catalysis, Springer, 1997, p. 2244.

Structural transformations

- suggested transformations of the $VOHPO_4 \cdot 0.5\ H_2O$ precursor during the formation of the final VPO catalyst and the reaction cycle:



1. oxydehydration
2. topotactic transformation
3. reduction
4. isovalent transformation
5. reduction/oxidation

🟥 V^{4+}

● V^{5+}

C.J. Kiely, G.J. Hutchings, Appl. Catal. A: General 325 (2007) 194.

Preparation of supported VPO catalysts

- **preparation of VPO/SBA-15 catalysts according to Li et al.:**

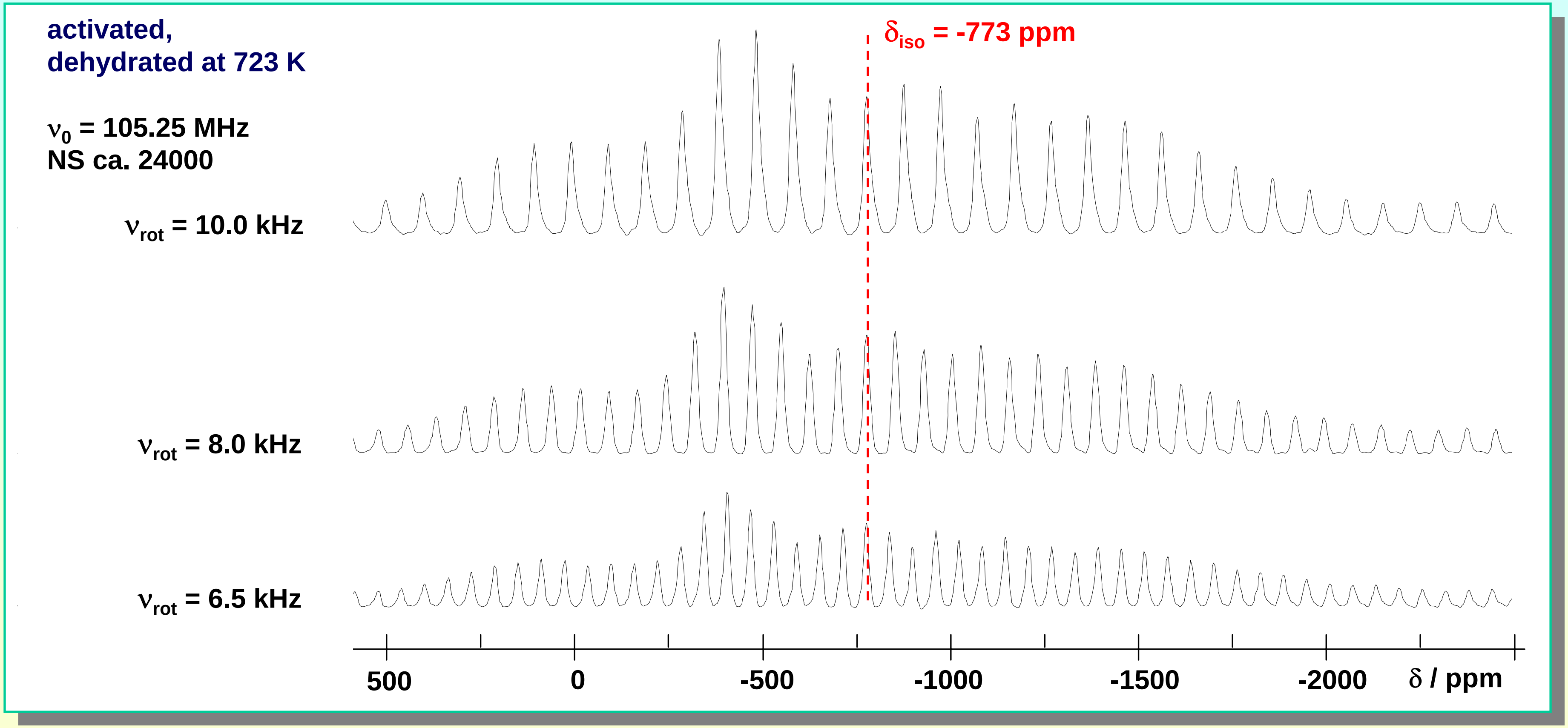
  - siliceous SBA-15 is added to isobutyl/benzyl alcohols (1 : 1) with V_2O_5, PEG 6.000 and H_3PO_4
  - VPO loadings of 20 to 60 wt.%
  - activation in a flow of 1.5 % n-butane, 17.5 % O_2 and balance N_2 (100 ml/min) at 673 K for 15 h

- **ICP-AES and nitrogen adsorption:**

Samples	P / V	BET surface m^2 / g	Pore volume cm^3 / g
SBA-15	-	1164	1.25
20%VPO/SBA-15	1.09	662	0.80
60%VPO/SBA-15	1.04	456	0.54

X.-K. Li et al., J. Catal. 238 (2006) 232.

^{51}V MAS NMR of 60%VPO/SBA-15



activated,
dehydrated at 723 K

ν_0 = 105.25 MHz
NS ca. 24000

Material	δ_{iso}	$\Delta\delta$	η_δ	C_{QCC}	η_Q
60%VPO/SBA-15	**-773 ppm**	**-900 ppm**	**0.10**	**1.99 MHz**	**0.59**

M. Hunger et al., poster AC-03, EUROMAR 2008, St. Petersburg, Russia.

^{51}V MAS NMR spectroscopy of vanadium orthophosphates

- ^{51}V MAS NMR investigations of V^{5+} species in $VOPO_4$:

Material	δ_{iso}	$\Delta\delta$	η_δ	C_{QCC}	η_Q	References
60%VPO/ SBA-15	-773 ppm	-900 ppm	0.10	1.99 MHz	0.59	present Study
α_I-$VOPO_4$	-691 ppm	820 ppm	0.00	1.55 MHz	0.55	[1]
α_{II}-$VOPO_4$	-776 ppm -755 ppm	582 ppm 922 ppm	0.67 0.08	0.83 MHz 0.63 MHz	0.52 0.09	[1] [2]
β-$VOPO_4$	-691 ppm -735 ppm	818 ppm 818 ppm	0.00 0.05	1.99 MHz 1.45 MHz	0.59 0.44	[1] [2]
γ-$VOPO_4$/1	-755 ppm	955 ppm	0.15	0.55 MHz	0.68	[2]
γ-$VOPO_4$/2	-739 ppm	942 ppm	0.07	1.32 MHz	0.55	[2]

- $\Delta\delta$ values of 900 to 1300 ppm indicate distorted VO_6 octahedra

[1] O.B. Lapina et al., J. Mol. Catal. A: Chem. 162 (2000) 381.
[2] R. Siegel et al., Magn. Reson. Chem. 42 (2004) 1022.

^{31}P MAS NMR spectroscopy of vanadium orthophosphates

- ^{31}P MAS NMR studies of phosphorous atoms at vanadium V^{5+} species in $VOPO_4$ phases:

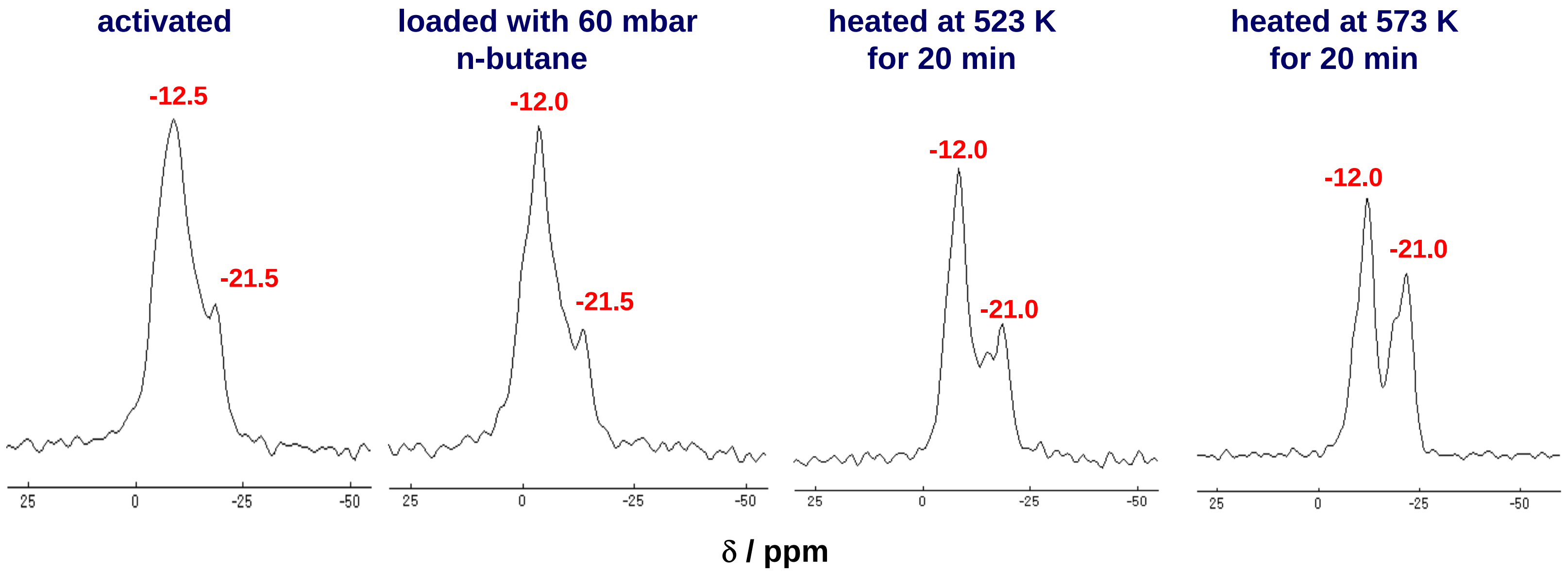
^{31}P MAS NMR signals	**V^{5+} phases**	**References**
-20.5 ppm	**α_{II}-$VOPO_4$**	**[3]**
-11.5 ppm	**β-$VOPO_4$**	**[3]**
-21.2 ppm, -17.3 ppm (ca. 1:1) **-14.9 ppm (very weak shoulder)**	**γ-$VOPO_4$**	**[3]**
-17.6 ppm, -8.4 ppm (ca. 1:1) **-6.5 ppm (very weak shoulder)**	**δ-$VOPO_4$**	**[3]**
2.7 to 3.6 ppm	**α_{I}-$VOPO_4$**	**[4, 5, 6]**
3.9 ppm	**$VOPO_4 \cdot n\ H_2O$**	**[4]**

[1] M.T. Sananes-Schulz et al., J. Catal. 166 (1997) 388.
[2] M.T. Sananes, A. Tuel, Solid State Nuclear Magn. Reson., 6 (1996) 157.
[3] F. Ben Abdelouahab et al., J. Catal. 134 (1992) 151.
[4] S.A. Ennaciri et al., Eur. J. Solid State Inorg. Chem. 30 (1993) 227.
[5] K.E. Birkeland et al., J. Phys. Chem. B 101 (1997) 6895.
[6] K. Ait-Lachgar et al., J. Catal. 177 (1998) 224.

^{31}P MAS NMR of 60%VPO/SBA-15

60%VPO/SBA-15 activated at 673 for 15 h

ν_0 = 161.98 MHz, ν_{rot} = 10 kHz, NS = 200



activated | **loaded with 60 mbar n-butane** | **heated at 523 K for 20 min** | **heated at 573 K for 20 min**

-21.5 to -21.0 ppm: P at V^{5+} in α_{II}- and γ-$VOPO_4$

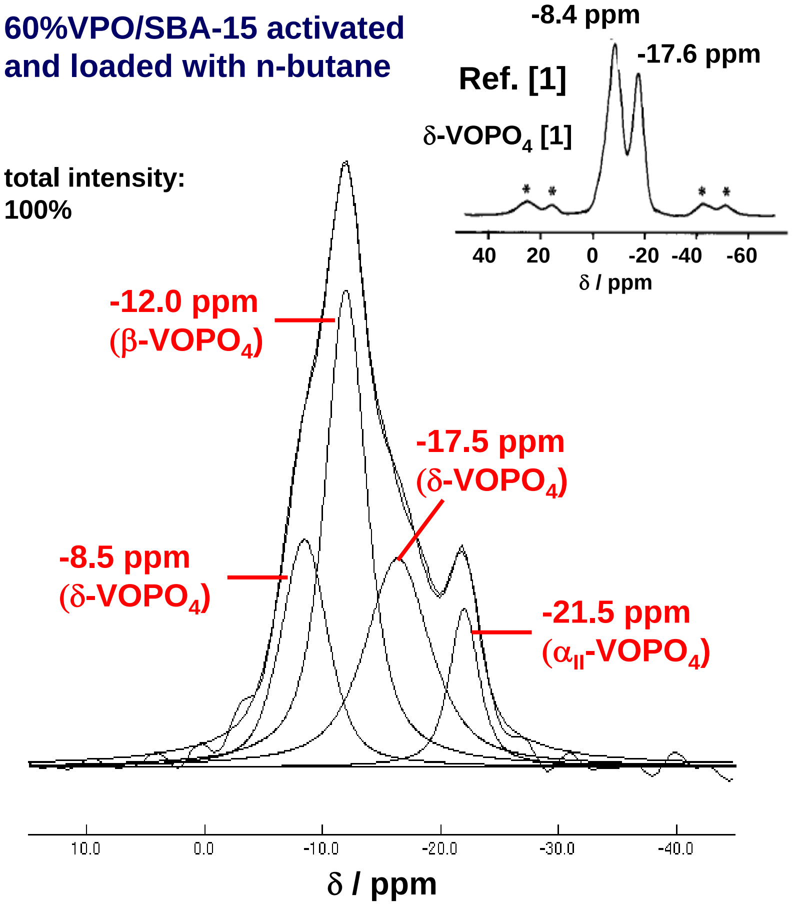
-8 and -18 ppm: P at V^{5+} in δ-$VOPO_4$ → **decrease upon conversion of n-butane**

-11.5 to -12.5 ppm: P at V^{5+} in β-$VOPO_4$

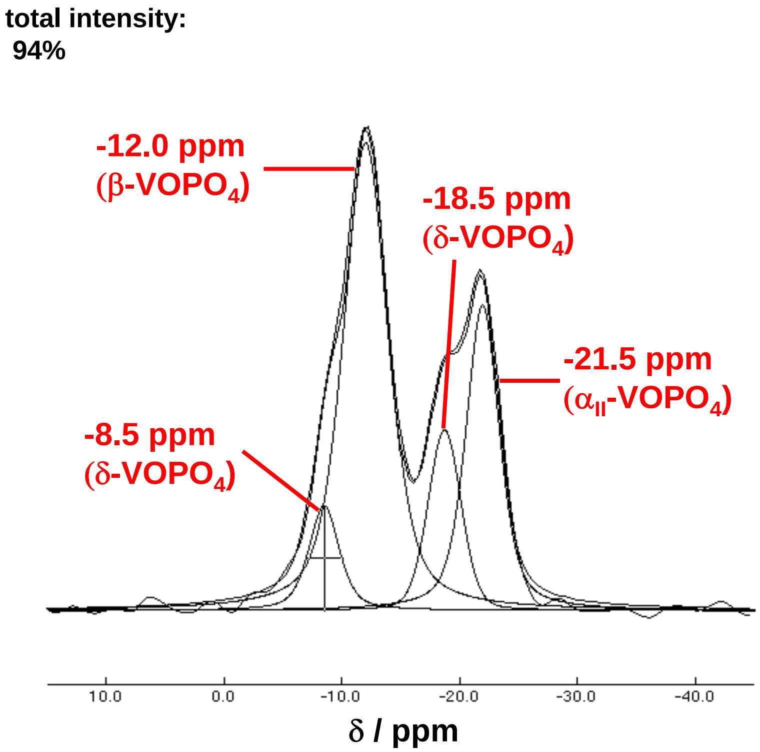
M. Hunger et al., poster AC-03, EUROMAR 2008, St. Petersburg, Russia.

Simulation of ^{31}P MAS NMR spectra

60%VPO/SBA-15 activated and loaded with n-butane

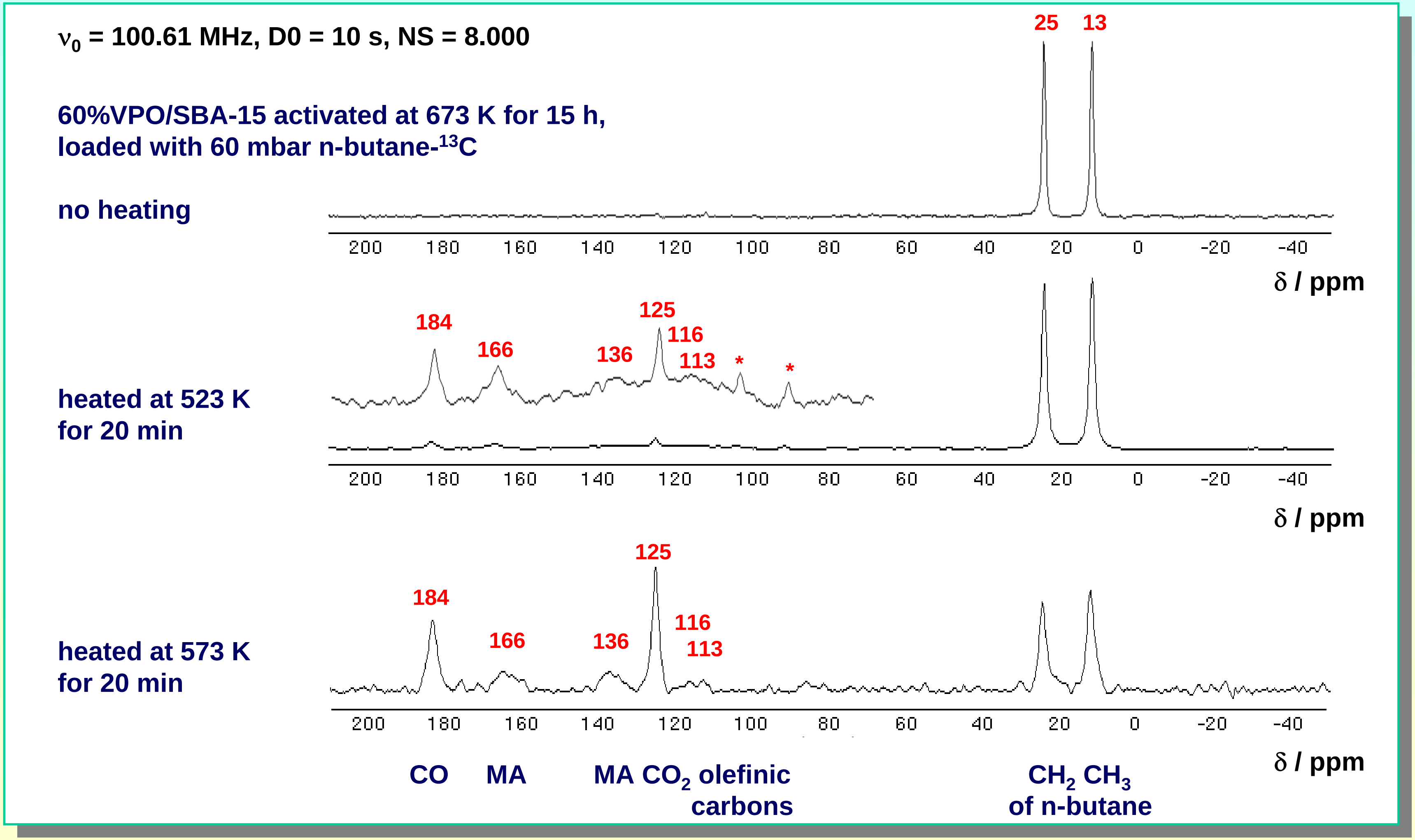


60%VPO/SBA-15 activated, loaded with n-butane, and heated at 573 K



[1] F. Ben Abdelouahab et al., J. Catal. 134 (1992) 151.

^{13}C MAS NMR of n-butane on 60%VPO/SBA-15



ν_0 = 100.61 MHz, D0 = 10 s, NS = 8.000

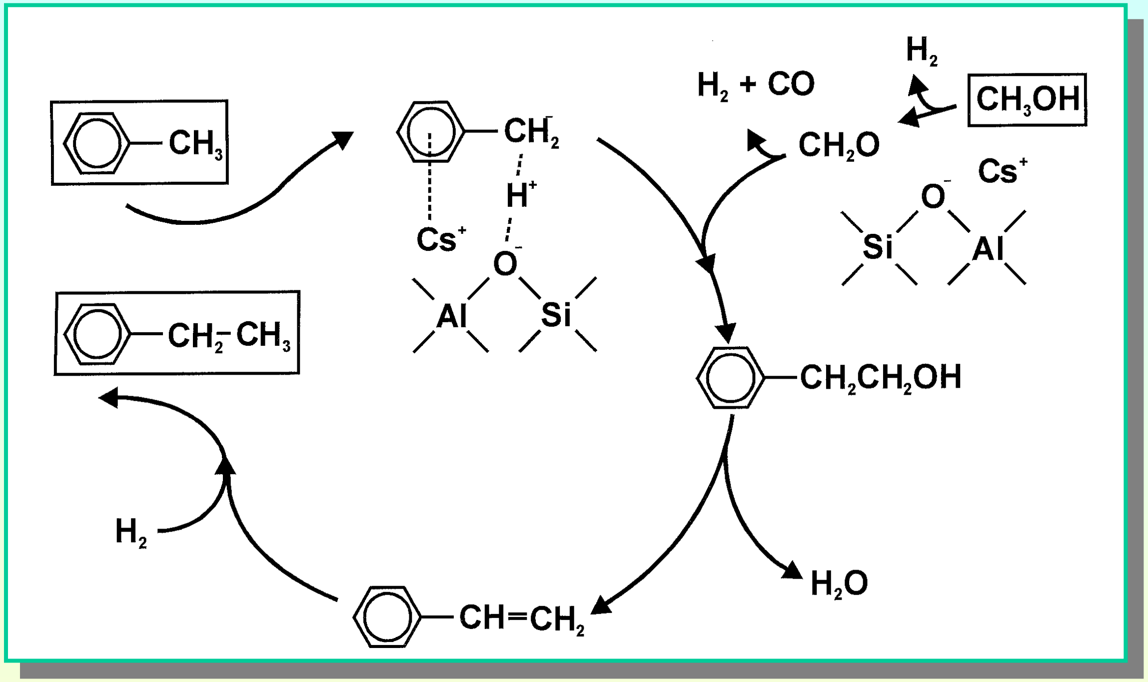
60%VPO/SBA-15 activated at 673 K for 15 h, loaded with 60 mbar n-butane-^{13}C

M. Hunger et al., poster AC-03, EUROMAR 2008, St. Petersburg, Russia.

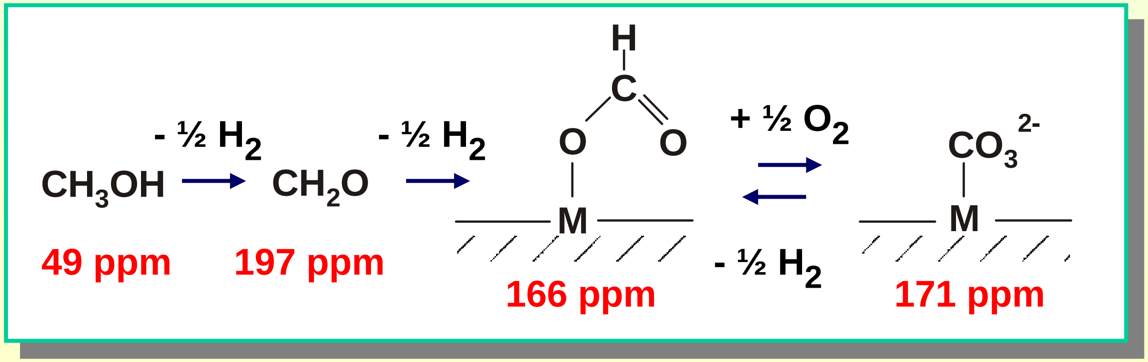
Investigation of base sites and of reactions catalyzed by basic zeolites

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

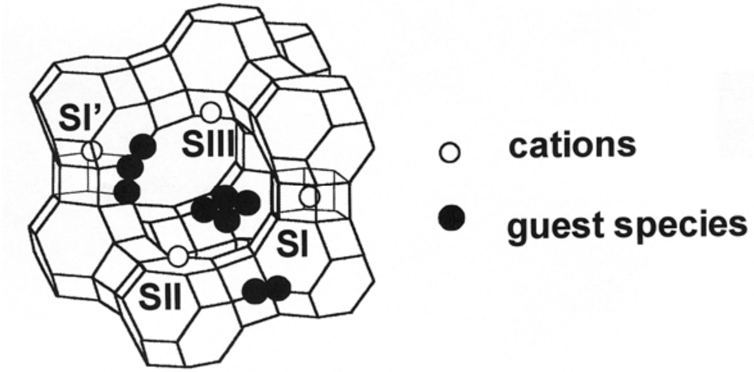


- proposed surface species:
  - formate (δ_{13C} = 166 ppm)
  - carbonate (δ_{13C} = 171 ppm)

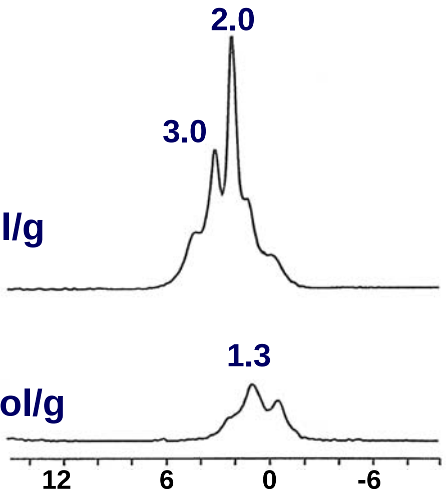


NMR characterization of the calcined zeolite CsOH/Cs,Na-X

- **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



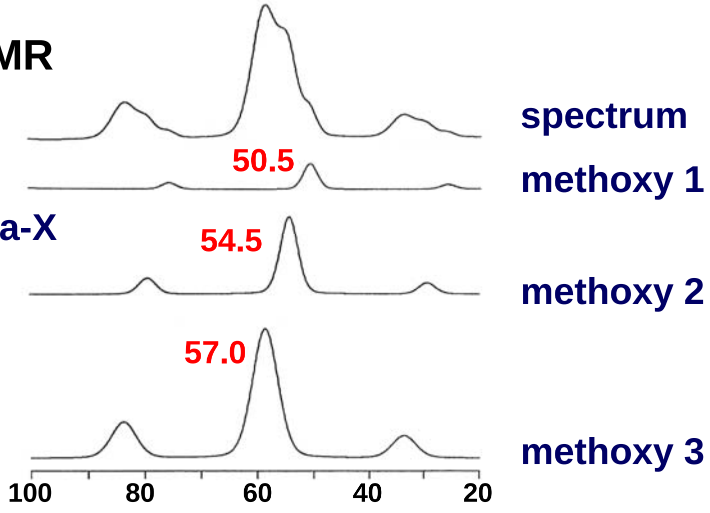
Cs,Na-X:
c_{OH} = 0.3 mmol/g

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

δ_{1H}/ppm

^{13}C MAS NMR

CsOH/Cs,Na-X
+ CH_3I

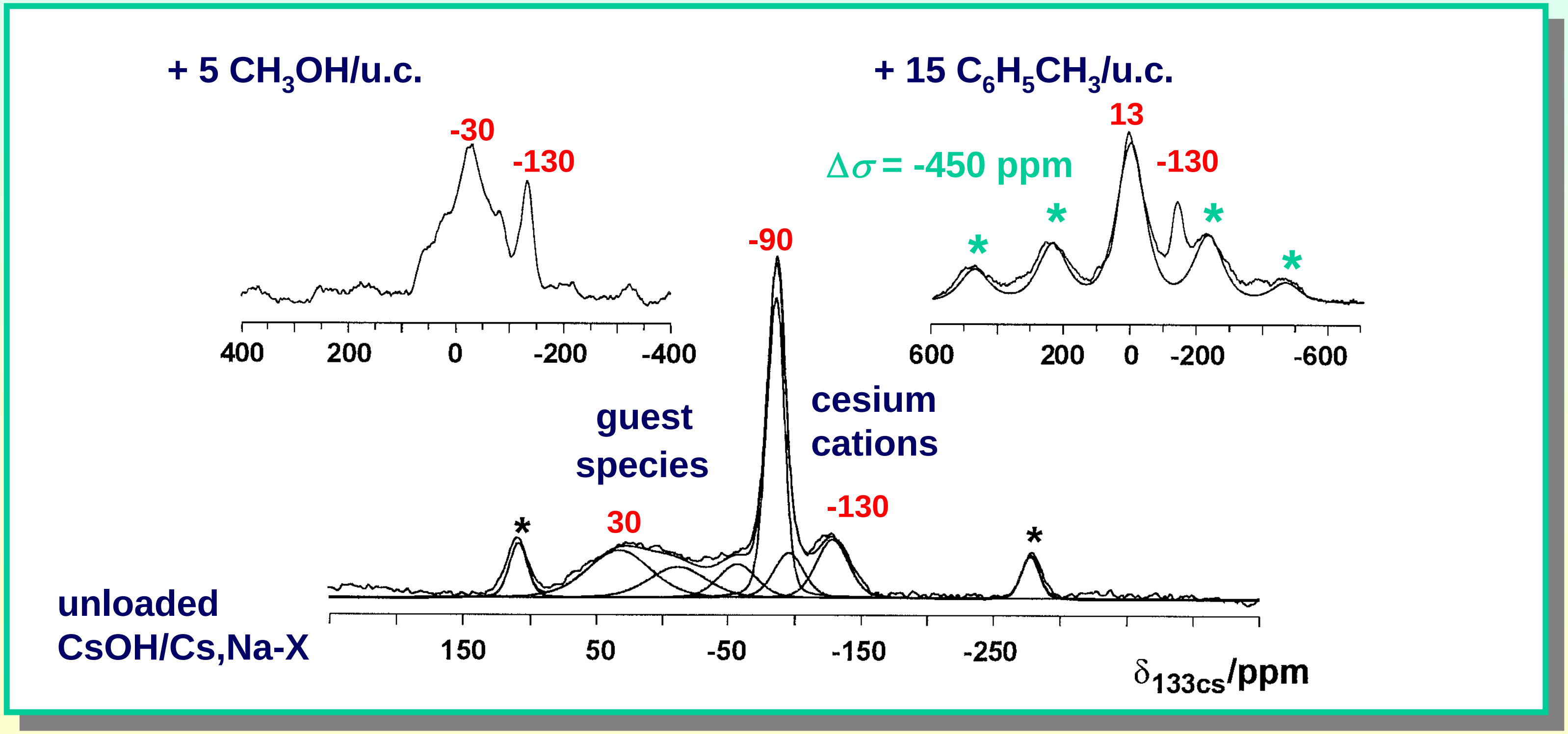


δ_{13C}/ppm

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**

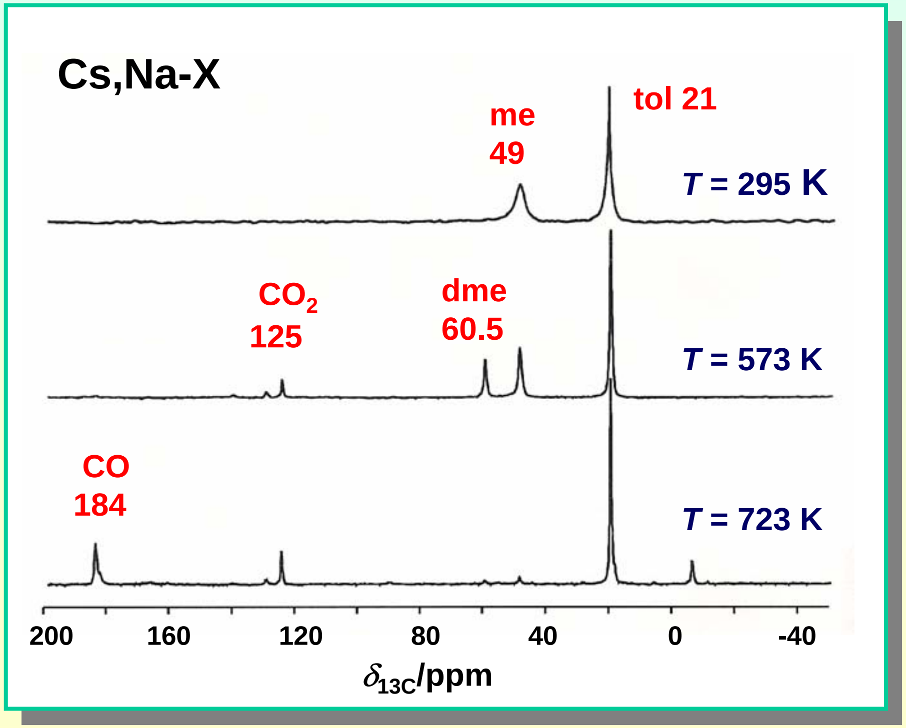


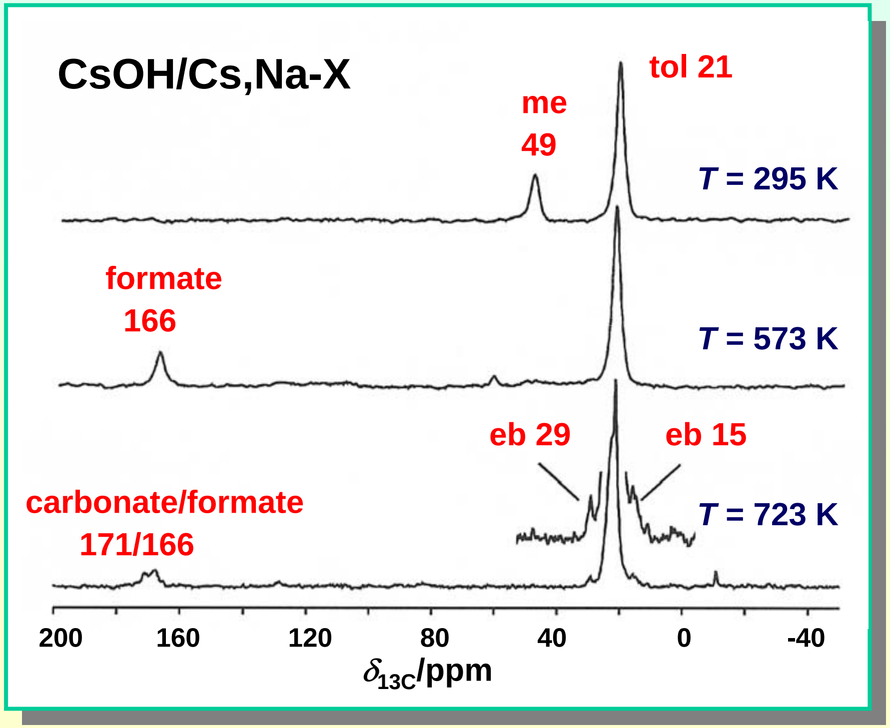
M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

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.

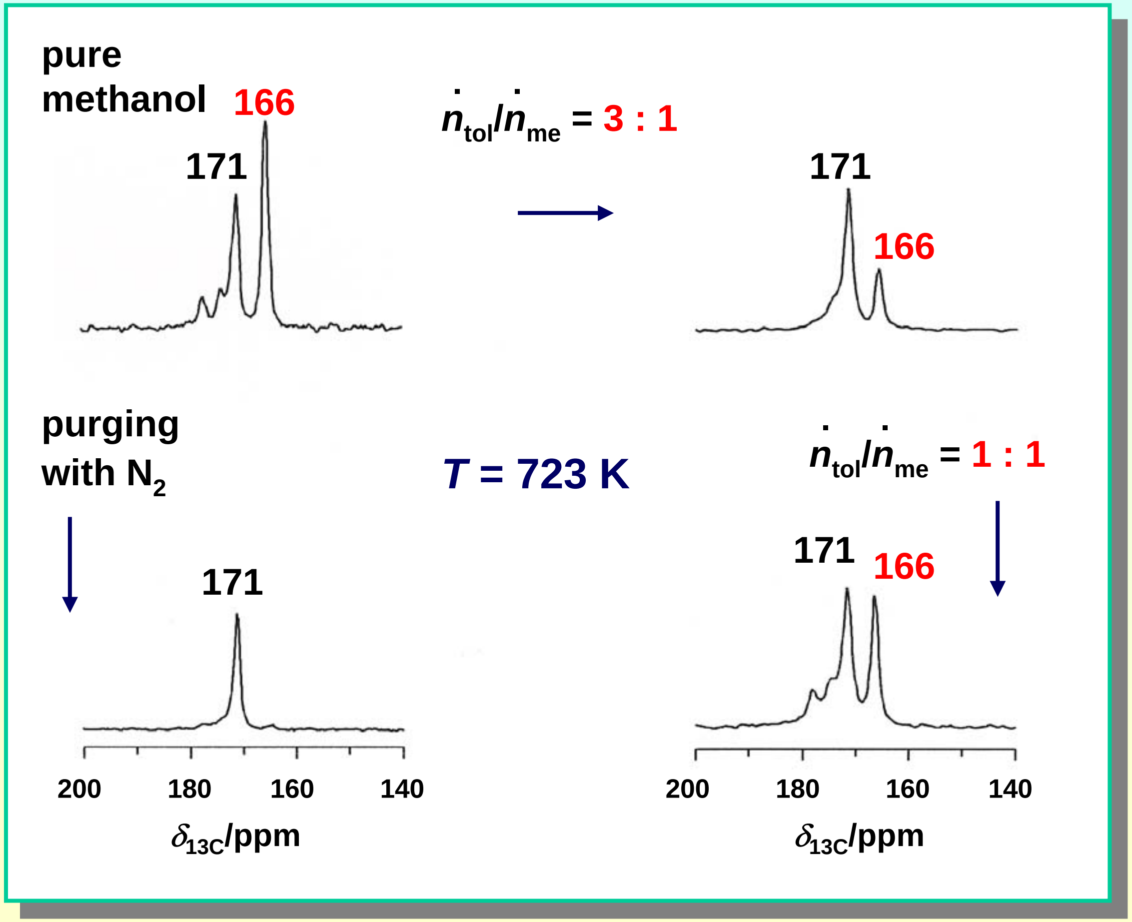
Reactivity of formate species on zeolite CsOH/Cs,Na-X under flow conditions

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

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

→ **carbonate species are chemically stable**

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

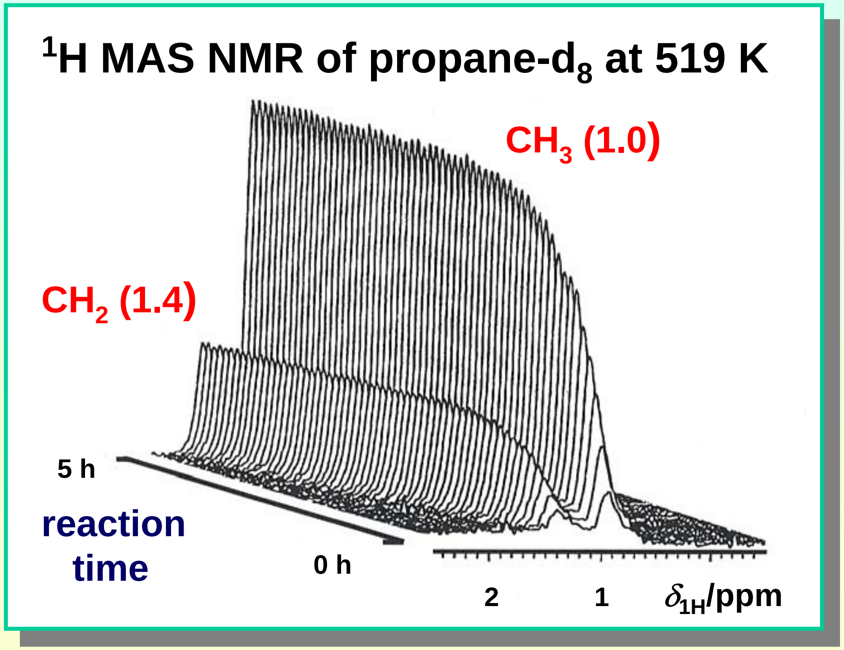


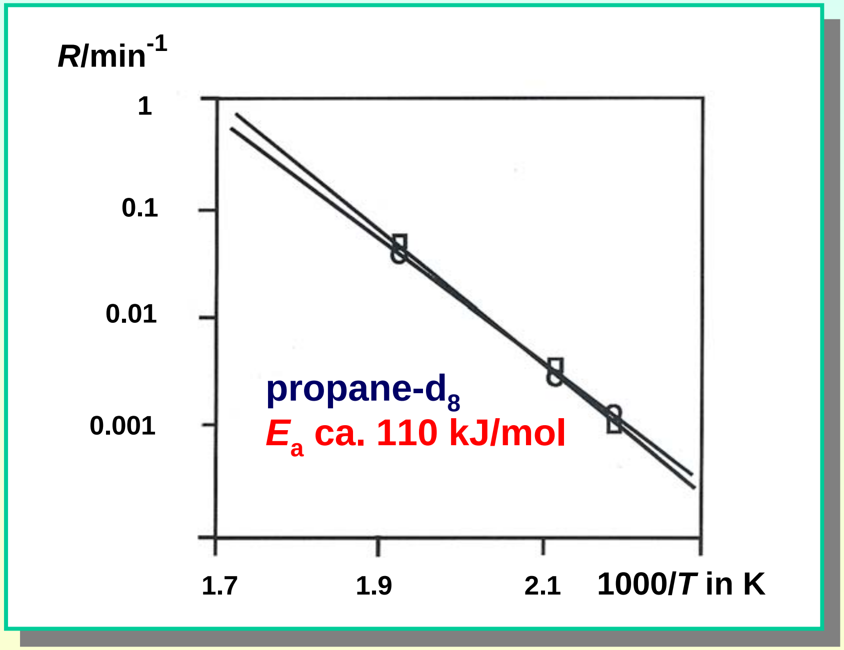
M. Hunger et al., J. Mol. Catal. A: Chem. 156 (2000) 153.

Investigation of the H/D exchange on acidic catalysts

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

A.G. Stepanov et al., Catal. Lett. 54 (1998) 1

B:

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

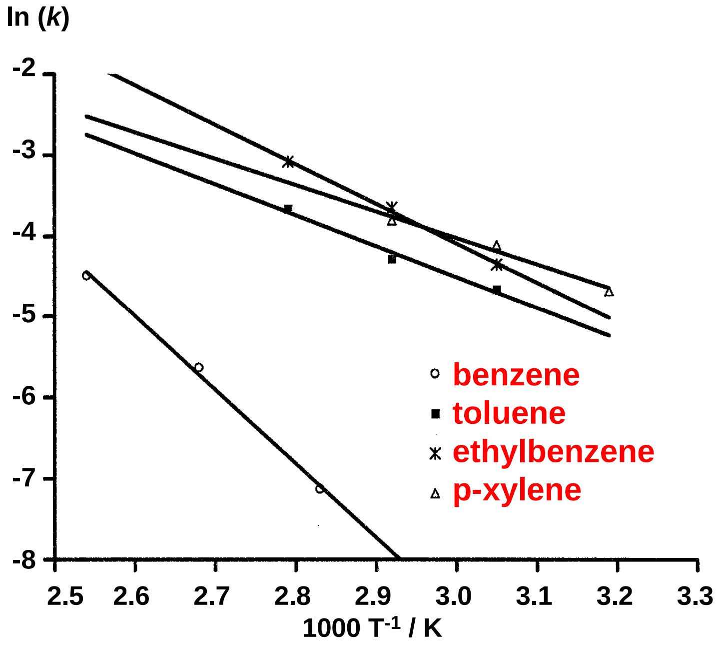
→ formation carbenium ions

J. Sommer et al., J. Catal. 181 (1999) 265.

H/D exchange between deuterated reactants and protons of surface OH groups

- **H/D exchange with deuterated alkylaromatics on zeolites H,Na-Y, La,Na-Y, and H-ZSM-5**

deuterated alkylaromatics on H,Na-Y



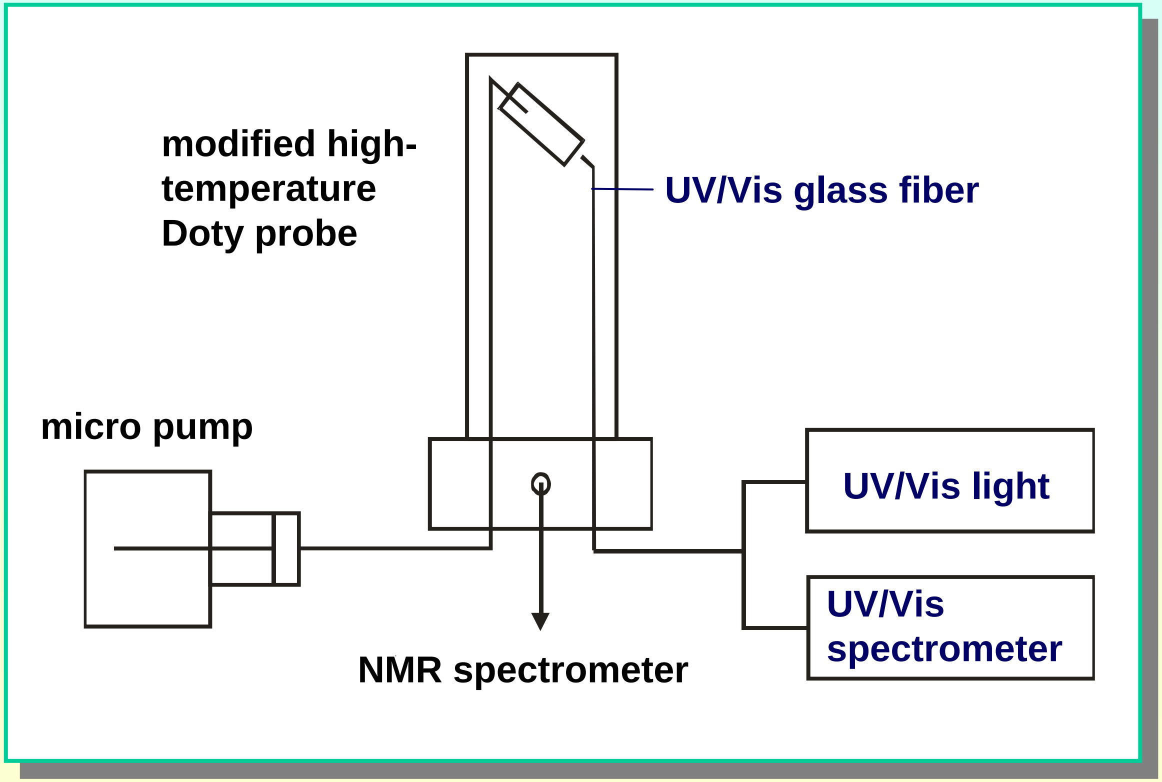
correlation of activation energies E_A of H/D exchange and low-field shifts $\Delta\delta_{1H}$ upon adsorption CD_3CN:

catalyst	molecule	E_A / kJ mol^{-1}	$\Delta\delta_{1H}$ / ppm
H,Na-Y	benzene	76	5.1
La,Na-Y	benzene	67	5.7
H-ZSM-5	benzene	46	7.9
H,Na-Y	benzene	76	
	ethylbenzene	41	
	toluene	32	
	p-xylene	27	

J. Huang et al., Microporous Mesoporous Mater. 99 (2007) 86.

H/D exchange studied by ^{1}H MAS NMR-UV/Vis

- **injection of micro-pulses give start point for H/D exchange at elavated temperature**



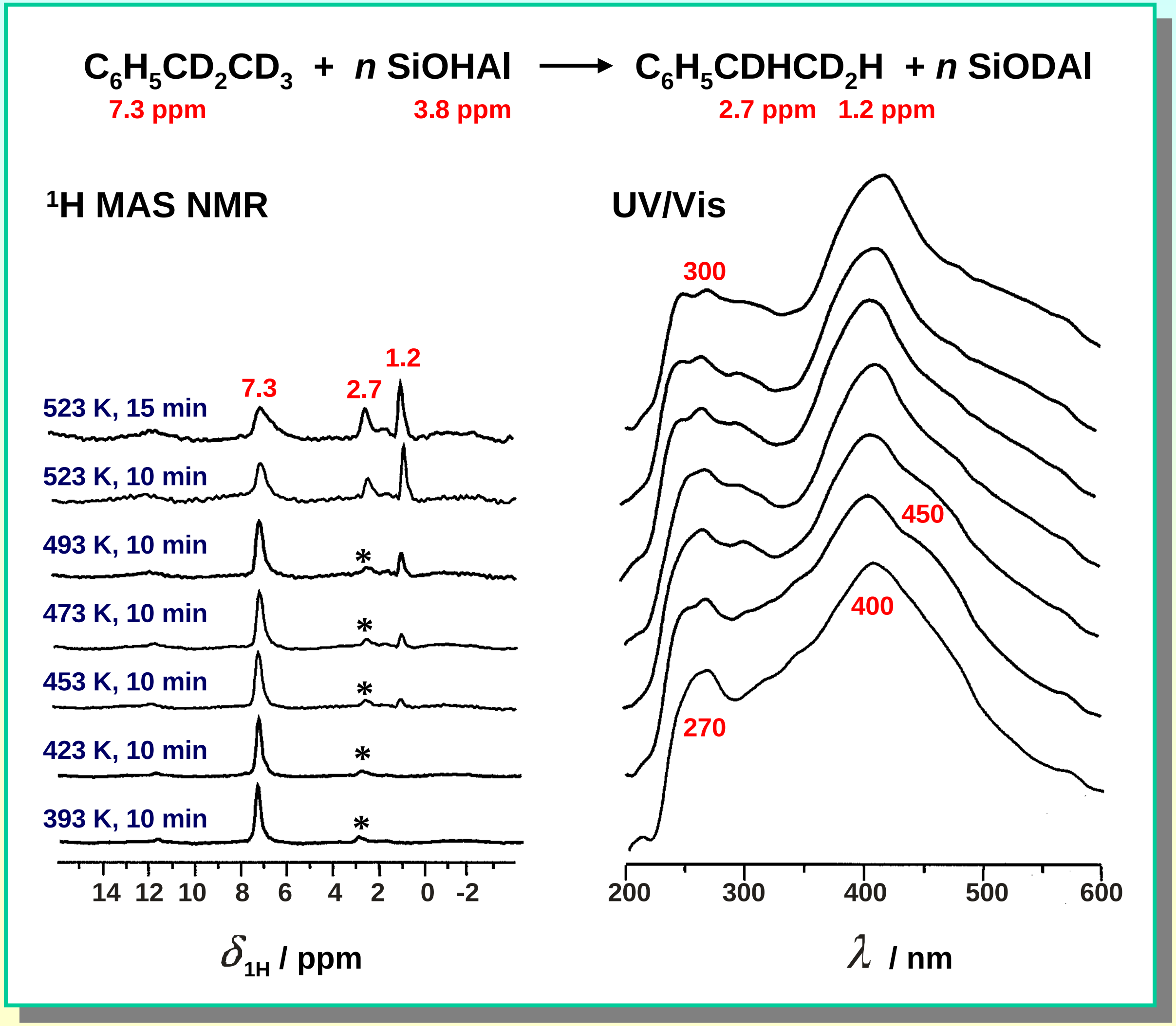
- **pump Mikro g/5 of Fa. ProMinent, Germany, for single pulses with volumes of 2 to 50 µl**

J. Huang, et al., ChemPhysChem 9 (2008) 1107.

Study of the side-chain H/D exchange of ethylbenzene on dealuminated zeolite Y

- ^{1}H MAS NMR studies under pulsed-flow conditions:
  - steamed zeolite deH-Y (n_{Si}/n_{Al} = 5.4)
  - pulses of 7.8 mg ethyl-d_5-benzene
  - 32 scans per spectrum with repetition time of 10 s at 9.4 T
  - sample spinning rate of *ca.* 2 kHz

- message:
  - regioselective H/D exchange at 443 to 463 K (^{1}H MAS NMR)
  - different types of carbenium ions (UV/Vis)

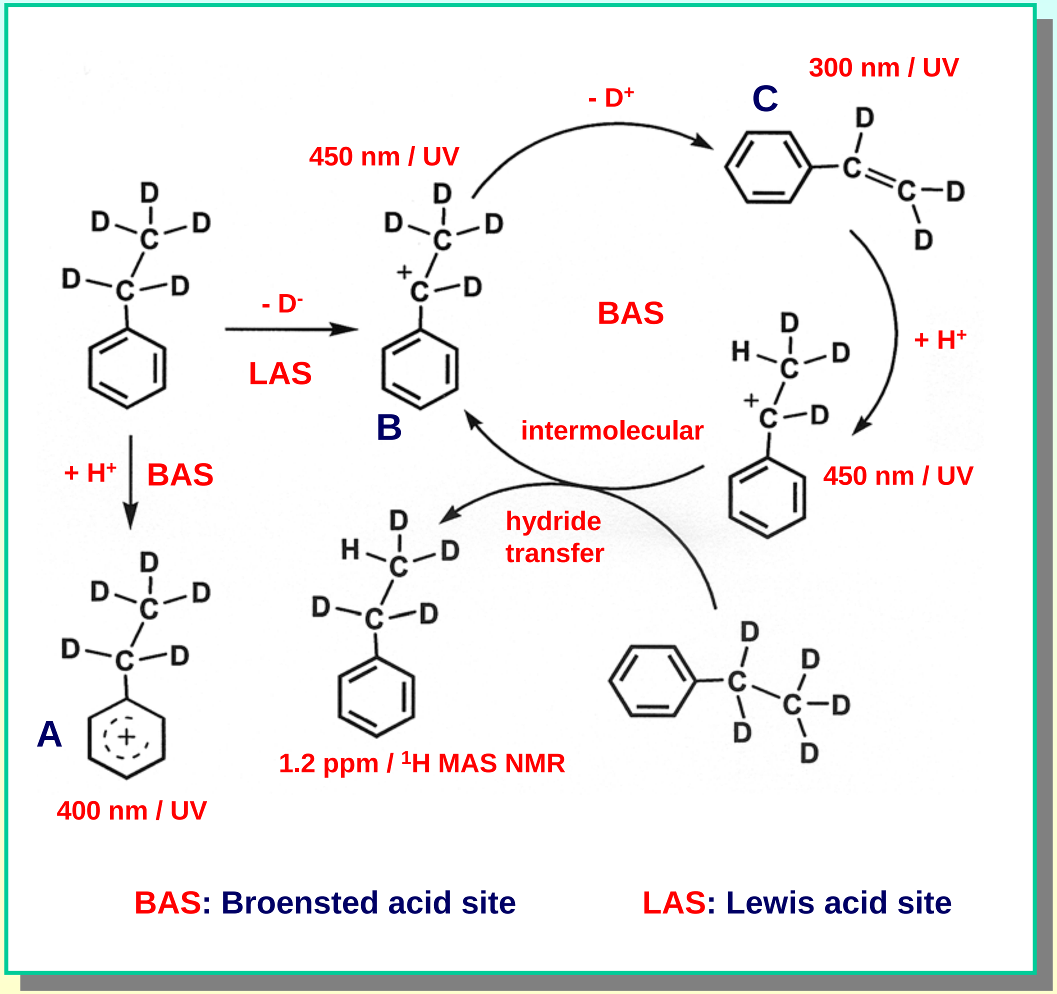


$C_6H_5CD_2CD_3$ + *n* SiOHAl $\longrightarrow$ $C_6H_5CDHCD_2H$ + *n* SiODAl

J. Huang, et al., ChemPhysChem 9 (2008) 1107.

Mechanism of the regioselctive side-chain H/D exchange of ethylbenzene on deH-Y

- ^{1}H MAS NMR results:
  - selective H/D exchange of methyl groups (1.2 ppm)
  - activation energy of 194 kJ/mol indicates hydride transfer
- UV/Vis results:
  - ethylcyclohexadienyl carbenium ions at BAS (400 nm), A
  - sec-ethylphenyl carbenium ions at LAS (450 nm), B
  - styrene at BAS (300 nm), C

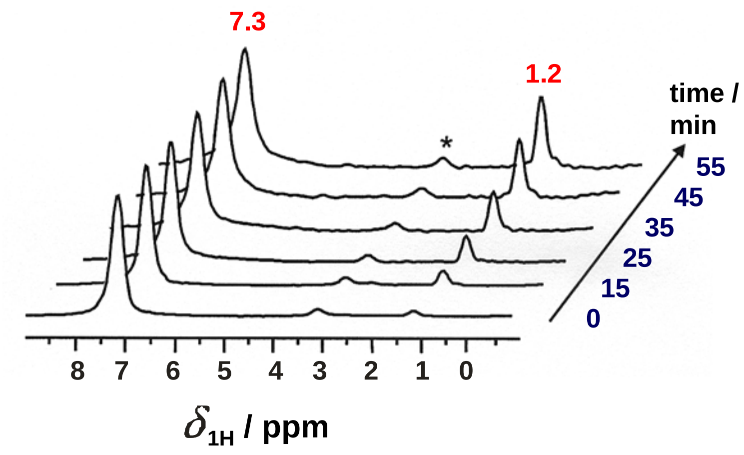


J. Huang, et al., ChemPhysChem 9 (2008) 1107.

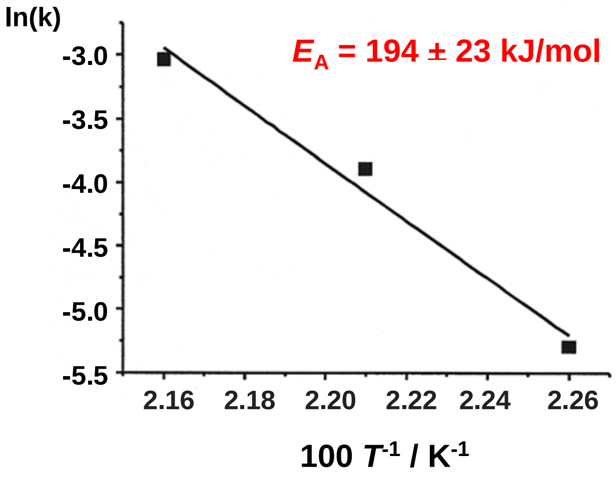
Study of the side-chain H/D exchange of ethylbenzene on dealuminated zeolite Y

- *in situ* pulsed-flow ^{1}H MAS NMR study of the regioselective H/D exchange of the side-chain of ethyl-d_5-benzene on dealuminated zeolite deH-Y (n_{Si}/n_{Al} = 5.4, 22 Al^{ex}/u.c, 10.9 SiOHAl /u.c)

^{1}H MAS NMR



Arrhenius plot



- message:
  - activation energy of the regioselective H/D exchange (194 kJ/mol) indicates that a hydride transfer reaction is the rate determining step

J. Huang, et al., ChemPhysChem 9 (2008) 1107.

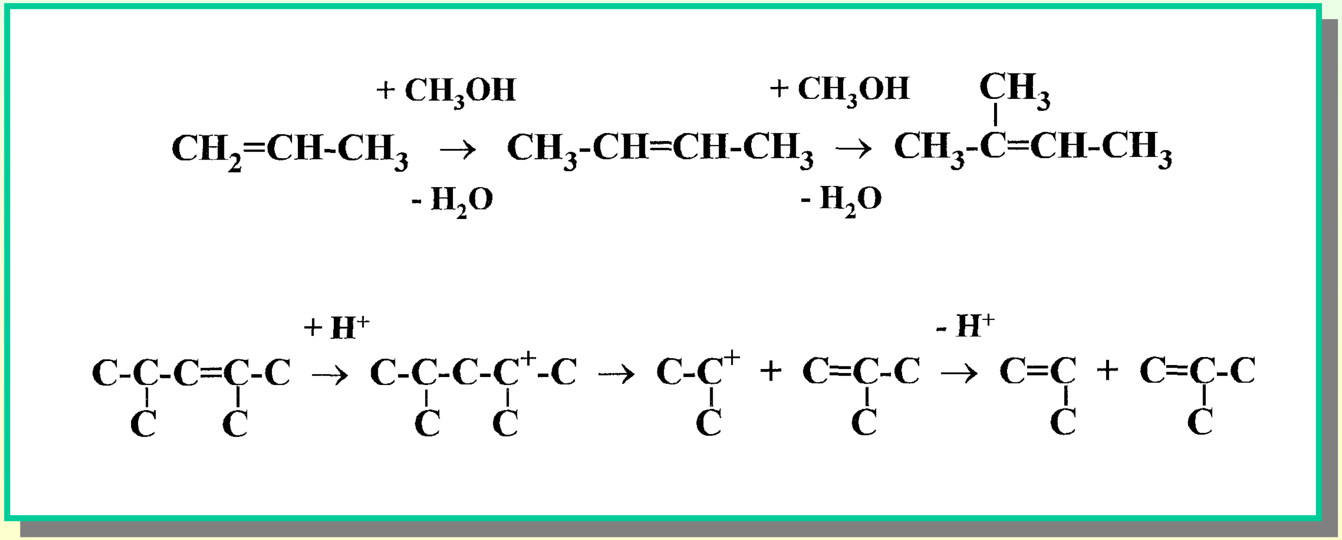
In situ MAS NMR-UV/Vis investigations of organic deposits formed during the methanol to olefin conversion on acidic catalysts

Methanol to olefin (MTO) conversion on acidic zeolite catalysts

1996: **Norsk Hydro/Norway, demonstration unit, 0.5 t ethene and propene per year, H-SAPO-34 used as catalyst**

2005: **Dalian/China, test unit, 10 000 t olefins per year**

2005: **Shaanxi/China, start of the construction of a commercial plant, 800 000 t olefins per year**



$$CH_2{=}CH{-}CH_3 \xrightarrow[-\,H_2O]{+\,CH_3OH} CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[-\,H_2O]{+\,CH_3OH} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3$$

$$C{-}\underset{C}{\underset{|}{C}}{-}C{=}\underset{C}{\underset{|}{C}}{-}C \xrightarrow{+\,H^+} C{-}\underset{C}{\underset{|}{C}}{-}C{-}\underset{C}{\underset{|}{C^+}}{-}C \rightarrow C{-}\underset{C}{\underset{|}{C^+}} + C{=}\underset{C}{\underset{|}{C}}{-}C \xrightarrow{-\,H^+} C{=}\underset{C}{\underset{|}{C}} + C{=}\underset{C}{\underset{|}{C}}{-}C$$

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

Periods of the methanol conversion on acidic zeolites

I: Induction period of the methanol conversion on zeolite catalysts

Formation of first C-C bonds by reaction of surface methoxy groups and alkylation of organic impurities

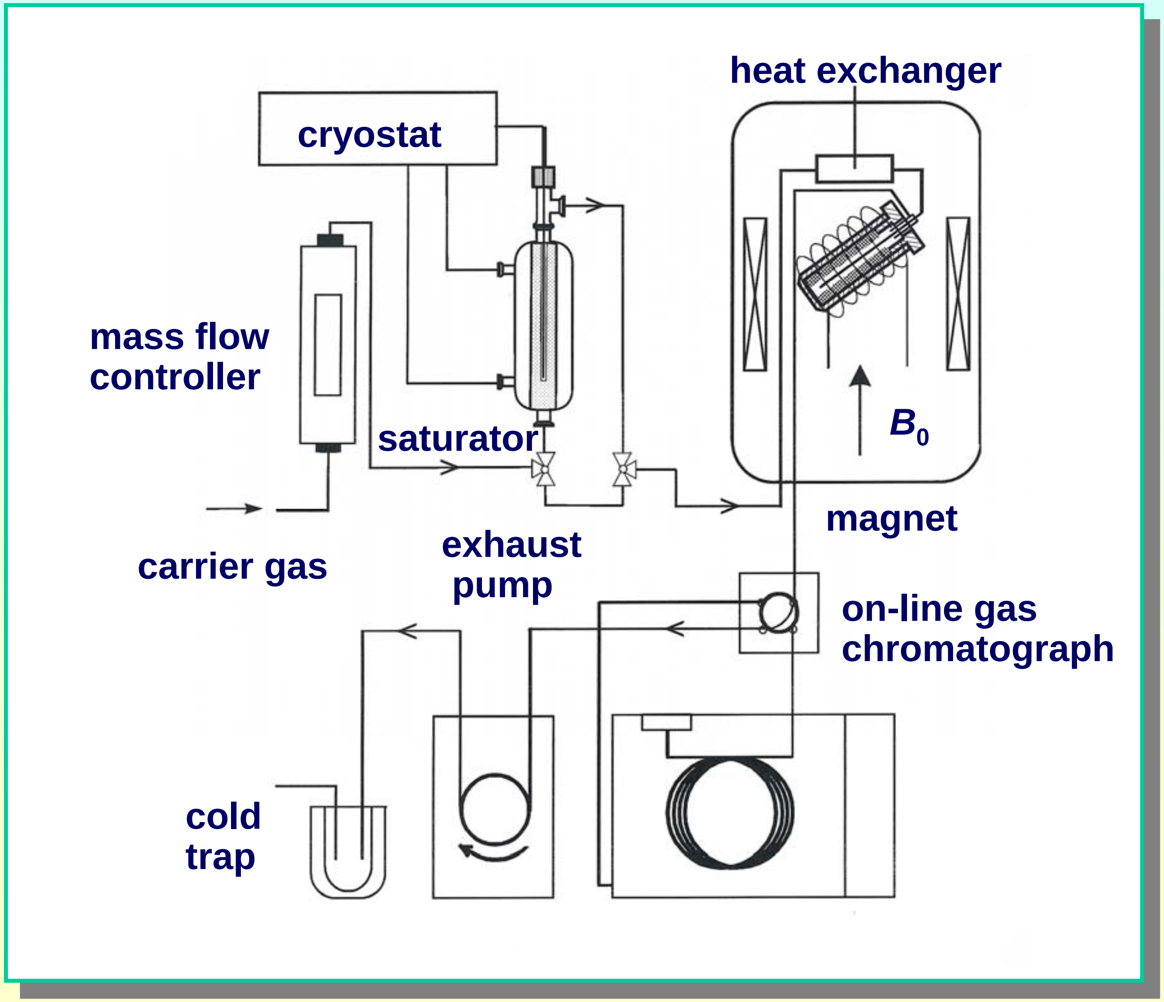
II: Steady-state of the methanol conversion on zeolite catalysts

Formation of light olefins by methylation and dealkylation of catalytically active hydrocarbon-pool compounds (olefinic and aromatic deposits)

III: Catalyst deactivation during methanol conversion on zeolites

Formation of inactive coke deposits affecting the methanol conversion and the selectivity to ethylene and propylene

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

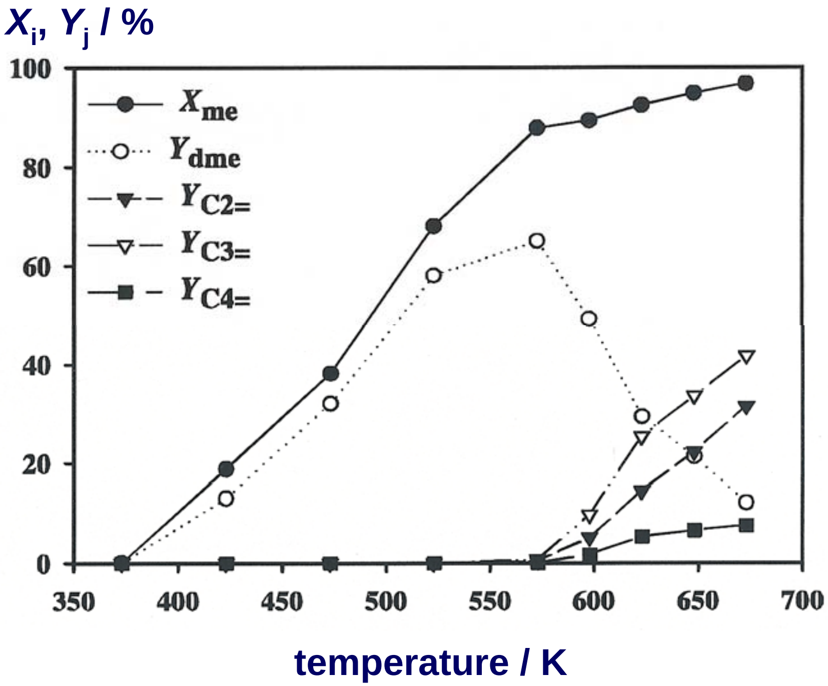


M. Hunger et al., Catal. Lett. 57 (1999) 199.

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

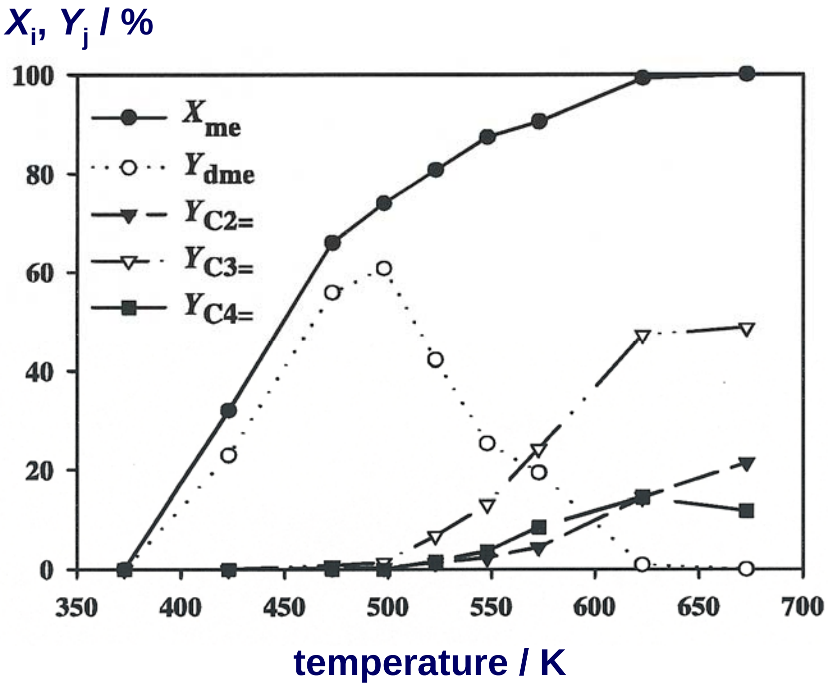
fixed-bed reactor

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



spinning (2 kHz) MAS NMR rotor reactor

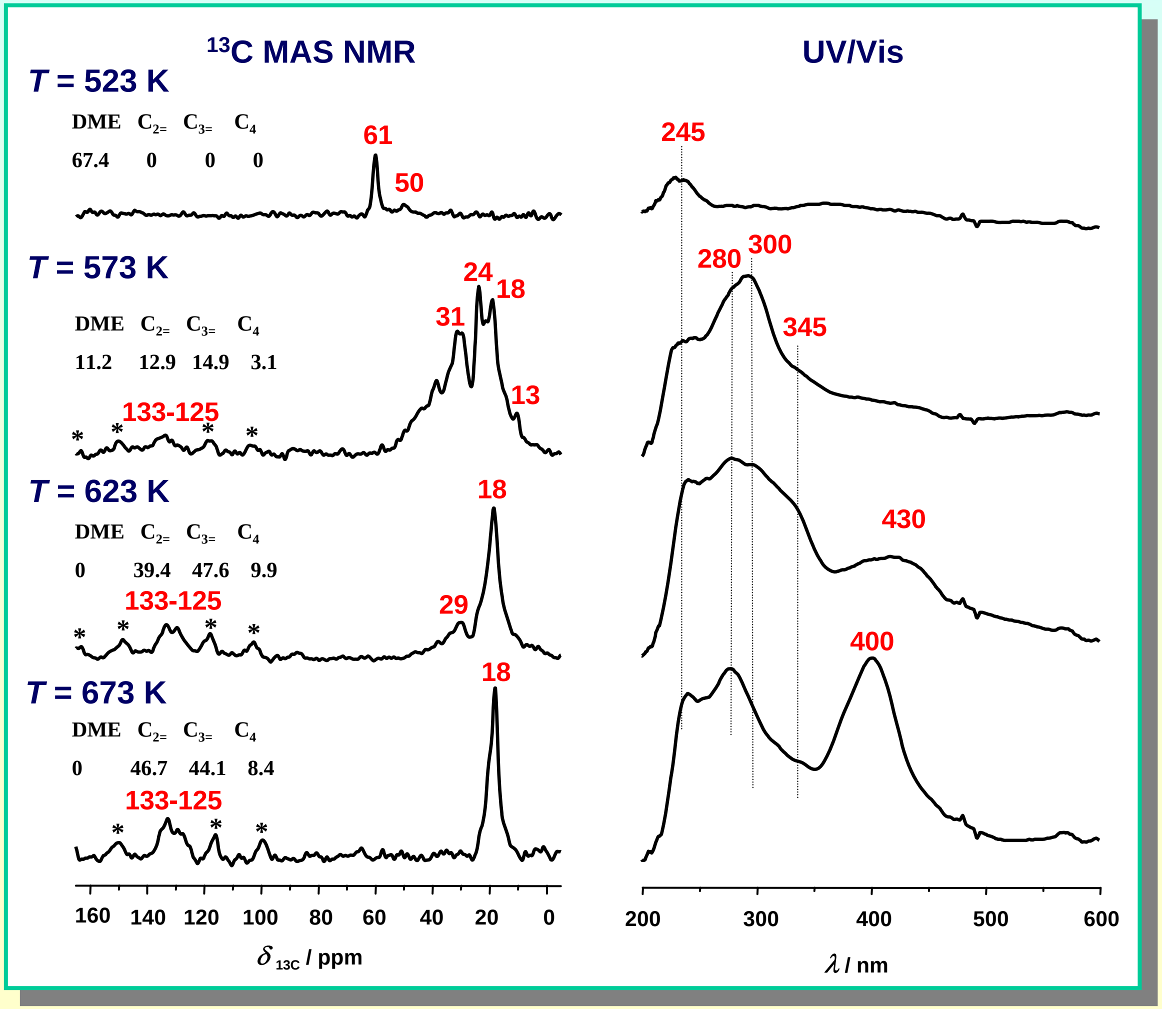
W_{cat}/F_{me} = 25 gh/mol



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

In situ MAS NMR-UV/Vis study of the formation of organic deposits

In situ ^{13}C MAS NMR-UV/Vis spectroscopy of deposit formation on H-SAPO-34 at 523 to 673 K for 3 h under continuous-flow conditions (W_{cat}/F_{me} = 25 gh/mol)



T = 523 K

DME	$C_{2=}$	$C_{3=}$	C_4
67.4	0	0	0

T = 573 K

DME	$C_{2=}$	$C_{3=}$	C_4
11.2	12.9	14.9	3.1

T = 623 K

DME	$C_{2=}$	$C_{3=}$	C_4
0	39.4	47.6	9.9

T = 673 K

DME	$C_{2=}$	$C_{3=}$	C_4
0	46.7	44.1	8.4

NMR:

- **separation of alkyl groups (13-31) and aromatic compounds (125-133)**

UV/Vis:

- **sensitive for carbenium cations (300, 345, 430 nm)**
- **separation of aromatics (280 nm) and polycyclic aromatics (400 nm)**

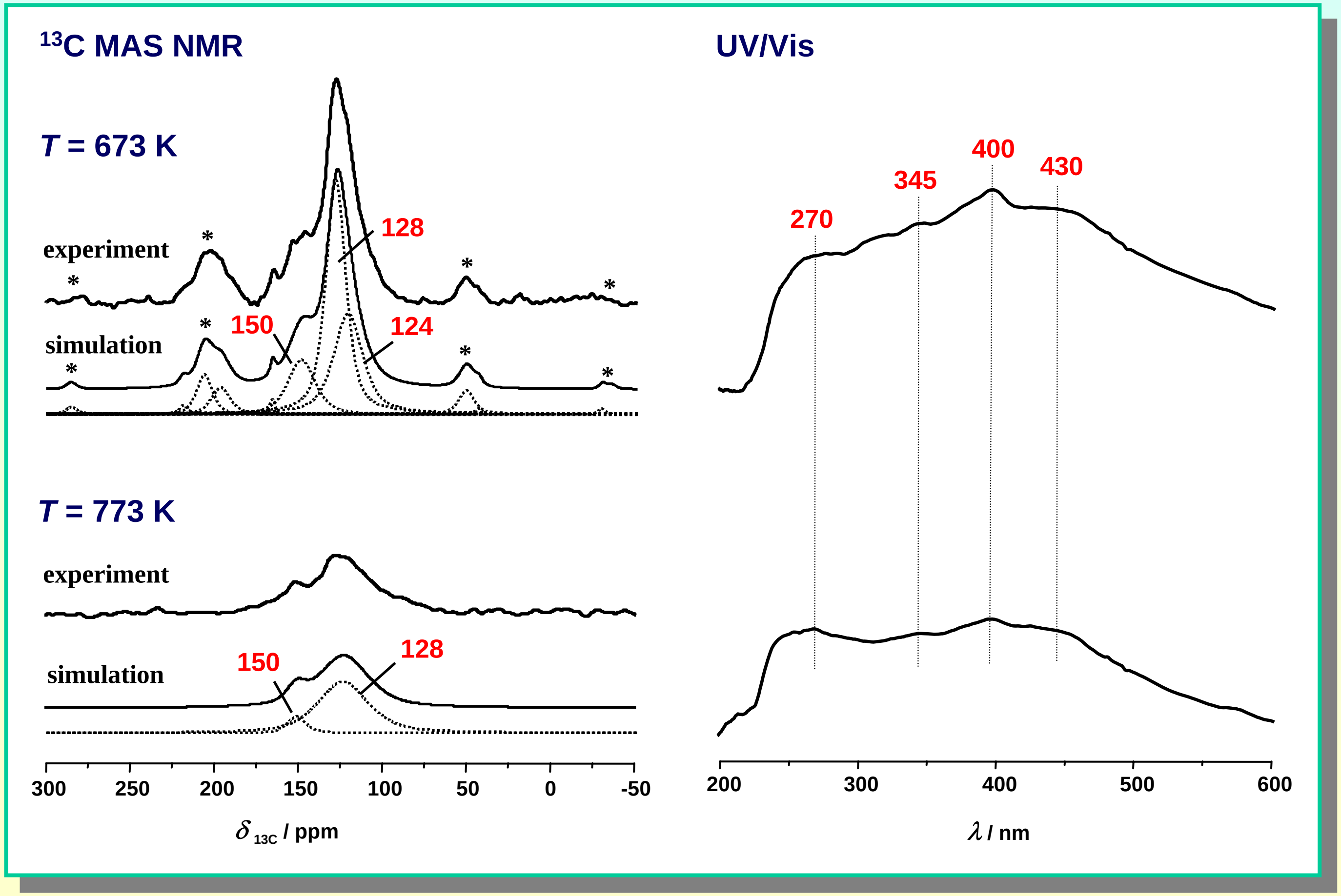
On-line GC:

- **determination of volatile reaction products**

Y. Jiang et al., Microporous Mesoporous Mater. 105 (2007) 132.

Regeneration of coked MTO catalyst

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



→

decrease of all aromatics including coke compounds (400 nm)

new band of phenolic species (270 nm)

Y. Jiang et al., Microporous Mesoporous Mater. 105 (2007) 132.

Results of the quantitative evaluation

Quantitative evaluation of the ^{13}C MAS NMR spectra of coked H-SAPO-34 regenerated by burning with synthetic air at 673 and 773 K 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

→ **nearly total removal of coke compounds (UV/Vis bands at 280 nm and 400 nm), but formation of oxygenated species (270 nm)**

Y. Jiang et al., Microporous Mesoporous Mater. 105 (2007) 132.

Summary I

applications of *in situ* NMR 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**

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 for the study of surface sites under reaction conditions
- 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 MS

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Fonds der Chemischen Industrie

Literature

M. Hunger, *In situ NMR spectroscopy in heterogeneous catalysis*, Catal. Today 97 (2004) 3-12.

M. Hunger, J. Weitkamp, *In situ Magnetic Resonance Techniques: Nuclear Magnetic Resonance*, in: B.M. Weckhuysen (ed.), *In situ Spectroscopy of Catalysts*, American Scientific Publishers, Stevenson Ranch, California, 2004, p. 177-218.

M. Hunger, W. Wang, *Characterization of Solid Catalysts in the Functioning State by Nuclear Magnetic Resonance Spectroscopy*, Adv. Catal. 50 (2006) 149-225.

M. Hunger, *In situ flow MAS NMR spectroscopy: State of the art and applications in heterogeneous catalysis*, Prog. Nucl. Magn. Reson. Spectrosc., doi.org/10.1016/j.pnmrs.2007.08.001.

Behavior of the high-temperature CF MAS NMR probe

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

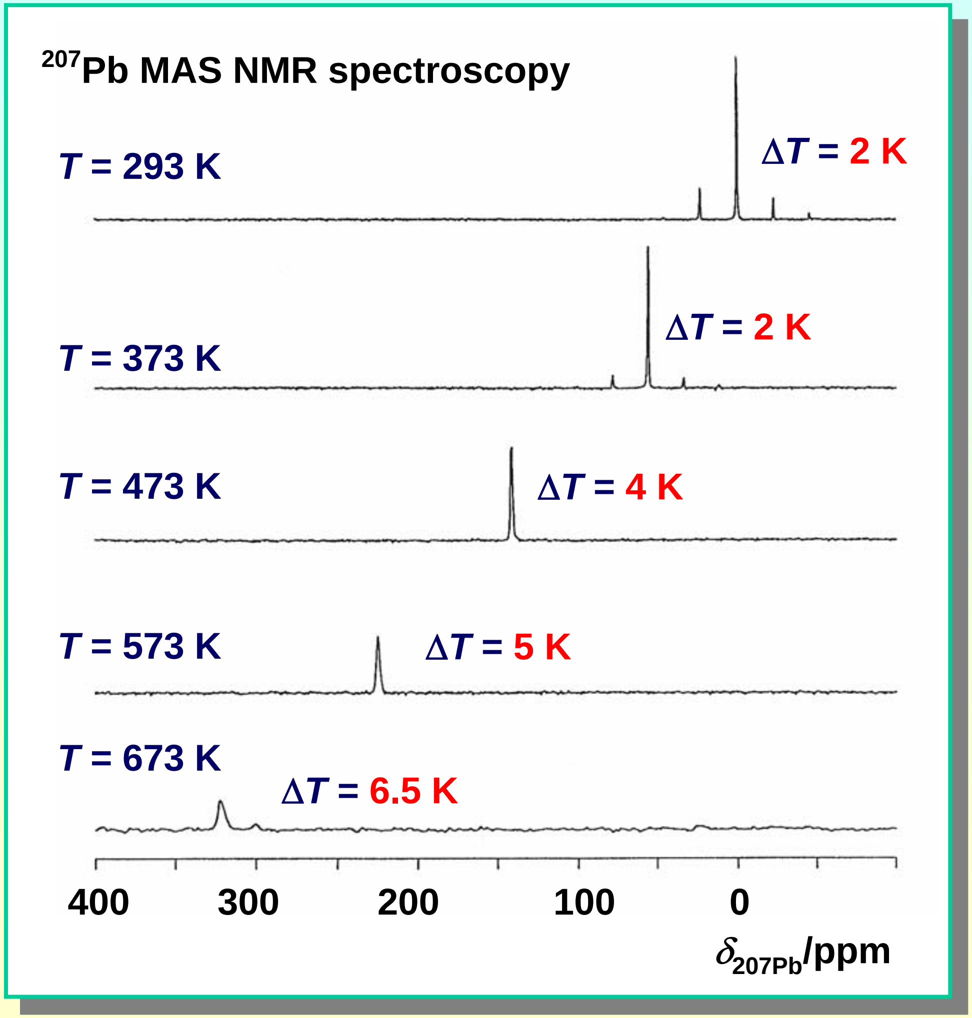
  $\Delta T / \Delta\delta$ = 1.29 K / ppm [1]

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

  ν_0 = 83.2 MHz

  ν_{rot} = 2.5 kHz

  F_{N2} = 15 ml/min



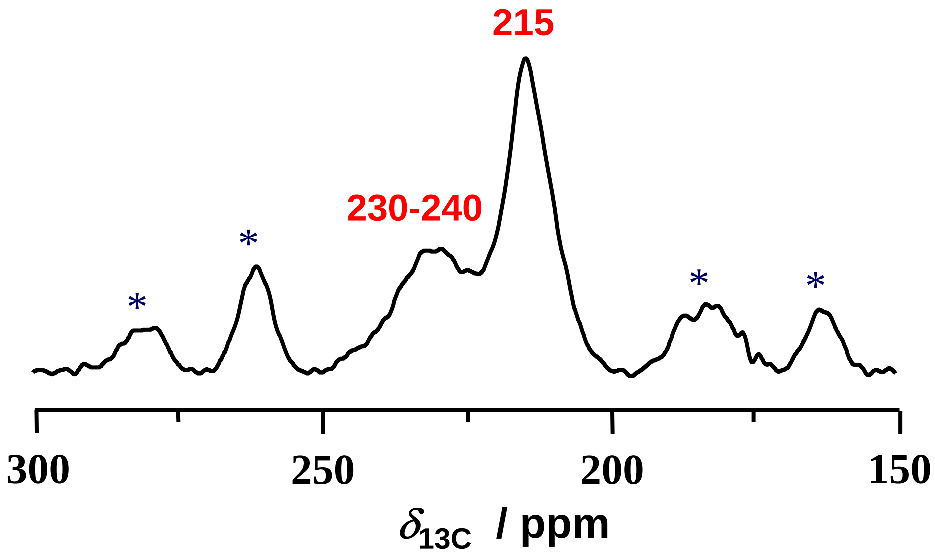
[1] D.B. Ferguson et al., Anal. Chem. 67 (1995) 3342.

Probing Lewis acid sites of dealuminated zeolite H-Y

H-Y (n_{Si}/n_{Al} = 2.7):
46.5 SiOHAl / u.c.

deH-Y (n_{Si}/n_{Al} = 5.4):
10.9 SiOHAl / u.c.
22 extra-framework Al / u.c.

^{13}C CP MAS NMR spectrum of dehydrated (723 K) zeolite deH-Y after adsorption of 2-^{13}C-acetone



215 ppm: acetone on Brønsted acid sites or physical adsorbed acetone
230-240 ppm: acetone on extra-framework aluminum (Lewis acid sites)

Assignment of UV/Vis bands

Assignments of UV/Vis bands (π-π^* transitions) observed during the methanol-to-olefin conversion on H-SAPO-34 at 523 to 673 K

Bands at ν / nm	Assignments
220-245	neutral dienes
254-280	neutral aromatics and polyalkylaromatics
270	neutral phenols
300-320	monoenylic carbenium ions
345-380	dienylic carbenium ions
390-410	neutral polycyclic aromatics
430-470	trienylic carbenium ions

H.G. Karge *et al.,* Stud. Surf. Sci. Catal. 49 (1989) 1327; J. Mohan, Organic Spectroscopy Principles and Applications, Alpha Science International Ltd., Harrow, U.K., 2002, p. 137; A.V. Demidov, Mater. Chem. Phys. 39 (1994) 13; I. Kirisci *et al.,* Chem. Rev. 99 (1999) 2085; R. Ahmad *et al.,* J. Catal. 218 (2003) 365-374.