

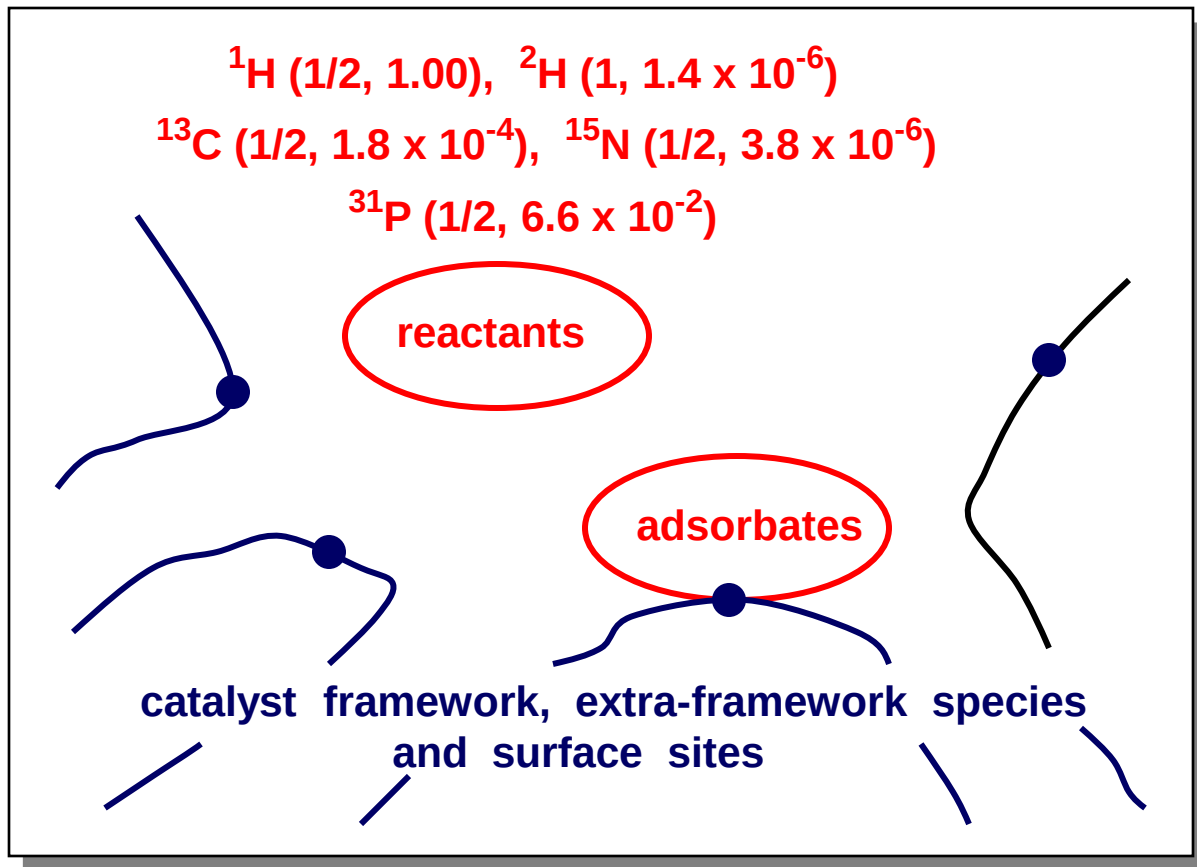
State of the Art and Applications of In Situ Solid-State NMR Spectroscopy in Heterogeneous Catalysis

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Examples of nuclei accessible for in situ NMR in heterogeneous catalysis



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

isotope (nuclear spin, relative sensitivity in comparison with ^1H)

Specific problems of in situ 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 ^1H 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:

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

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

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

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

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

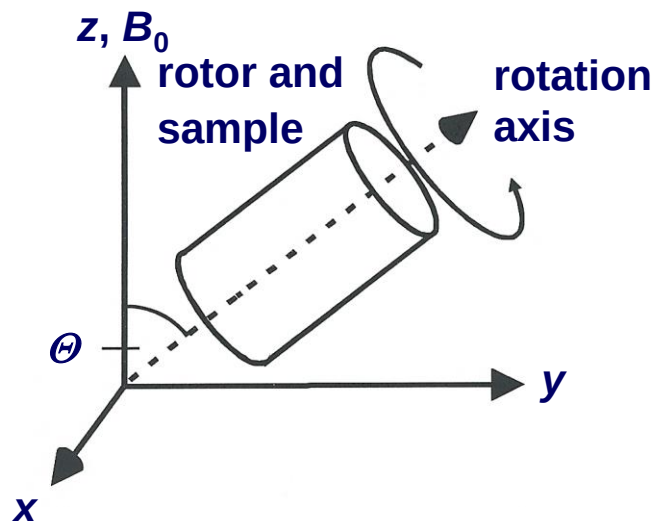
H_{J} : indirect or J-coupling of nuclei via their bond electrons
 $\nu_{\text{J}} \leq 5 \times 10^2 \text{ s}^{-1}$

Solid-state NMR techniques

spin $I = \frac{1}{2}$:

- magic angle spinning (**MAS**)

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



spin $I > \frac{1}{2}$:

- double oriented rotation (**DOR**)

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

$$\rightarrow \theta = 30.6^\circ$$

$$\theta = 70.1^\circ$$

- 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

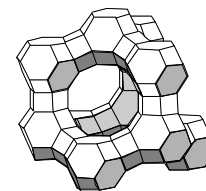
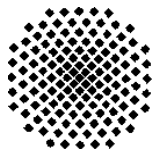
characteristics:

- 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:

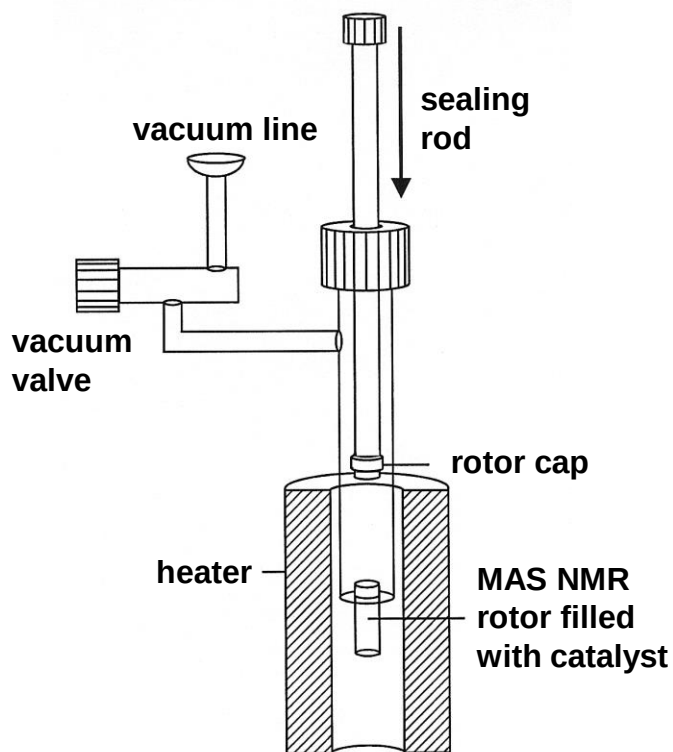
- self-made equipments
- study of reactions under steady state conditions



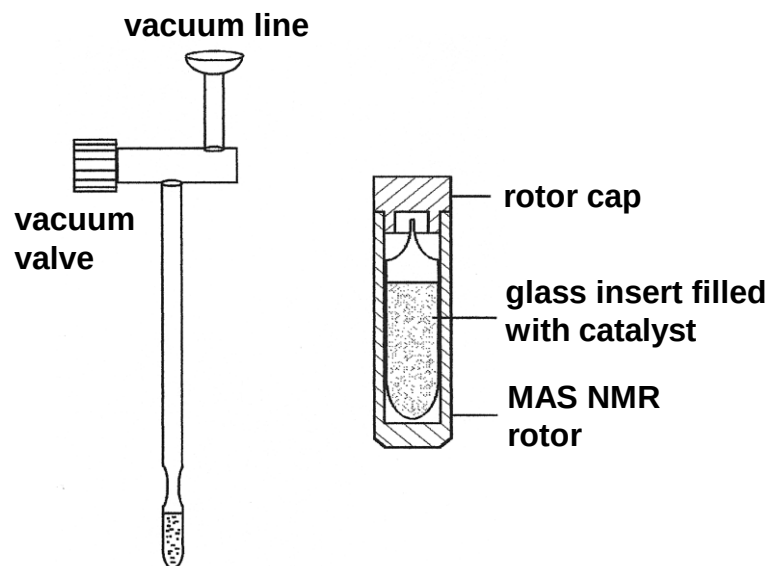
***Experimental techniques applied for studies
under batch and continuous-flow conditions***

Handling of dehydrated catalysts under batch conditions

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

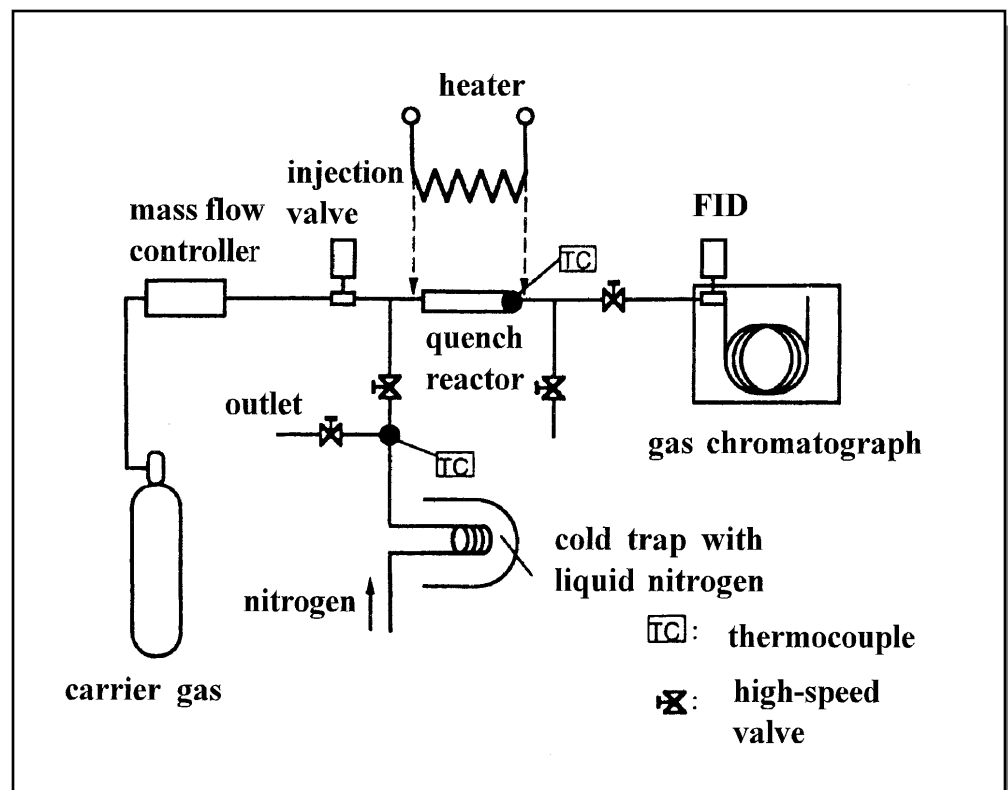


dehydration of catalysts inside of glass inserts (e.g. commercial Wilmad MAS NMR inserts for 4 mm and 7 mm rotors)



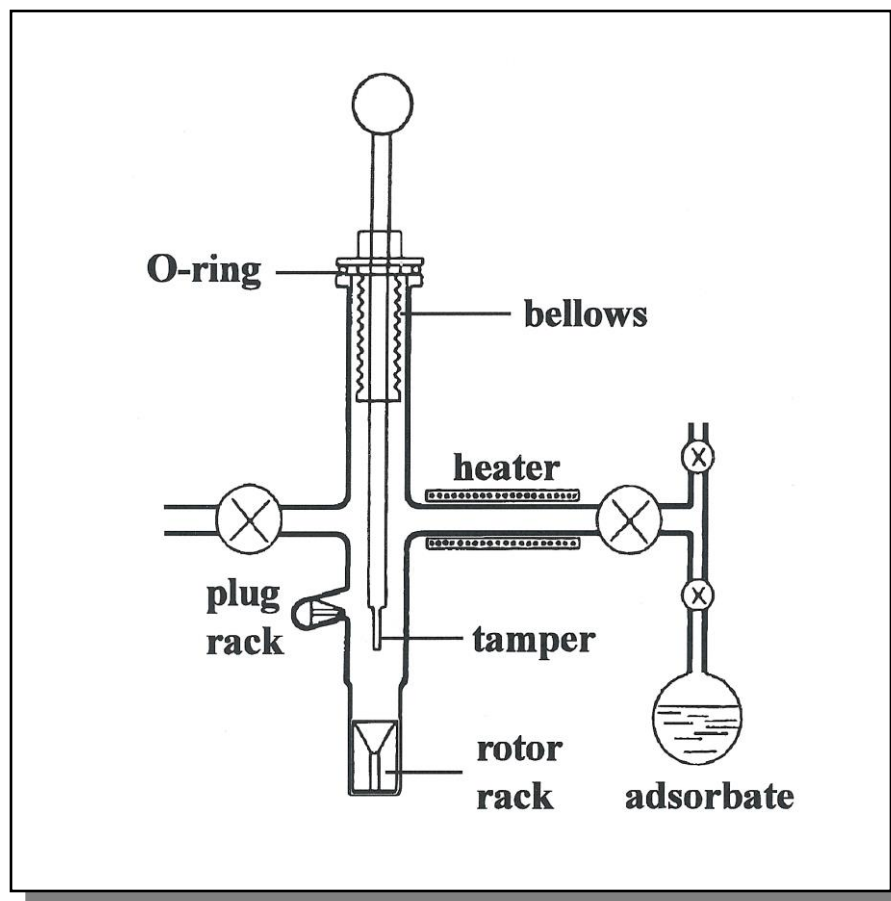
Go-and-stop experiments using an external reactor

- 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



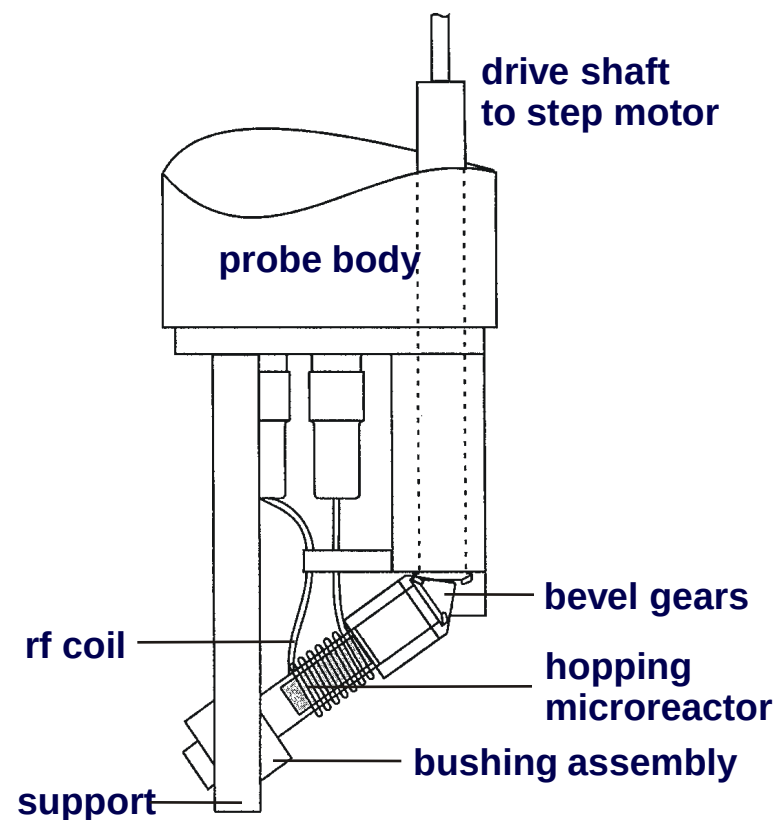
Approach for batch and continuous-flow experiments in an external reactor

- 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

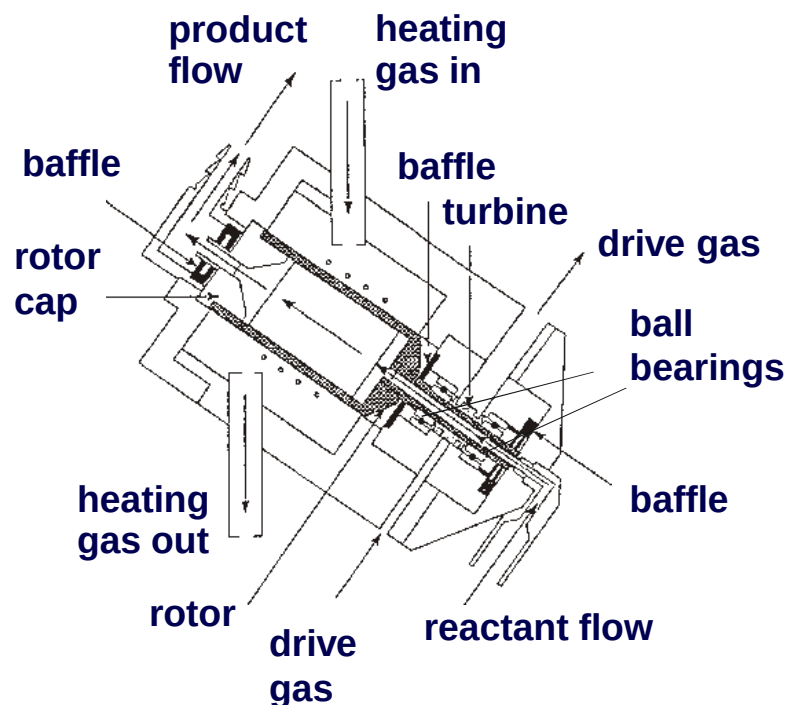


Approaches for *in situ* flow MAS NMR spectroscopy

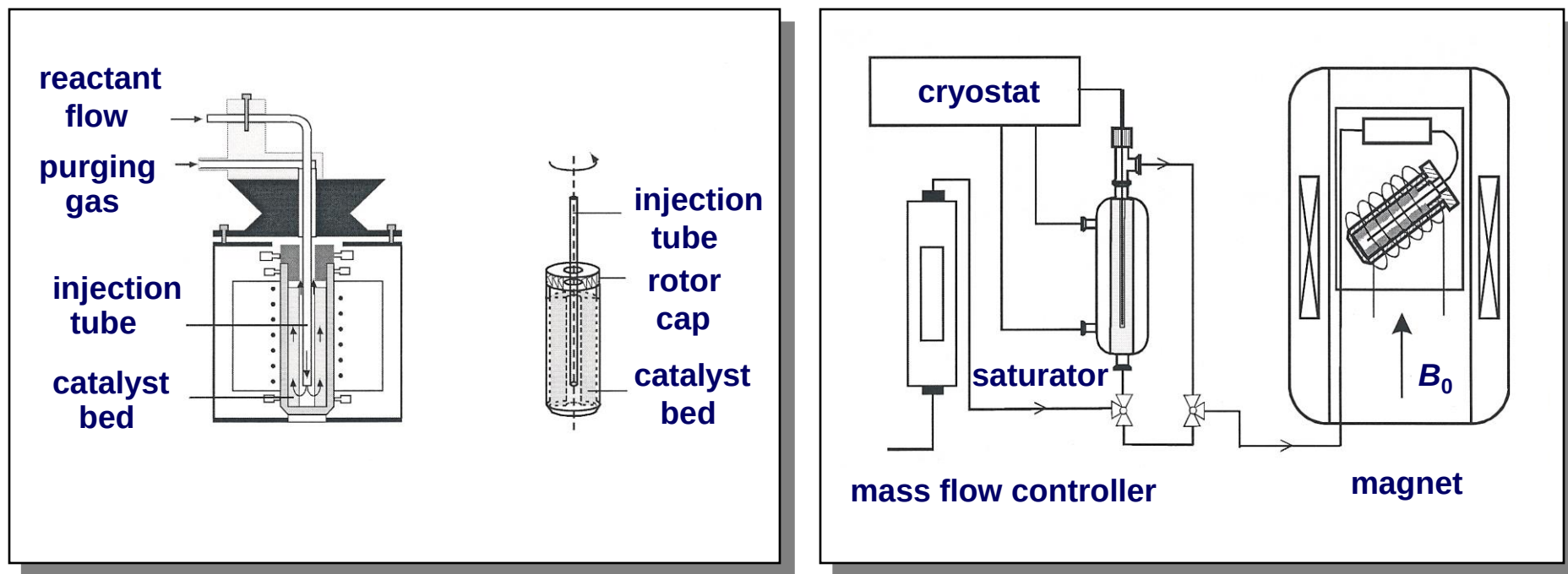
flow MAS NMR probe with hopping microreactor (GRASSHopper II)



flow MAS NMR probe with ball bearings

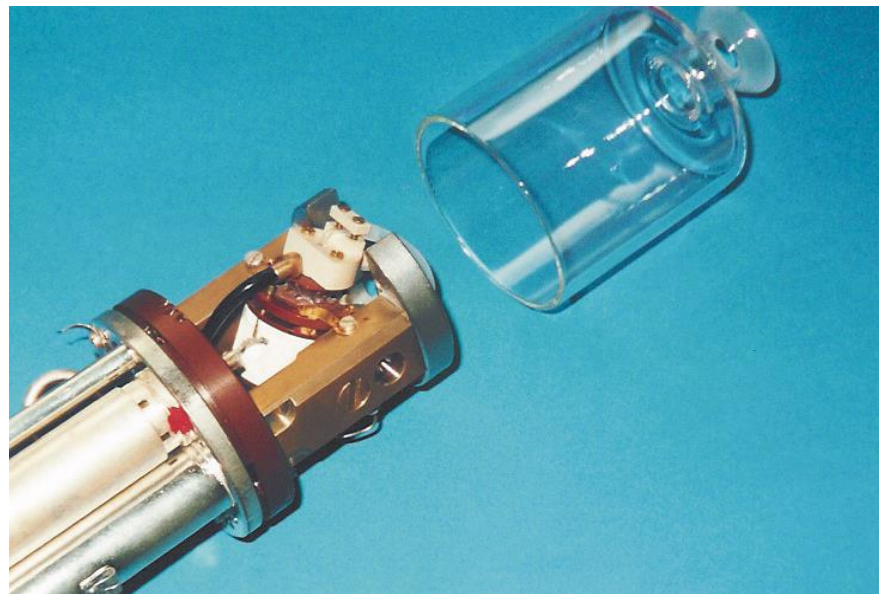
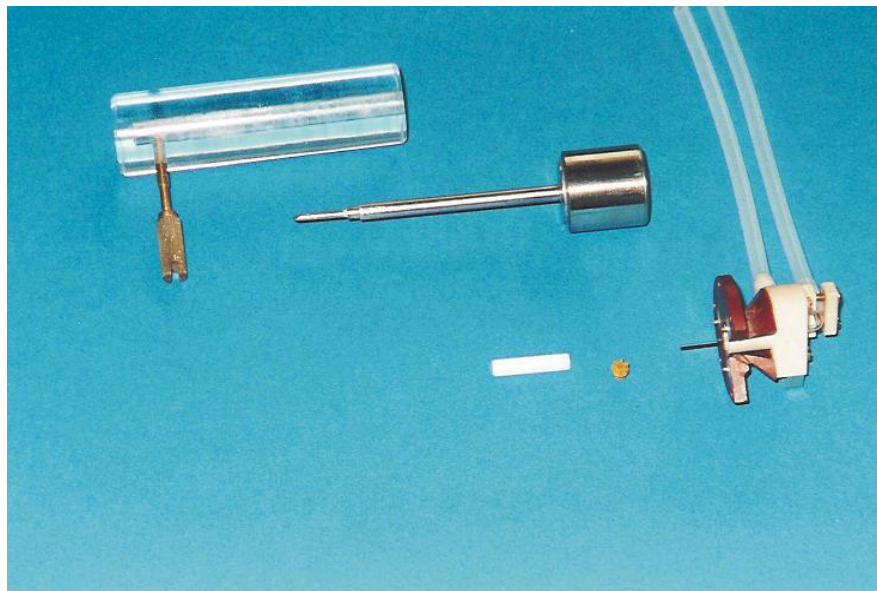


Continuous-flow (CF) MAS NMR technique



- continuous injection of reactants into a spinning MAS NMR rotor reactor ($T < 923 \text{ K}$)

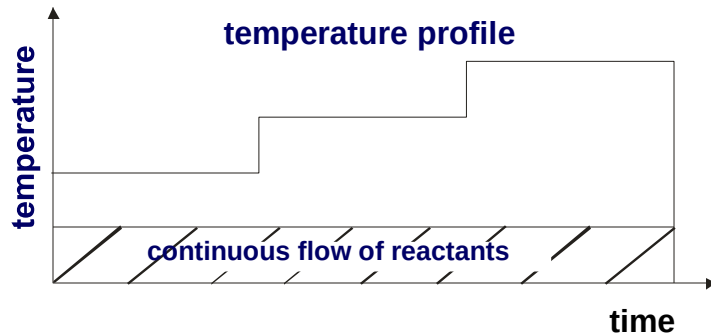
Continuous-flow (CF) MAS NMR technique



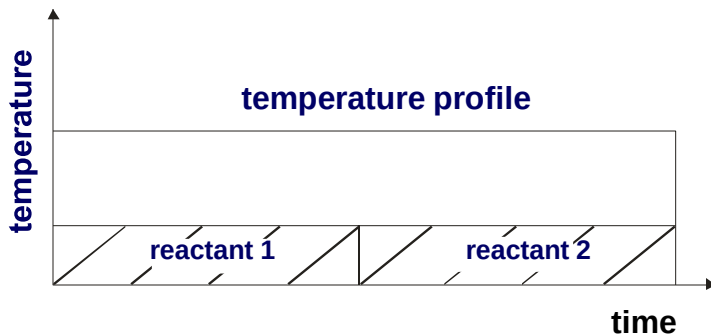
- **modified 4 mm Bruker MAS NMR probe equipped with an injection system**

Types of flow experiments I

- continuous-flow experiment



- switched-flow experiment



- continuous-flow experiment:

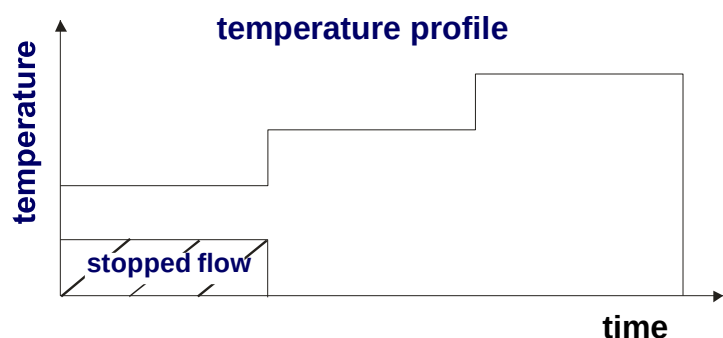
- study of adsorption or conversion of reactants at constant or different temperatures
- study of formation of stable deposits of catalyst deactivation

- switched-flow experiment:

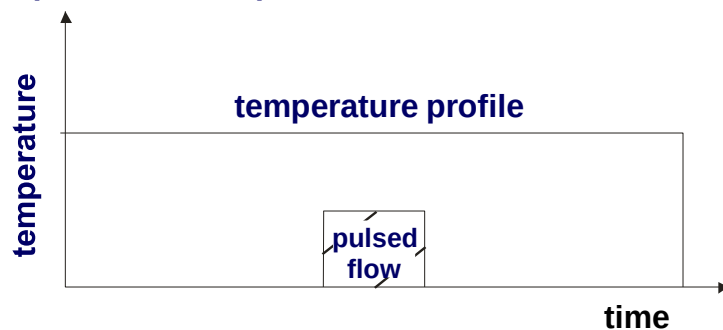
- change of isotopic enrichment in reactants
- study of the response of the composition of reaction products or deposits on the change of reactants

Types of flow experiments II

- stopped-flow experiment



- pulsed-flow experiment



- stopped-flow experiment:

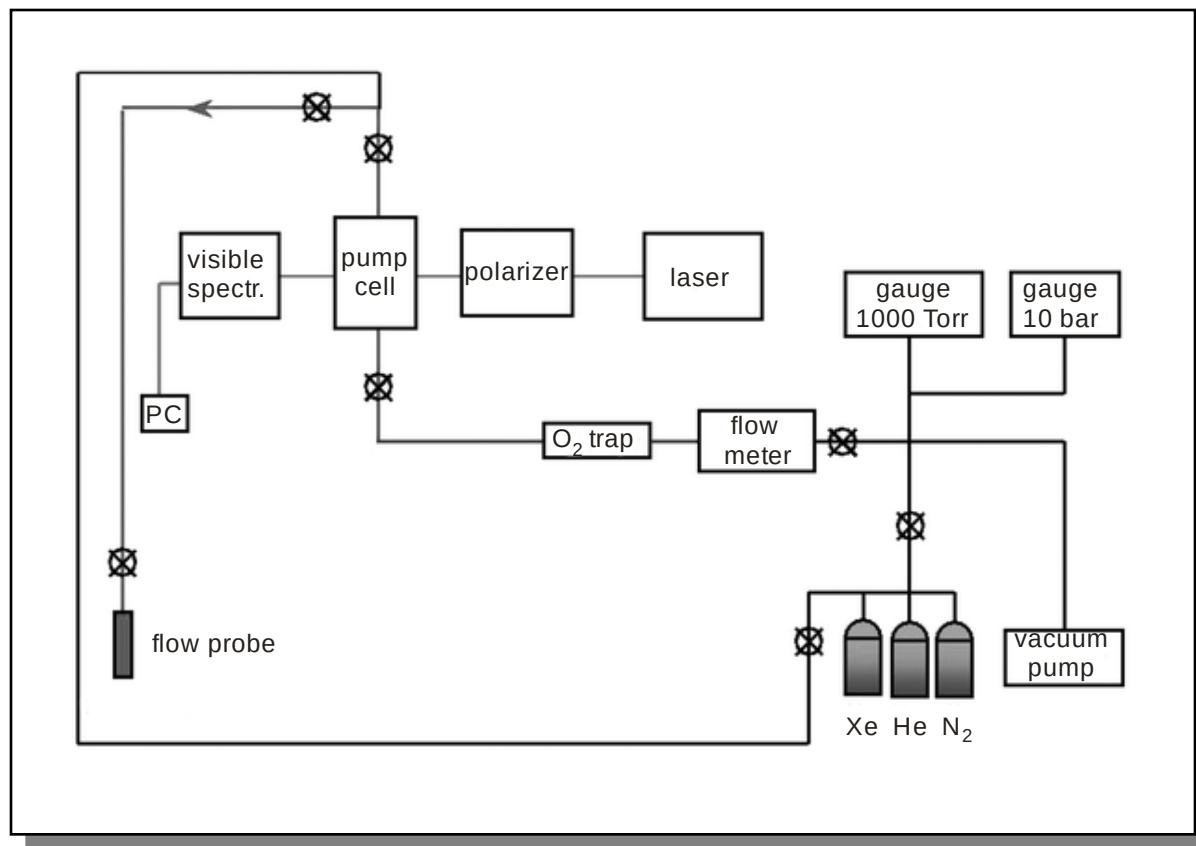
- preparation of intermediates on the catalyst
- study of the reactivity and conversion of intermediates at constant or different temperatures

- pulsed-flow experiment:

- study of the time dependence of the conversion of reactants
- study of the isotopic exchange of reactants at high temperatures

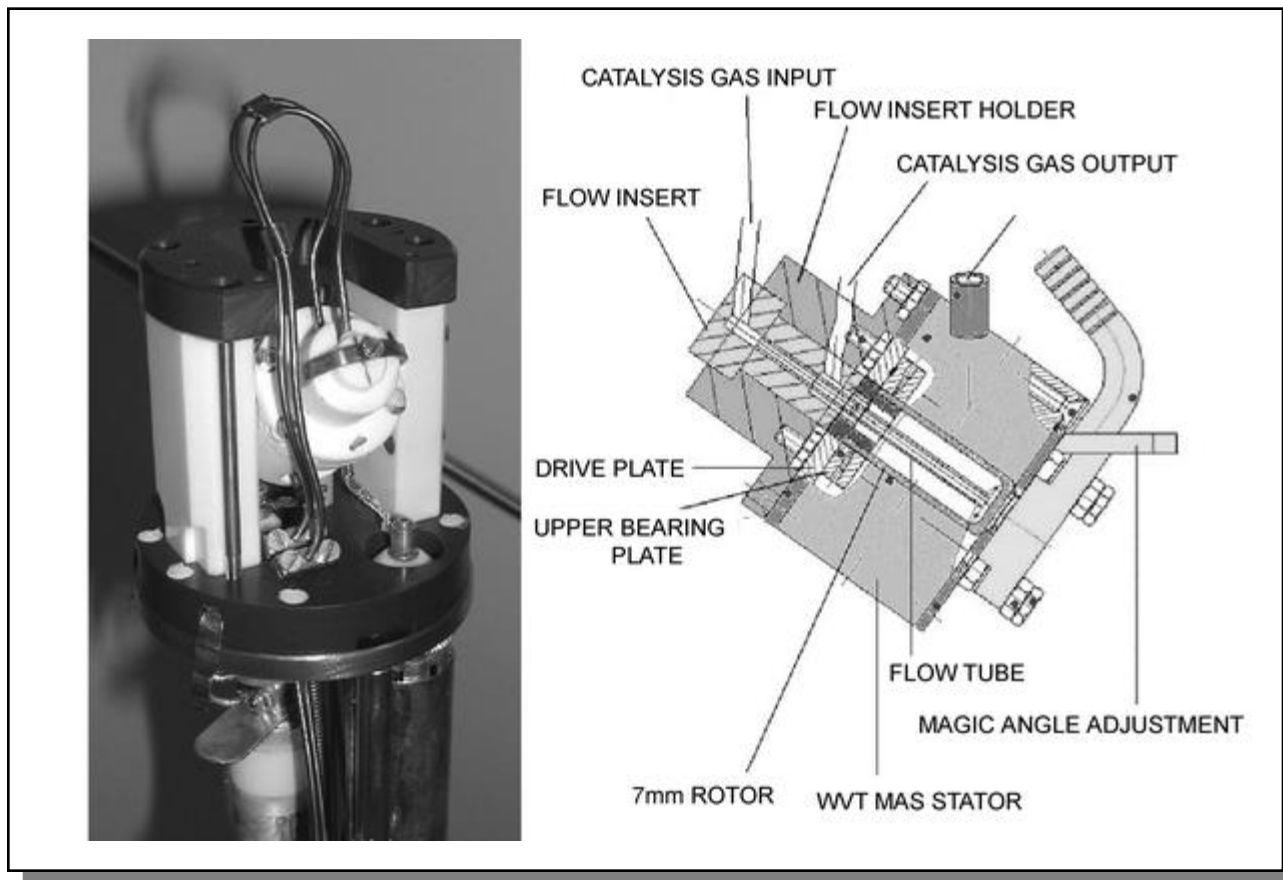
Flow experiments with laser-polarized xenon

- 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

CF MAS NMR probe of Bruker BioSpin

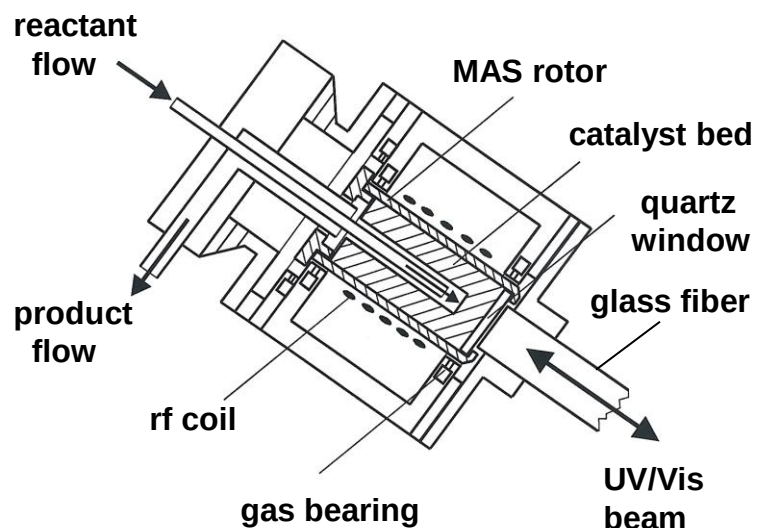


- **MASCAT probe design with 7 mm MAS NMR rotor and temperatures up to 623 K**

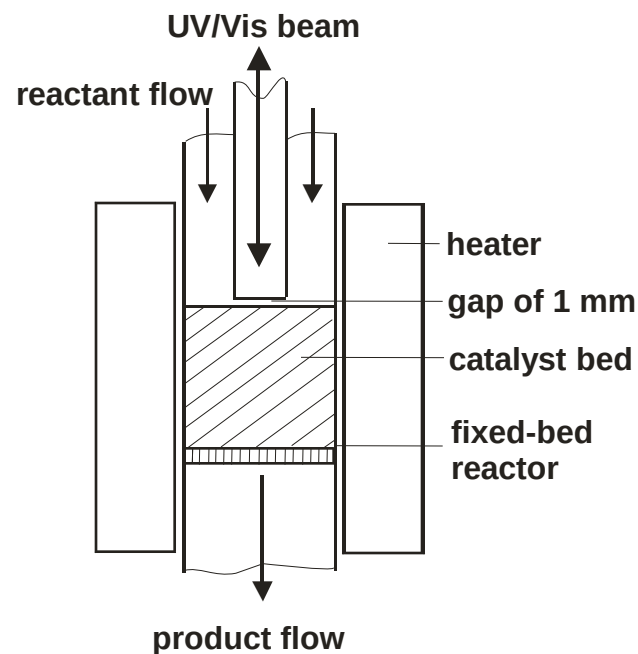
Technique of MAS NMR-UV/Vis spectroscopy

- 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

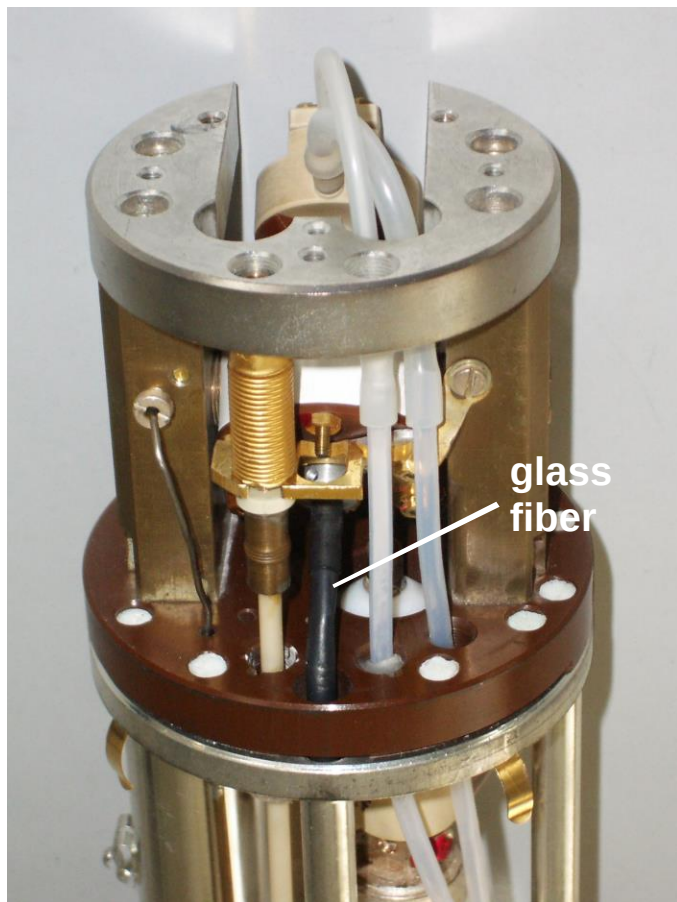
MAS NMR-UV/Vis probe



fixed-bed reactor

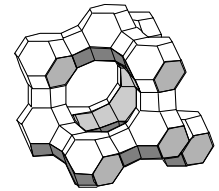
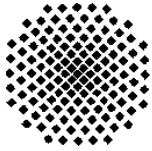


Technique of in situ flow MAS NMR



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

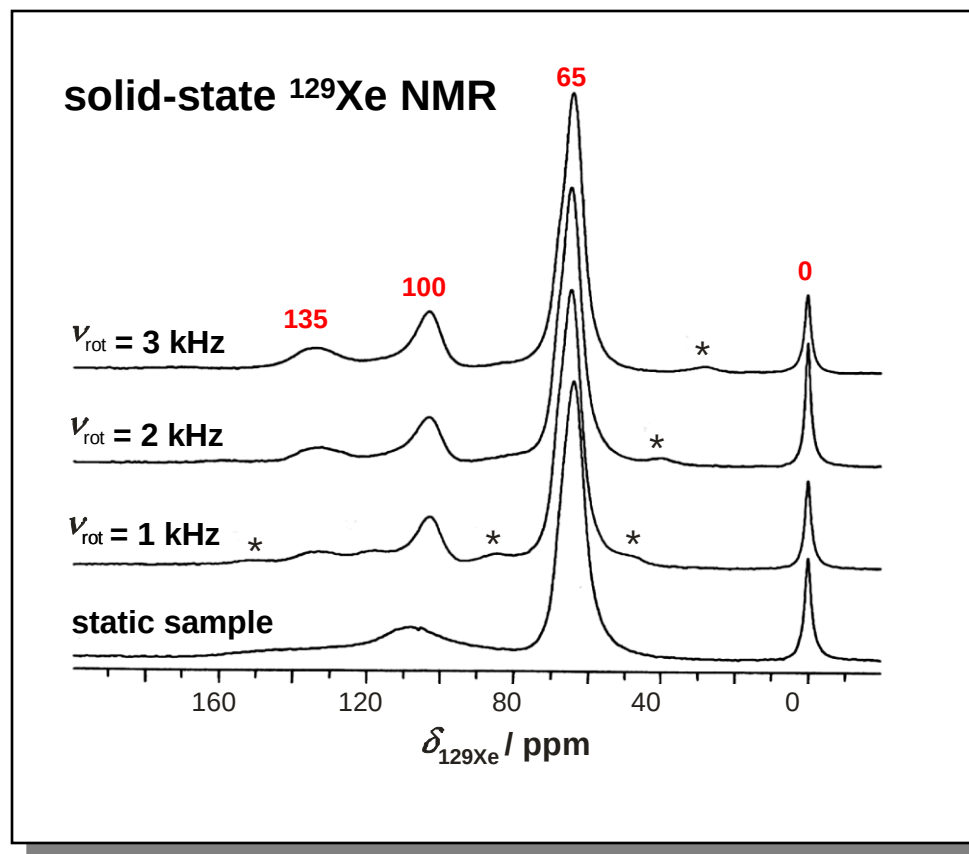




Investigation of the pore system of solid catalysts

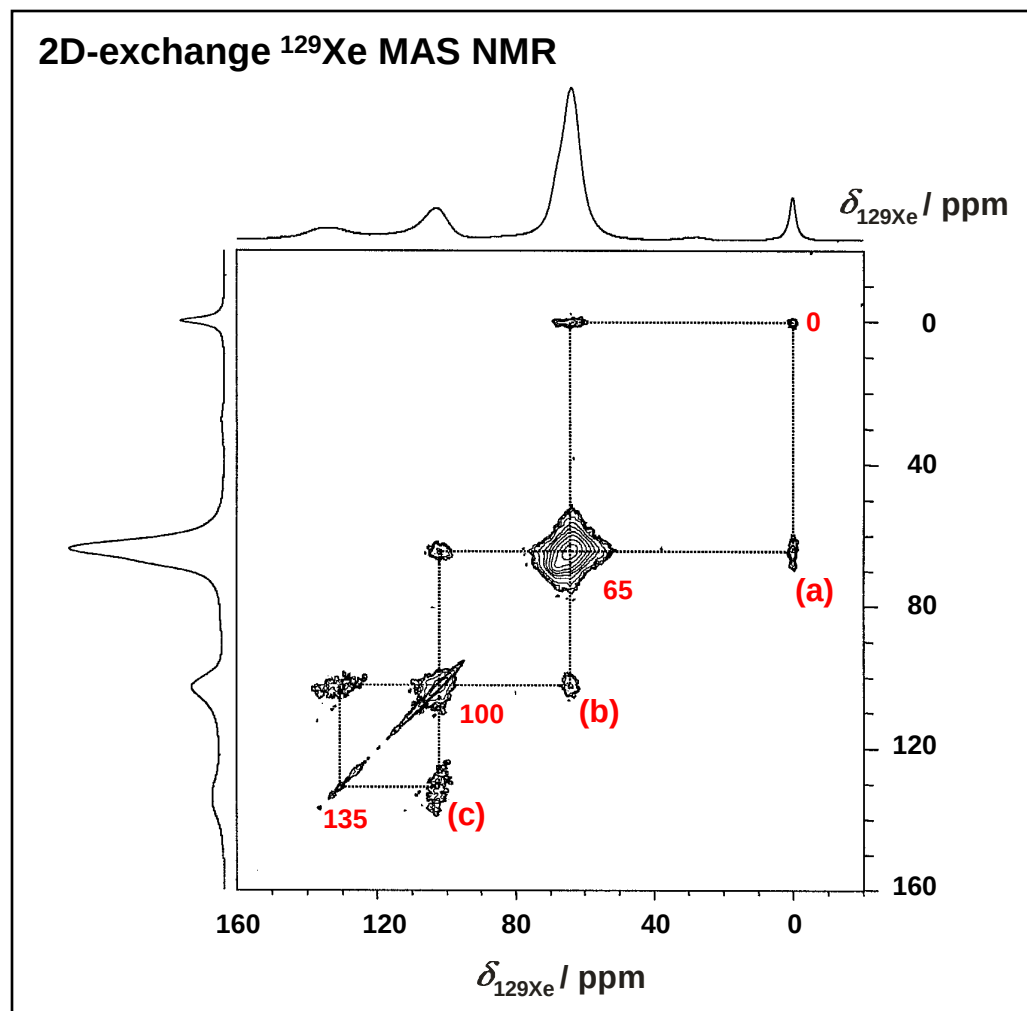
Advantage of MAS for NMR studies of laser-polarized xenon in porous solids

- solid-state ^{129}Xe NMR spectroscopy of laser-polarized xenon adsorbed on zeolite ITQ-6:
 - helium flow of $100 \text{ cm}^3 \text{ min}^{-1}$ 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



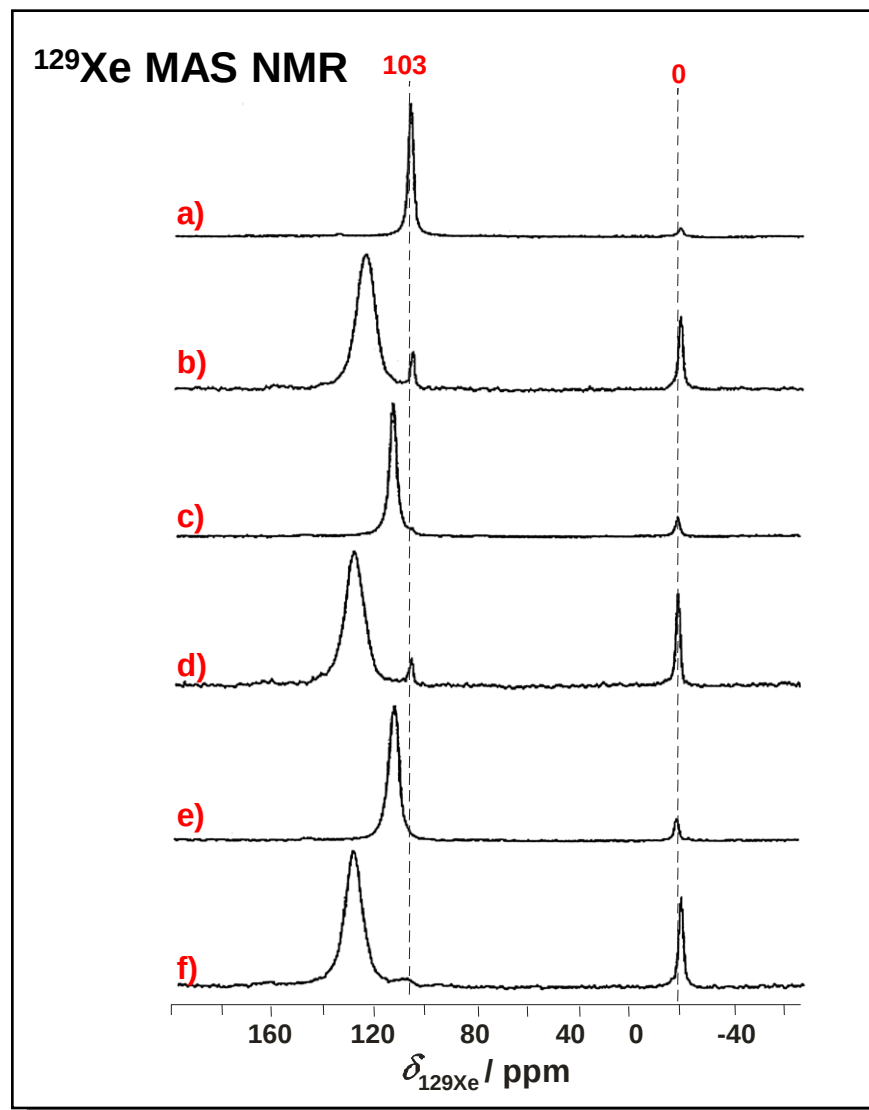
Study of xenon exchange dynamics in zeolite ITQ-6

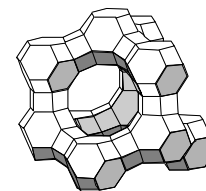
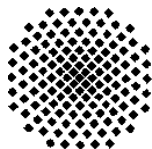
- 2D-exchange ^{129}Xe MAS NMR of laser-polarized xenon adsorbed on zeolite ITQ-6:
 - helium flow of $100 \text{ cm}^3 \text{ min}^{-1}$ with 1 % hyperpolarized xenon
 - magnetic field of 7.0 T
 - $\nu_{\text{rot}} = 3 \text{ kHz}$, repetition time of 2 s, and 8 scans per increment (256)
 - mixing time 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



Study of the location of reactant molecules in porous catalysts

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

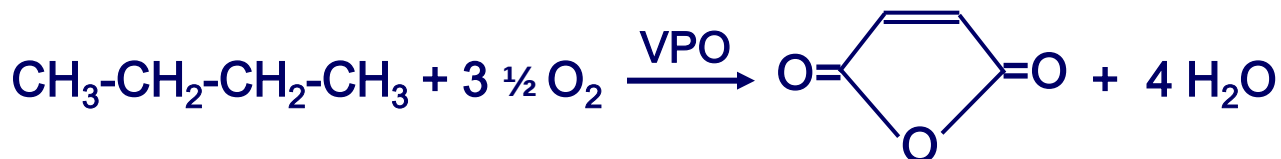




***Investigation of the selective oxidation of
alkanes on VPO catalysts***

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 $\text{VOHPO}_4 \cdot 0.5 \text{H}_2\text{O}$ in *n*-butane/air flow [2]:

reducing atm.	→	$(\text{VO})_2\text{P}_2\text{O}_7$ (V^{4+}) as bulk compound
oxidizing atm.	→	VOPO_4 phases on the particle surface (V^{5+})

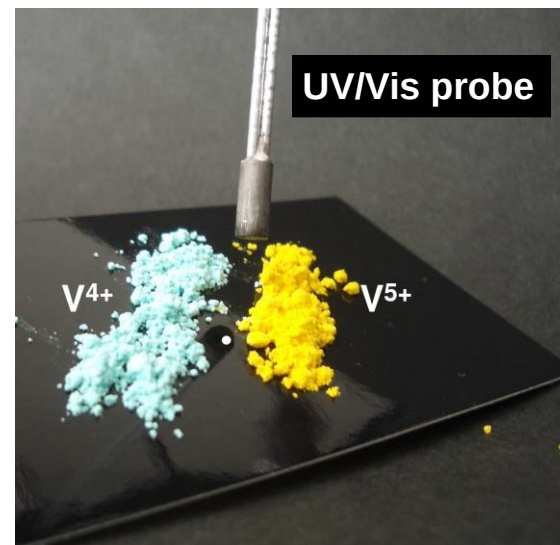
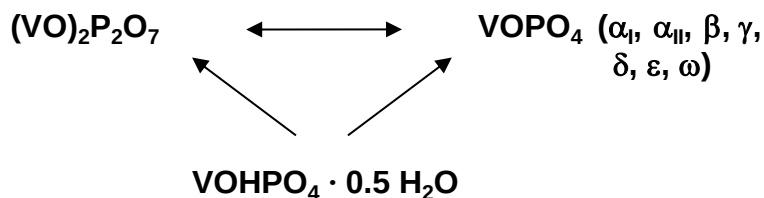
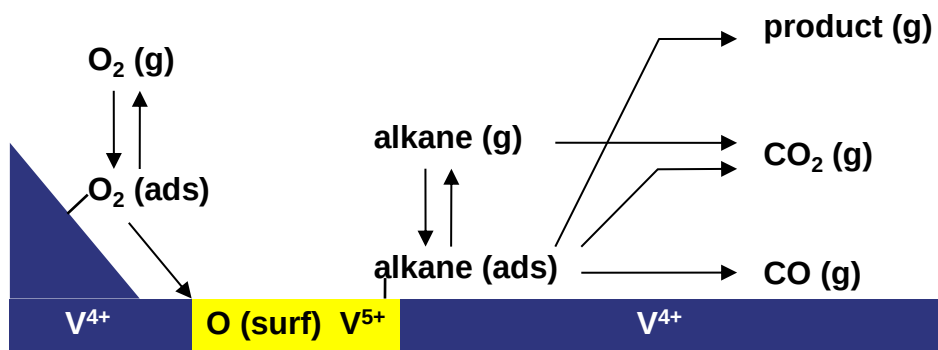
- activity increases sharply for P / V ratio reaching > 1

[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.

Oxidation states of vanadium in VPO catalysts

- suggested reaction mechanism of selective oxidation of alkanes on VPO catalysts (left) and experimentally observed color changes (right)



UV/Vis band of V^{4+} : 700 to 900 nm
UV/Vis band of V^{5+} : ca. 420 nm

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 V₂O₅, PEG 6.000 and H₃PO₄
 - VPO loadings of 20 to 60 wt.%
 - activation in a flow of 1.5 % *n*-butane, 17.5 % O₂ and balance N₂ (100 ml/min) at 673 K for 15 h
- ICP-AES and nitrogen adsorption:

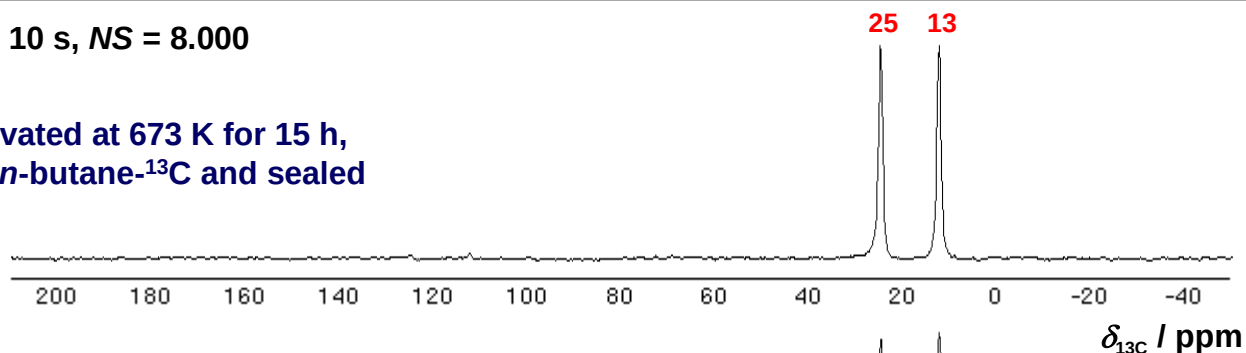
Catalysts	P / V	BET surface m ² / g	Pore volume cm ³ / g
SBA-15	-	1164	1.25
20%VPO/SBA-15	1.09	662	0.80
60%VPO/SBA-15	1.04	456	0.54
VPO bulk	1.02	13	-

^{13}C MAS NMR of *n*-butane conversion on 60%VPO/SBA-15 under batch conditions

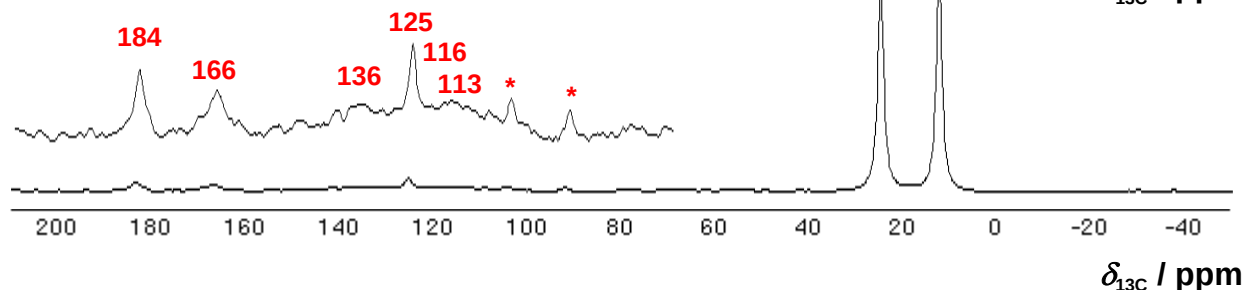
$\nu_0 = 100.61 \text{ MHz}$, $D_0 = 10 \text{ s}$, $NS = 8.000$

60%VPO/SBA-15 activated at 673 K for 15 h,
loaded with 60 mbar *n*-butane- ^{13}C and sealed
in a glass ampoule

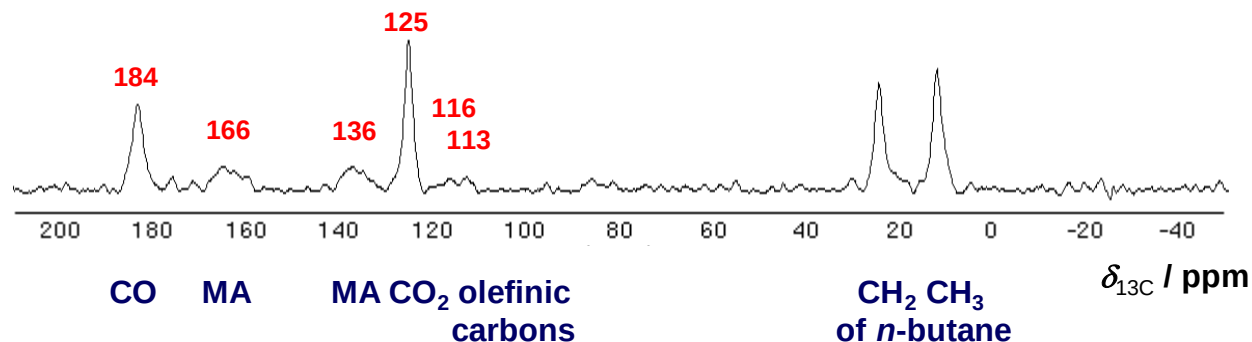
no heating



heated at 523 K
for 20 min



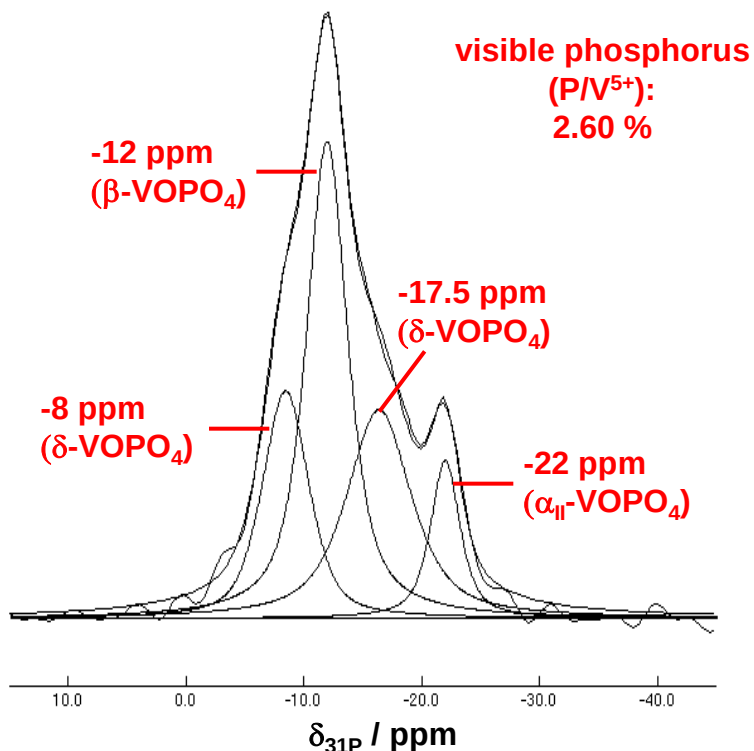
heated at 573 K
for 20 min



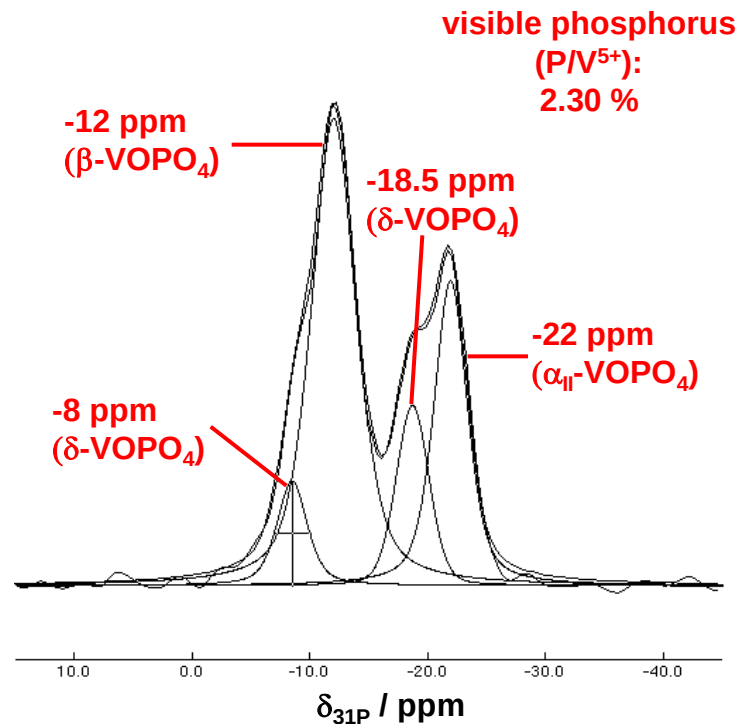
^{31}P MAS NMR spectra of oxidized and reduced 60%VPO/SBA-15

- VPO bulk catalysts recorded upon *n*-butane conversion under batch conditions in a sealed glass ampoule

60%VPO/SBA-15 activated and loaded with *n*-butane but no heating

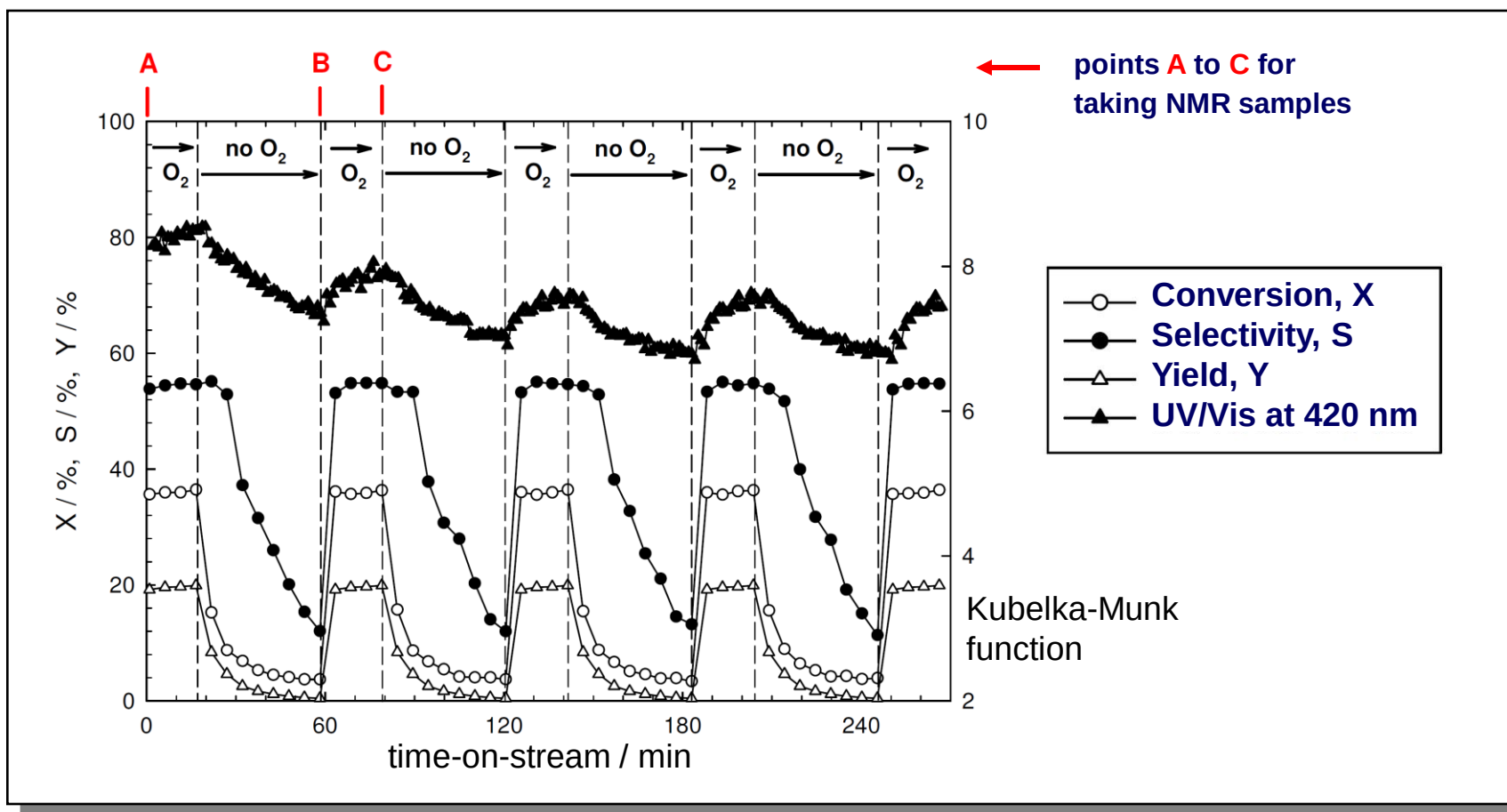


60%VPO/SBA-15 activated, loaded with *n*-butane, and heated at 573 K for 20 min



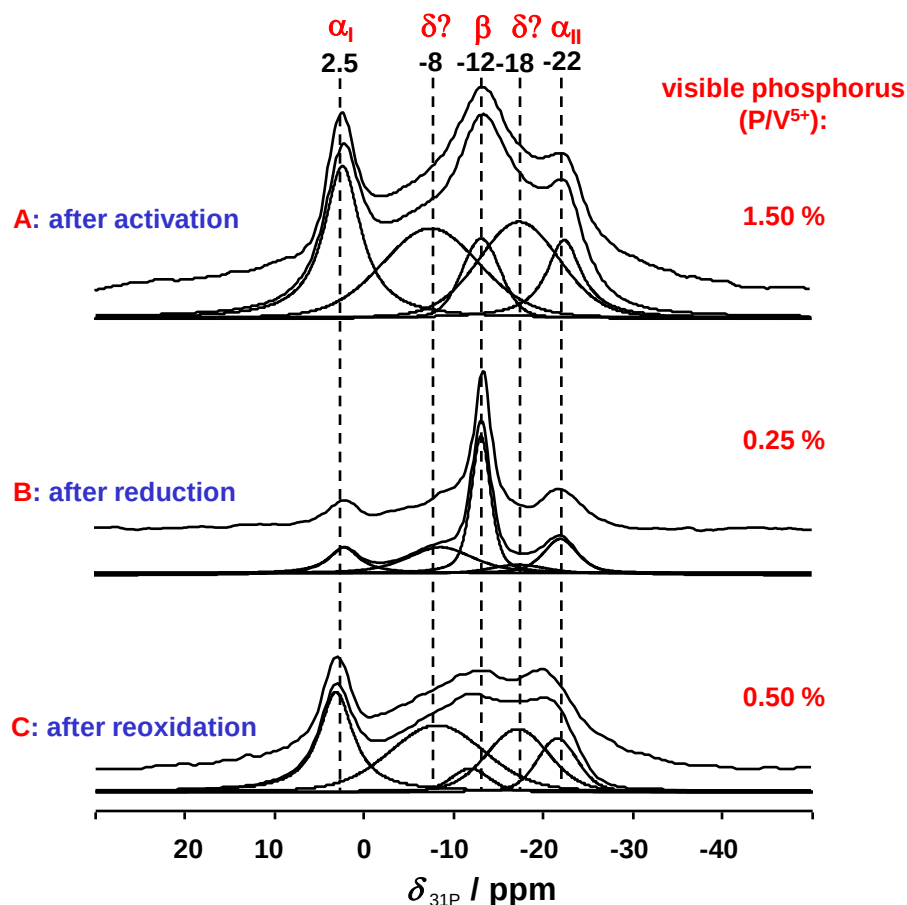
Treatment of VPO catalysts in a fixed-bed reactor

- conversion of *n*-butane on a VPO bulk catalysts at 678 K with a flow rate of 100 ml/min (1.5 vol.% *n*-butane) and switching between $\text{N}_2 + \text{O}_2$ and pure N_2



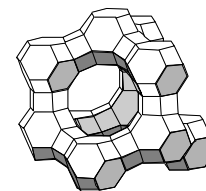
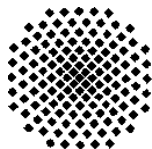
³¹P MAS NMR spectra of oxidized, reduced, and reoxidized VPO bulk catalysts

- VPO bulk catalysts recorded upon *n*-butane conversion at 678 K and switching between N₂ + O₂ and pure N₂ flow in a fixed-bed reactor



Materials	Signals	Ref.
γ -VOPO ₄	-21.2 ppm, -17.3 ppm (ca. 1:1) -14.9 ppm (very weak shoulder)	[1]
α_{II} -VOPO ₄	-20.5 ppm	[1]
δ -VOPO ₄	-17.6 ppm, -8.4 ppm (ca. 1:1) -6.5 ppm (very weak shoulder)	[1]
β -VOPO ₄	-11.5 ppm	[1]
α_I -VOPO ₄	2.7 to 3.6 ppm	[1-3]
VOPO ₄ · <i>n</i> H ₂ O	3.9 ppm	[2]

- [1] F.B. Abdelouhab et al., J. Catal. 134 (1992) 151.
 [1] K.E. Birkeland et al., J. Phys. Chem. B 101 (1997) 6895.
 [2] S.A. Ennaciri et al., Eur. J. Solid State Inorg. Chem. 30 (1993) 227.
 [3] K. Ait-Lachgar et al., J. Catal. 177 (1998) 224.



***Investigation of reactions catalyzed
by basic zeolites***

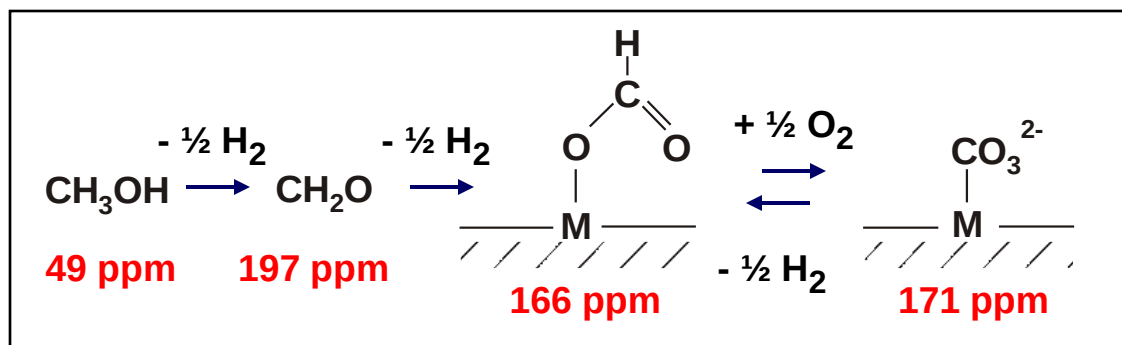
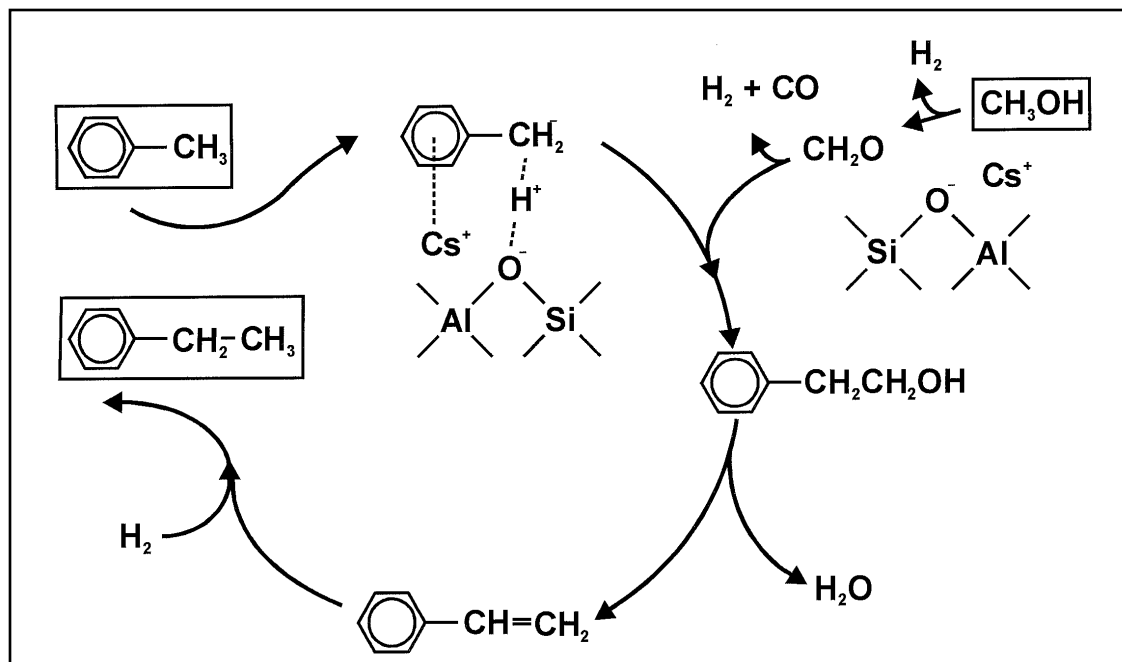
Side-chain alkylation of toluene with methanol on basic zeolites

- proposed reaction scheme:

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

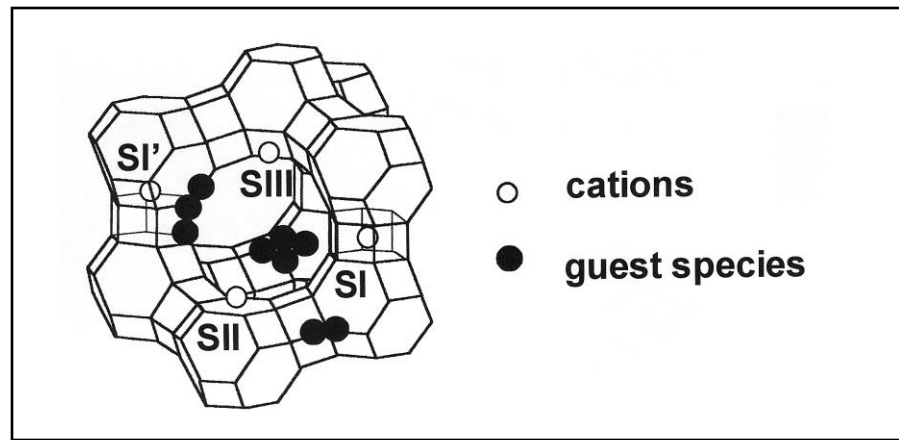
- proposed surface species:

- formate ($\delta_{13C} = 166$ ppm)
- carbonate ($\delta_{13C} = 171$ ppm)



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

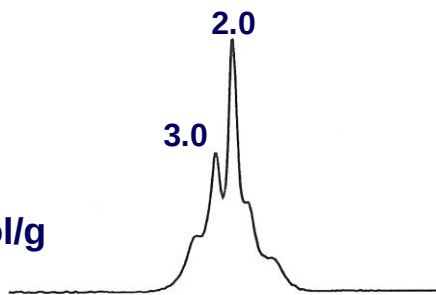
- zeolite Na-X ($n_{\text{Si}}/n_{\text{Al}} = 1.4$) exchanged with cesium cations (55 %) and impregnated with cesium hydroxide (24 CsOH/u.c.)



^1H MAS NMR

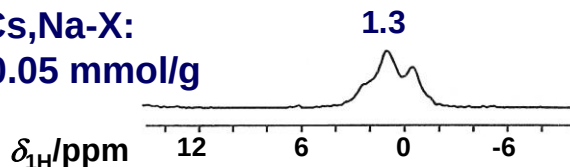
Cs,Na-X:

$c_{\text{OH}} = 0.3 \text{ mmol/g}$



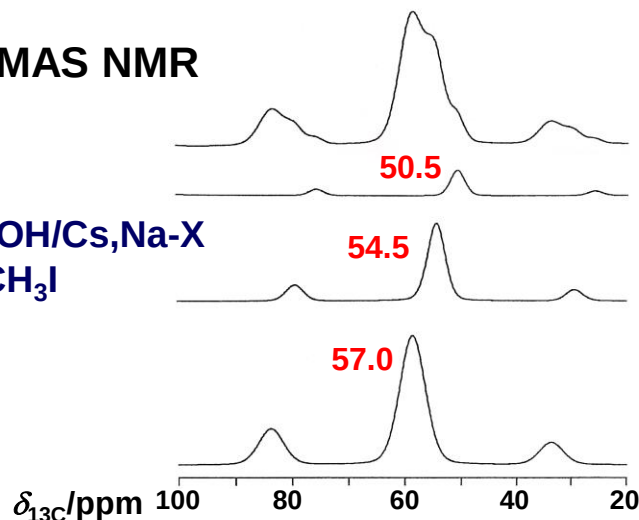
CsOH/Cs,Na-X:

$c_{\text{OH}} = 0.05 \text{ mmol/g}$



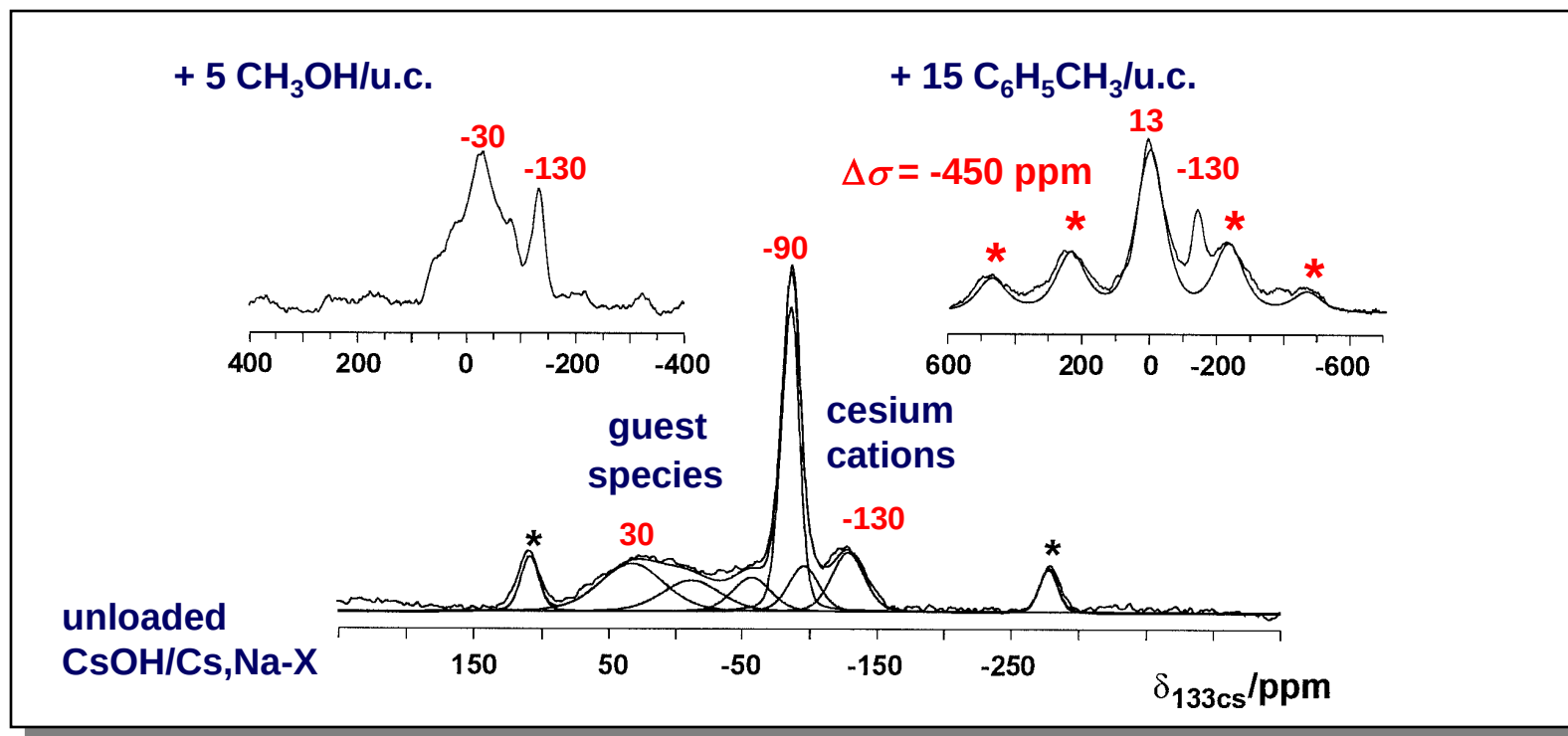
^{13}C MAS NMR

CsOH/Cs,Na-X
+ CH_3I



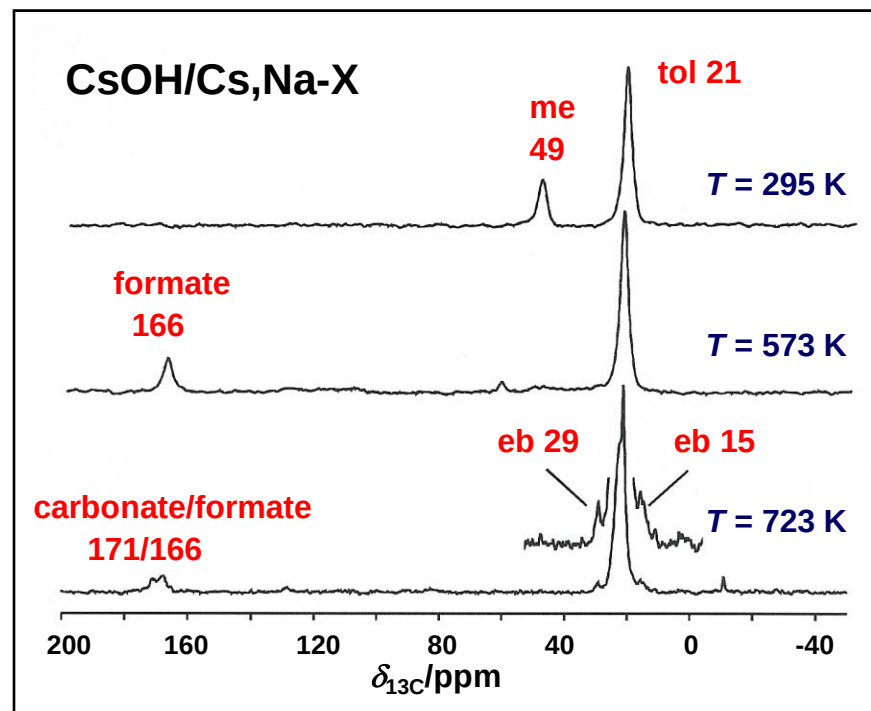
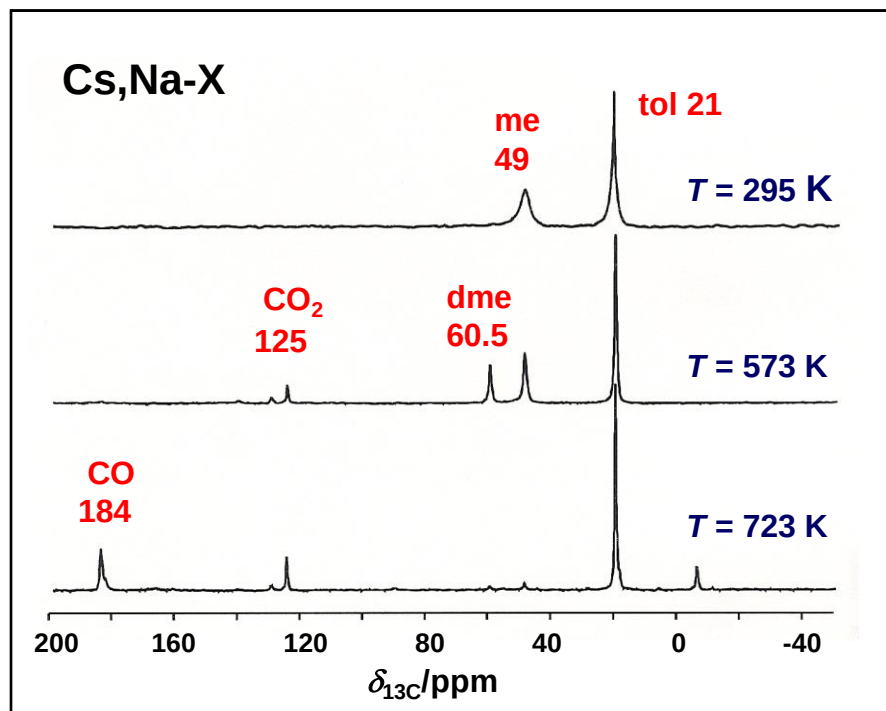
Adsorbate complexes formed by the reactants on zeolite CsOH/Cs,Na-X

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



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

^{13}C MAS NMR spectroscopy: $15 \text{ C}_6\text{H}_5^{13}\text{CH}_3/\text{u.c.}$
 $5 \text{ }^{13}\text{CH}_3\text{OH}/\text{u.c.}$

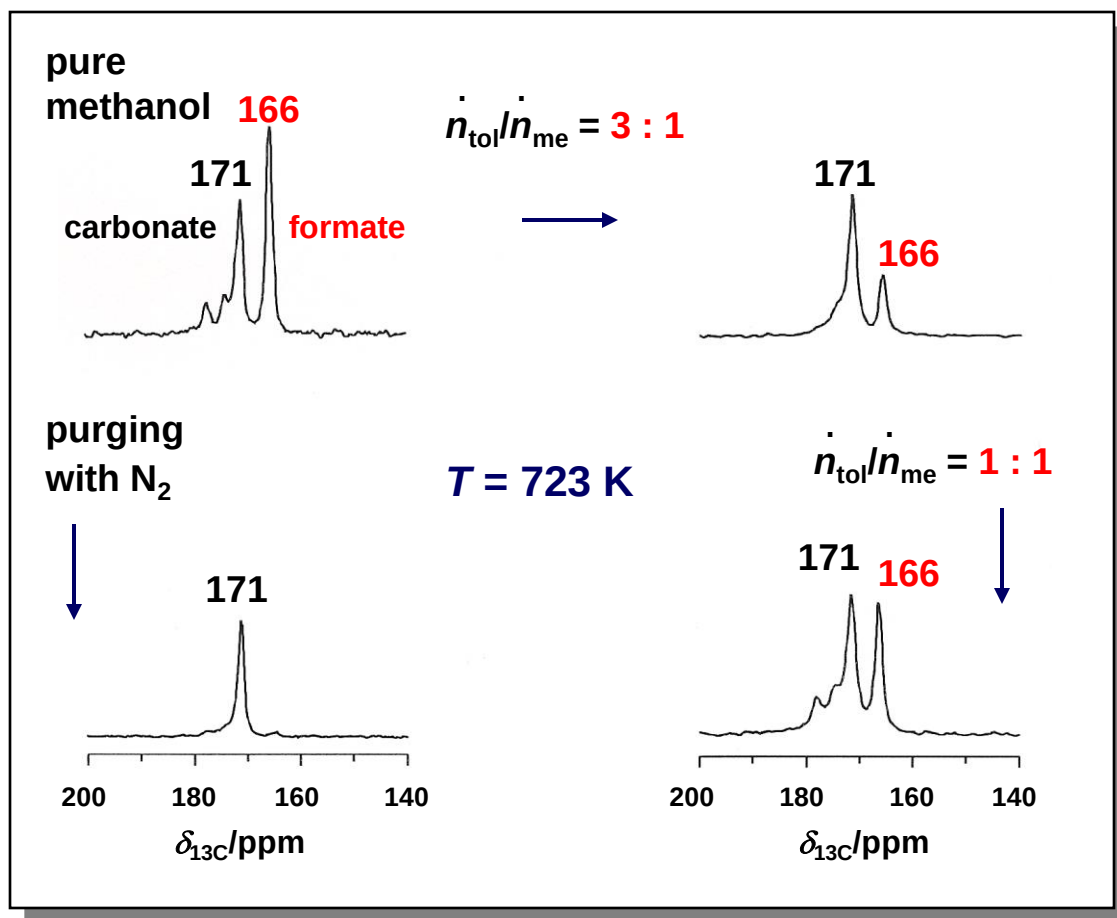


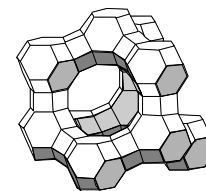
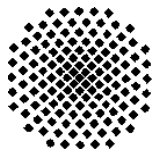
Reactivity of formate species on zeolite CsOH/Cs,Na-X under flow conditions

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

$$W_{\text{cat}}/F_{\text{me}} = 60 \text{ gh/mol}$$

- carbonate species are chemically stable
- formate species are consumed by toluene, which indicates their reactivity

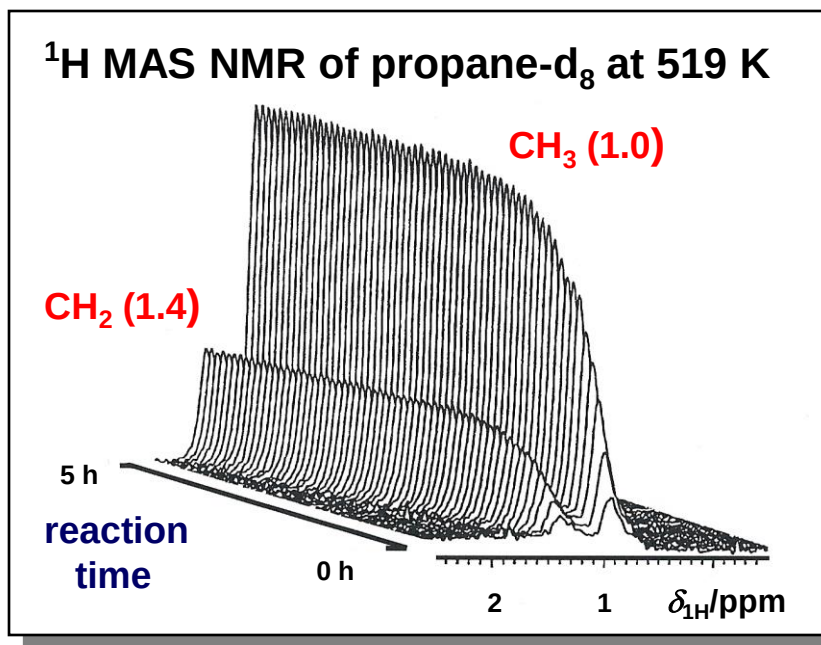




***Investigation of the H/D exchange
on acidic catalysts***

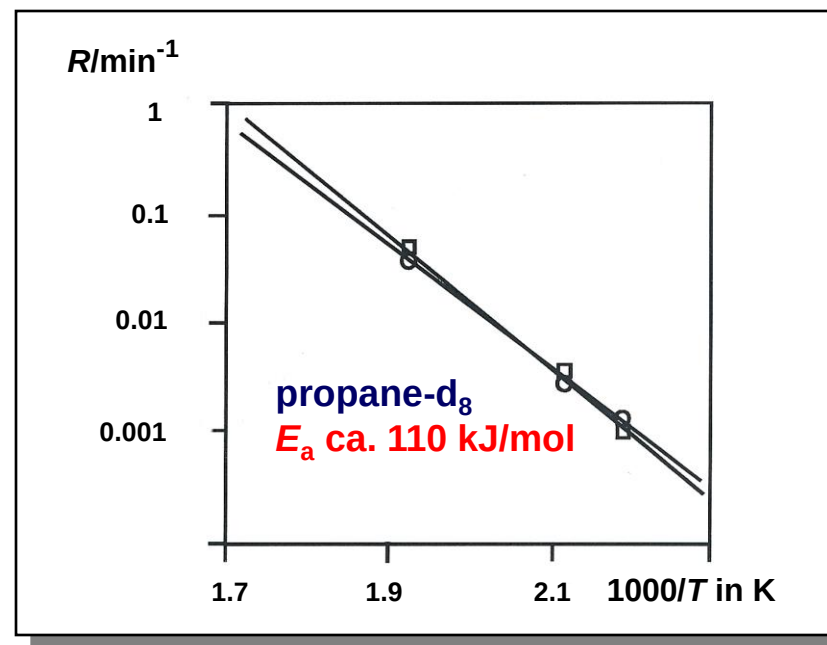
Evaluation of reaction mechanisms by H/D exchange on acidic zeolites

- 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

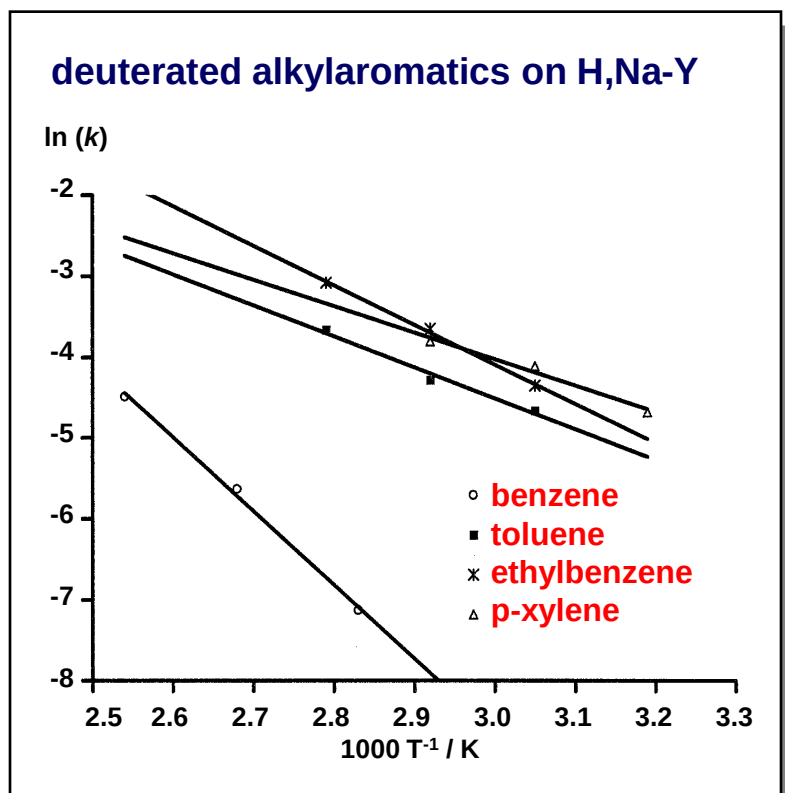


B:

- regiospecific H/D exchange
 - E_a of ca. 50 kJ/mol
- formation carbenium ions

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

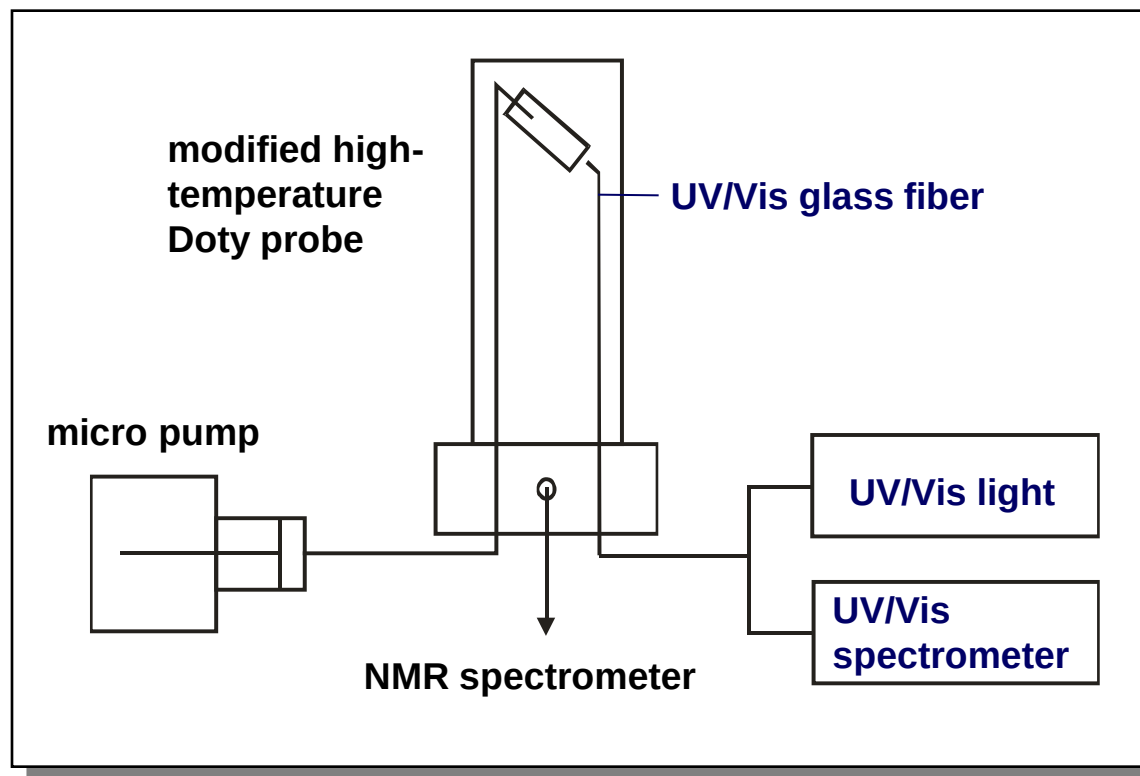


correlation of activation energies E_A of H/D exchange and low-field shifts $\Delta\delta_{1H}$ upon adsorption CD_3CN :

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	

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

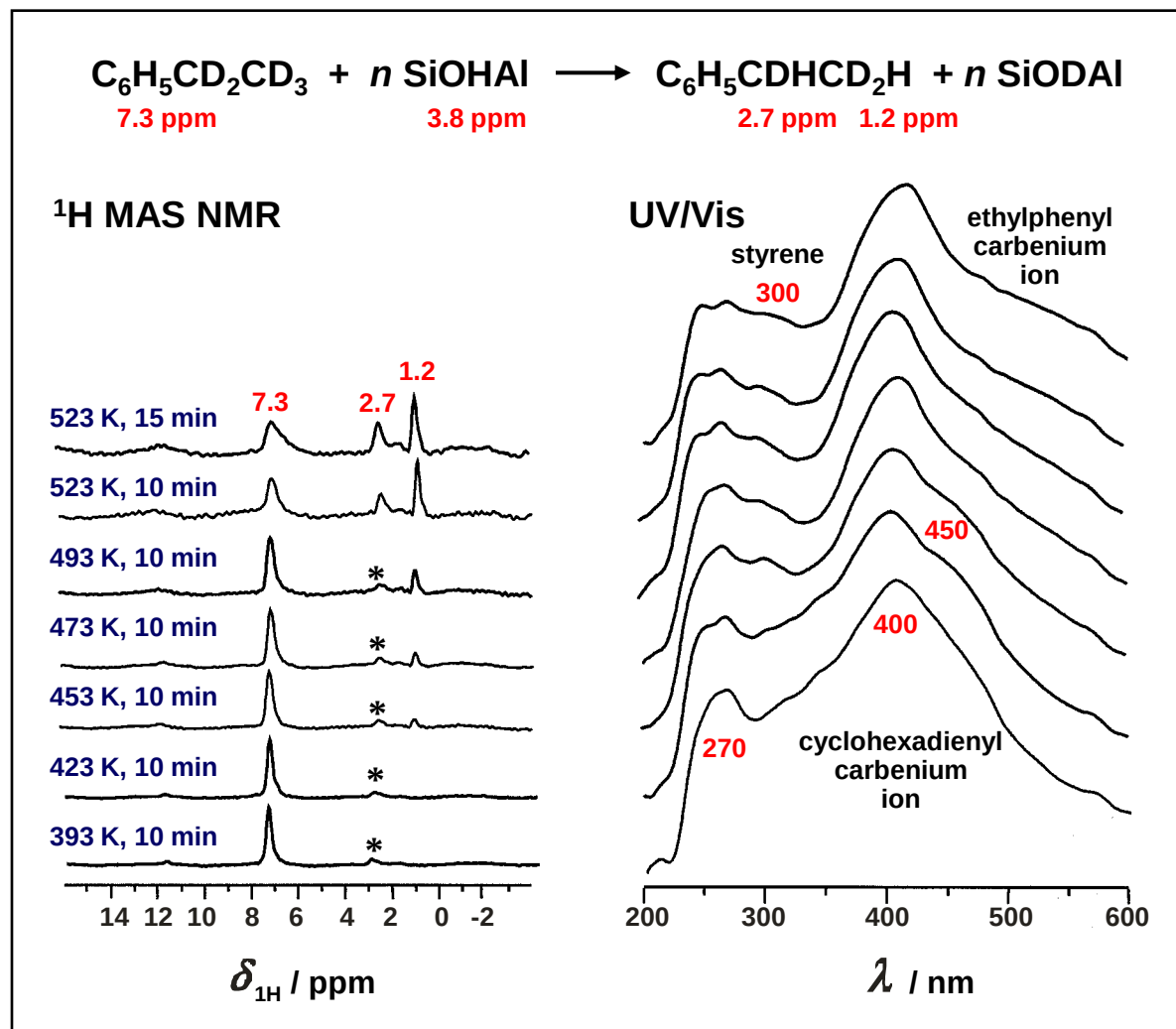
- injection of micro-pulses initiates the H/D exchange at elevated temperature



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

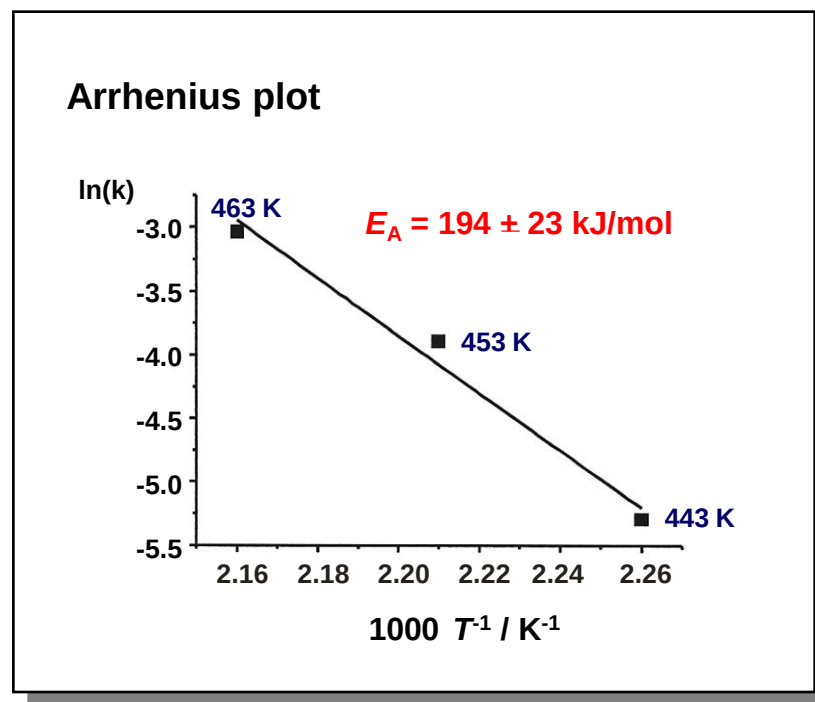
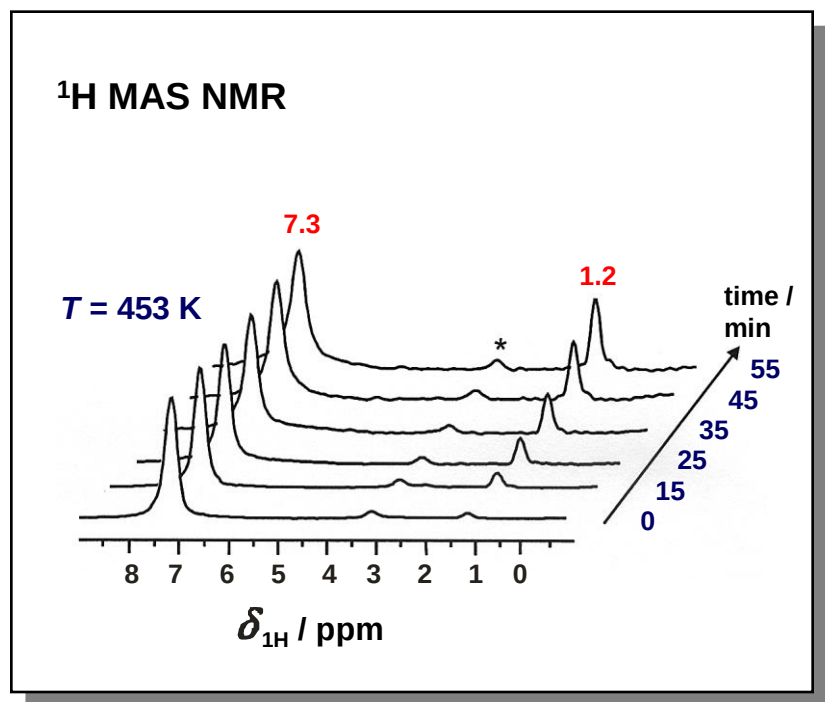
Study of the side-chain H/D exchange of ethylbenzene on dealuminated zeolite Y

- ^1H MAS NMR studies under pulsed-flow conditions:
 - steamed zeolite deH-Y ($n_{\text{Si}}/n_{\text{Al}} = 5.4$)
 - pulses of 7.8 mg ethyl- d_5 -benzene
 - 32 scans per spectrum with repetition time of 10 s
 - sample spinning rate of ca. 2 kHz
- message:
 - regioselective H/D exchange at 443 to 463 K (^1H MAS NMR)
 - different types of carbenium ions (UV/Vis)



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

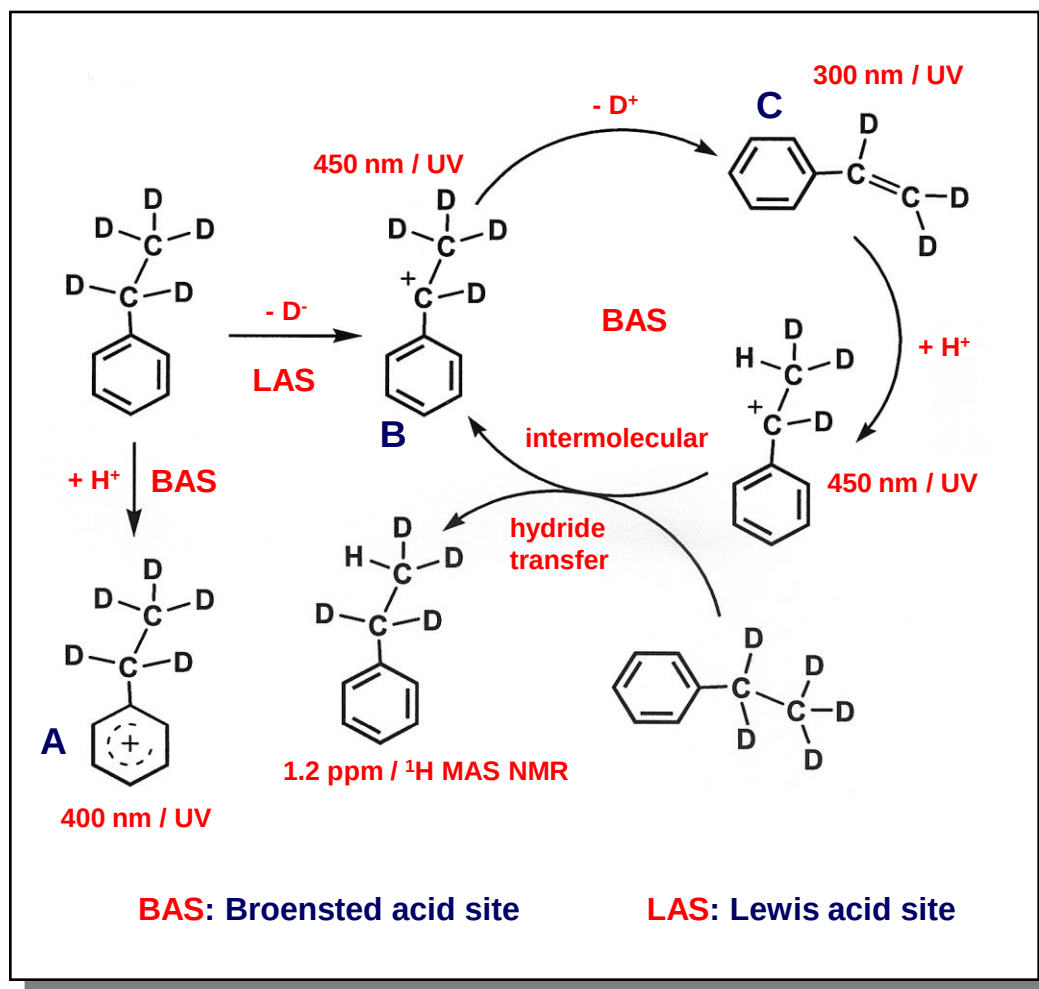
- in situ* pulsed-flow ^1H MAS NMR study of the regioselective H/D exchange of the side-chain of ethyl- d_5 -benzene on dealuminated zeolite deH-Y ($n_{\text{Si}}/n_{\text{Al}} = 5.4$, 22 Al^{ex}/u.c, 10.9 SiOHAl /u.c)

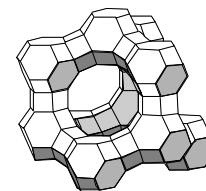
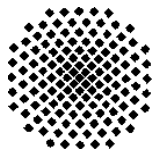


activation energy of the regioselective H/D exchange (194 kJ/mol) indicates that a hydride transfer reaction is the rate determining step

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

- ^1H 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





***In situ MAS NMR-UV/Vis investigation of
the methanol to olefin conversion
on acidic zeolites***

Periods of catalyst formation and aging during 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

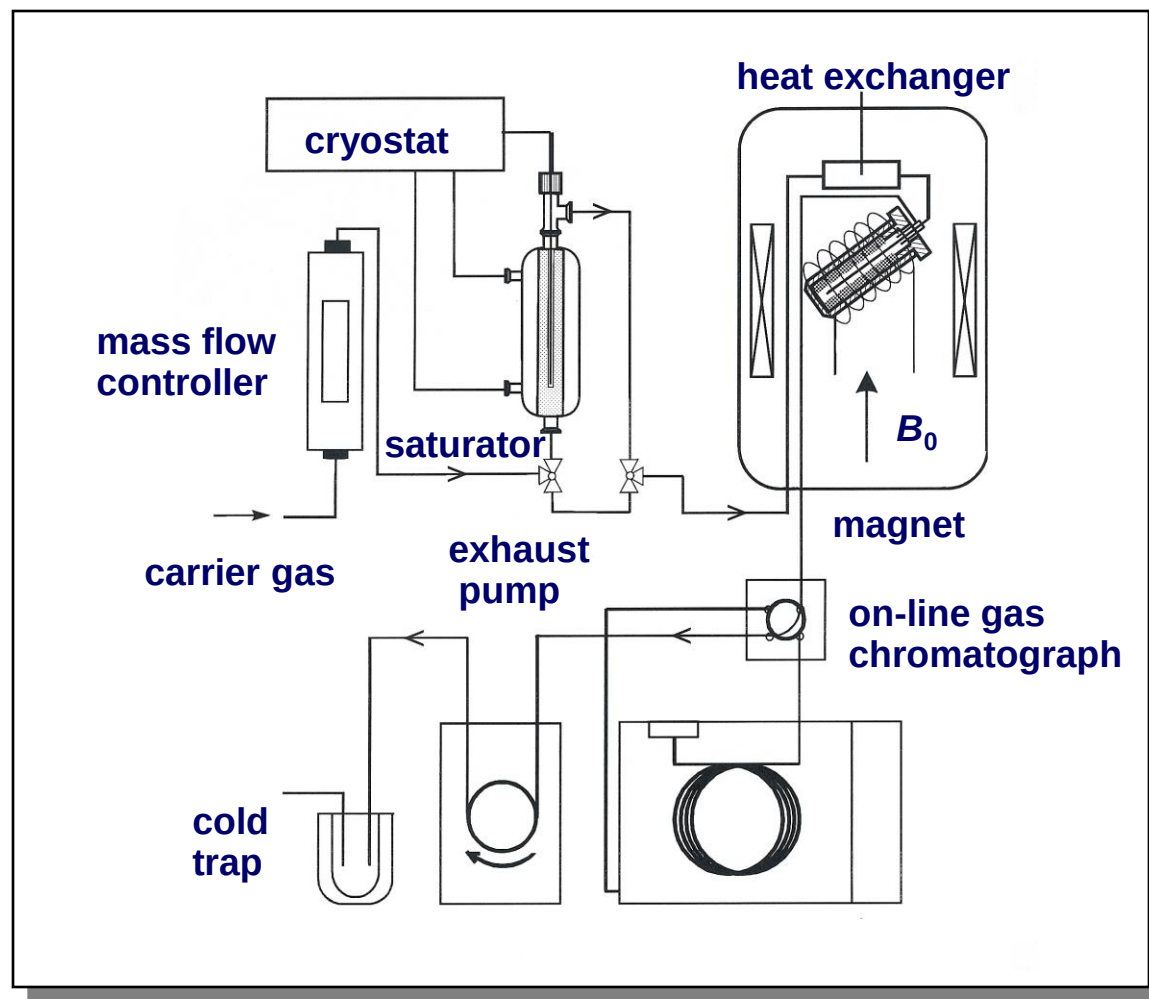
Formation of light olefins by methylation and dealkylation of catalytically active hydrocarbon-pool compounds (olefinic and aromatic deposits)



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

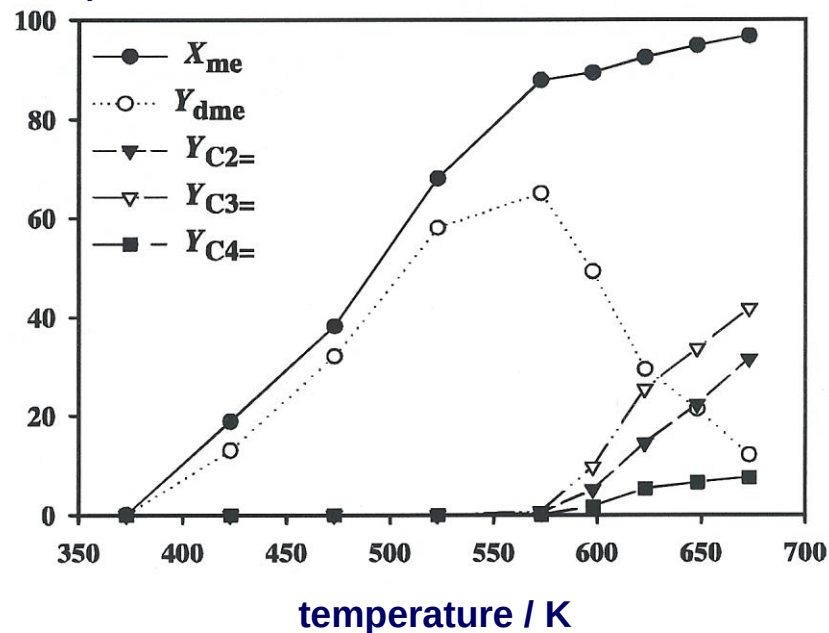


Conversion of methanol on H-ZSM-5 in a fixed-bed and in an MAS NMR rotor reactor

fixed-bed reactor

$$W_{\text{cat}}/F_{\text{me}} = 25 \text{ gh/mol}$$

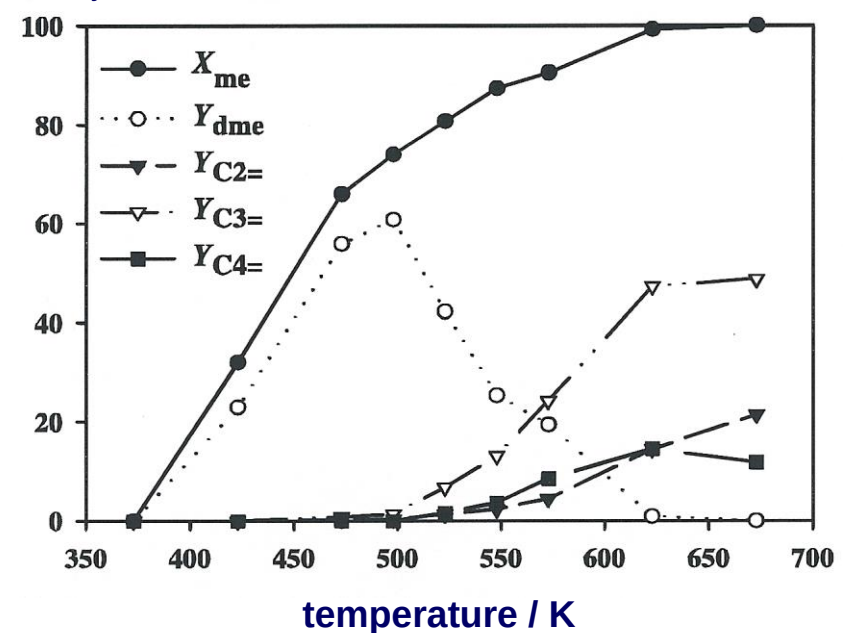
$X_i, Y_j / \%$



spinning (2 kHz) MAS NMR rotor reactor

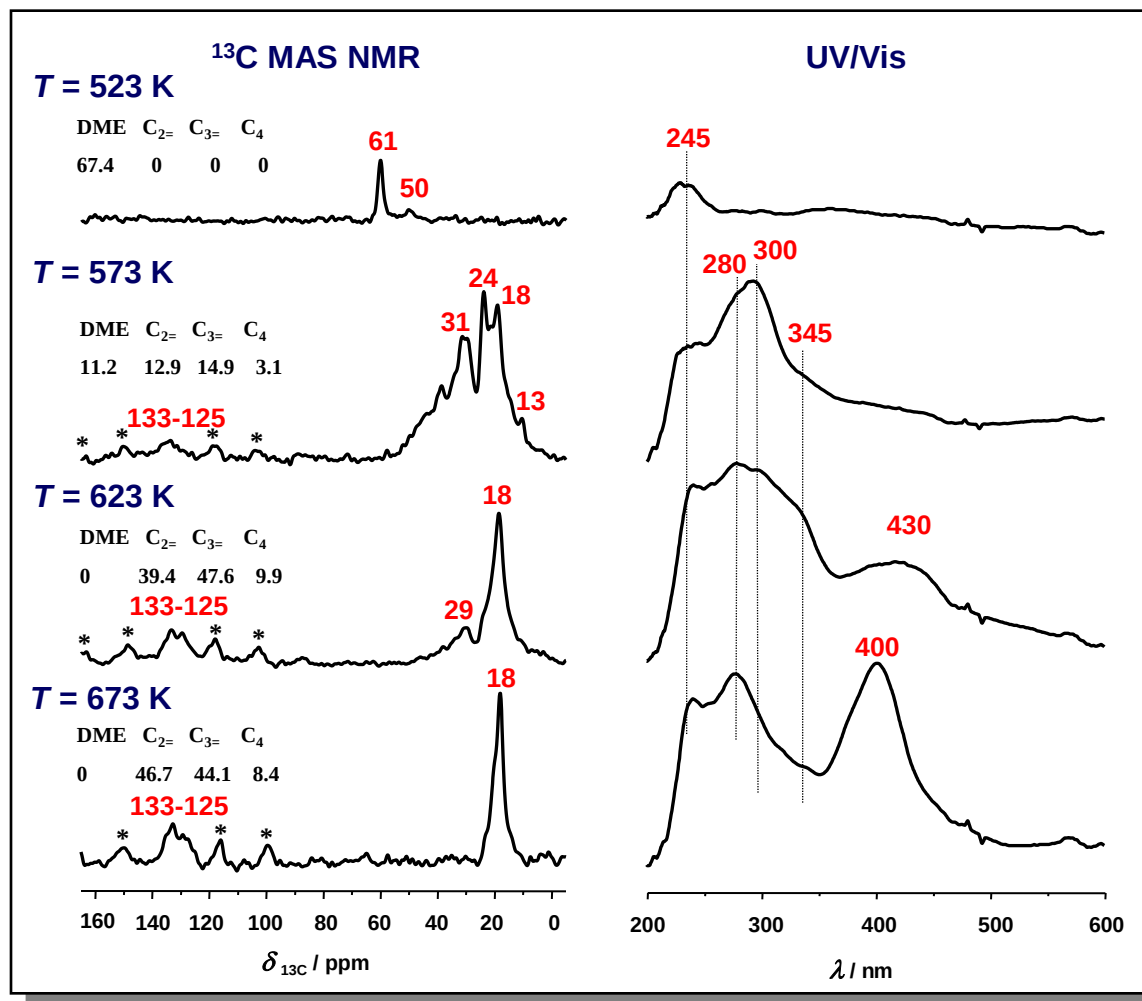
$$W_{\text{cat}}/F_{\text{me}} = 25 \text{ gh/mol}$$

$X_i, Y_j / \%$



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 ($W_{\text{cat}}/F_{\text{me}} = 25 \text{ gh/mol}$)**



NMR:

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

UV/Vis:

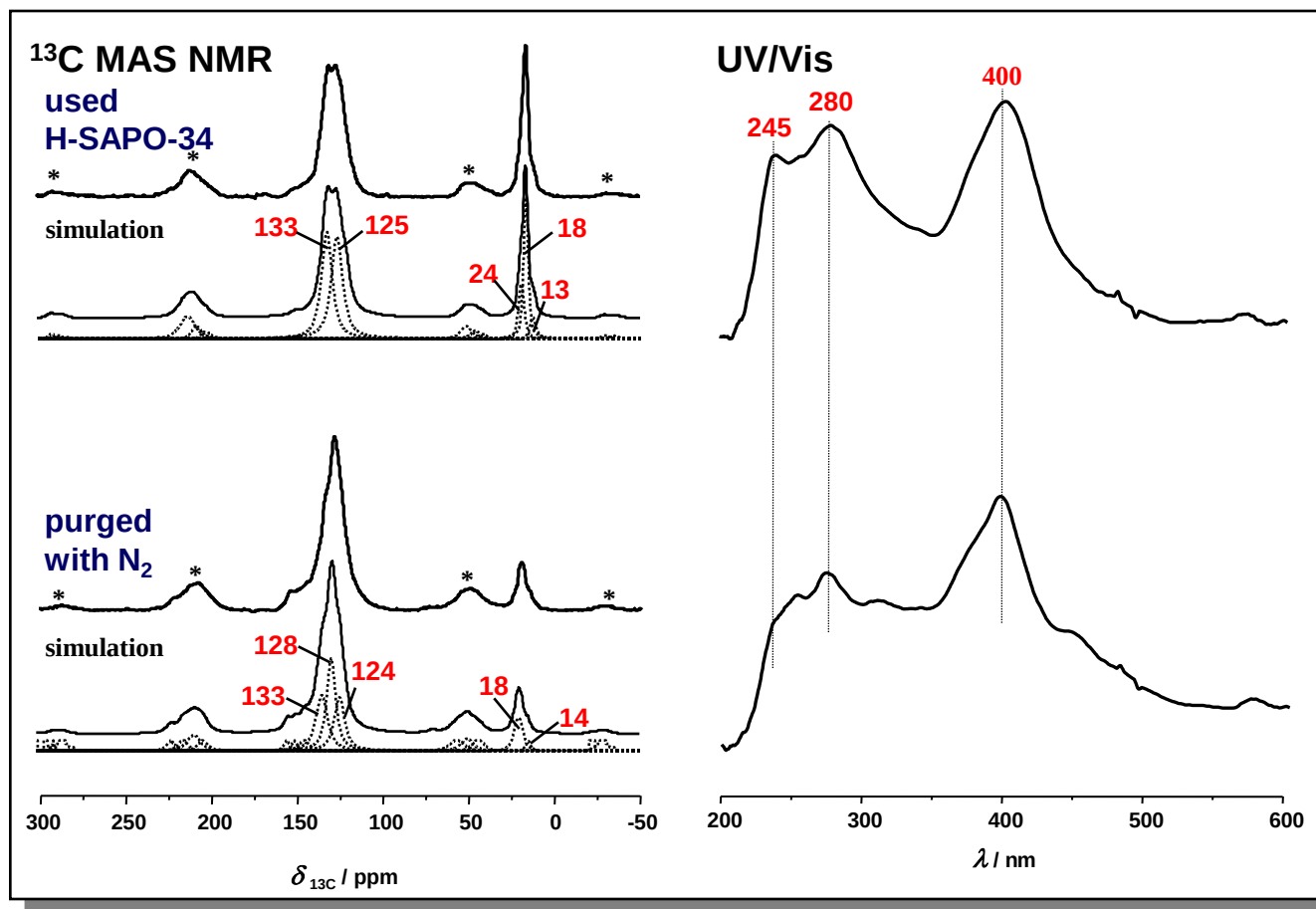
- sensitive for carbenium cations (300, 345, 430 nm)**
- separation of aromatics (280 nm) and polycyclic aromatics (400 nm)**

On-line GC:

- determination of volatile reaction products**

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

Occluded and stable organic deposits formed by conversion of methanol ($W/F = 25$ gh/mol) on H-SAPO-34 at 673 K for 3 h

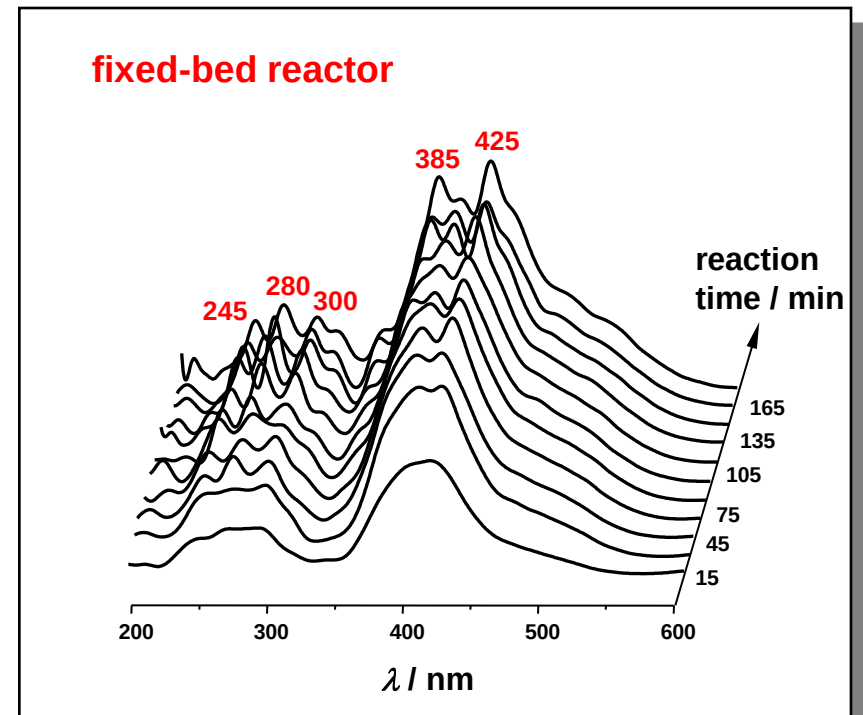
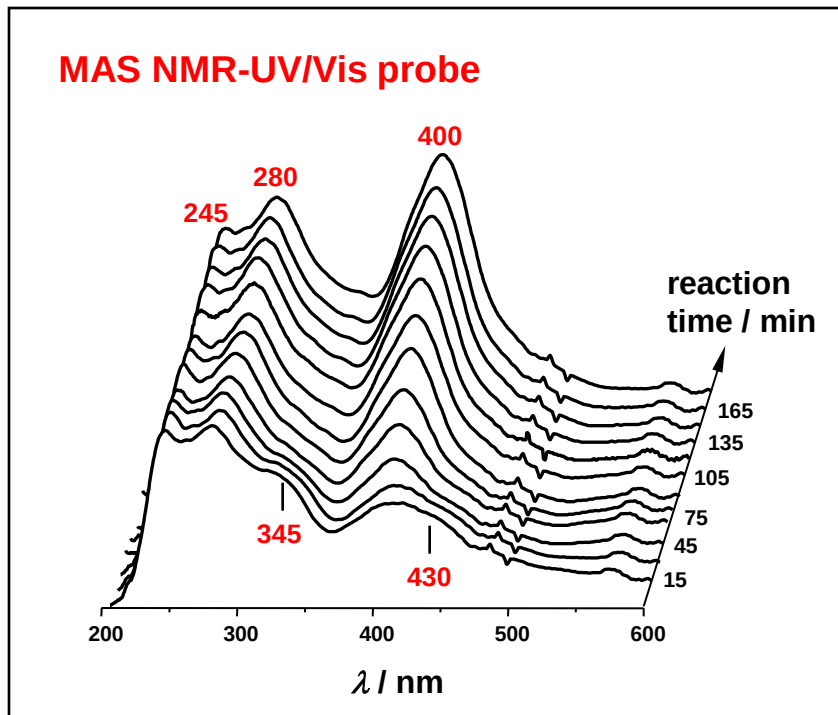


→
decrease of dienes
(245 nm) and
polyalkylaromatics
(280 nm)

stable polycyclic
aromatics (400 nm)

UV/Vis study of the formation of organic deposits in different reactors

In situ UV/Vis studies of deposit formation during methanol conversion on H-SAPO-34 at 673 K ($W_{\text{cat}}/F_{\text{me}} = 25 \text{ gh/mol}$)

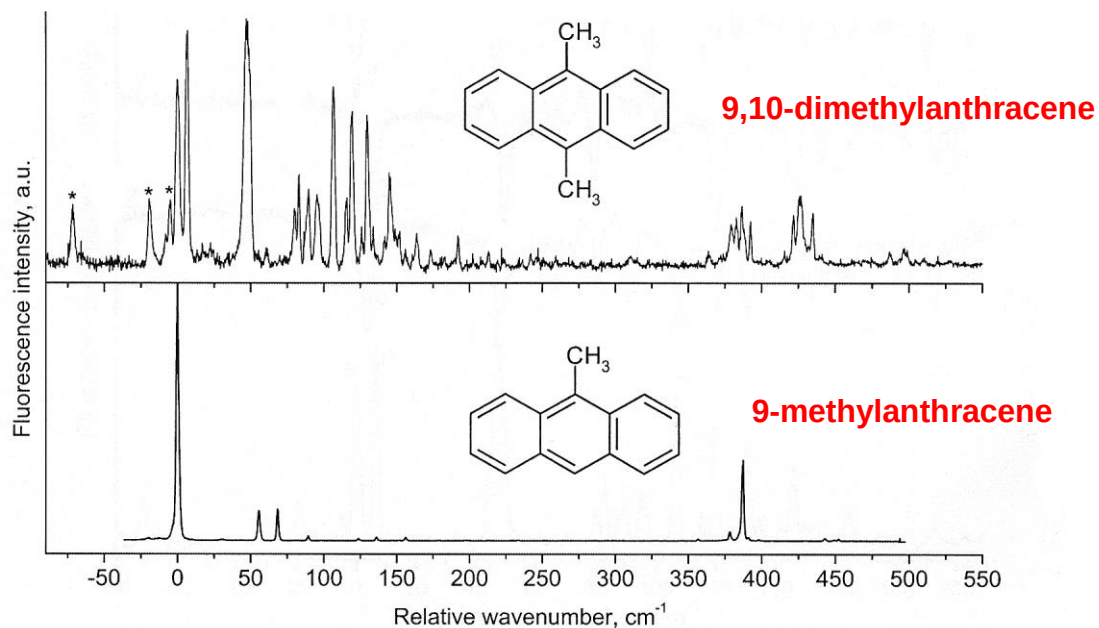


- continuous increase of the band at ca. 400 nm indicates formation of polycyclic aromatics
- simultaneously, the bands of di- and trienylic carbenium ions decrease (345 nm, 430 nm)

Assignment of the coke band

Possible assignment of the coke band at ca. 400 nm,
(Y. Stepanenko *et al.*, J. Mol. Spectrosc. 233 (2005) 15)

Laser-induced fluorescence excitation spectra

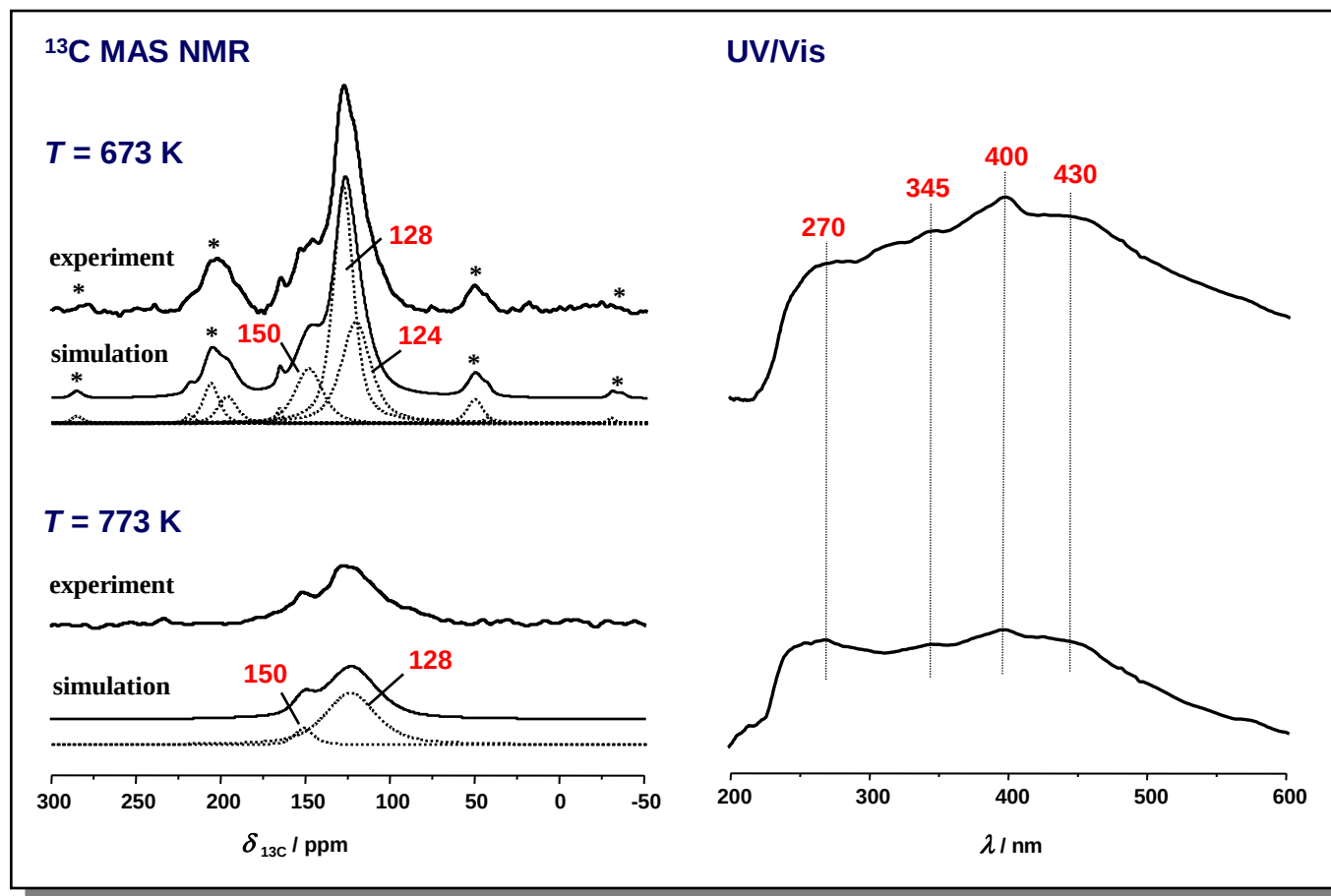


chain-like
polyaromatics
correspond to:

polymethyl-
anthracenes

Regeneration of coked MTO catalysts

- Regeneration of coked H-SAPO-34 by purging with synthetic air (20 vol.-% O₂, 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)

Regeneration of coked MTO catalysts

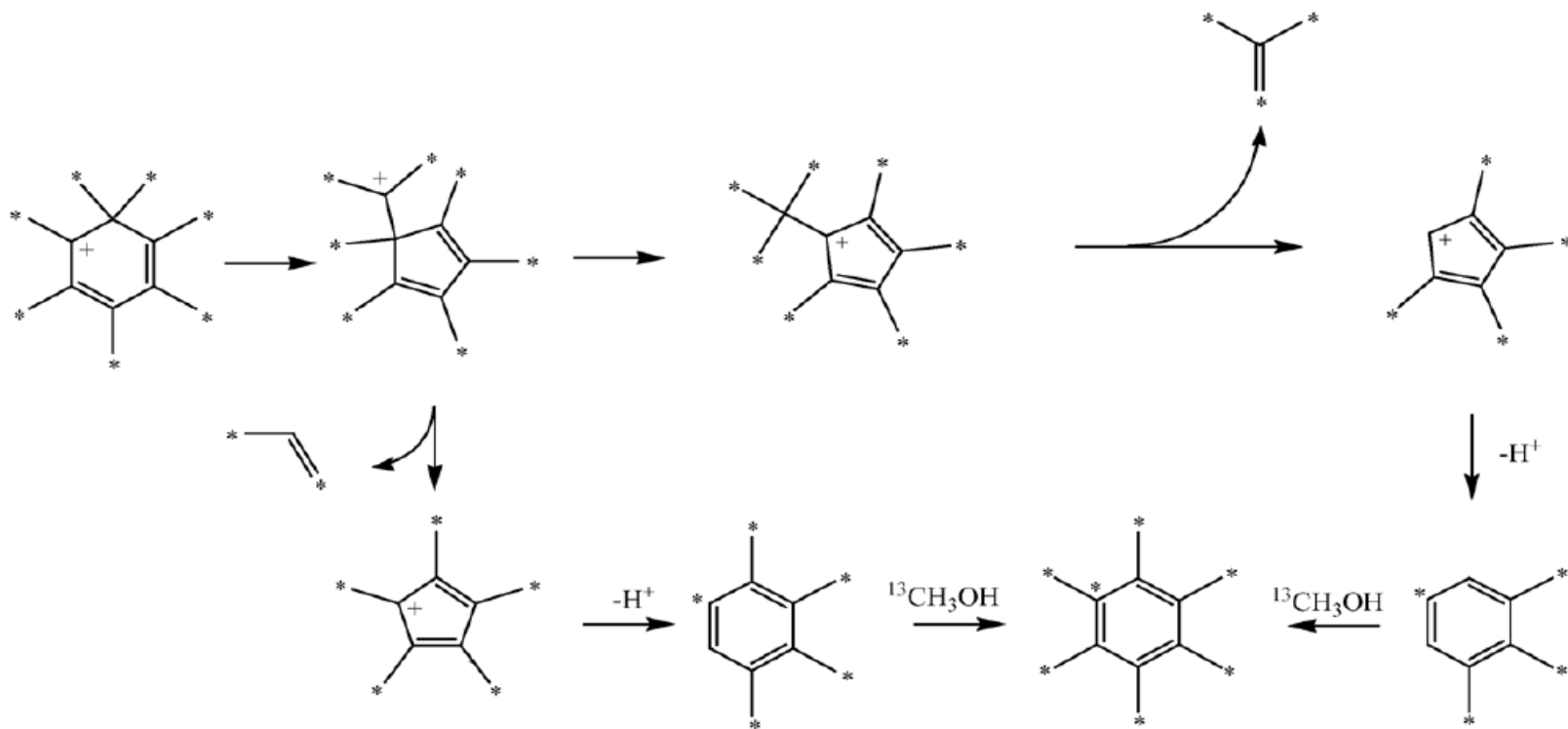
- Quantitative evaluation of the ^{13}C MAS NMR spectra of coked H-SAPO-34 regenerated by burning with synthetic air at 673 and 773 K for 2 h

Signal at $\delta_{^{13}\text{C}}$ /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

→ significant removal of coke compounds (UV/Vis bands at 280 nm and 400 nm) and formation of oxygenated species (270 nm)

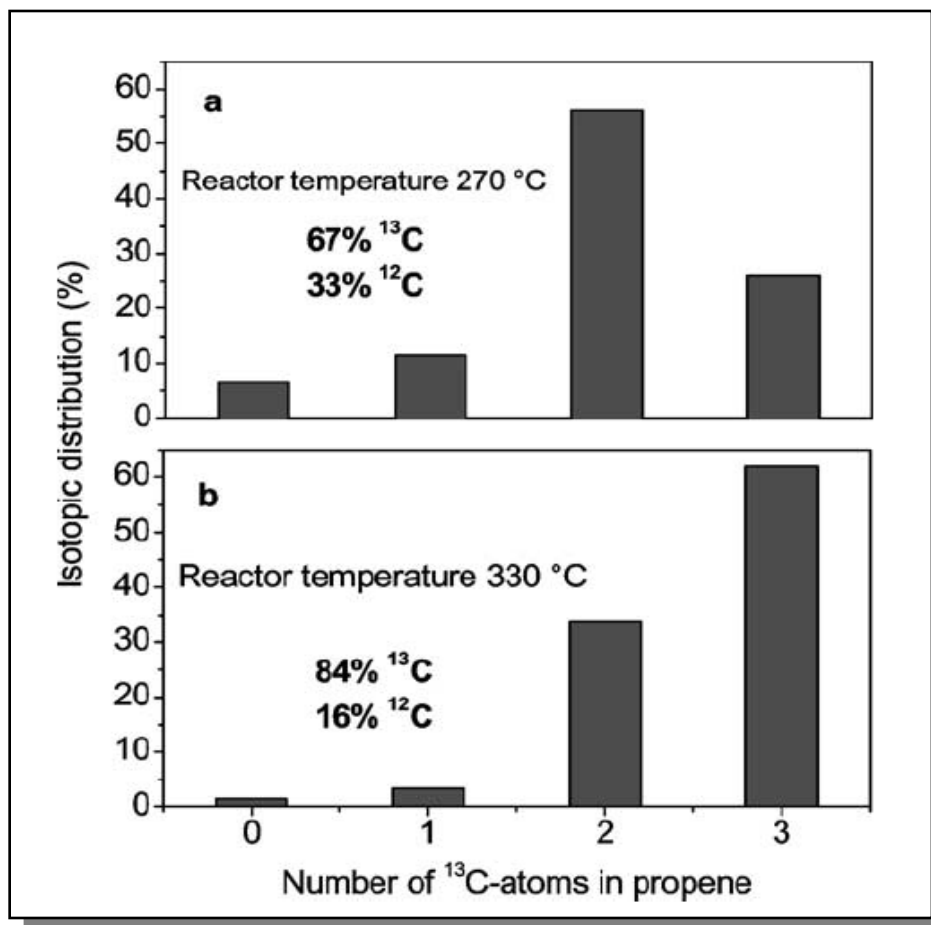
Studies of the reaction mechanism

Alkyl chain growing by paring reaction, M. Bjorgen et al., J. Catal. 221 (2004) 1:



Studies of the reaction mechanism

Co-reaction of $^{13}\text{CH}_3\text{OH}$ and $^{12}\text{C}_6\text{H}_6$ on zeolite H-Beta (12-ring channels),
M. Bjorgen et al., J. Catal. 221 (2004) 1

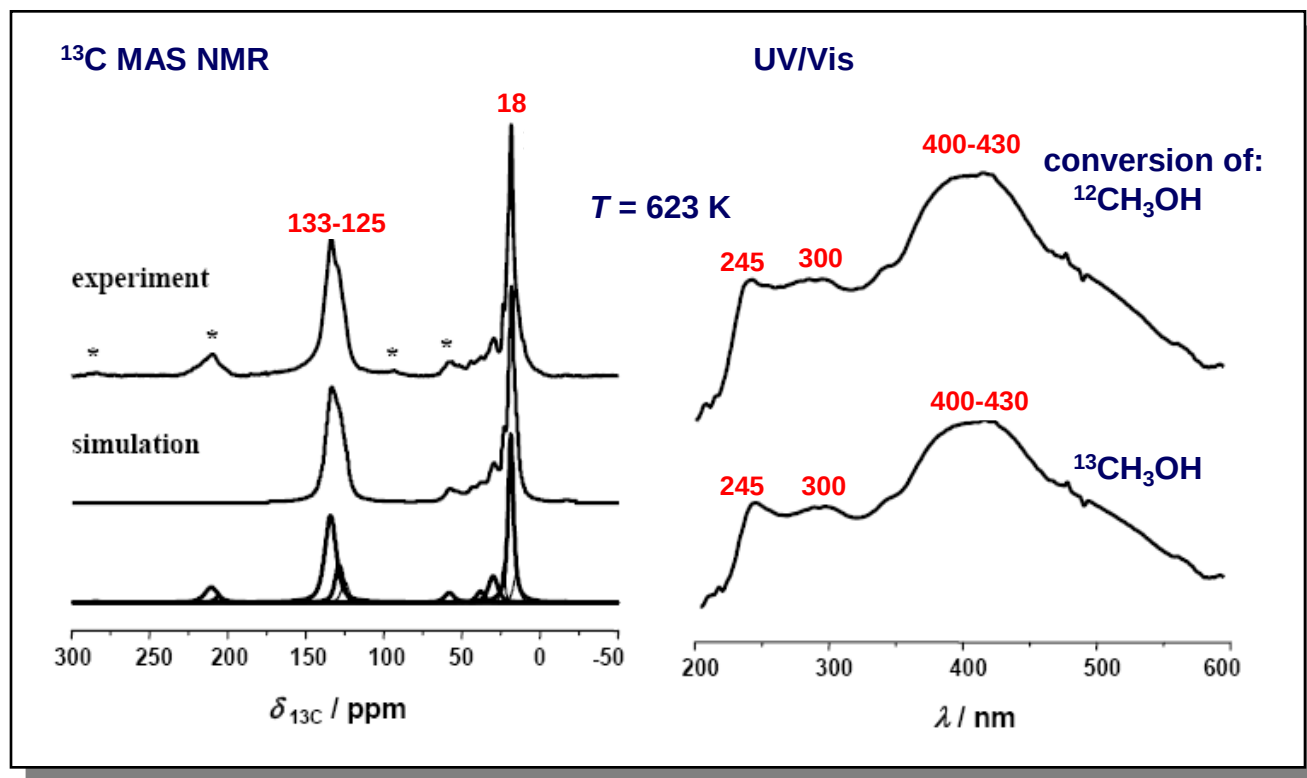


→
the majority of propene (and isobutene) product molecules contain ^{12}C atoms from non-enriched benzene rings

the isotopic distribution is in agreement with the paring reaction mechanism (on H-Beta)

Studies of the reaction mechanism

Evaluation of ^{13}C MAS NMR spectra recorded after sequential conversion of $^{12}\text{CH}_3\text{OH}$ for 6 h and $^{13}\text{CH}_3\text{OH}$ for 2 h on H-SAPO-34 ($W/F = 25$ gh/mol)



determination of the absolute number of ^{13}C atoms by spin-counting at room temperature

no change of the hydrocarbon pool upon switching as evidenced by UV/Vis

Studies of the reaction mechanism

Study of ^{13}C scrambling by sequential conversion of $^{12}\text{CH}_3\text{OH}$ for 6 h and $^{13}\text{CH}_3\text{OH}$ for 2 h on H-SAPO-34 ($W/F = 25 \text{ gh/mol}$)

Reaction temperature and type of ^{13}C atoms	Number of ^{13}C atoms for continuous conversion of $^{13}\text{CH}_3\text{OH}$	Number of ^{13}C atoms for sequential conversion of $^{12}\text{CH}_3\text{OH}$ and $^{13}\text{CH}_3\text{OH}$	Comparison with continuous conversion of $^{13}\text{CH}_3\text{OH}$
$T = 623 \text{ K}$ in alkyl groups in aromatic rings	2.74 mmol/g 3.28 mmol/g	0.61 mmol/g 1.00 mmol/g	22.3 % 30.5 %
$T = 673 \text{ K}$ in alkyl groups in aromatic rings	0.69 mmol/g 3.33 mmol/g	0.21 mmol/g 0.65 mmol/g	30.4 % 19.5 %



strong ^{13}C scrambling of carbon atoms in aromatic rings supports paring mechanism on H-SAPO-34

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 developments in the field of *in situ* NMR spectroscopy:

- improvement of the time-resolution of *in situ* NMR investigations by an introduction of pulsed-flow experiments
- application of modern solid-state NMR techniques such as MQMAS for the study of surface sites under reaction conditions
- enhancement of signal intensities by a continuous injection of laser-polarized ^{129}Xe into CF MAS NMR probes
- combination of NMR spectroscopy with other spectroscopic techniques such as Raman spectroscopy and mass spectrometry

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**Volkswagen-Stiftung
Hannover**

**Max-Buchner-Forschungs-
stiftung**

**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. 53 (2008) 105-127.

M. Hunger, *NMR Spectroscopy for the Characterization of Surface Acidity and Basicity*, in: G. Ertl, K. Knoezinger, F. Schueth, J. Weitkamp (eds.), *Handbook of Heterogeneous Catalysis*, Volume 2, Chapter 3.2.4.4, 2nd Edition, Wiley-VCH, Weinheim, 2008, p. 1163-1178.

Calibration of the high-temperature CF MAS NMR probe

- ^{207}Pb MAS NMR of $\text{Pb}(\text{NO}_3)_2$:

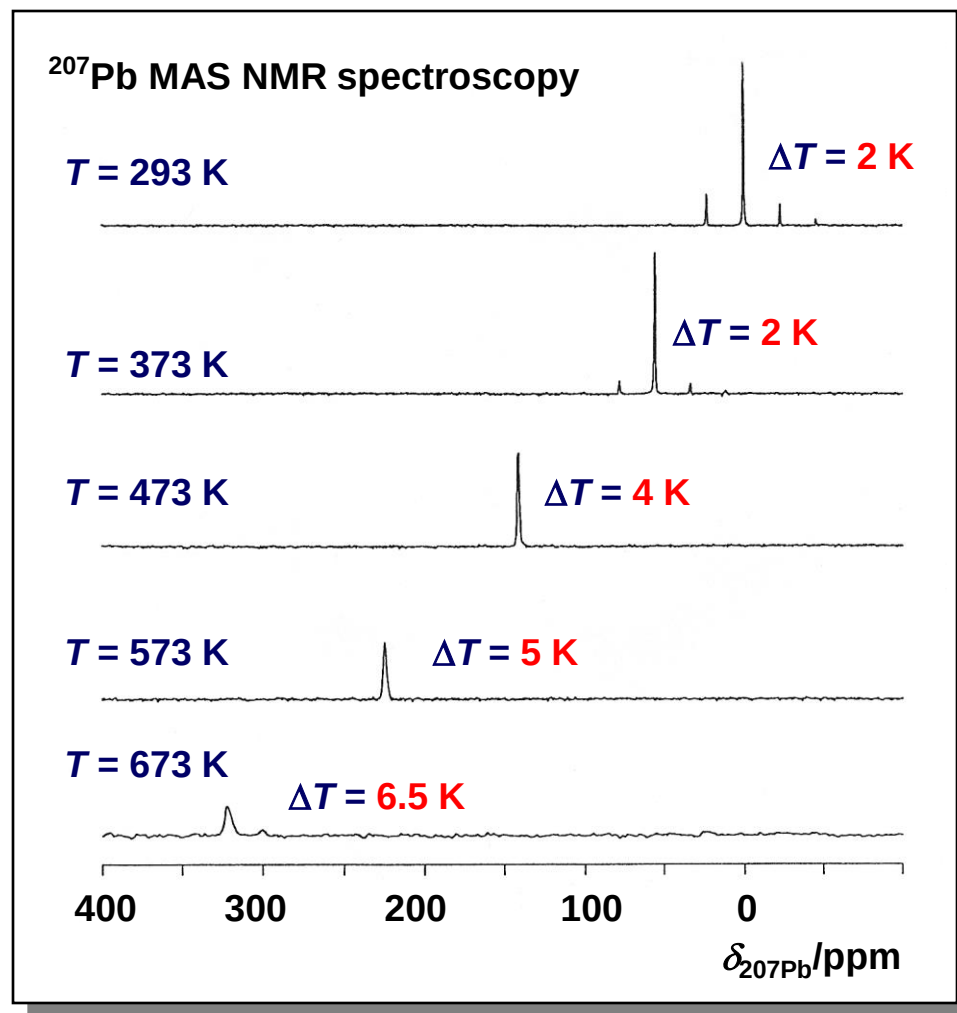
$$\Delta T / \Delta \delta = 1.29 \text{ K / ppm} \quad [1]$$

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

$$\nu_0 = 83.2 \text{ MHz}$$

$$\nu_{\text{rot}} = 2.5 \text{ kHz}$$

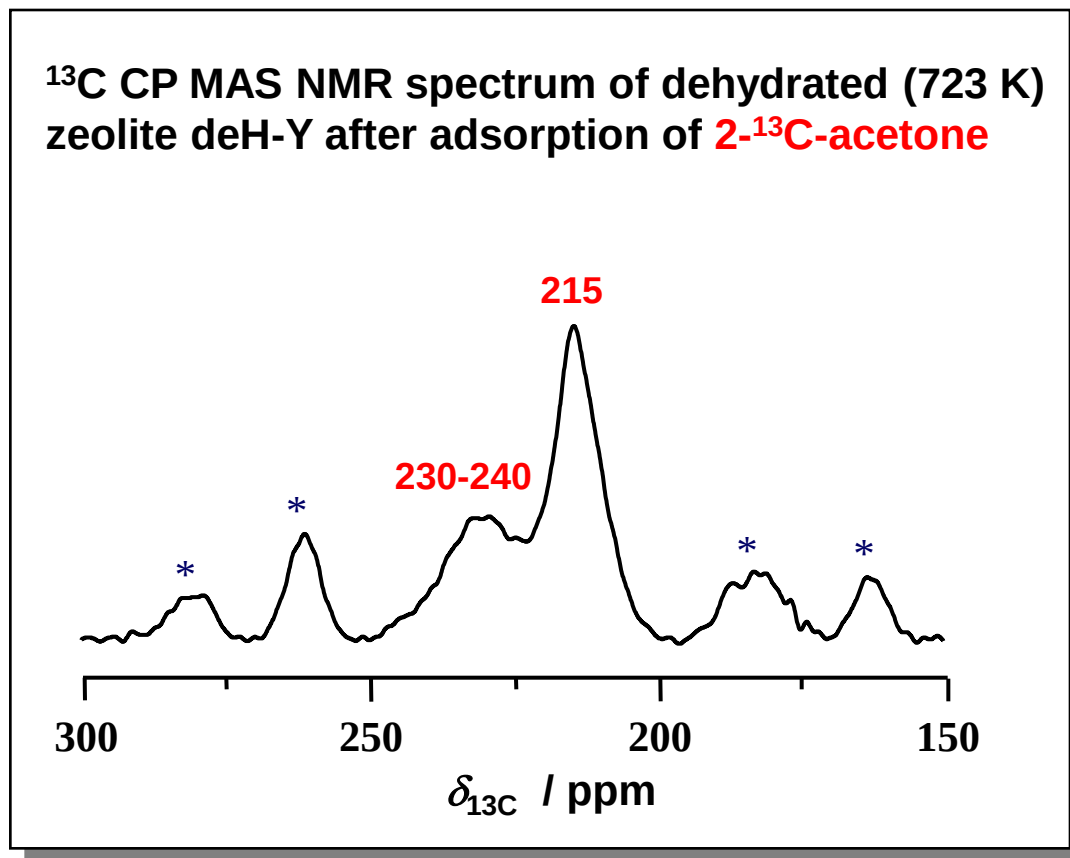
$$F_{\text{N}_2} = 15 \text{ ml/min}$$



Probing Lewis acid sites of dealuminated zeolite H-Y

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

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



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

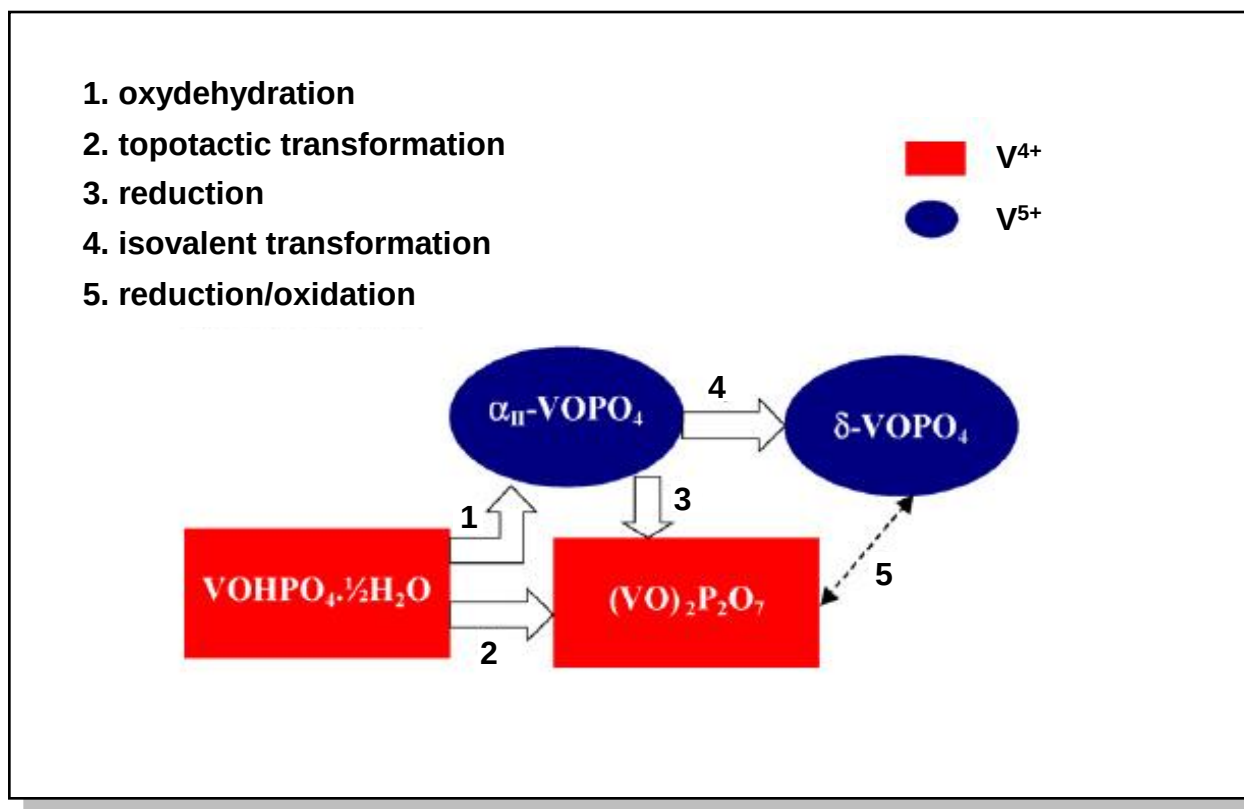
Assignments of UV/Vis bands (π - π^* transitions) observed during the methanol-to-olefin conversion on H-SAPO-34 at 523 to 673 K

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.

Structural transformations of vanadyl phosphates

- suggested transformation of the $\text{VOHPO}_4 \cdot 0.5 \text{H}_2\text{O}$ precursor during the formation of active VPO bulk catalysts



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

activated,
dehydrated at 723 K

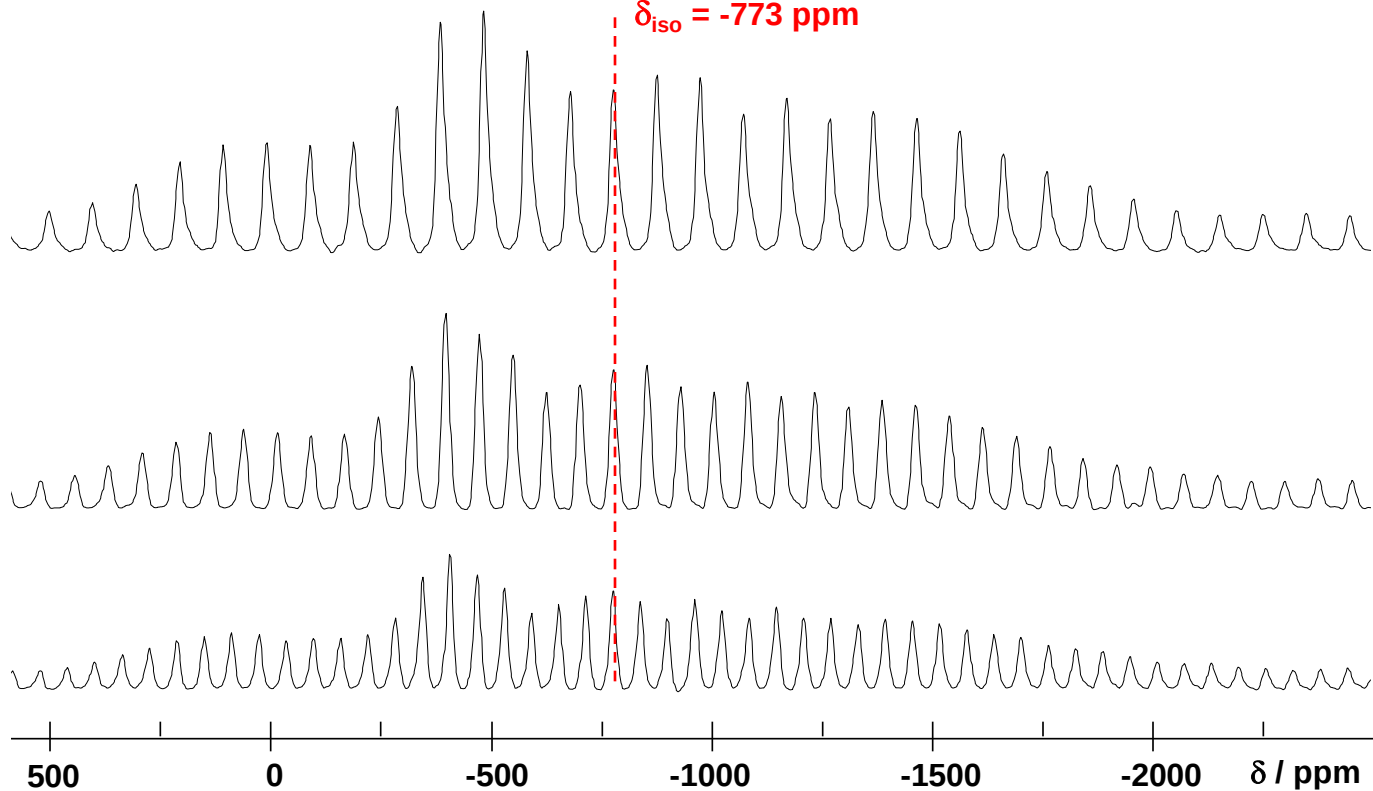
$\nu_0 = 105.25$ MHz
NS ca. 24000

$\nu_{\text{rot}} = 10.0$ kHz

$\nu_{\text{rot}} = 8.0$ kHz

$\nu_{\text{rot}} = 6.5$ kHz

$\delta_{\text{iso}} = -773$ ppm



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

^{51}V MAS NMR spectroscopy of vanadium orthophosphates

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

Materials	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
$\alpha_{\text{I}}\text{-VOPO}_4$	-691 ppm	820 ppm	0.00	1.55 MHz	0.55	[1]
$\alpha_{\text{II}}\text{-VOPO}_4$	-776 ppm -755 ppm	582 ppm 922 ppm	0.67 0.08	0.83 MHz 0.63 MHz	0.52 0.09	[1] [2]
$\beta\text{-VOPO}_4$	-691 ppm -735 ppm	818 ppm 818 ppm	0.00 0.05	1.99 MHz 1.45 MHz	0.59 0.44	[1] [2]
$\gamma\text{-VOPO}_4/1$	-755 ppm	955 ppm	0.15	0.55 MHz	0.68	[2]
$\gamma\text{-VOPO}_4/2$	-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

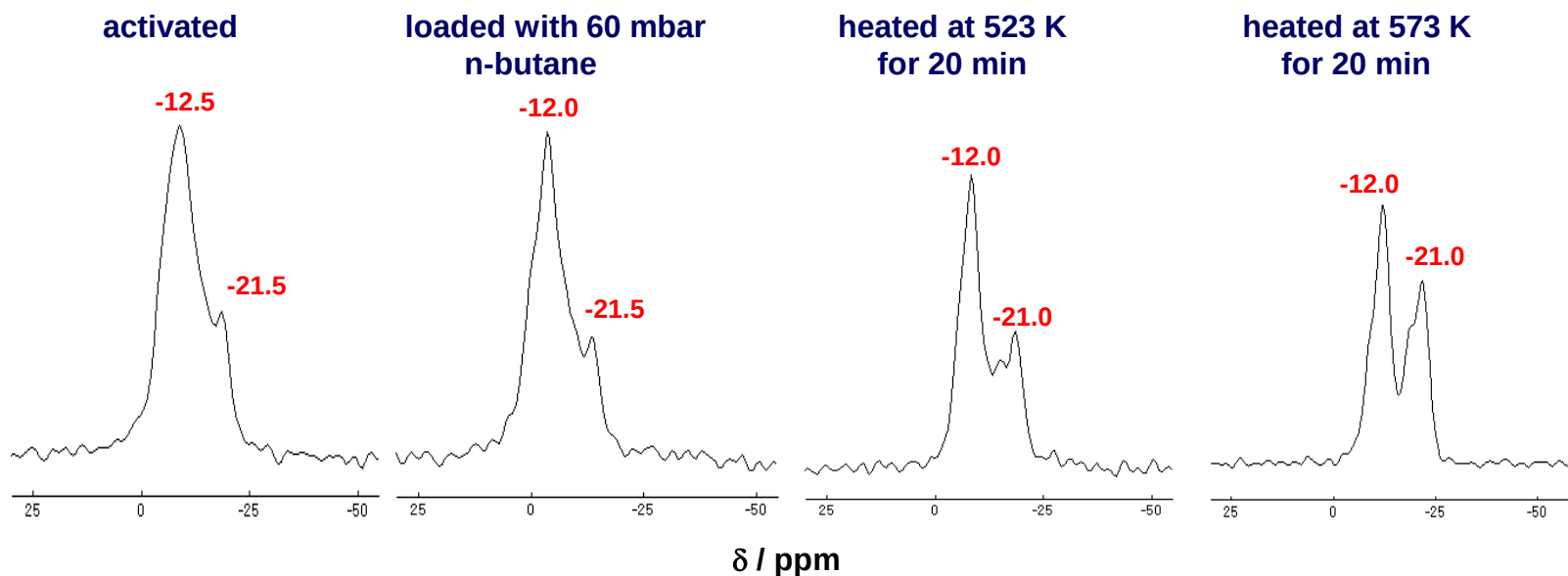
[1] O.B. Lapina et al., J. Mol. Catal. A: Chem. 162 (2000) 381.

[2] R. Siegel et al., Magn. Reson. Chem. 42 (2004) 1022.

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

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

$\nu_0 = 161.98$ MHz, $\nu_{\text{rot}} = 10$ kHz, NS = 200



-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

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



decrease upon conversion of n-butane

³¹P MAS NMR spectroscopy of vanadium orthophosphates

- **³¹P MAS NMR studies of phosphorous atoms at vanadium V⁵⁺ species in VOPO₄ phases:**

³¹P MAS NMR signals	V⁵⁺ phases	References
-20.5 ppm	α_{II}-VOPO₄	[3]
-11.5 ppm	β-VOPO₄	[3]
-21.2 ppm, -17.3 ppm (ca. 1:1) -14.9 ppm (very weak shoulder)	γ-VOPO₄	[3]
-17.6 ppm, -8.4 ppm (ca. 1:1) -6.5 ppm (very weak shoulder)	δ-VOPO₄	[3]
2.7 to 3.6 ppm	α_I-VOPO₄	[4, 5, 6]
3.9 ppm	VOPO₄ · n H₂O	[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.

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

