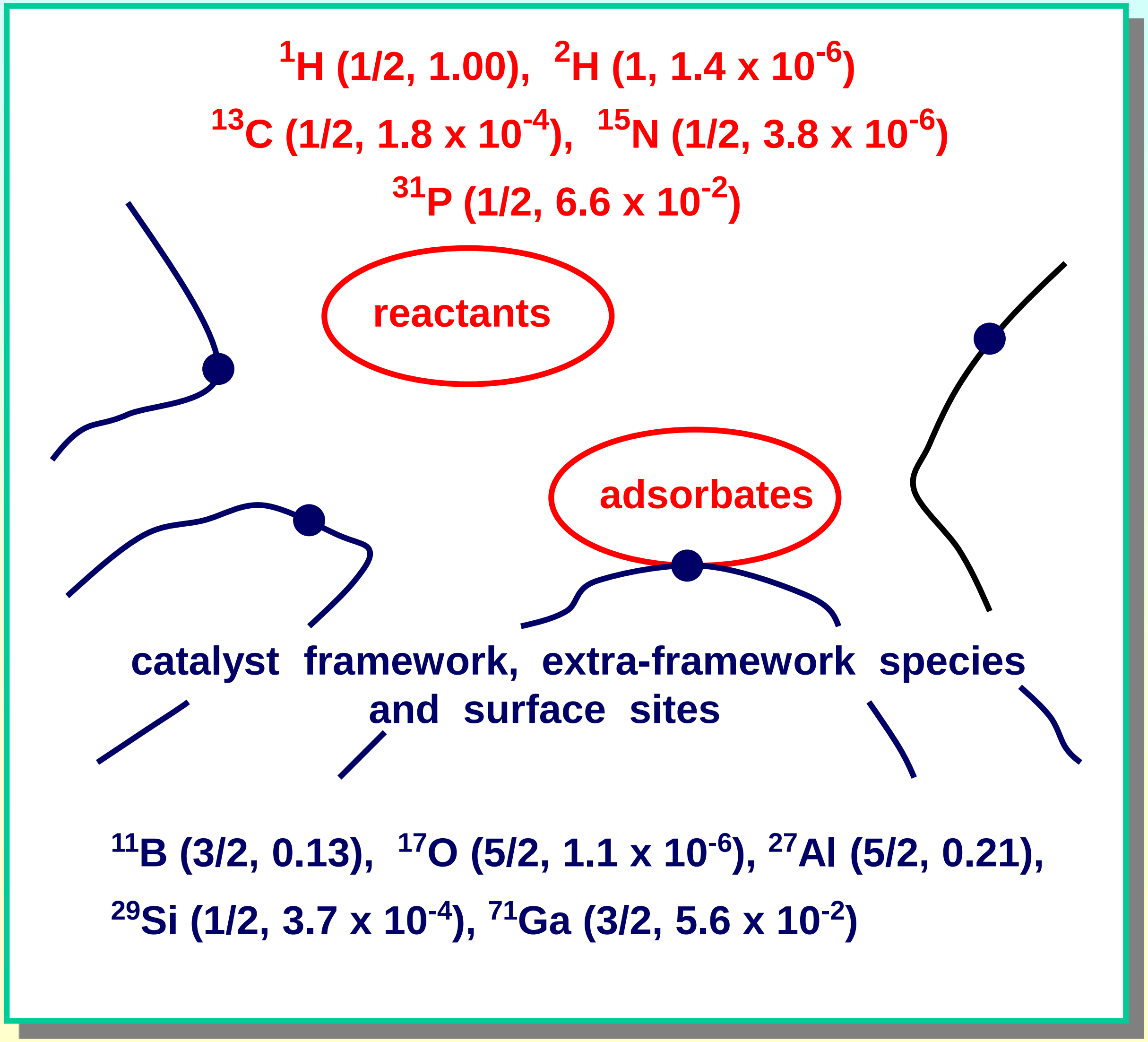
In situ MAS NMR spectroscopy under flow conditions: State of the art and applications

MDR XIX, June 25, 2007

Michael Hunger

Components of heterogeneous reaction systems



^{1}H (1/2, 1.00), ^{2}H (1, 1.4 x 10^{-6})
^{13}C (1/2, 1.8 x 10^{-4}), ^{15}N (1/2, 3.8 x 10^{-6})
^{31}P (1/2, 6.6 x 10^{-2})

reactants

adsorbates

catalyst framework, extra-framework species
and surface sites

^{11}B (3/2, 0.13), ^{17}O (5/2, 1.1 x 10^{-6}), ^{27}Al (5/2, 0.21),
^{29}Si (1/2, 3.7 x 10^{-4}), ^{71}Ga (3/2, 5.6 x 10^{-2})

interesting NMR parameters:

- **isotropic chemical shift values**
- **anisotropy of chemical shift**
- **quadrupolar interaction**
- **intensities of species under study**

Batch contra flow experiments

- 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 of flow MAS NMR spectroscopy

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 $\nu_{\mathrm{CS}} \leq 5 \times 10^3\ \mathrm{s}^{-1}$

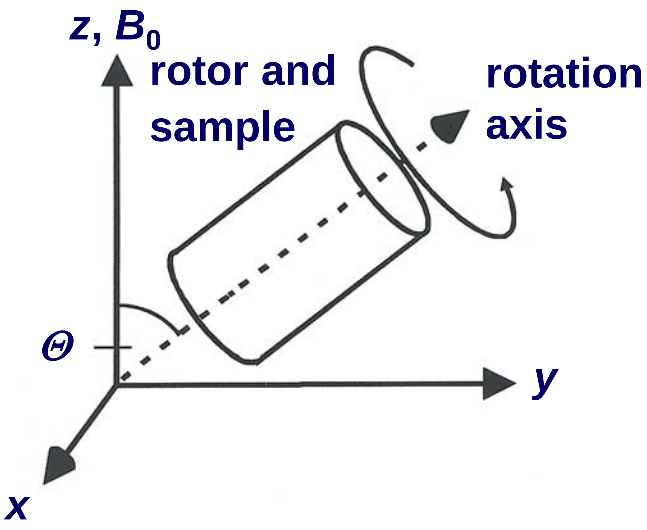
H_{J} : indirect or J-coupling of nuclei via their bond electrons $\nu_{\mathrm{J}} \leq 5 \times 10^2\ \mathrm{s}^{-1}$

Solid-state NMR techniques

spin *I* = ½ :

- **magic angle spinning (MAS)**

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



spin *I* > ½ :

- **double oriented rotation (DOR)**

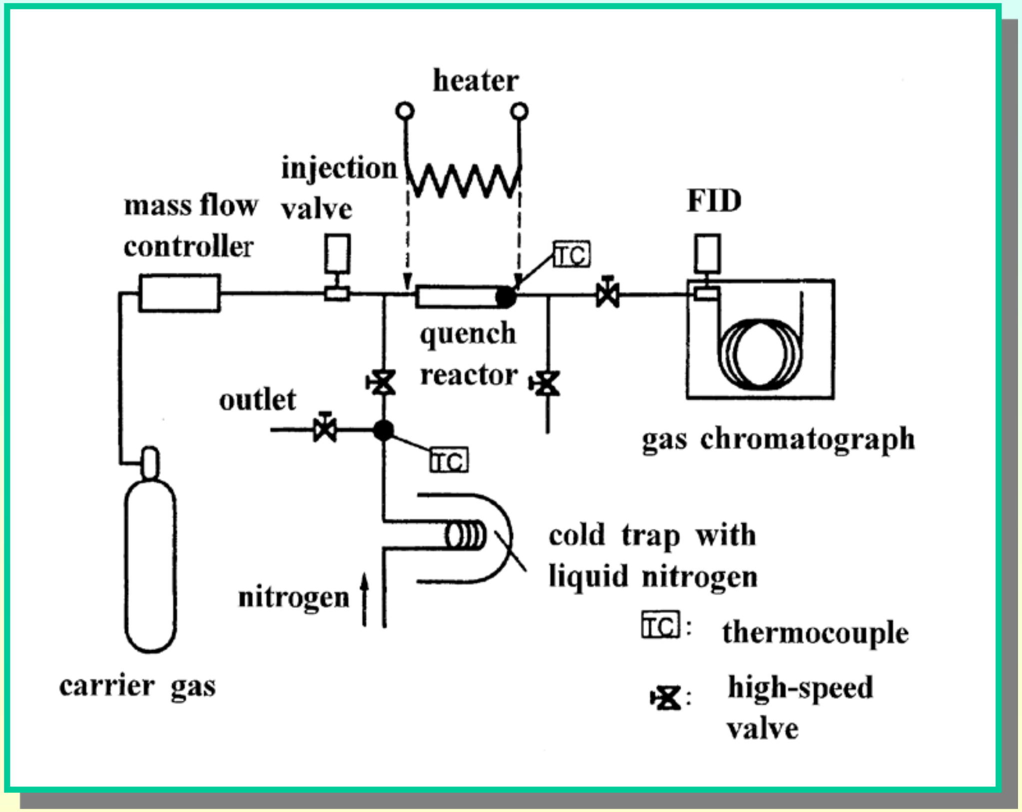
$$\nu_{2QI} = f\,\{35\cos^4\Theta - 30\cos^2\Theta + 3\} \longrightarrow \begin{matrix}\Theta = 30.6^{o} \\ \Theta = 70.1^{o}\end{matrix}$$

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

Ex situ go-and-stop technique 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**

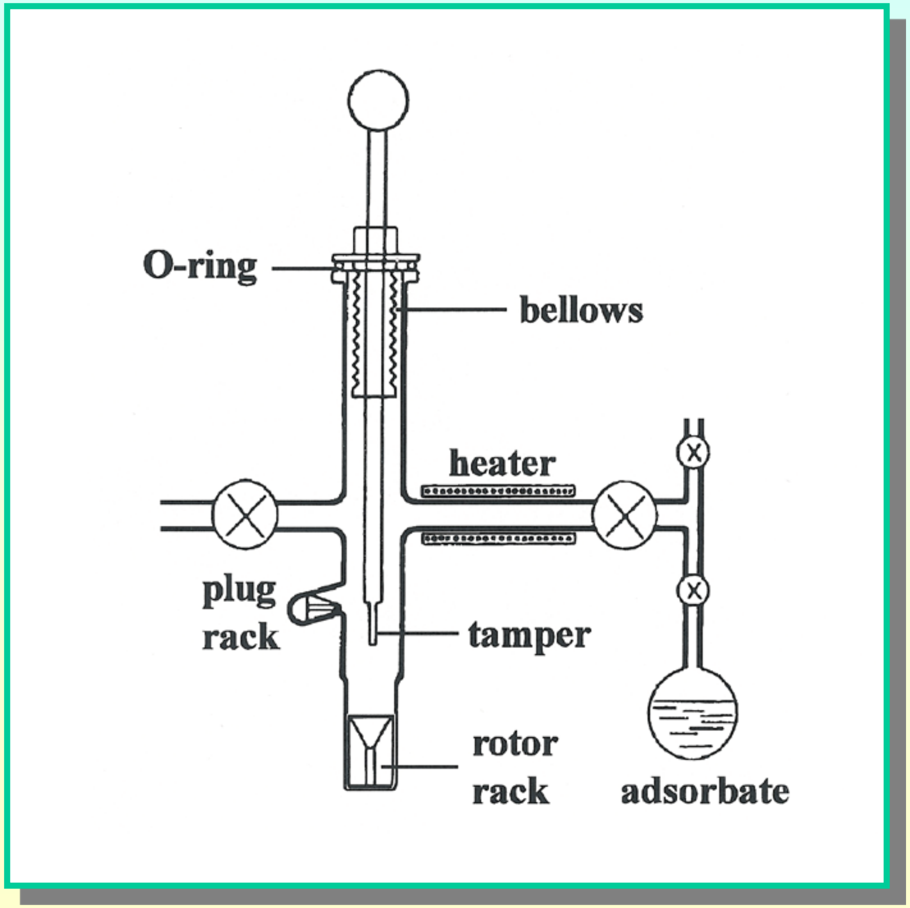
- **NMR investigations:**
  - **transfer of the catalyst loaded with reaction products into an MAS NMR rotor**
  - **measurements performed at room temperature**



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

Ex situ approach for batch and flow experiments in an external reactor

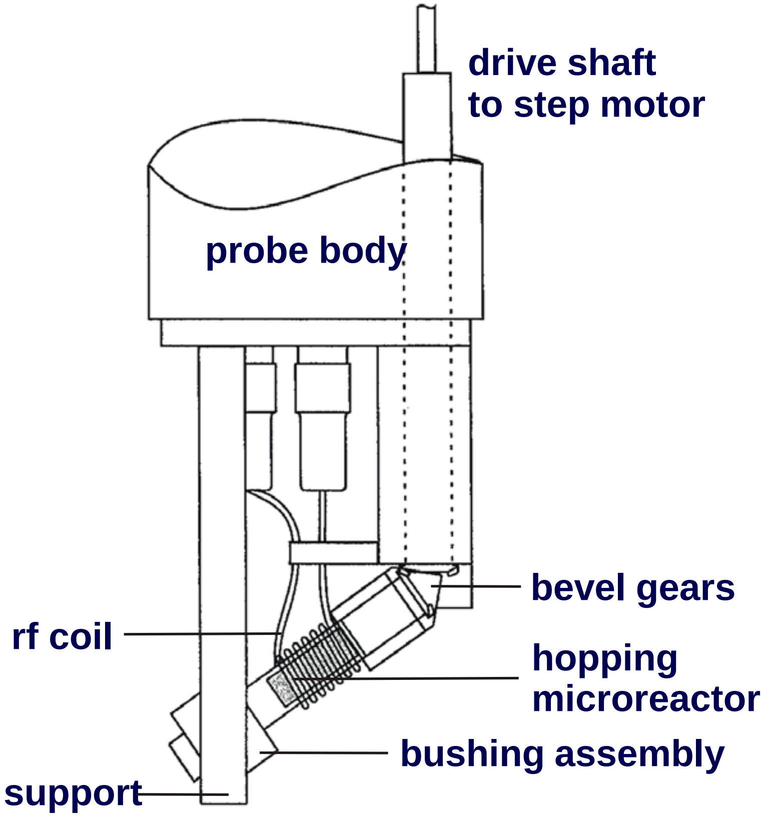
- apparatus for evacuation, loading and catalysis on solid materials in an external reactor
- no contact to air during the transfer of the catalyst material into an MAS NMR rotor
- sealing of the MAS NMR rotor inside the apparatus



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

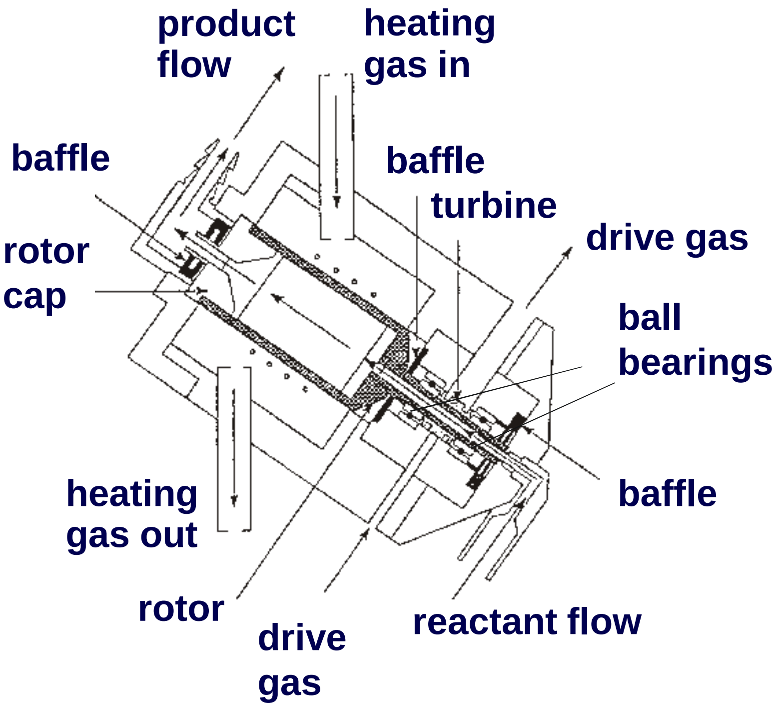
Approaches for in situ flow MAS NMR spectroscopy

flow MAS NMR probe with hopping microreactor (GRASSHopper II)



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

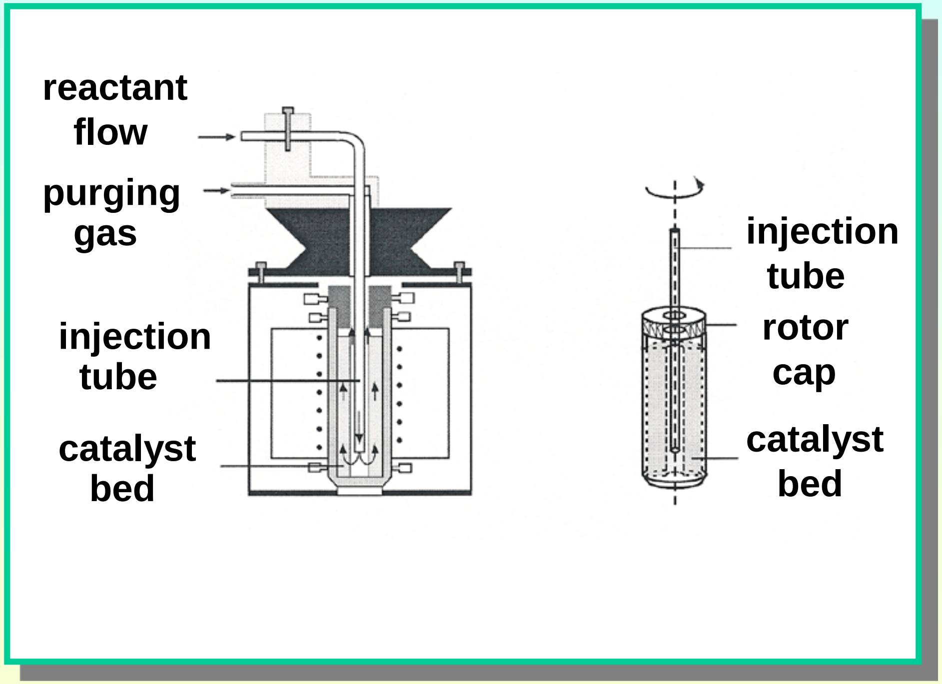
flow MAS NMR probe with ball bearings

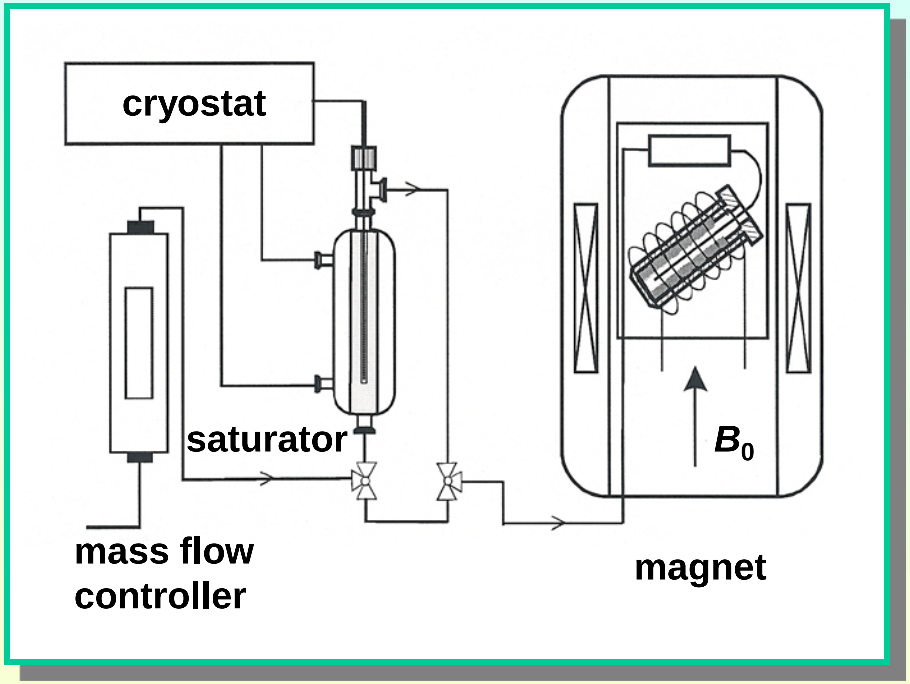


P.K. Isbester et al., Catal. Today 49 (1999) 363.

Technique of in situ flow MAS NMR

scheme of an *in situ* MAS NMR probe

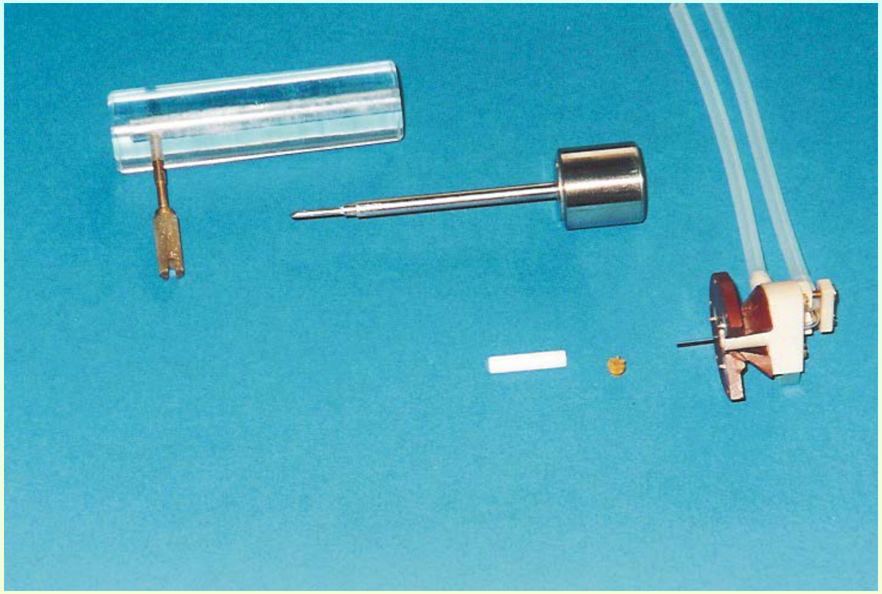


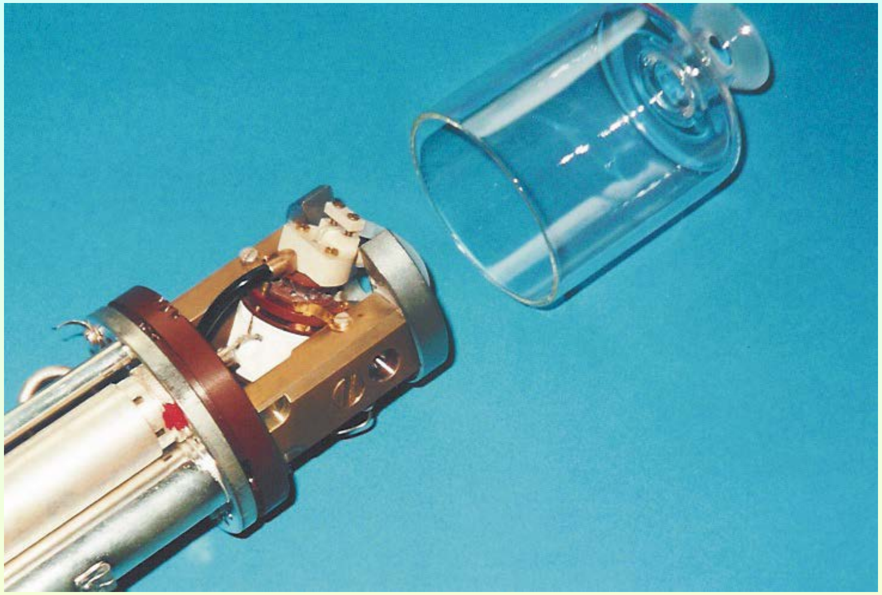


- **injection of reactants into a spinning MAS NMR rotor reactor**

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

Technique of in situ flow MAS NMR



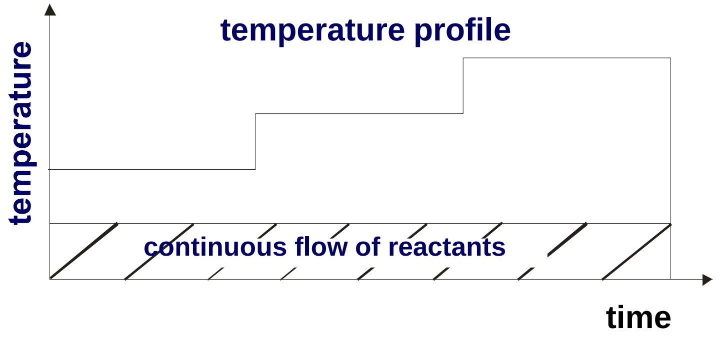


- **modified 4 mm Bruker MAS NMR probe equipped with an injection system**

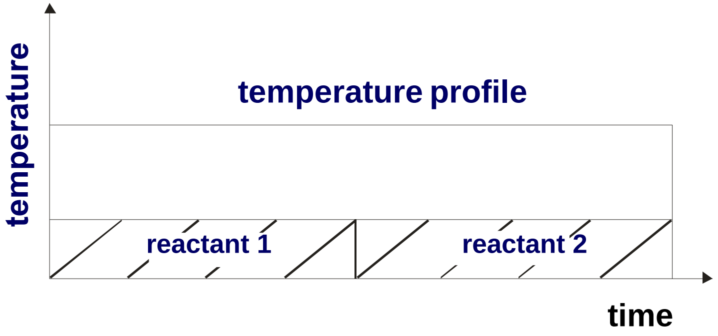
A. Buchholz et al., Microporous & Mesoporous Mater. 57 (2003) 157.

Types of flow experiments I

- continuous-flow experiment



- switched-flow experiment

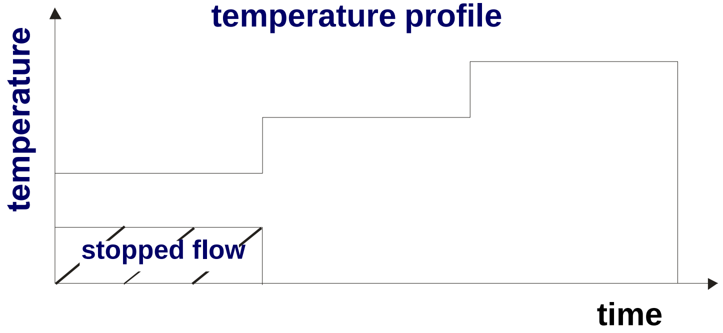


- **continuous-flow experiment:**
  - study of adsorption or conversion of reactants at constant or different temperatures
  - study of formation of stable deposits of catalyst deactivatrion

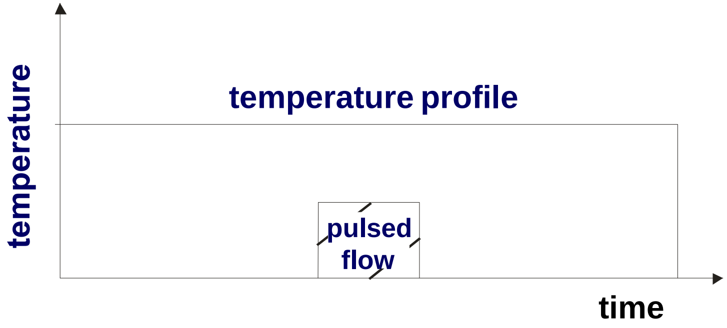
- **switched-flow experiment:**
  - change of isotopic enrichment in reactants
  - study of the response of the composition of reaction products or deposits on the change of reactants

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**

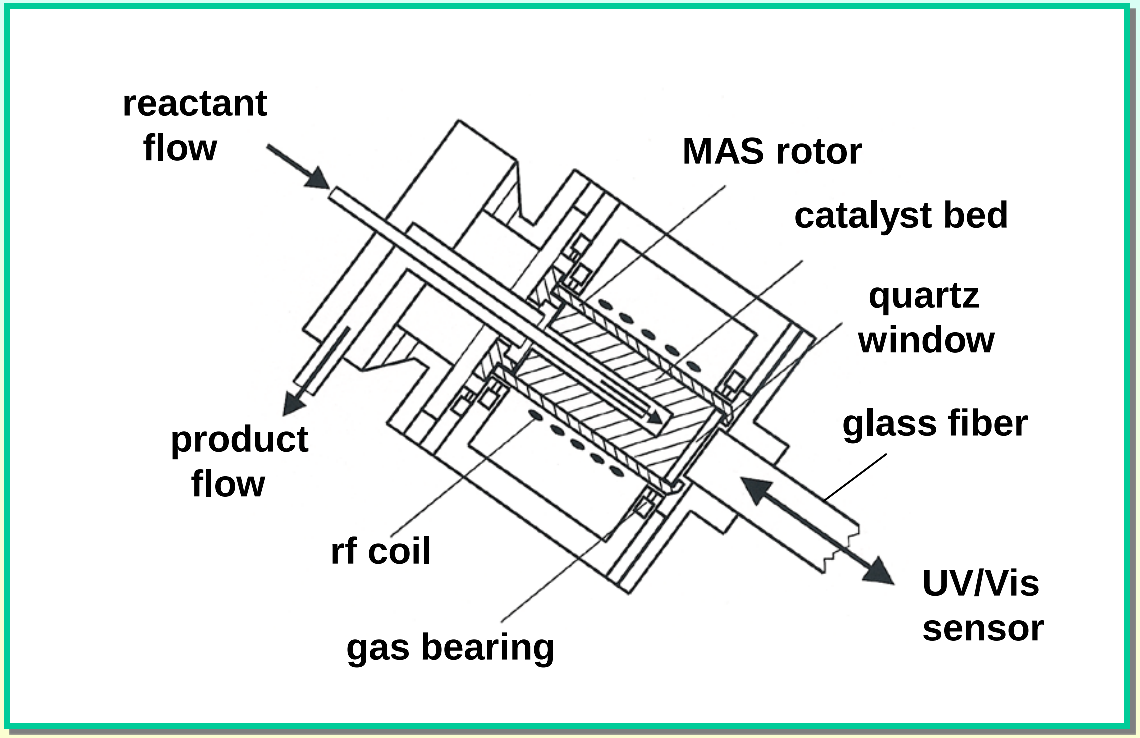
Pulsed-flow technique

- **injection of liquid reactants into the spinning MAS NMR rotor via a micro-pulse pump**

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

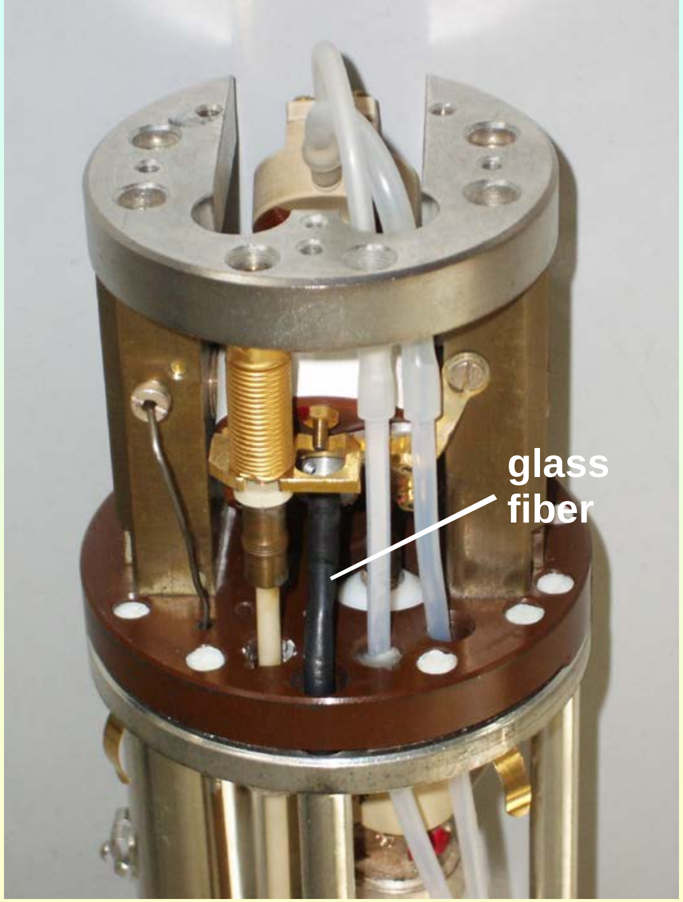
Technique of in situ flow MAS NMR

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

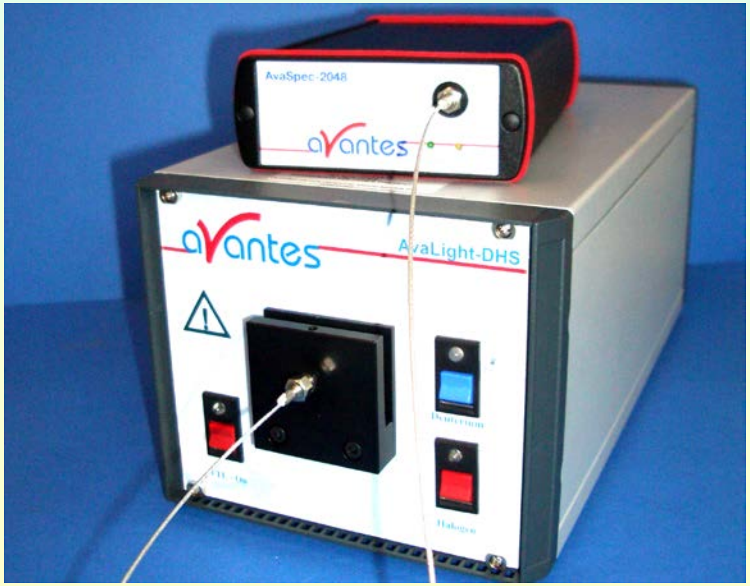


M. Hunger, W. Wang, Chem. Commun. (2004) 584.

Technique of in situ flow MAS NMR



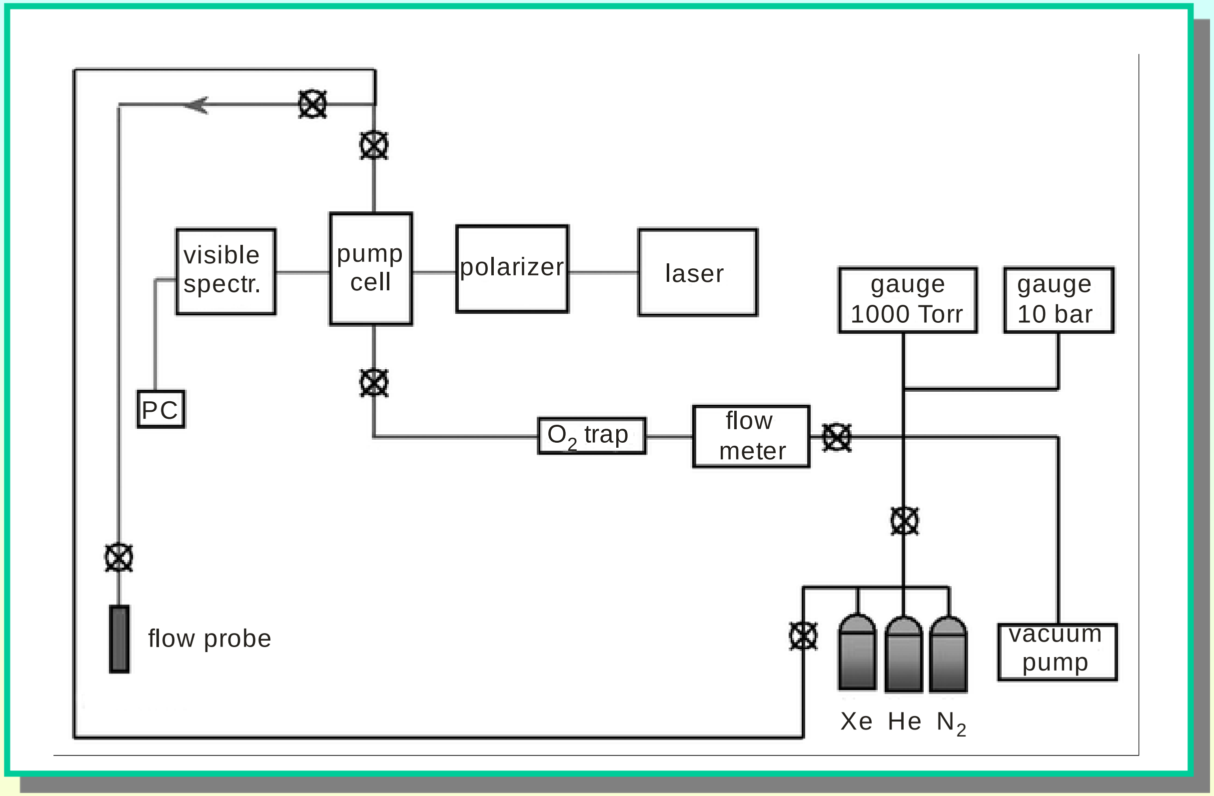
7 mm flow Bruker MAS NMR probe equipped with a glass fiber (left) and UV/Vis light source and spectrometer of Avantes (bottom)



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

Flow experiments with laser-polarized xenon

- **continuous injection of laser-polarized xenon:**
  - **- optical pumping of the D1 transition 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**

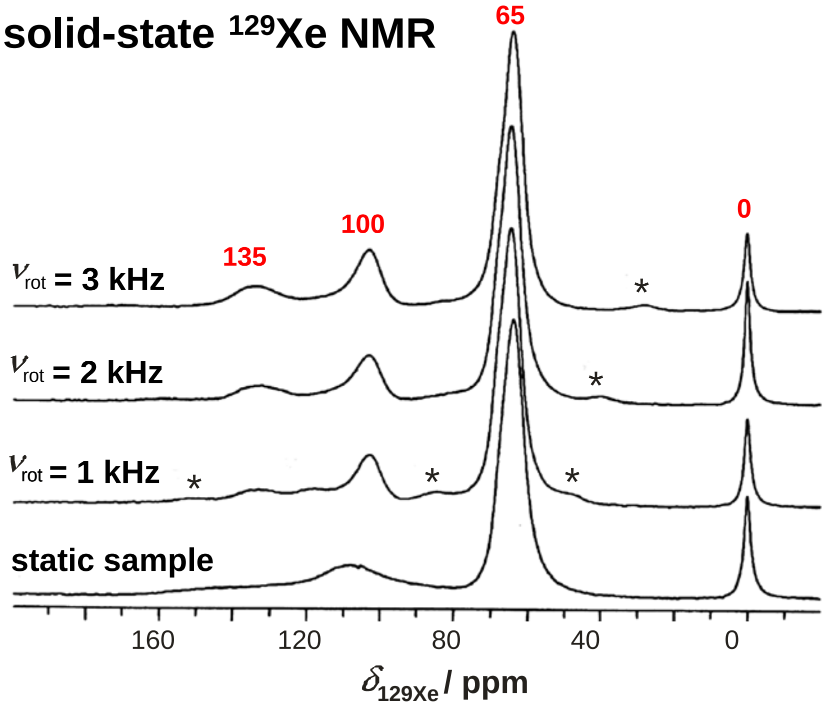
A. Nossov et al., Phys. Chem. Chem. Phys. 5 (2003) 4479.

Applications of flow MAS NMR spectroscopy in materials science and heterogeneous catalysis

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 small cages**
  - **signal at 135 ppm corresponds to xenon in channels**



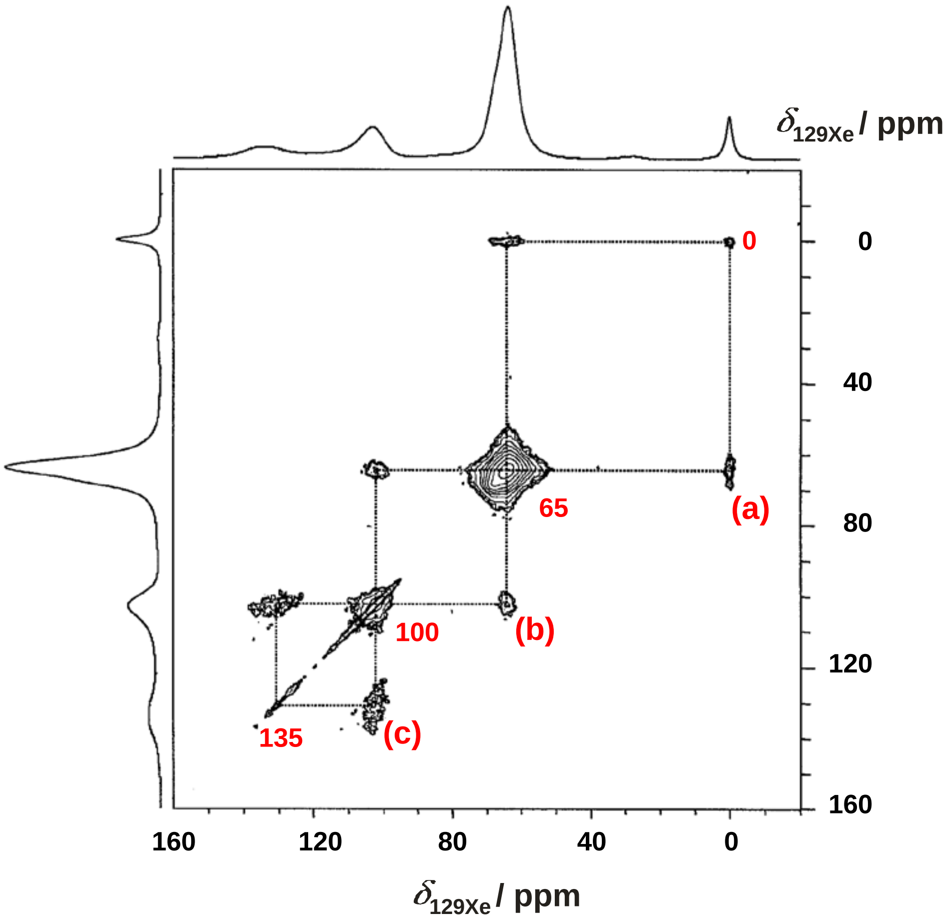
A. Nossov et al., Phys. Chem. Chem. Phys. 5 (2003) 4479.

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

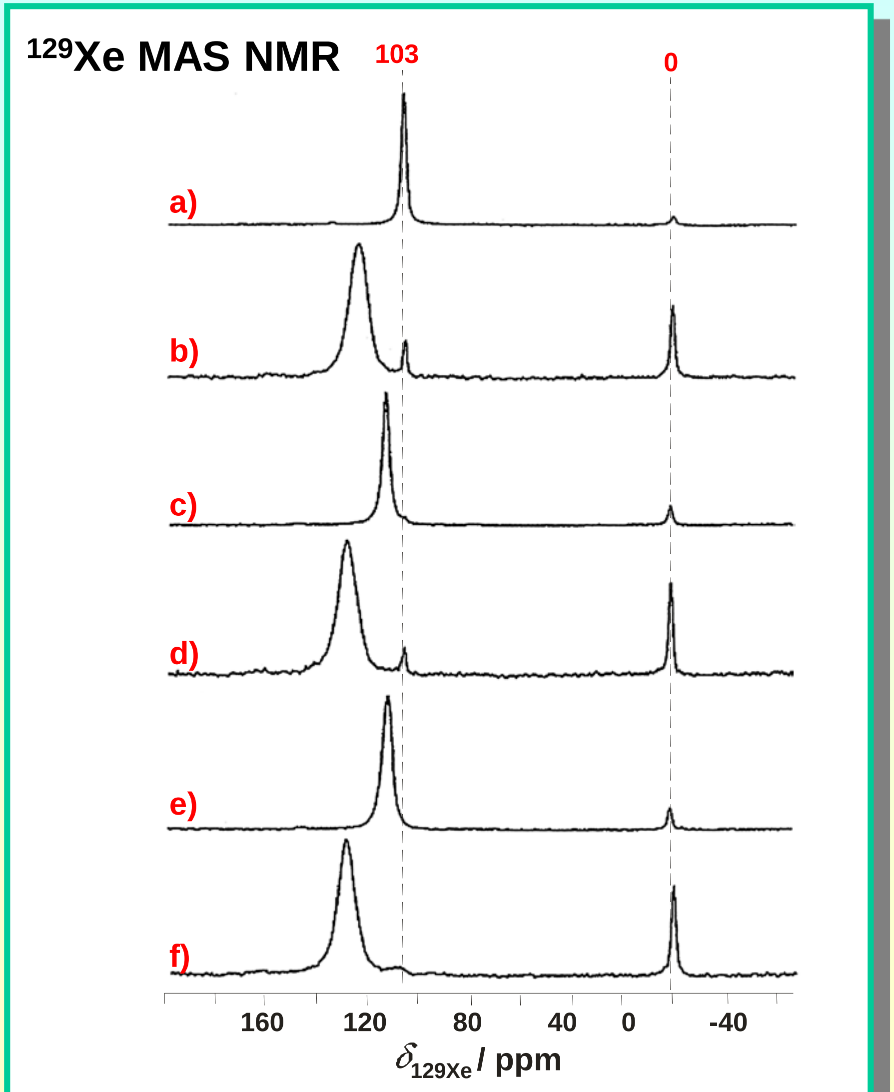


A. Nossov et al., Phys. Chem. Chem. Phys. 5 (2003) 4479.

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 .

Study of the coordination change of aluminum in H-SAPO-34

- ^{1}H MAS NMR of H-SAPO-34:
  - continuous flow of nitrogen saturated with water vapor
  - magnetic field of 9.4 T
  - ν_{rot} = 8.0 kHz
  - ^{1}H MAS NMR signals:

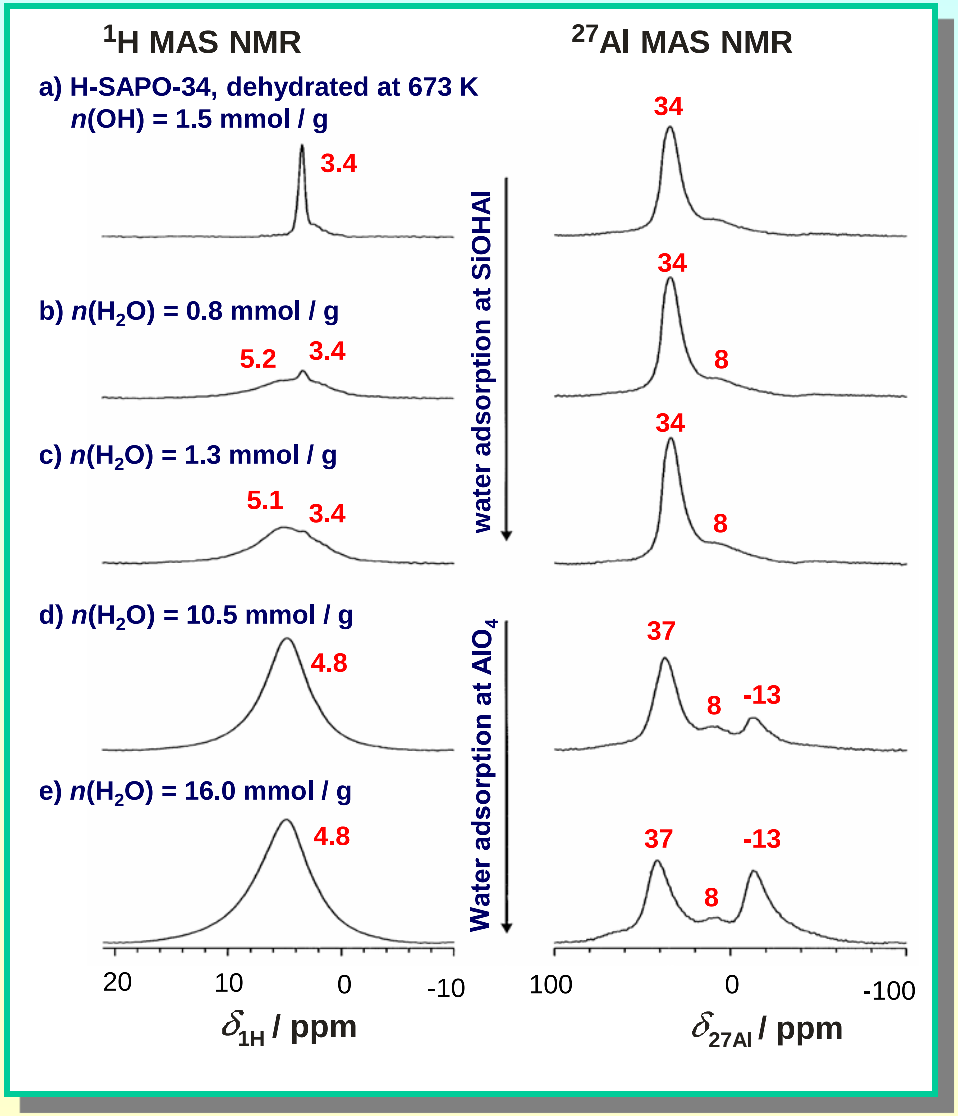
3.4 ppm	SiOHAl
4.8 ppm	bulk water
5.1 ppm	hydrogen bonded water

  - ^{27}Al MAS NMR signals:

34 ppm	Al^{IV}
8 ppm	perturbed Al^{IV}
-13 ppm	Al^{VI}

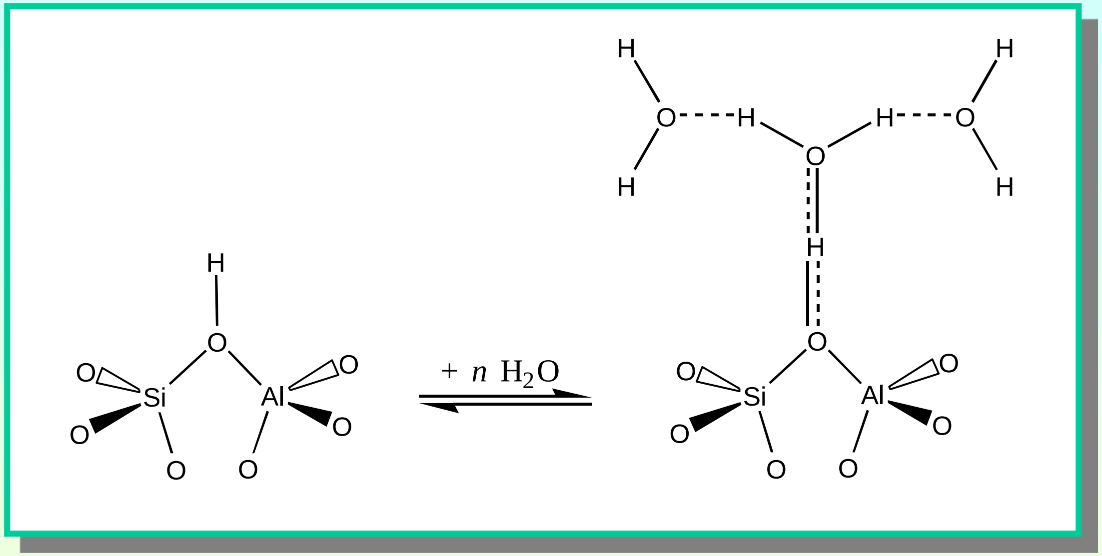
- two-step adsorption process:
  - exclusive adsorption at SiOHAl (a-c)
  - adsorption at AlO_4 (d, e)

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

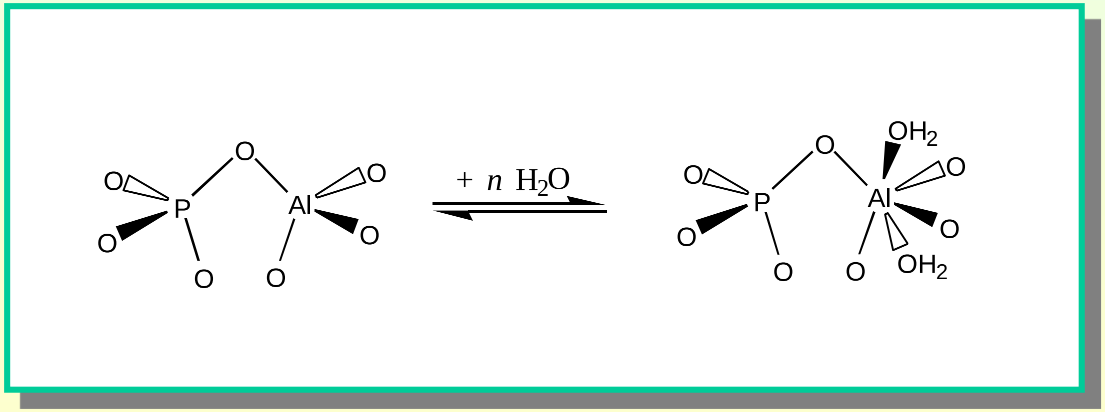


Study of the coordination change of aluminum in H-SAPO-34

- **first step of water adsorption:**
  - **exclusive adsorption at SiOHAl (spectra a-c)**



- **second step of water adsorption:**
  - **coordination to AlO_4 tetrahedra leading to octahedrally coordinated framework Al (spectra d, e)**



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

Study of toluene hydrogenation on Pt/ZrO_2-SO_4 under continuous-flow conditions

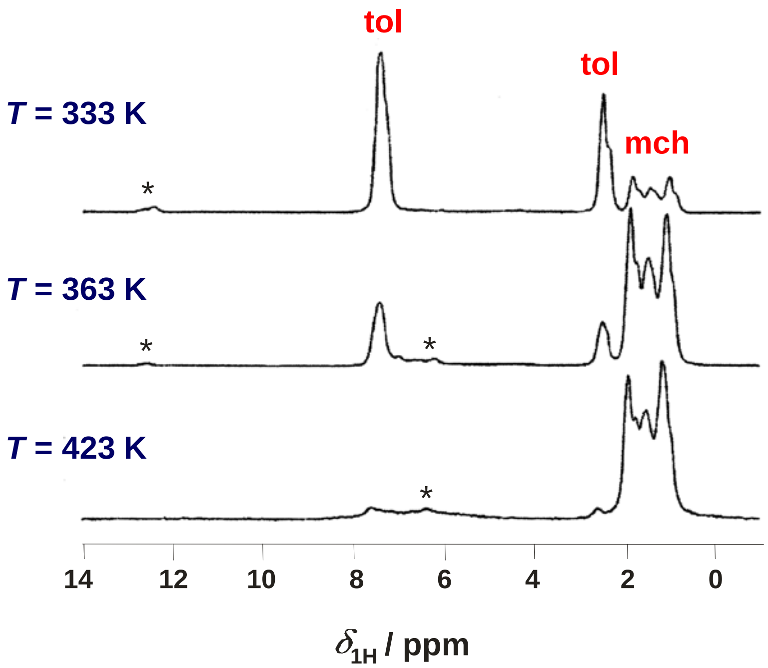
- ^{1}H MASNMR spectroscopy under continuous flow of H_2:
  - hydrogen flow of 100 cm^3 min^{-1} with 1 % hyperpolarized xenon
  - 16 scans per spectrum with repetition time of 10 s in magnetic field of 9.4 T
  - sample spinning rate of 2.1 kHz

- signal assignment:
  - signals at 2.1-2.6 ppm and 6.9-7.6 ppm due to toluene
  - signals at 0.9-1.8 ppm are caused by methylcyclohexane
  - change of signals is fully reversible uppon variation of reaction temperature

$$(C_6H_5)CH_3 \;+\; 5/2\ H_2 \longrightarrow (C_6H_{10})CH_3$$

toluene **hydrogen** **methylcyclohexane**

^{1}H CF MAS NMR



V. Sundaramurthy et al, C.R. Chimie 9 (2006) 459 .

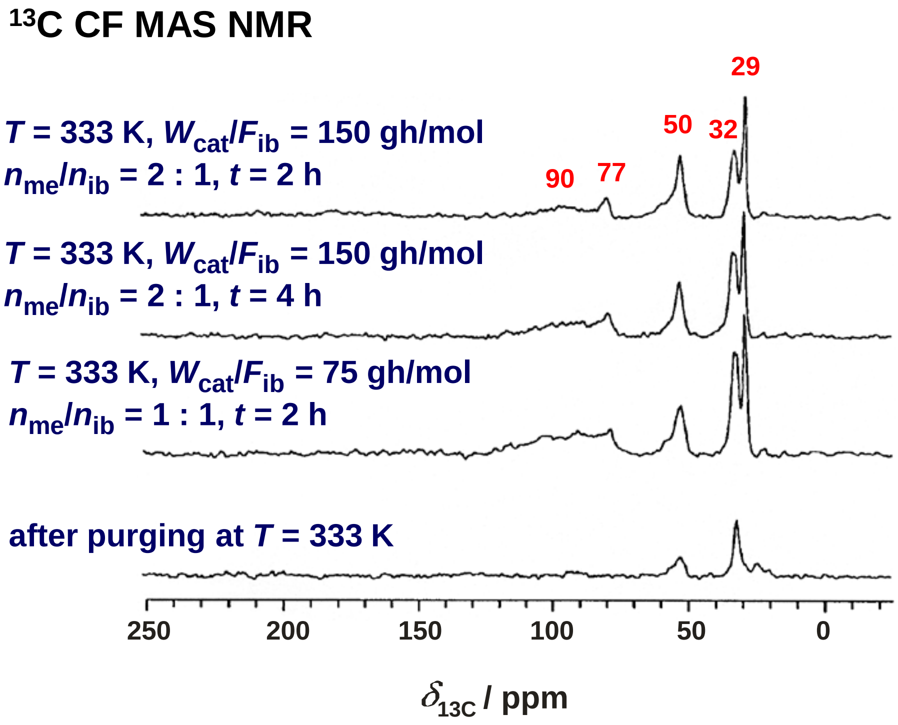
Study of the synthesis of methyl-tert-butylether (MTBE) on zeolite H-Beta

- **^{13}C MAS NMR spectroscopy under continuous flow of isobutene and methanol:**
  - **- 720 scans per spectrum with repetition time of 10 s in magnetic field of 9.4 T**
  - **- sample spinning rate of 2.5 kHz**
  - **- isotops in natural abundance**

- **signal assignment:**
  - **- 32 and 50 ppm: due to methyl groups of isobutene and methanol**
  - **- 77-90 ppm: alkoxy species**
  - **- 29 ppm: methyl groups of alkoxy species**

$$(CH_3)_2C{=}CH_2 + CH_3OH \longleftrightarrow (CH_3)_3COCH_3$$

isobutene **methanol** **MTBE**

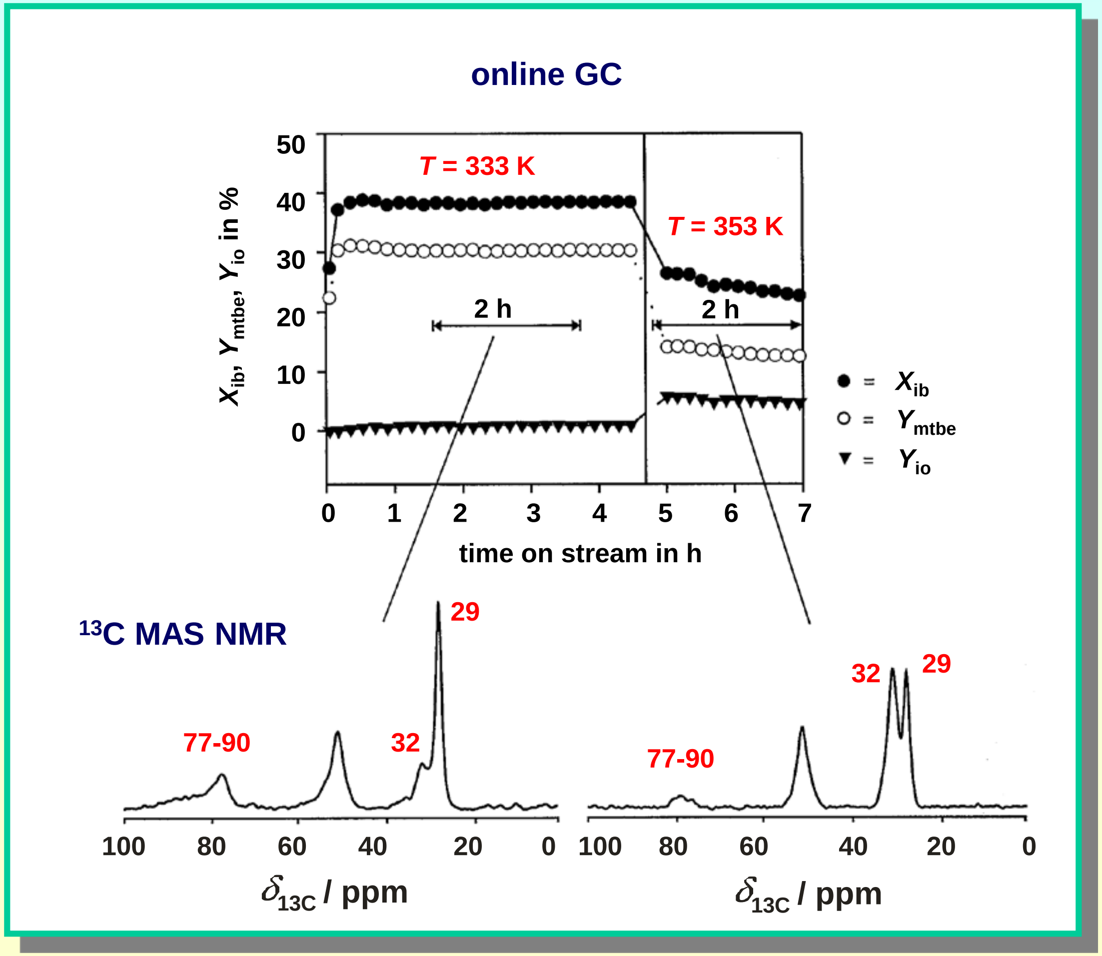


T. Horvath et al, Appl. Catal. A: General 193 (2000) 227.

Study of the synthesis of MTBE on zeolite H-Beta under continuous-flow conditions

- **^{13}C MAS NMR spectroscopy under continuous flow of isobutene and methanol:**
  - **flow of W_{cat}/F_{ib} = 150 gh/mol**
  - **720 scans per spectrum with repetition time of 10 s in magnetic field of 9.4 T**
  - **sample spinning rate of 2.8 kHz**

- **message:**
  - **simultaneous change of the yield of MTBE (online GC) and signals of alkoxy species indicates catalytic role of these surface compounds**



T. Horvath et al, Appl. Catal. A: General 193 (2000) 227.

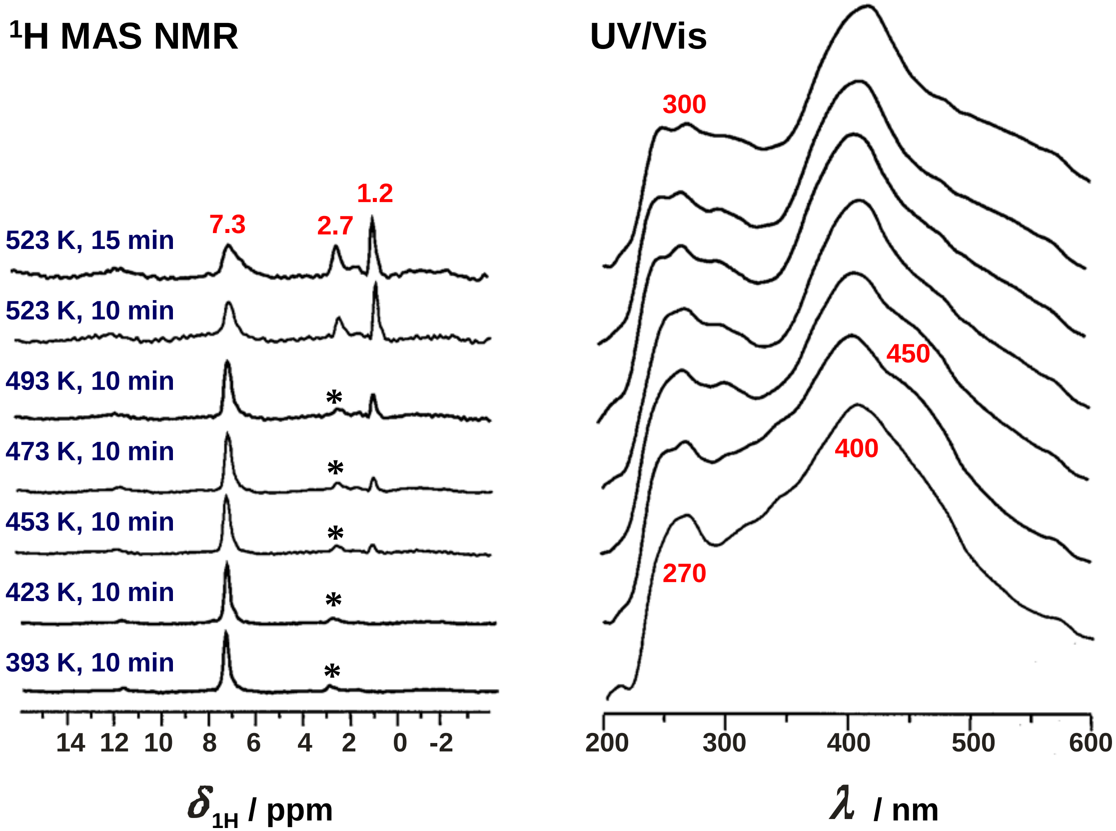
Study of the side-chain H/D exchange of ethylbenzene on dealuminated zeolite Y

- ^{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)

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

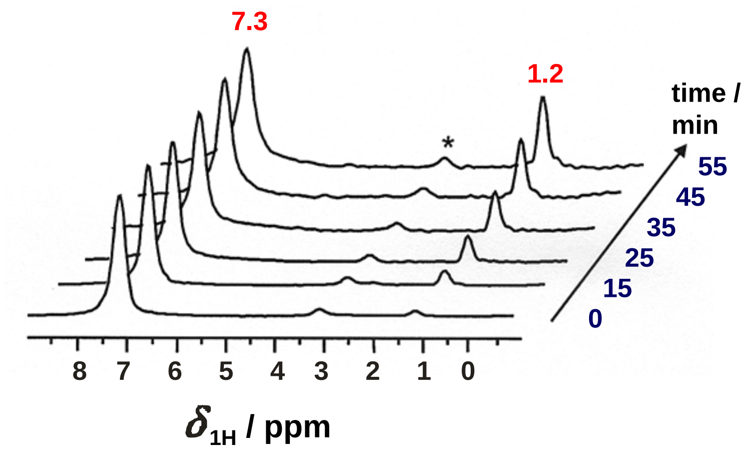
7.3 ppm   3.8 ppm   2.7 ppm   1.2 ppm



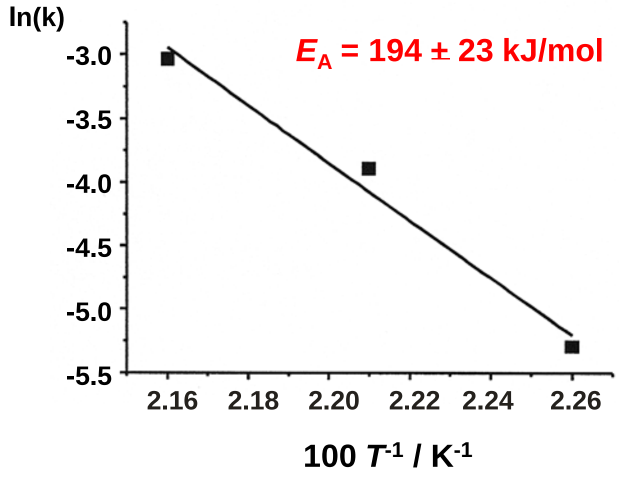
J. Huang et al, submitted.

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:**

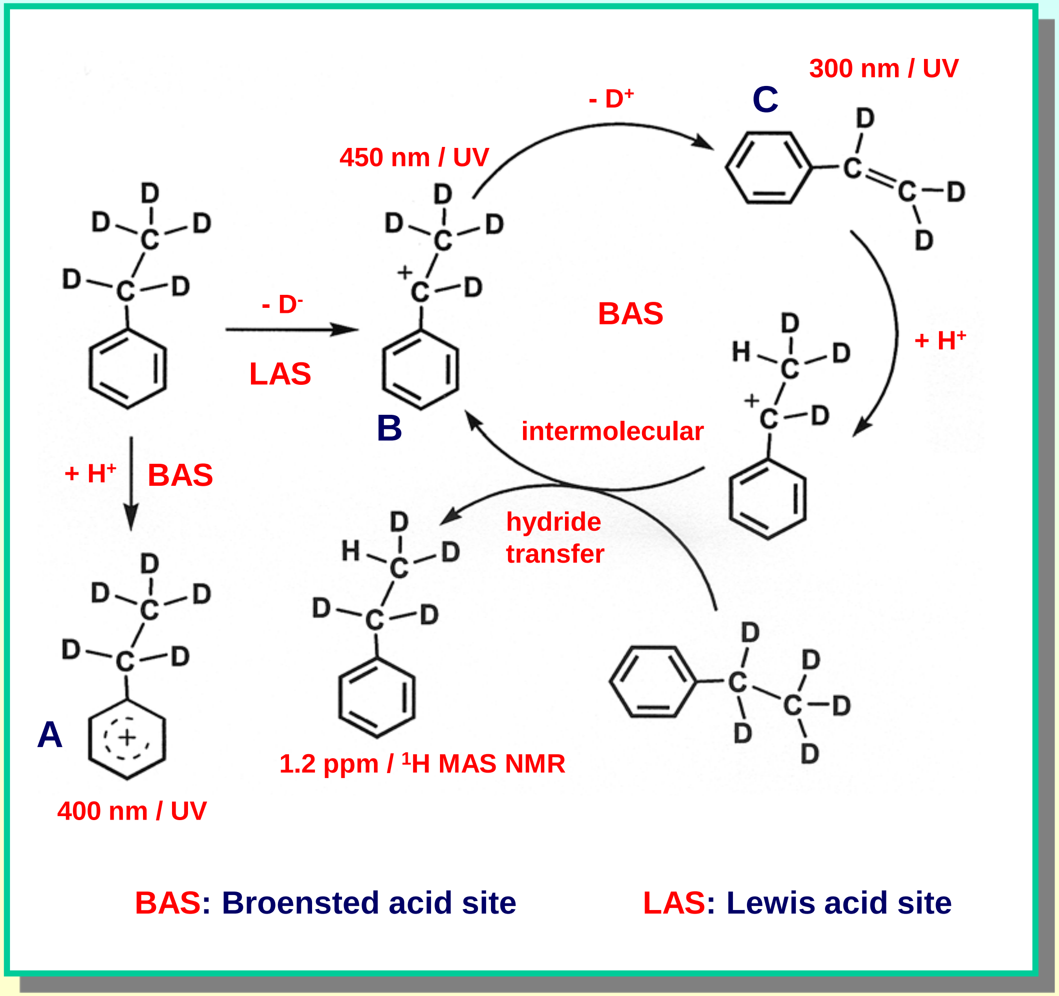
  - activation energy of the regioselective H/D exchange (194 kJ/mol) indicates that a hydride transfer reaction is the rate determining step

J. Huang et al, submitted.

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

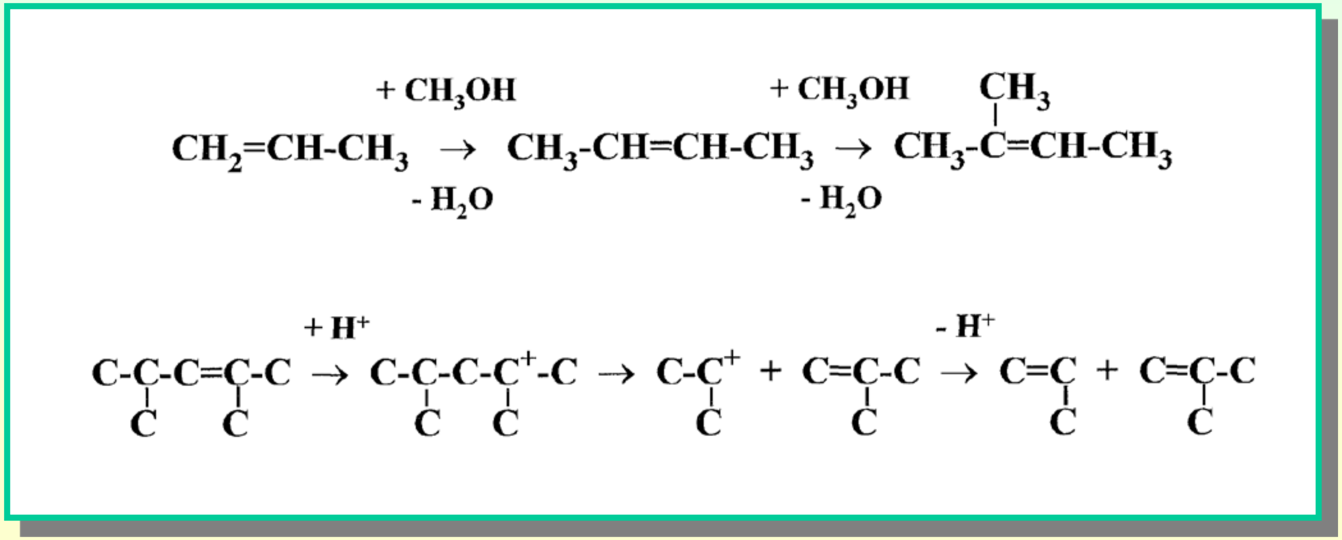


J. Huang et al, submitted.

Methanol-to-olefin (MTO) conversion on acidic zeolites

reaction mechanisms proposed in the literature:

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

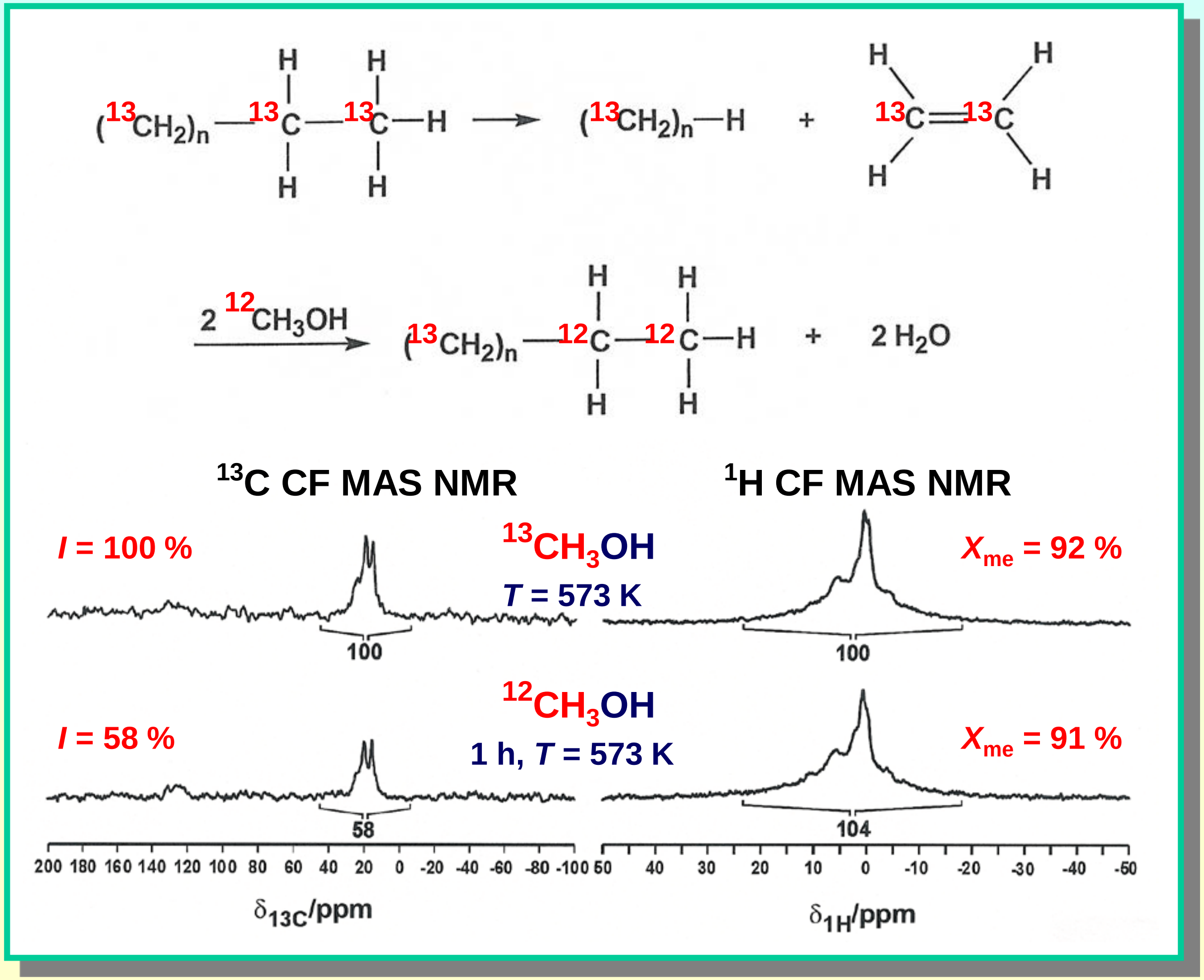


$$CH_2{=}CH{-}CH_3 \xrightarrow[-\,H_2O]{+\,CH_3OH} CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[-\,H_2O]{+\,CH_3OH} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3$$

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

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

Role of alkylated carbon pool compounds in the MTO process



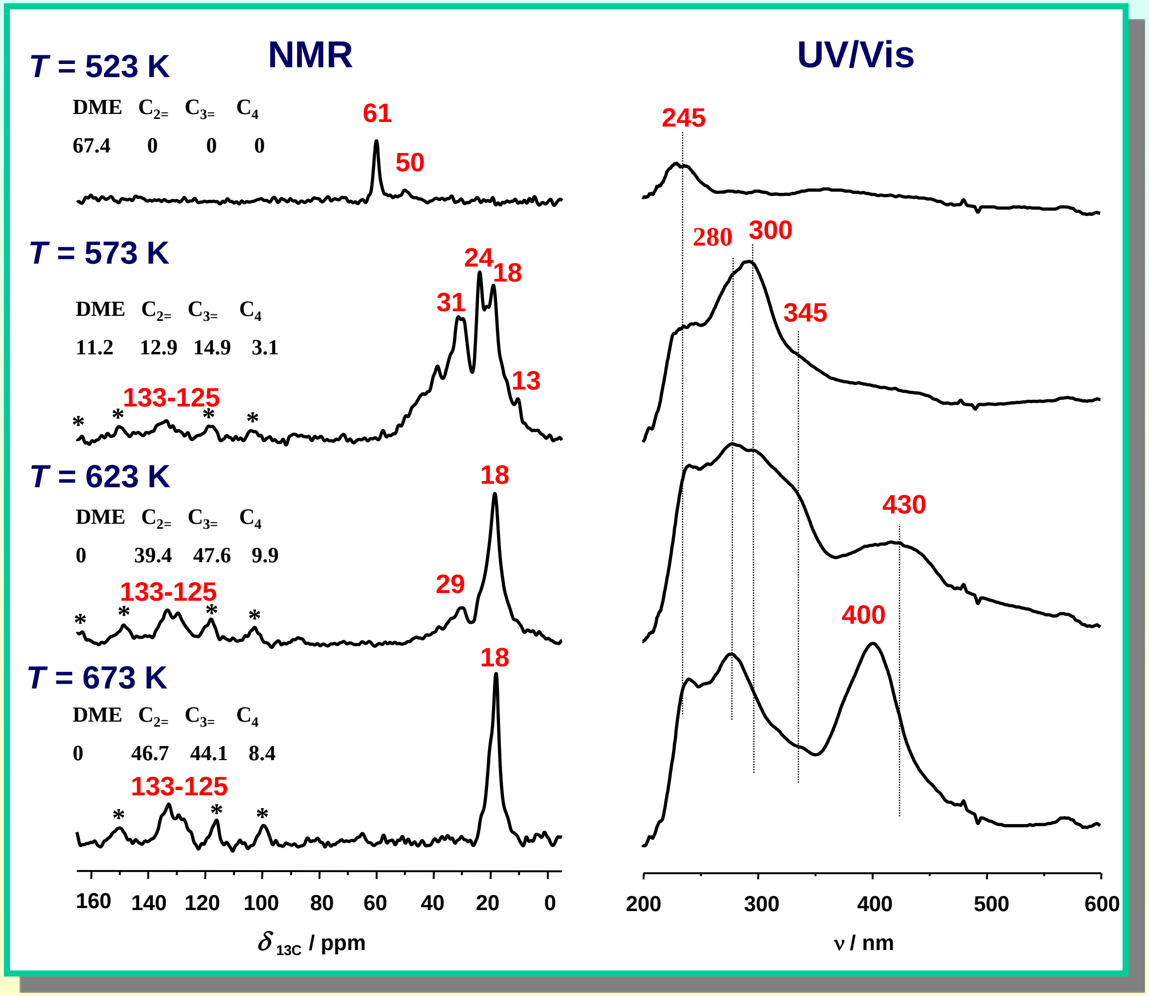
switching of the reactant flow induces a decrease of the ^{13}C-isotopes in the alkyl groups:

- → **alkyl groups are involved in the formation of olefins**
- → **carbon pool plays an active role in the MTO process**

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

Study of the formation of organic deposits

In situ ^{13}C MAS NMR-UV/Vis spectroscopy of coke formation on H-SAPO-34 at 523 to 673 K for 3 h 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) doi.org/10.1016/j.micromeso.2007.05.028.

Assignments of UV/Vis bands

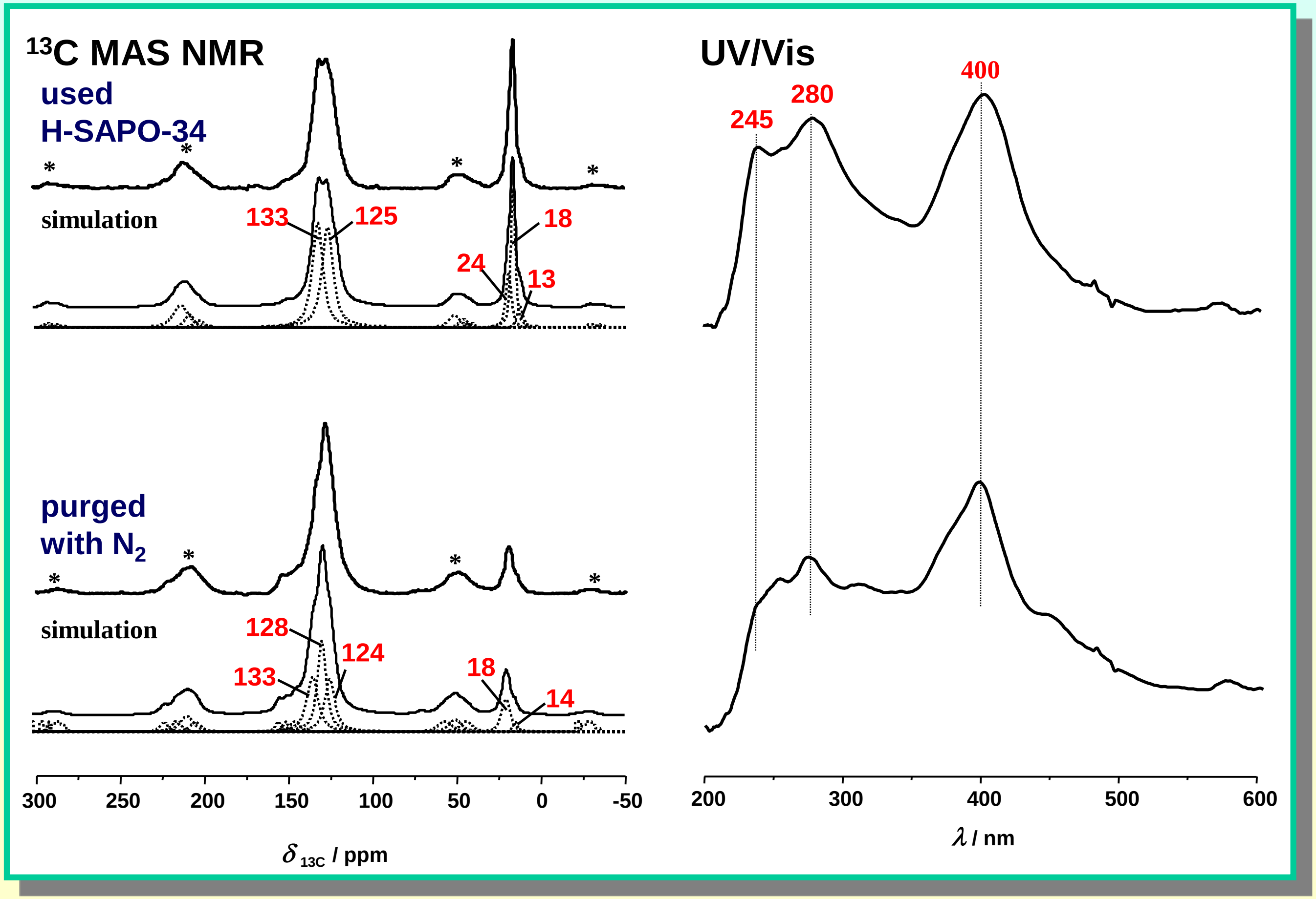
UV/Vis bands (π-π* transitions) observed during methanol-to-olefin conversion on H-SAPO-34 at 523-673 K

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

Ref.: 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.

Study of the stability 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)

Y. Jiang et al., Microporous Mesoporous Mater. (2007) doi.org/10.1016/j.micromeso.2007.05.028.

Results of catalyst purging

Quantitative evaluation of the ^{13}C MAS NMR spectra of used H-SAPO-34 before and after purging with N_2

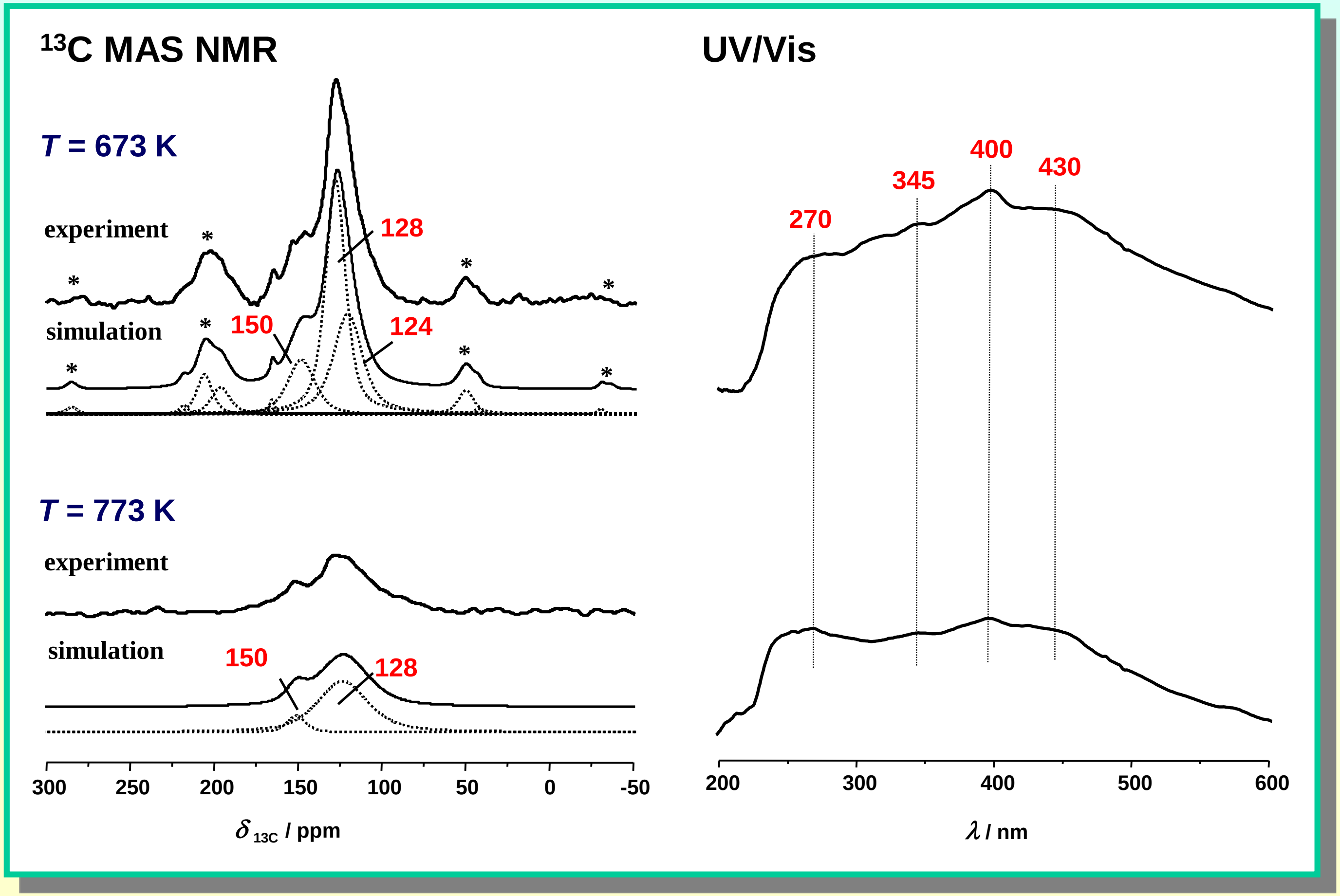
Signal at δ_{13C} /ppm	Assignments	Number in mmol/g		
		reaction at 623 K	reaction at 673 K	purging with N_2 at 673 K
16-21	methyl groups bound to aromatics	1.87	0.53	0.31
14-15 and 22-29	ethyl groups bound to aromatics	0.21	0.08	0.03
23-24 and 33-37	isopropyl groups bound to aromatics	0.15	-	-
125-137	alkylated and non-alkylated aromatic rings	0.55	0.56	0.41

→ **agrees with the stronger decrease of UV/Vis bands of alkylated aromatics (280 nm) than of polycyclic aromatics (400 nm)**

Y. Jiang et al., Microporous Mesoporous Mater. (2007) doi.org/10.1016/j.micromeso.2007.05.028.

Study of catalyst regeneration

Regeneration of the 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 poly-cyclic coke (400 nm)

new band of phenolic species (270 nm)

Y. Jiang et al., Microporous Mesoporous Mater. (2007) doi.org/10.1016/j.micromeso.2007.05.028.

Results of catalyst regeneration

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

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

Y. Jiang et al., Microporous Mesoporous Mater. (2007) doi.org/10.1016/j.micromeso.2007.05.028.

Summary

Advantages of *in situ* flow MAS NMR spectroscopy in materials science and heterogeneous catalysis:

- **allows application of laser-polarized xenon for studies of pore systems in solid materials and location of adsorbate complexes**
- **different flow protocols lead to a number of experiments with different messages**
- **required lifetime of intermediates in the case of continuous-flow experiments corresponds to duration of free induction decay**
- **response of spectroscopic parameters on the change of reaction conditions may deliver hints to a catalytic role of surface species**
- **combination with other analytical methods leads to complementary messages**

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Temperature behavior of the flow MAS NMR probe

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

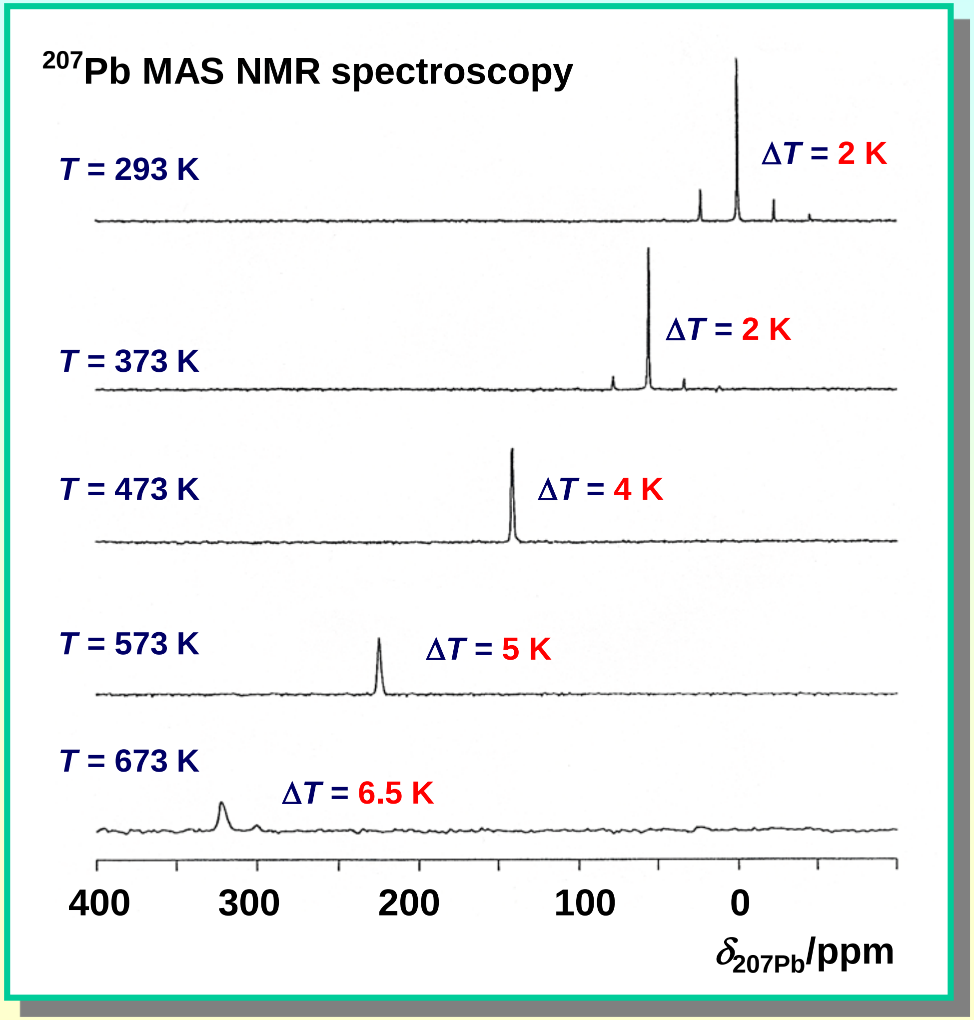
  $\Delta T / \Delta \delta$ = 1.29 K / ppm *

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

  ν_0 = 83.2 MHz

  ν_{rot} = 2.5 kHz

  F_{N2} = 15 ml/min



^{207}Pb MAS NMR spectroscopy

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