Solid-State NMR as an Analytical Tool for the Development of Catalyst Systems

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Solid-state NMR of solid catalysts

I. Synthesis of catalysts ⟷
- nature and local structure of framework atoms
- framework defects and amorphous phases

↓

II. Modification of catalysts ⟷
- incorporation and release of framework atoms
- nature and location of extra-framework species and cations

↓

III. Tailoring of surface sites ⟷
- number, strength, and accessibility of Brønsted acid sites
- presence and strength of base sites
- presence of Lewis acid sites

↓

IV. Catalytic applications ⟷
- adsorbate complexes and intermediates formed on surface sites
- reaction mechanisms
- reasons of catalyst deactivation

↓

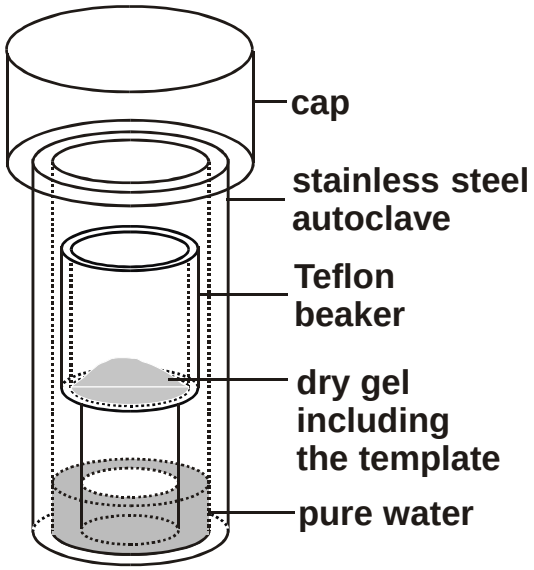
topics I to IV

I. Synthesis of catalysts

I. Synthesis of catalysts

steam-assisted dry-gel conversion (SAC) for the synthesis of zeolites

autoclave volume: 110 cm^3
Teflon beaker: 14.5 cm^3

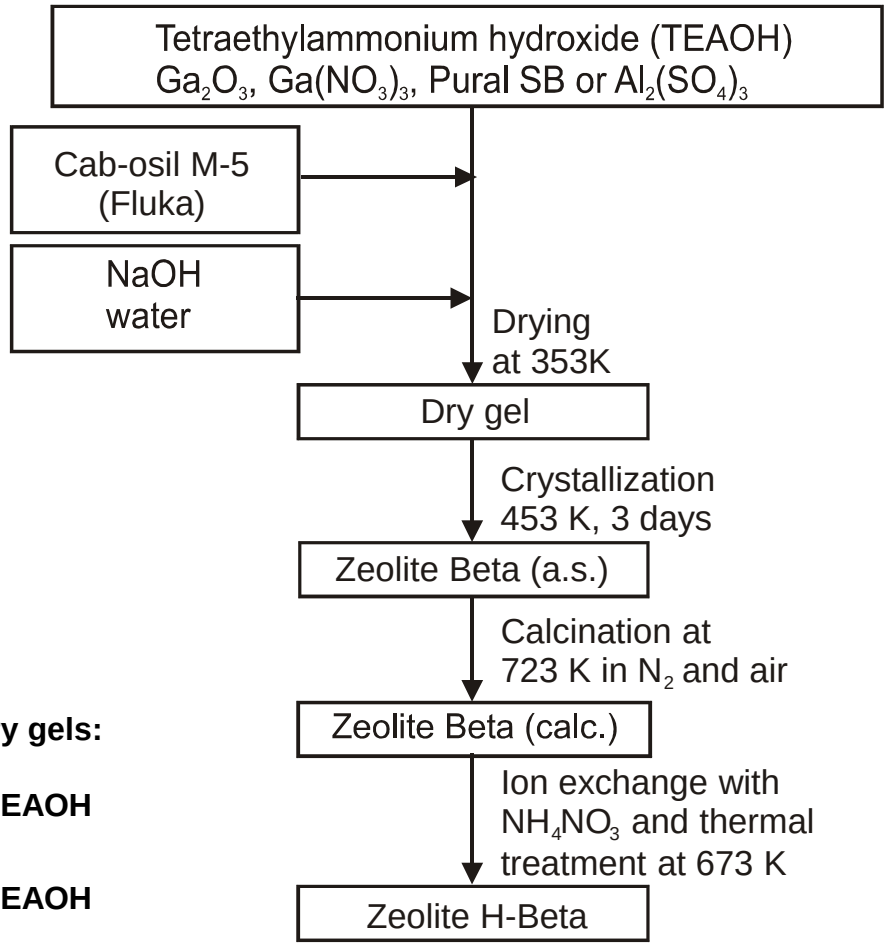


molar compositions of the dry gels:

17.0 –76.1 SiO_2 : Ga_2O_3 :
0.5-2.2 Na_2O : 6.2-27.9 TEAOH

25.2 –68.0 SiO_2 : Al_2O_3 :
0.7-2.0 Na_2O : 9.3-25.2 TEAOH

zeolite [Al]Beta and [Ga]Beta

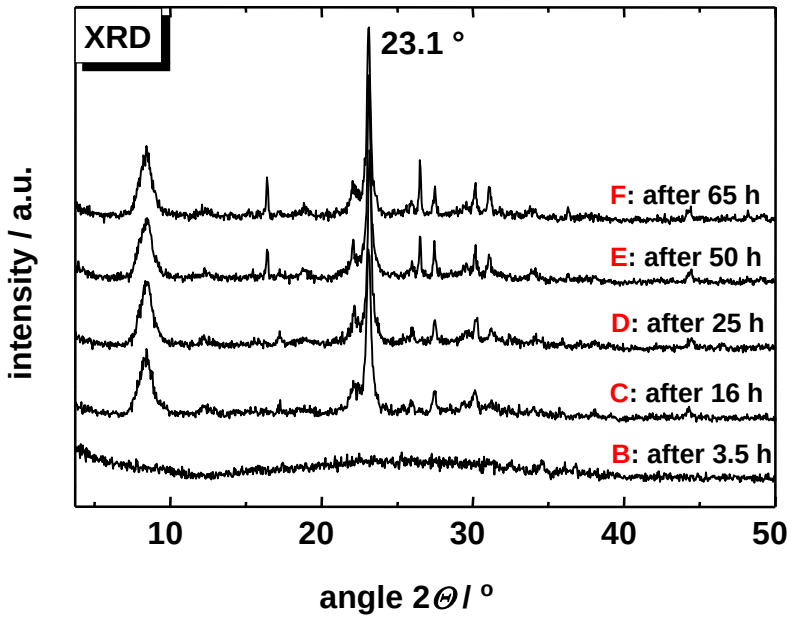


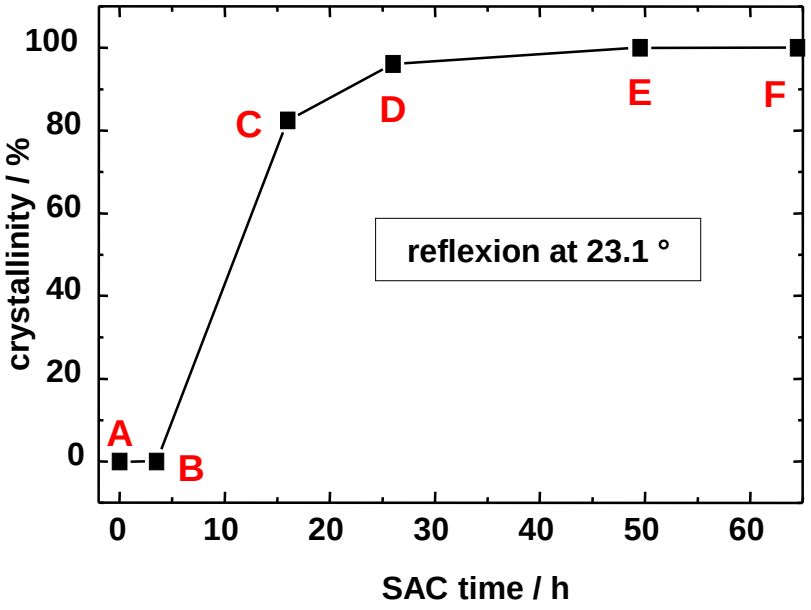
A. Arnold et al., Microporous Mesoporous Mater. 62 (2003) 97.

I. Synthesis of catalysts

synthesis of [Ga]Beta (n_{Si}/n_{Ga} = 8.5) by steam-assisted dry-gel conversion (SAC)

powder X-ray diffractograms and crystallinity as a function of the dry-gel conversion time





sample A: dry gel taken before conversion

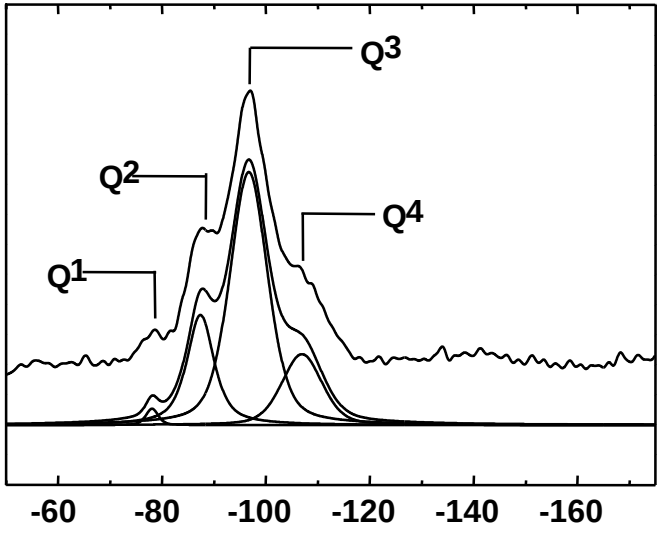
samples B to F: materials taken after conversion for 3.5 to 65 h

I. Synthesis of catalysts

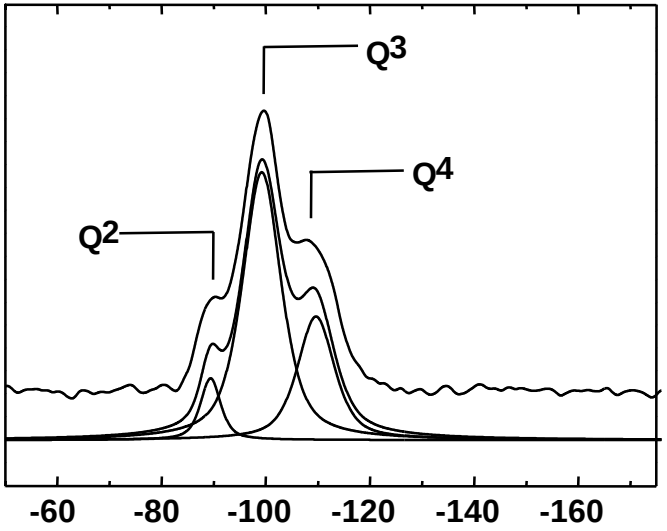
synthesis of [Ga]Beta (n_{Si}/n_{Ga} = 8.5) by steam-assisted dry-gel conversion (SAC)

^{29}Si MAS NMR spectra recorded after different SAC times

A: fresh dry-gel particles (0 h)



B: SAC time of 3.5 h



Q^1: silicon with one Si-O-Si bond, Si(1Si,3OH), at *ca.* -78 ppm

Q^4: silicon with four Si-O-Si bonds, Si(4Si), at *ca.* -107 ppm

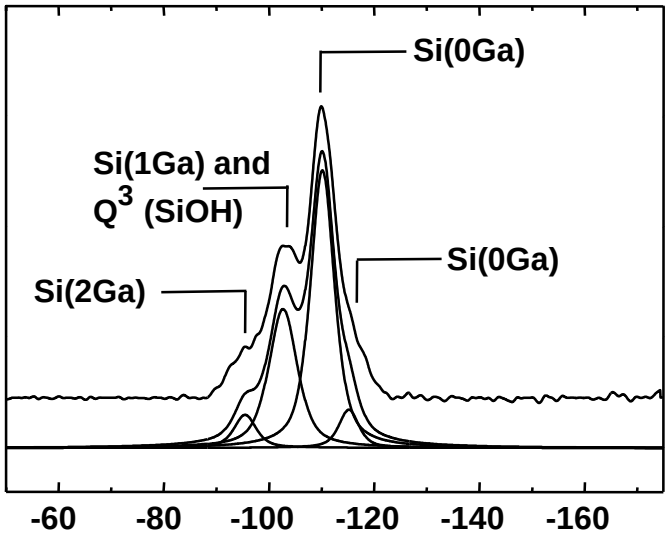
A. Arnold et al., Microporous Mesoporous Mater. 62 (2003) 97.

I. Synthesis of catalysts

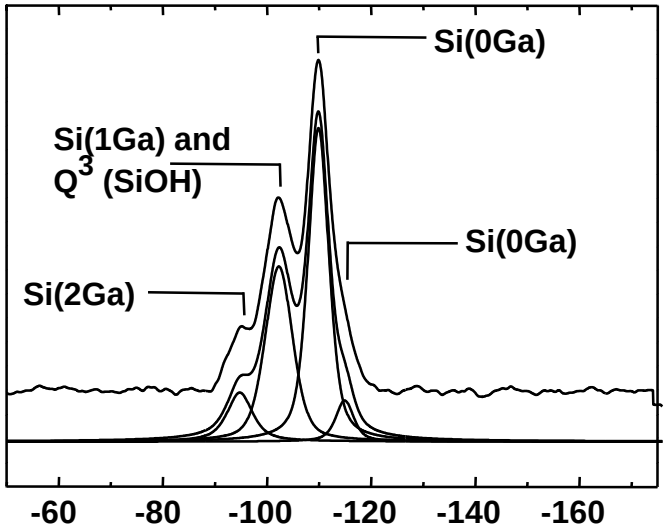
synthesis of [Ga]Beta (n_{Si}/n_{Ga} = 8.5) by steam-assisted dry-gel conversion (SAC)

^{29}Si MAS NMR spectra recorded after different SAC times

C: SAC time of 16 h



F: SAC time of 65 h



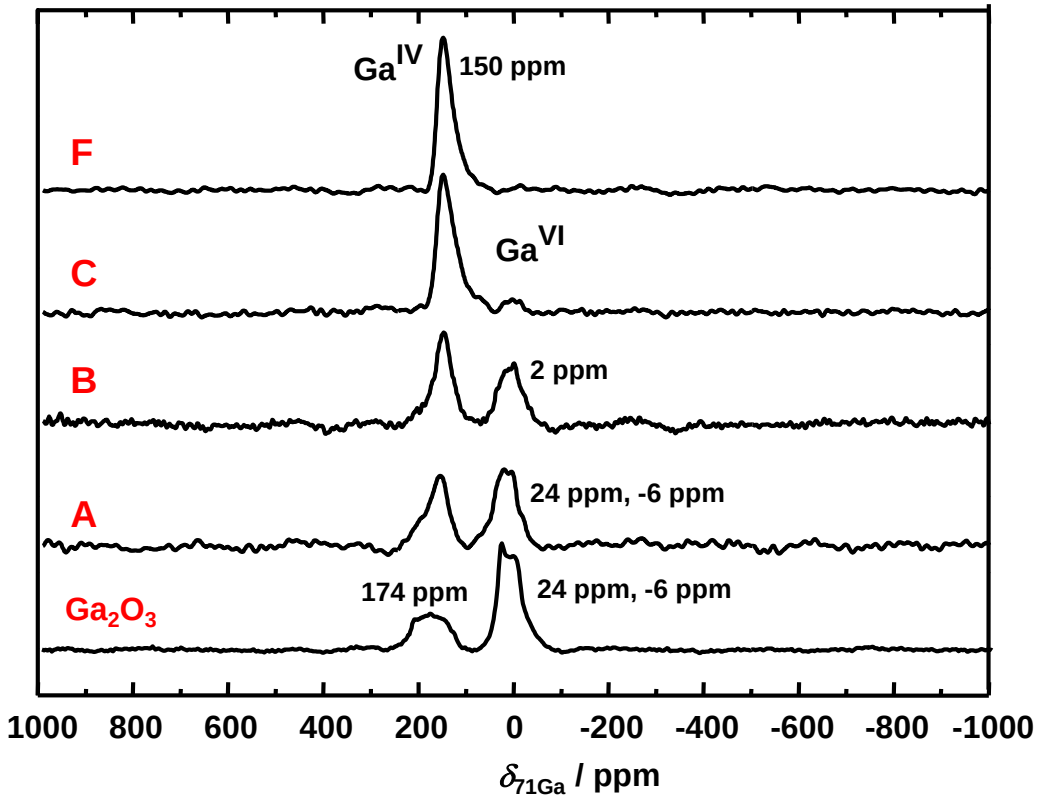
Si(1Ga): framework silicon with one Si-O-Ga and three Si-O-Si bonds, Si(3Si,1Ga), at -101 ppm is overlapped by the Q^3 signal, Si(3Si,1OH), at *ca.* -103 ppm

Si(2Ga): framework silicon with two Si-O-Ga and two Si-O-Si bonds, Si(2Si,2Ga), at -95 ppm

I. Synthesis of catalysts

synthesis of [Ga]Beta (n_{Si}/n_{Ga} = 8.5) by steam-assisted dry-gel conversion (SAC)

^{71}Ga MAS NMR spectra (B_0 = 17.6 T) recorded after different SAC times



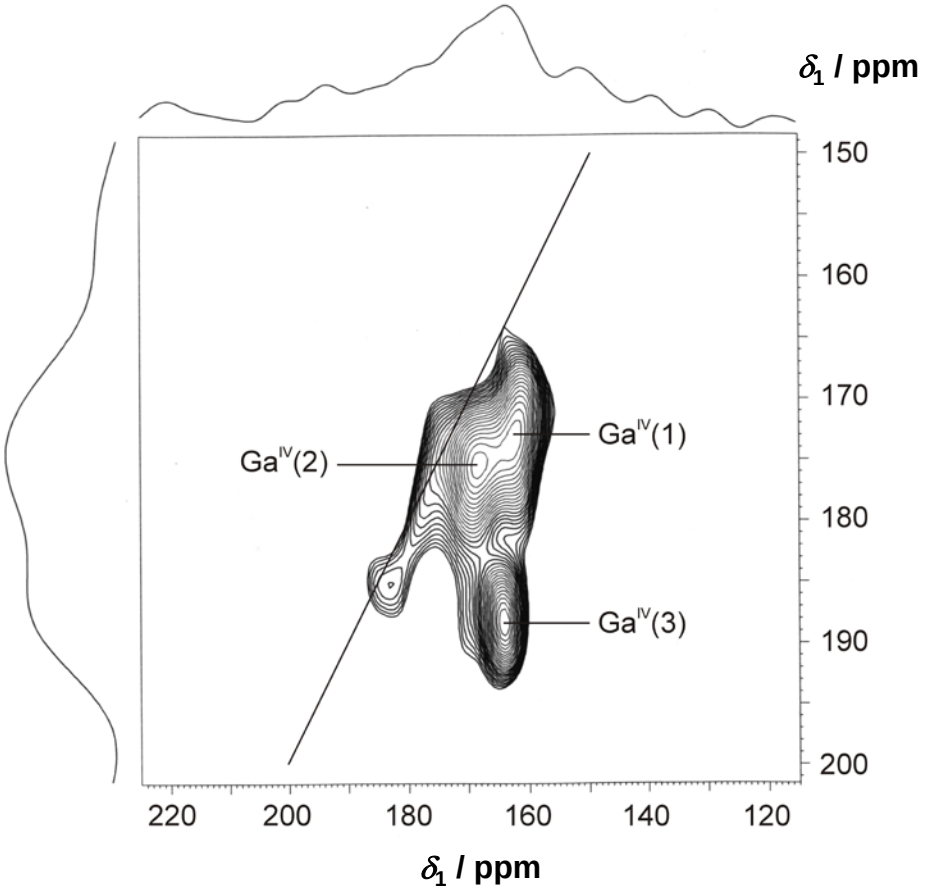
gallium coordination:	
Ga^{IV} /%	Ga^{VI} /%
100	0
93	7
58	42
45	55
34	66

complete incorporation of gallium atoms into tetrahedral sites for long SAC times

I. Synthesis of catalysts

synthesis of [Ga]Beta (n_{Si}/n_{Ga} = 8.5) by steam-assisted dry-gel conversion (SAC)

two-dimensional ^{71}Ga MQMAS NMR spectroscopy (B_0 = 11.8 T) of [Ga]Beta sample F (65 h)



Ga^{IV}(1, 2):
framework gallium species,
***SOQE* = 2.2 and 1.8 MHz,**
δ_{iso} = 172 and 168 ppm

Ga^{IV}(3):
extra-framework gallium species at defect sites or in an amorphous phase,
***SOQE* = 4.7 MHz,**
δ_{iso} = 176 ppm

A. Arnold et al., Microporous Mesoporous Mater. 62 (2003) 97.

I. Synthesis of catalysts

synthesis of flame-derived silica-alumina with different aluminum contents

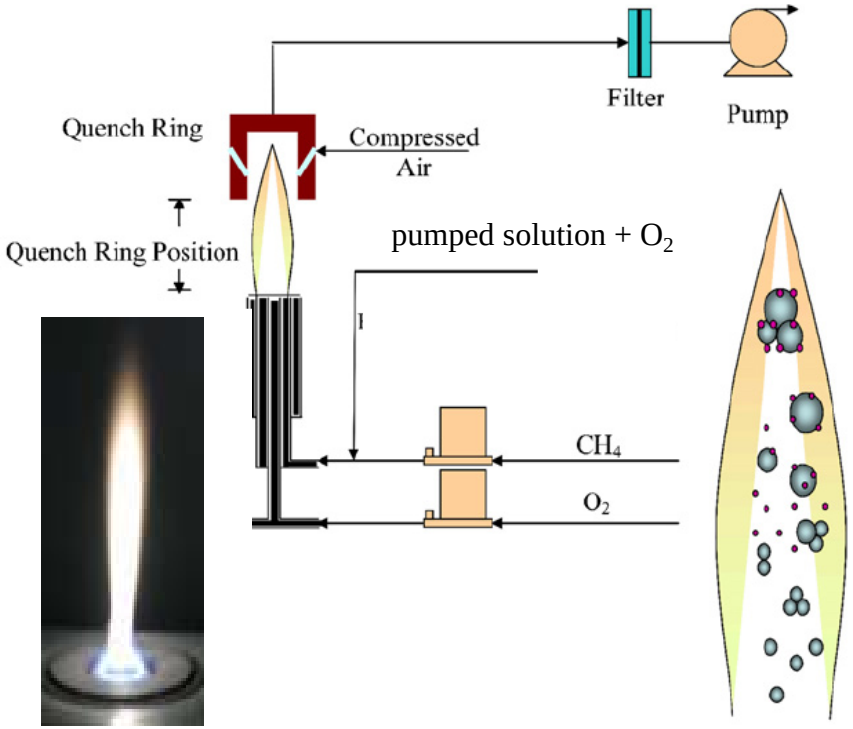
preparation of flame-made silica-alumina (SA) catalysts:

dissolving aluminum(III) acetylacetonate and tetraethoxysilane acetic acid grade in a 1:1 (vol%) mixture of acetic acid and methanol

this solution was pumped through a capillary with 5 ml/min and nebulized with 5 l/min O_2

the spray was ignited by a methane/ oxygen flame (1.5/0.9 L/min) resulting in an approximately 6 cm long flame

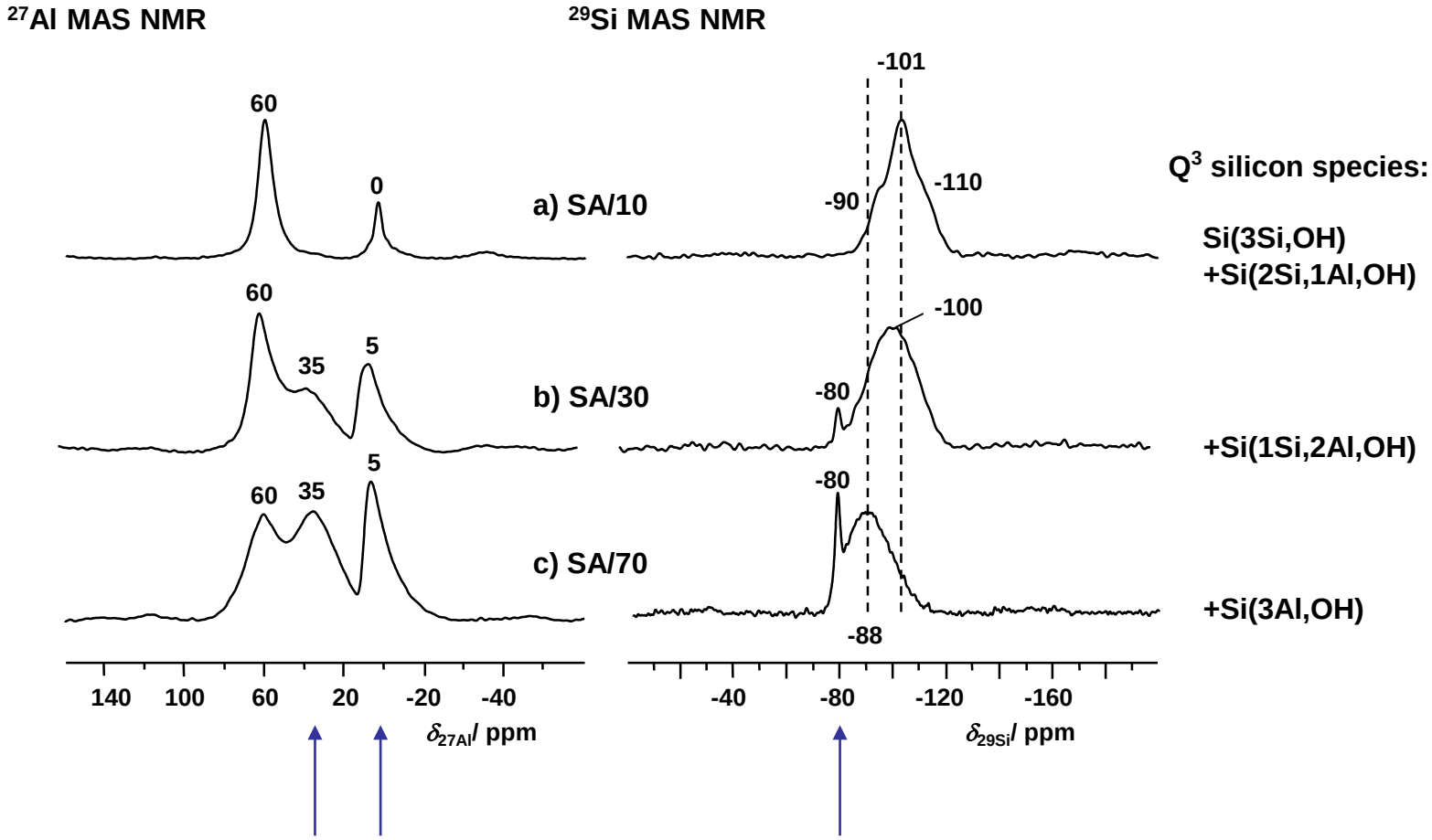
particles (*ca.* 20 nm) were collected on a cooled Whatman GF6 filter



J. Huang et al., Angew. Chem. Int. Ed. 49 (2010) 7776.

I. Synthesis of catalysts

synthesis of flame-derived silica-alumina with different aluminum contents

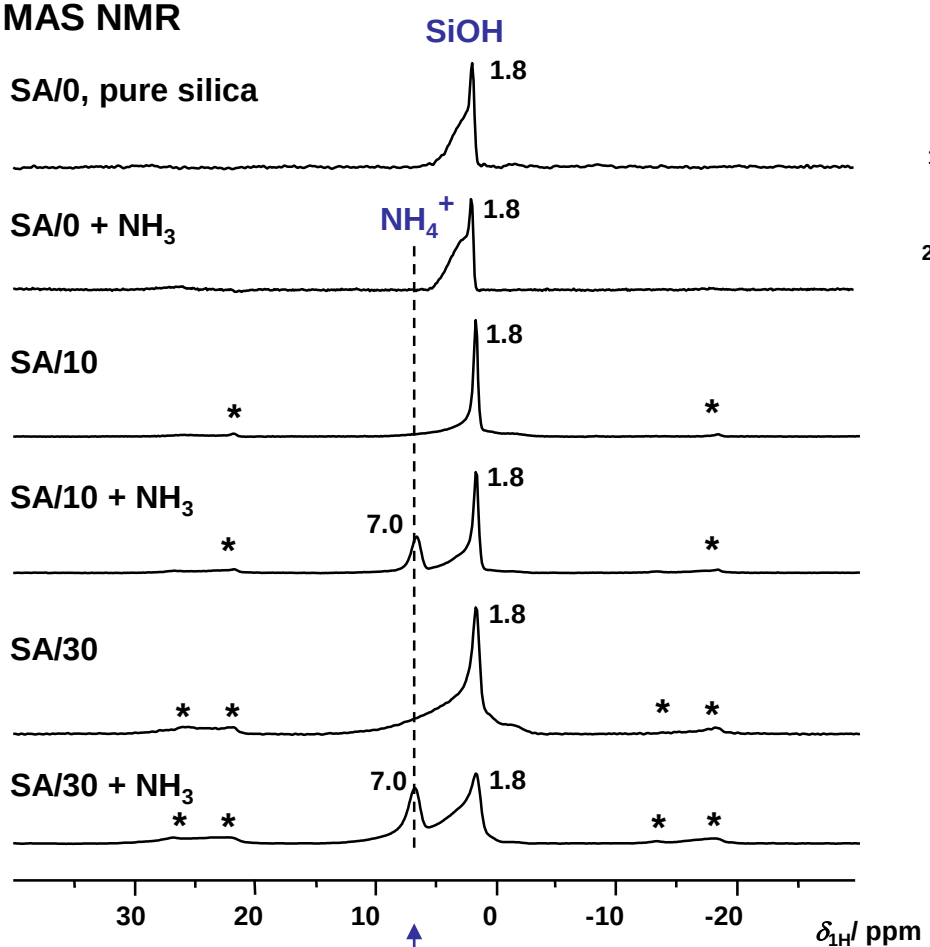


formation of andalusite phases (Al_2SiO_5) with δ_{29Si} = -79.8 ppm (M. Mägi *et al.*, J. Phys. Chem. 88 (1984) 1518) and octahedrally (δ_{27Al} = 5 ppm) as well as pentacoordinated aluminum atoms (δ_{27Al} = 35 ppm)

I. Synthesis of catalysts

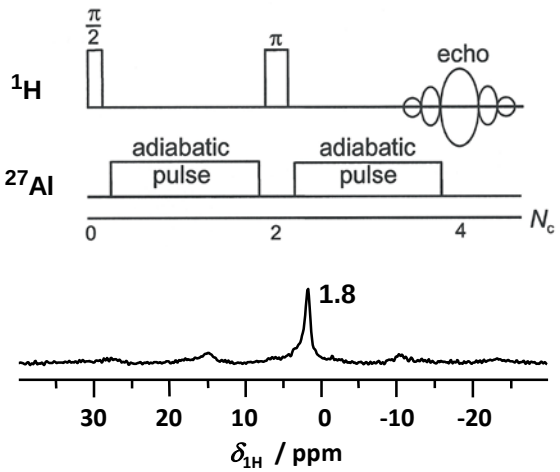
synthesis of flame-derived silica-alumina with different aluminum contents

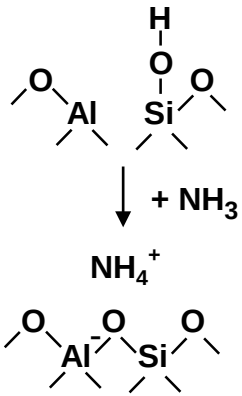
^{1}H MAS NMR



increases up to a molar aluminum content of 70 %

^{1}H/^{27}Al TRAPDOR MAS NMR of SA/70





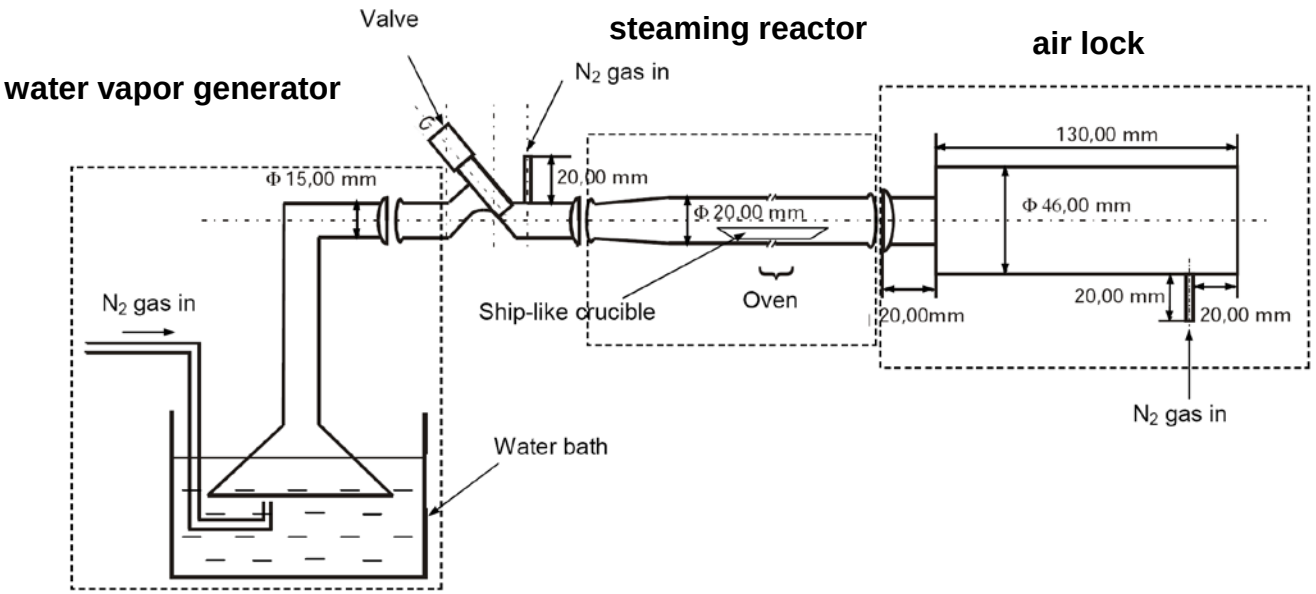
J. Huang et al., Angew. Chem. Int. Ed. 49 (2010) 7776.

II. Modification of catalysts

II. Modification of catalysts

dealumination of zeolite H,Na-Y by steaming

materials and steaming procedure:

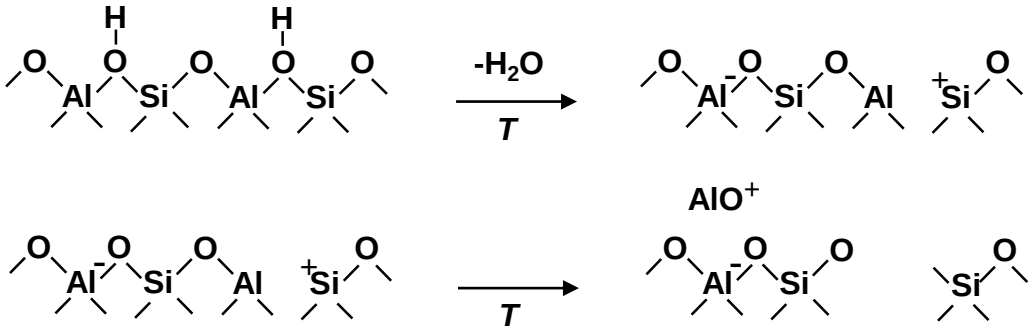


commercial zeolite Na-Y (n_{Si}/n_{Al} = 2.7) → **ammonium exchange (93%)** → **calcination and steaming at 748 K, flowing nitrogen (100 ml/min) at a water vapor a pressure of 81.5 kPa** → **dealuminated zeolite deH,Na-Y/81.5 (n_{Si}/n_{Al} = 6.0)**

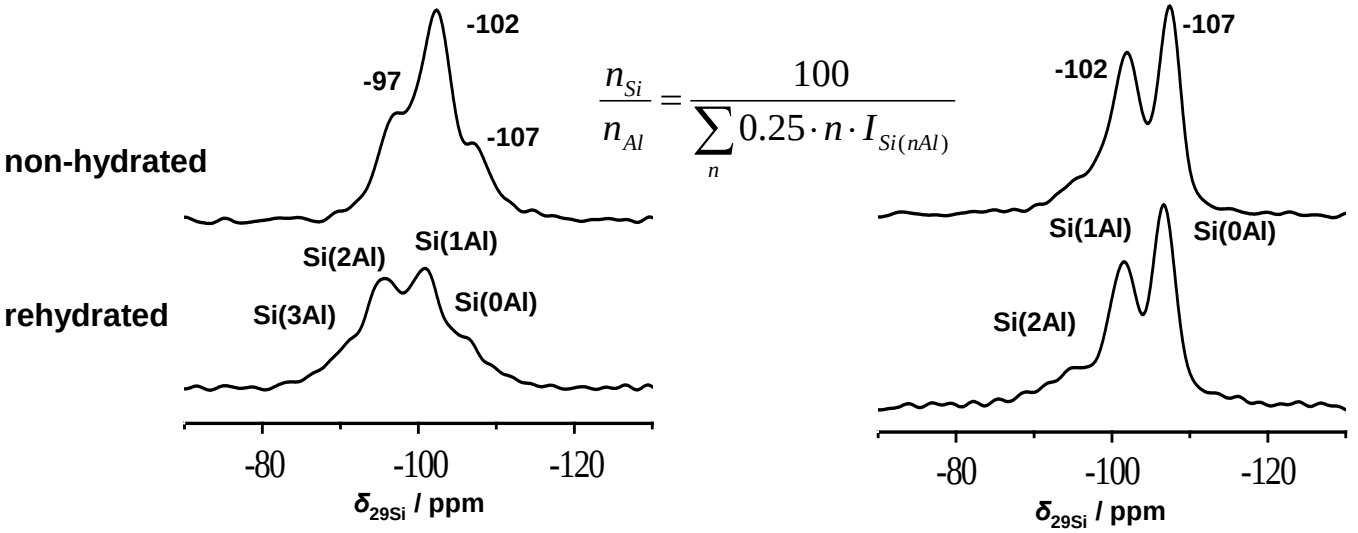
→ **transfer into gas-tight glass tubes and MAS NMR rotors** → **NMR characterization in the non-hydrated state**

II. Modification of catalysts

dealumination of zeolite H,Na-Y by steaming



^{29}Si MAS NMR spectroscopy of zeolites H,Na-Y (left) and deH,Na-Y/81.5 (right)



$$\frac{n_{Si}}{n_{Al}} = \frac{100}{\sum_n 0.25 \cdot n \cdot I_{Si(nAl)}}$$

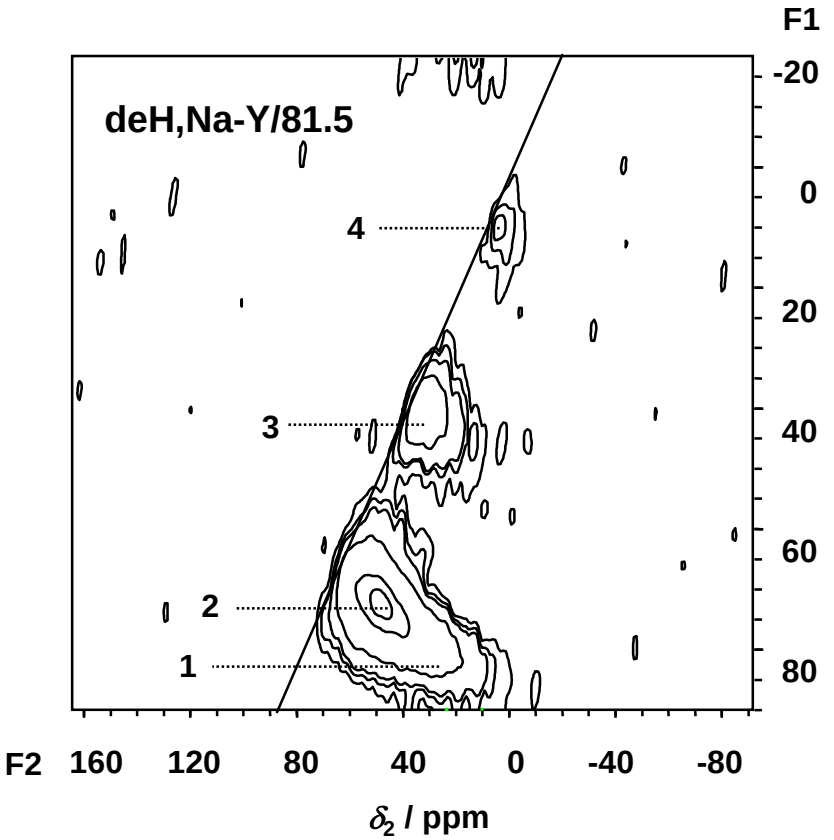
n_{Si}/n_{Al} = 2.7, 51.9 Al^{fr} / u.c.

n_{Si}/n_{Al} = 6.0, 27.4 Al^{fr}/u.c and 24.5 Al^{ex}/u.c

II. Modification of catalysts

dealumination of zeolite H,Na-Y by steaming

^{27}Al MQMAS NMR spectroscopy of non-hydrated zeolite deH,Na-Y/81.5



signal 1: Al^{IV}
- ***SOQE*** **= 15.0±1.0 MHz**
- **δ_{iso} = 70±10 ppm**

signal 2: Al^{IV}
- ***SOQE*** **= 8.0±0.5 MHz**
- **δ_{iso} = 65±5 ppm**

signal 3: Al^{V}
- ***SOQE*** **= 7.5±0.5 MHz**
- **δ_{iso} = 35±5 ppm**

signal 4: Al^{VI}
- ***SOQE*** **= 5.0±0.5 MHz**
- **δ_{iso} = 10±5 ppm**

B_0 = 17.6 T, ν_{rot} = 30 kHz

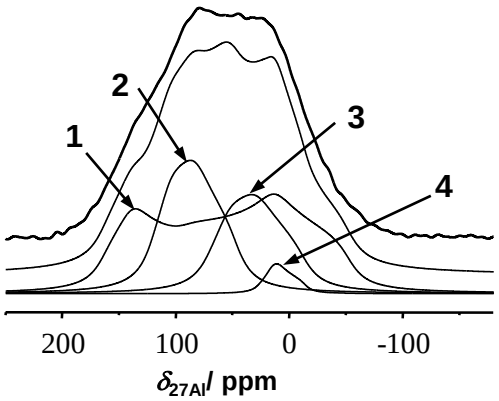
J. Jiao et al., Phys. Chem. Chem. Phys. 7 (2005) 3221.

II. Modification of catalysts

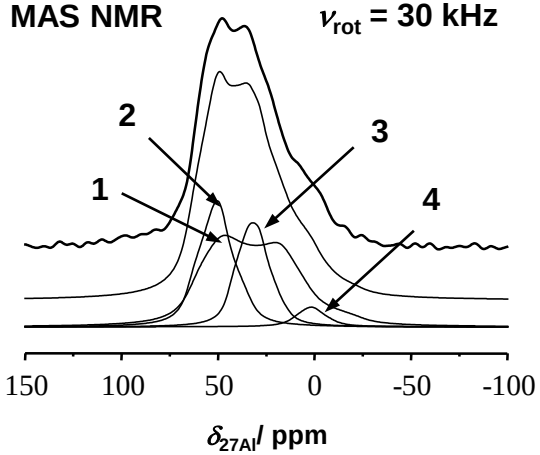
dealumination of zeolite H,Na-Y by steaming

^{27}Al solid-state NMR spectroscopy of zeolite deH,Na-Y/81.5 at B_0 = 17.6 T

^{27}Al spin-echo NMR



^{27}Al MAS NMR ν_{rot} = 30 kHz



Signals	1	2	3	4
Assignments of Al species	Al^{IV}/H^+ $Al^{IV}/Al^{V,x+}$	Al^{IV}/Na^+ cluster Al^{IV}	$Al^{V,x+}$ cat.	cluster Al^{VI}
δ_{iso} / ppm	70±10	65±5	35±5	10±5
C_{QCC} / MHz	15.0±1.0	8.0±0.5	7.5±0.5	5.0±0.5
η_Q	0.3	0.8	0.7	0.7
I in %	48 (27+21)	27 (7+20)	21	4

extra-framework Al cations ($Al^{V,x+}$) — **10.9 $Al^{V,x+}$/u.c.**

extra-framework Al_2O_3 clusters — **12.5 Al^{cl}/u.c.**

in comparison with 24.5 Al^{ex}/u.c. determined by ^{29}Si MAS NMR

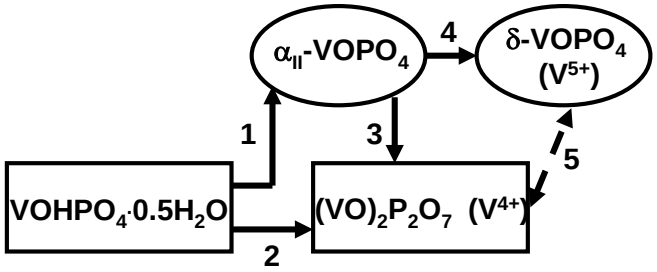
J. Jiao et al., Phys. Chem. Chem. Phys. 7 (2005) 3221.

II. Modification of catalysts

supporting of VPO catalysts on mesoporous SBA-15 materials

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

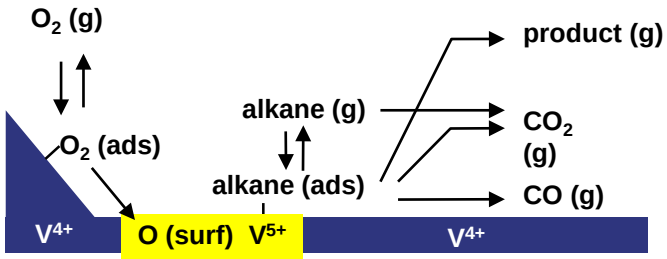
- **siliceous SBA-15 is added to isobutyl/benzyl alcohols (1 : 1) with V_2O_5, PEG 6.000 and H_3PO_4**
- **VPO loadings of 20 to 60 wt.%**
- **activation in a flow of 1.5 % n-butane, 17.5 % O_2 and balance N_2 (100 ml/min) at 673 K for 15 h**



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

ICP-AES and nitrogen adsorption:

Materials	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

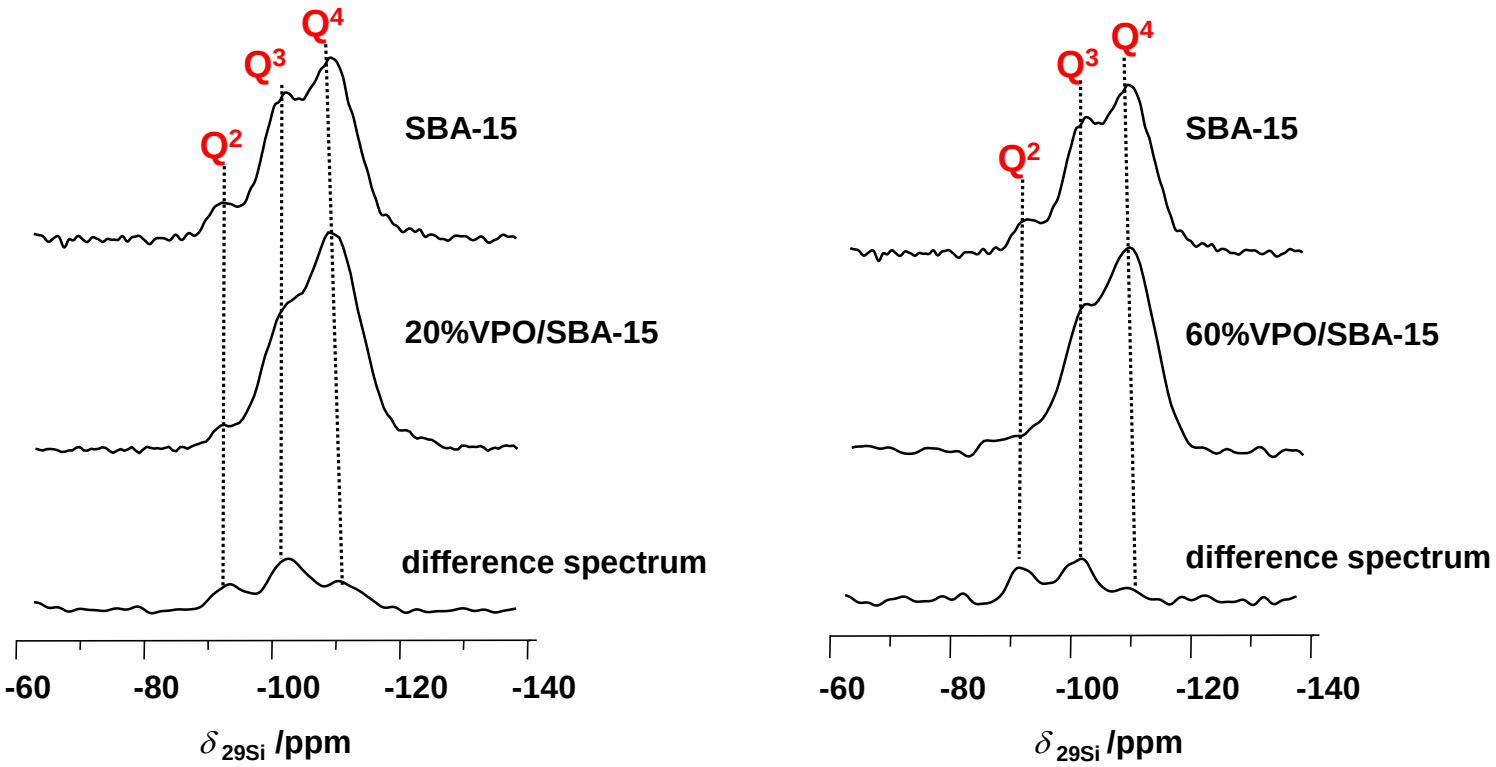


$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 3\,½\,O_2 \xrightarrow[678\ K]{VPO} O{=}\!\!<\!\!\rangle{=}O + 4\,H_2O$$

II. Modification of catalysts

supporting of VPO catalysts on mesoporous SBA-15 materials

^{29}Si MAS NMR spectroscopy of VPO/SBA-15



Q^2: silicon with one Si-O-Si bond, Si(2Si,2OH), at *ca.* -93 ppm

⋮

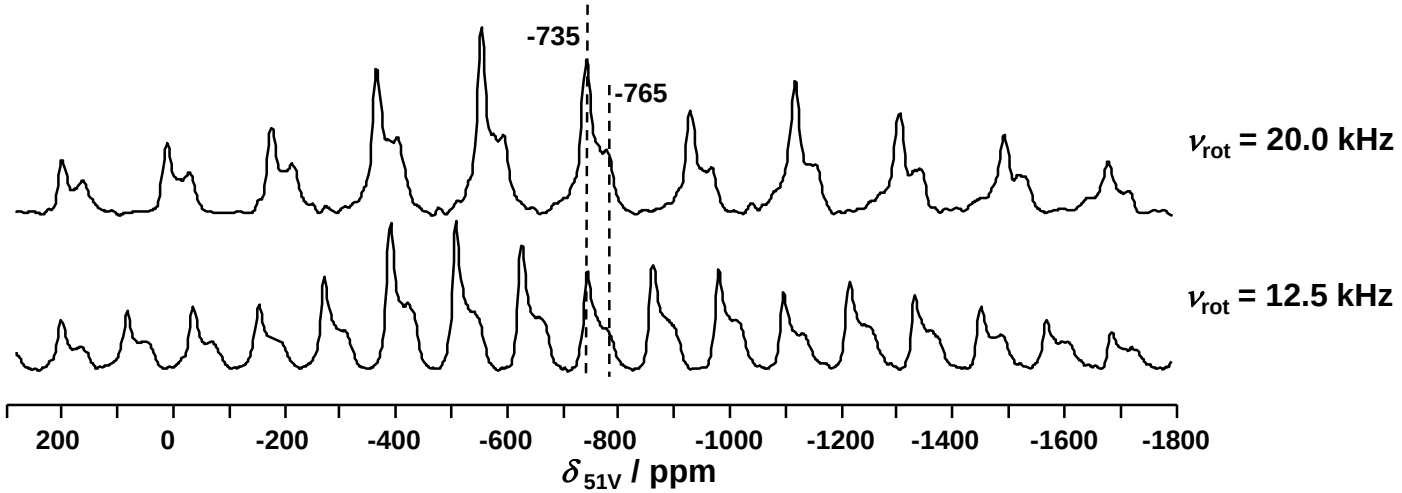
Q^4: silicon with four Si-O-Si bonds, Si(4Si), at *ca*. -110 ppm

VPO compounds cover the silanol groups of the internal mesoporous surface of the SBA-15 support

II. Modification of catalysts

supporting of VPO catalysts on mesoporous SBA-15 materials

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



Materials	δ_{iso} / ppm	$\Delta\delta_{cs}$ / ppm	η_{cs}	C_Q / MHz	η_Q
60%VPO/SBA-15	-735 -765	900 950	0.10 0.10	2.00 1.90	0.60 0.60
α_{II}-$VOPO_4$ *)	-755	992	0.08	0.63	0.09
β-$VOPO_4$ *)	-735	818	0.05	1.45	0.44

*) R. Siegel et al., Mag. Res. Chem. 42 (2004) 1022. O.B. Lapina et al., Prog. Nucl. Magn. Reson. Spetrosc. 53 (2008) 128.

J. Frey et al., Solid State Nucl. Magn. Reson. 35 (2009) 130

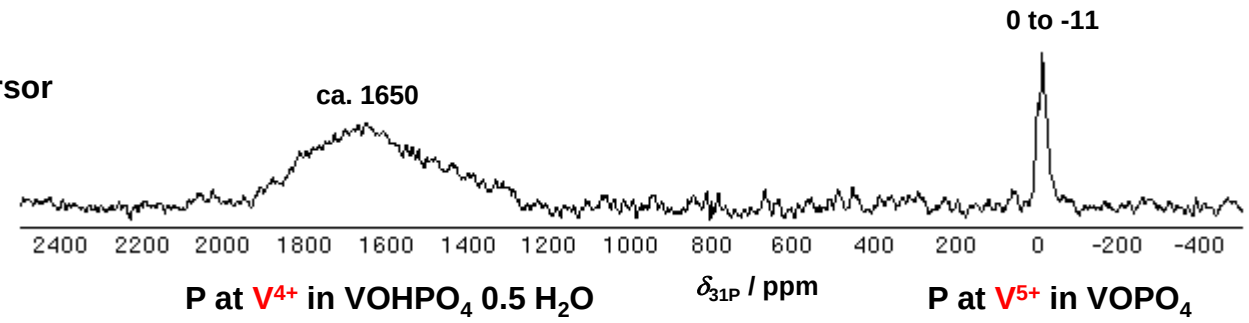
II. Modification of catalysts

supporting of VPO catalysts on mesoporous SBA-15 materials

^{31}P MAS NMR spectroscopy of 60%VPO/SBA-15 before and after activation

non-activated precursor

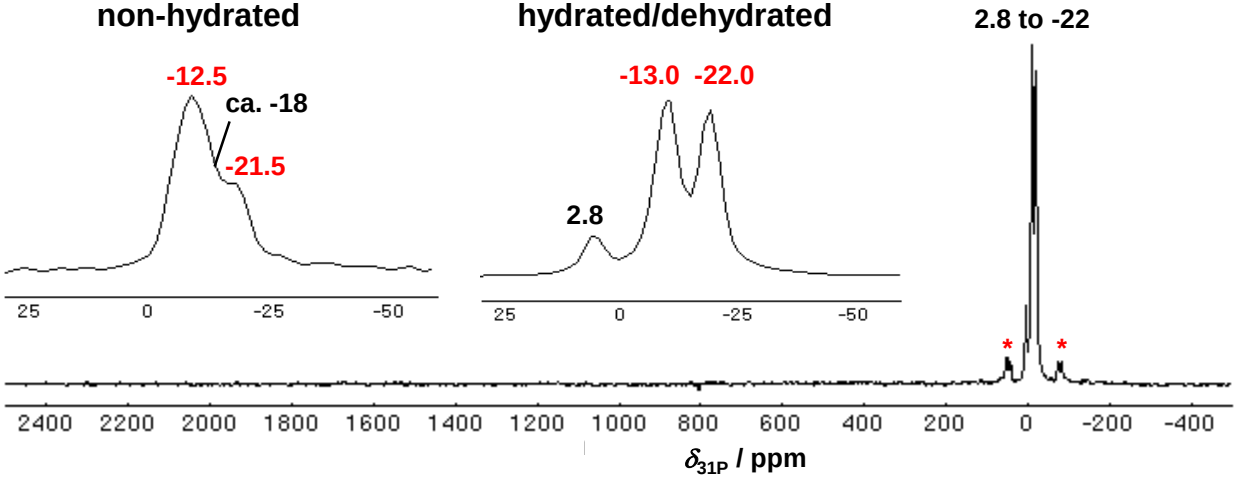
ν_0 = 161.98 MHz
ν_{rot} = 10 kHz
NS ca. 1650



P at V^{4+} in $VOHPO_4$ 0.5 H_2O **P at V^{5+} in $VOPO_4$**

activated at 673 K for 15 h

ν_0 = 161.98 MHz
ν_{rot} = 10 kHz
NS ca. 1000



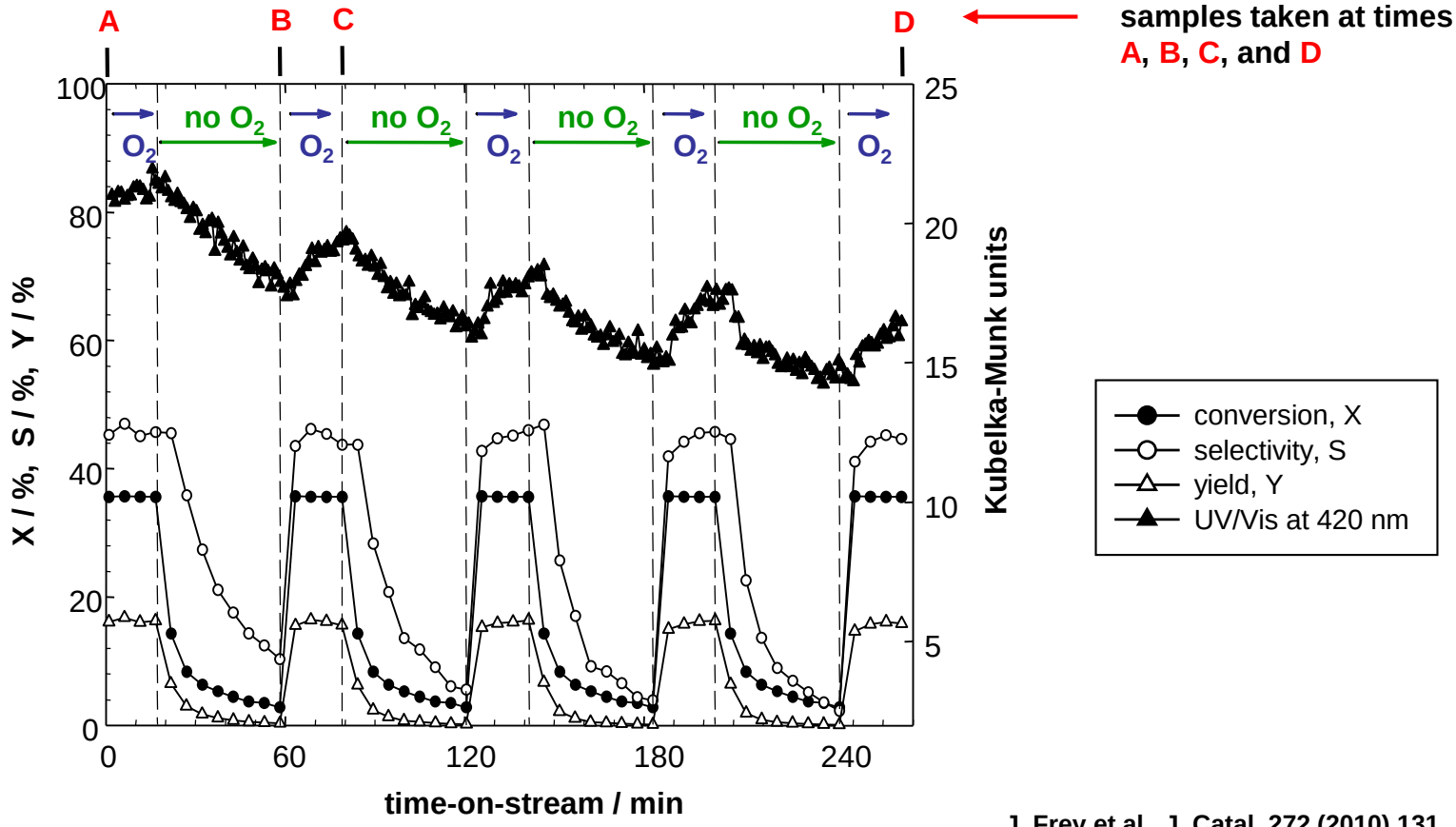
P at V^{5+} in $VOPO_4$ phases, such as β-$VOPO_4$ (-13 ppm) and α_{II}-$VOPO_4$ (-22 ppm)

J. Frey et al., Solid State Nucl. Magn. Reson. 35 (2009) 130

II. Modification of catalysts

supporting of VPO catalysts on mesoporous SBA-15 materials

selective oxidation of *n*-butane to maleic anhydride at 678 K with sequential switching on (15 min) and off (40 min) of the gaseous oxygen

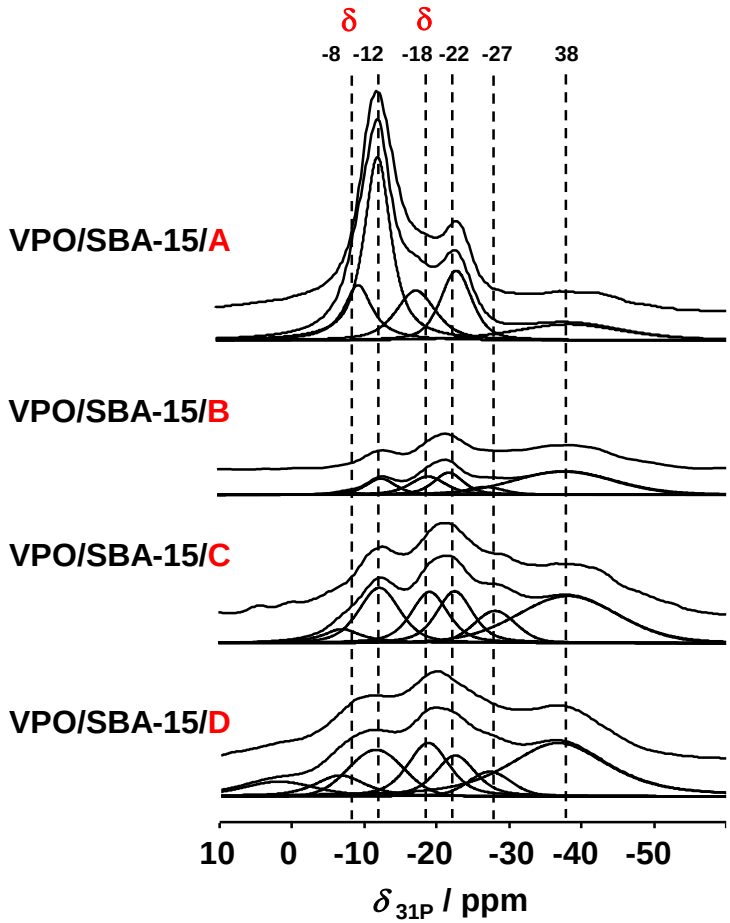


J. Frey et al., J. Catal. 272 (2010) 131

II. Modification of catalysts

supporting of VPO catalysts on mesoporous SBA-15 materials

^{31}P MAS NMR spectra of VPO/SBA-15/A to VPO/SBA-15/D:



Catalysts	Type	Contents of P/V^{5+} and P/SiO_2	Contents of P/V^{5+} in δ-$VOPO_4$ phases
VPO/bulk	A	0.5 %	
	B	0 %	
	C	0.35 %	
	D	0.4 %	
VPO/ SBA-15	A	2.6 %	0.80 %
	B	0.3 %	0.05 %
	C	0.9 %	0.20 %
	D	1.3 %	0.30 %

J. Frey et al., J. Catal. 272 (2010) 131

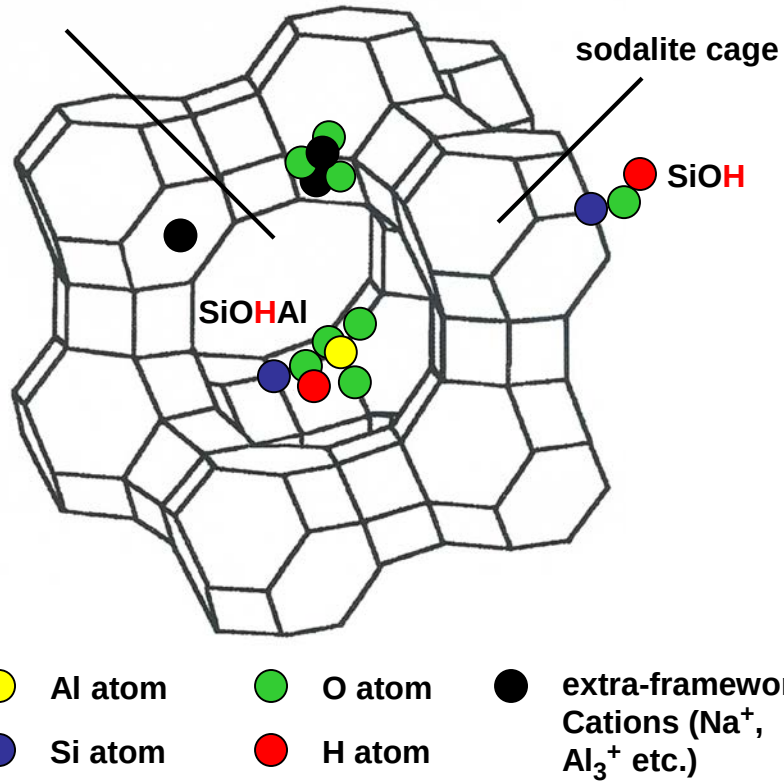
III. Tailoring of surface sites

III. Tailoring of surface sites

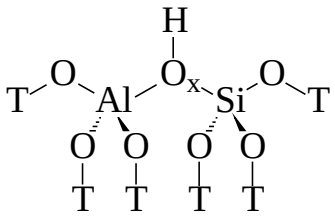
nature of acid sites on solid catalysts

structure of zeolite Y (FAU, faujasite): large-pore zeolite with 12-ring windows (0.74 nm)

supercage (1.23 nm)



Brønsted acid sites:



bridging OH group (SiOHAl)

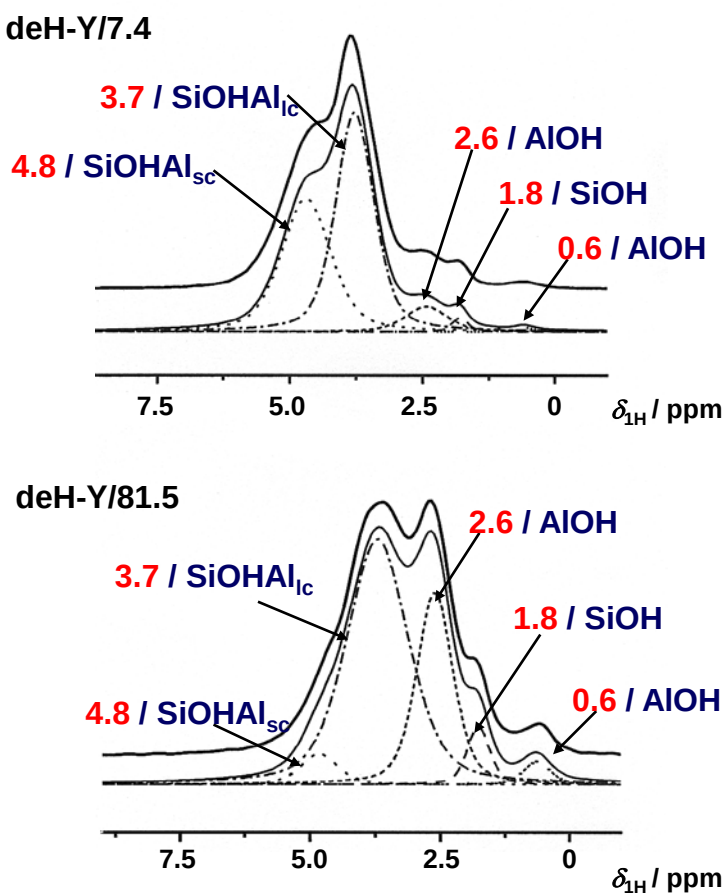
Lewis acid sites:

- **framework defects,**
- **extra-framework species (AlO^+, $AlOH^{2+}$ etc.)**

III. Tailoring of surface sites

modification of Brønsted acid sites on zeolites *via* steaming and dealumination

^{1}H MAS NMR



undisturbed metal OH (AlOH) groups:
-0.5 to 0.5 ppm

defect SiOH groups:
1.2 to 2.2 ppm

AlOH groups at extra-framework Al:
2.8 to 3.6 ppm

bridging OH groups in large cages and pores (SiOHAl$_{lc}$):
3.6 to 4.3 ppm

bridging OH groups in small cages (SiOHAl$_{sc}$):
4.6 to 5.2 ppm

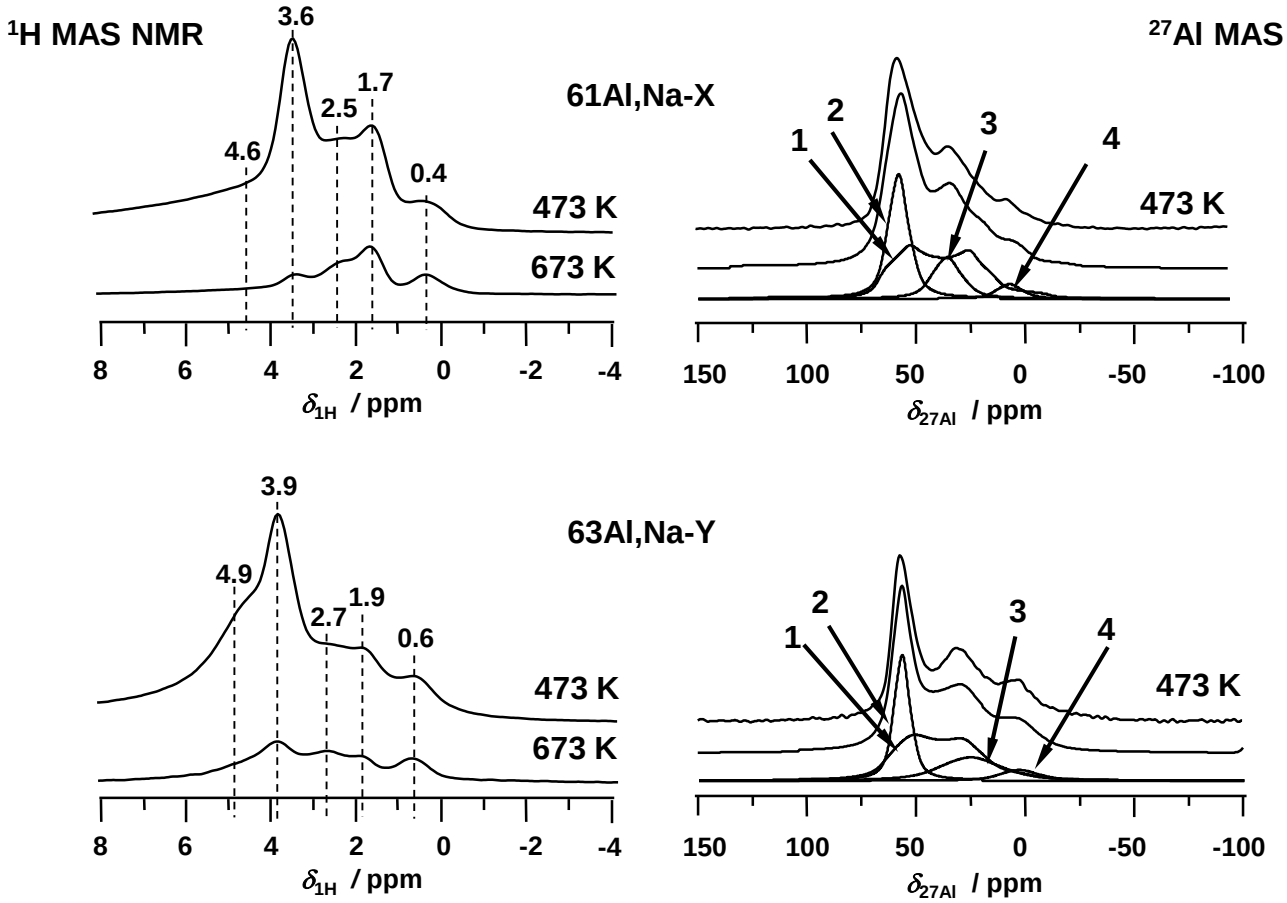
(hydrogen bonded SiOH and SiOHAl groups: 5.2 to 13 ppm)

J. Jiao et al., J. Phys. Chem B. 108 (2004) 14305.

III. Tailoring of surface sites

preparation of Brønsted acid sites on zeolites *via* exchange with multivalent cations

exchange of zeolite Na-Y (n_{Si}/n_{Al} = 2.7) in an 0.1 M $Al(NO_3)_3$ solution

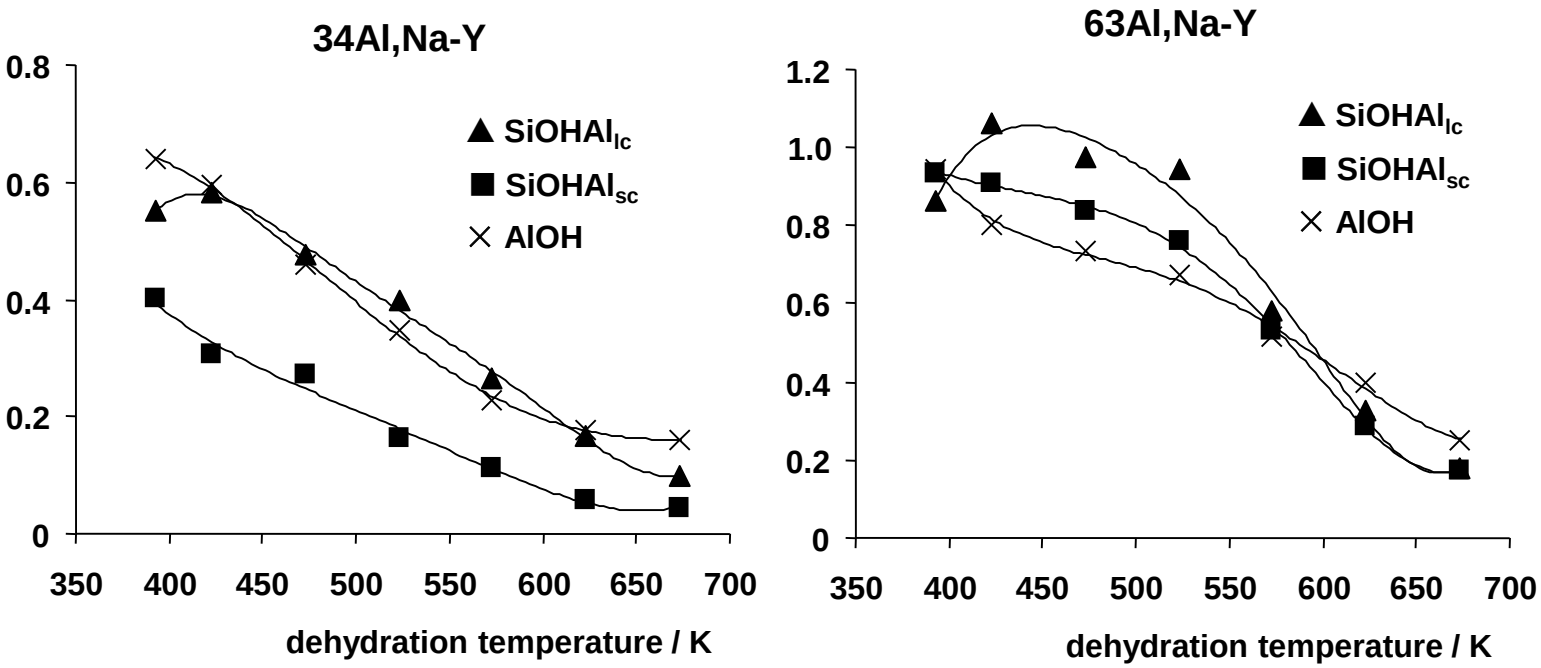


J. Huang et a.l, J. Phys. Chem. C 112 (2008) 3811.

III. Tailoring of surface sites

preparation of Brønsted acid sites on zeolites via exchange with multivalent cations

determination of the concentration of OH groups, n_{OH}, in mmol·g^{-1} by evaluation of the ^{1}H MAS NMR intensities

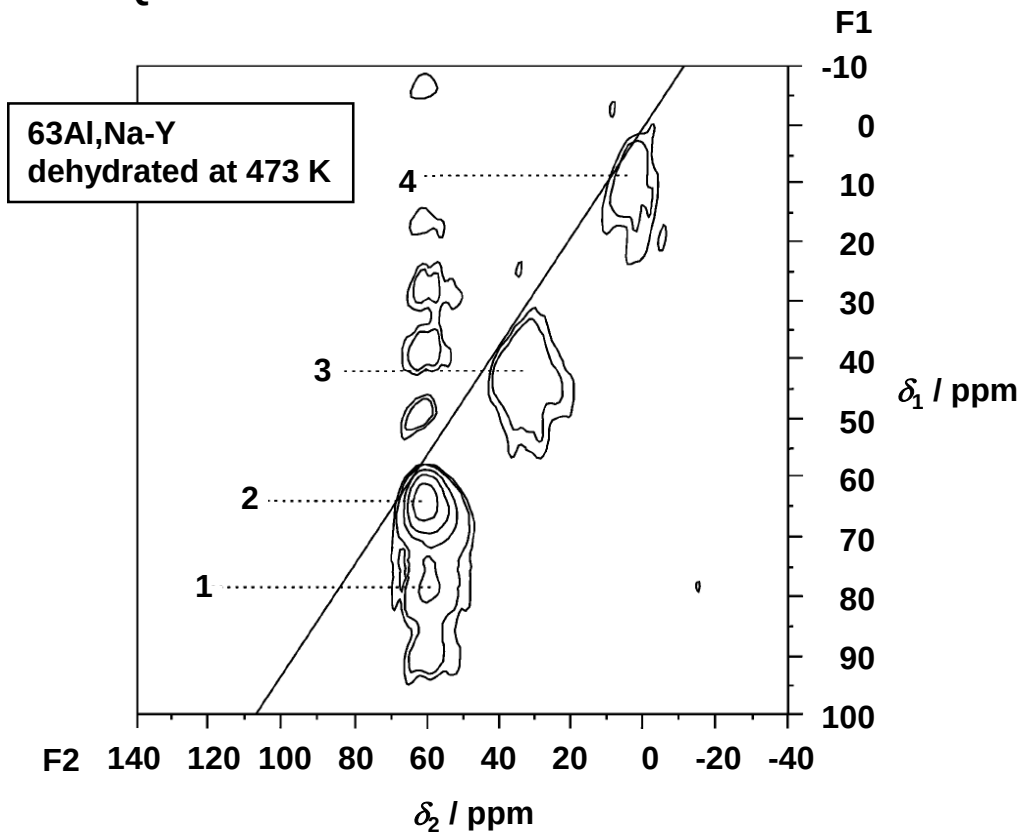


cation-exchange degree and dehydration temperature allow the tuning of the number of strongly polarising centers and Brønsted acid sites

III. Tailoring of surface sites

preparation of Brønsted acid sites on zeolites *via* exchange with multivalent cations

^{27}Al MQMAS NMR



signal 1: Al^{IV}
- ***SOQE*** **= 10.1 MHz**
- δ_{iso} **= 71 ppm**

signal 2: Al^{IV}
- ***SOQE*** **= 3.6 MHz**
- δ_{iso} **= 62 ppm**

signal 3: Al^{V}
- ***SOQE*** **= 7.6 MHz**
- δ_{iso} **= 39 ppm**

signal 4: Al^{VI}
- ***SOQE*** **= 6.2 MHz**
- δ_{iso} **= 6 ppm**

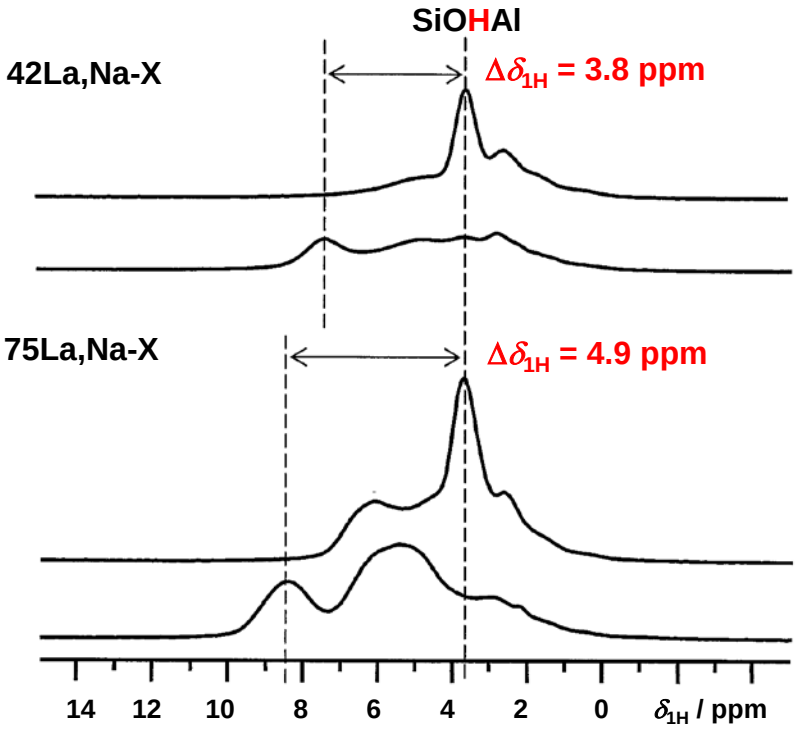
B_0 = 17.6 T, ν_{rot} = 30 kHz

J. Huang et a.l, J. Phys. Chem. C 112 (2008) 3811.

III. Tailoring of surface sites

characterization of the Brønsted acid strength *via* acetonitrile-induced low-field shift $\Delta\delta_{1H}$

^{1}H MAS NMR

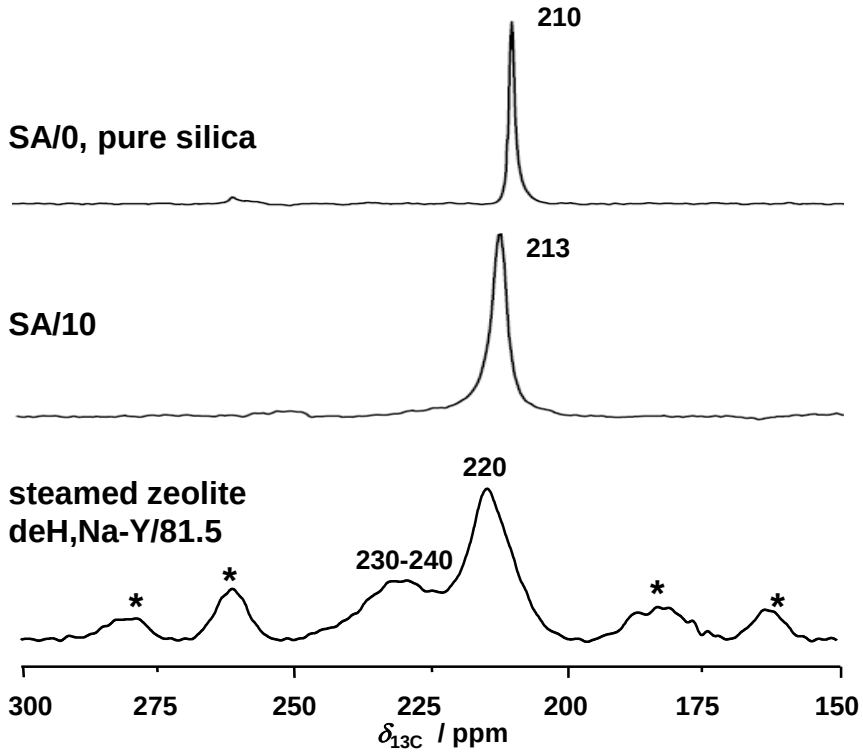


Low-field shift $\Delta\delta_{1H}$	Adsorbent and type of OH group
1.2 ppm	AlOH in MIL-53(Al)
3.6 ppm	H,Na-X (Si/Al= 1.3)
3.8 ppm	42La,Na-X and 32Al,Na-X (Si/Al = 1.4)
4.9 ppm	75La,Na-X (S/Al = 1.4)
5.1 ppm	H,Na-Y (Si/Al = 2.7)
5.3 ppm	34Al,Na-Y and 63Al,Na-Y (Si/Al = 2.7)
5.7 ppm	42La,Na-Y and 75La,Na-Y (Si/Al = 2.7)
6.5 ppm	steamed deH,Na-Y/81.5 (Si/Al = 6)
6.7 ppm	H-MOR (Si/Al = 10)
7.0 ppm	dealuminated H,Na-Y (Si/Al = 18)
7.9 ppm	H-ZSM-5 (Si/Al = 26)

III. Tailoring of surface sites

characterization of Brønsted and Lewis acid sites *via* ^{13}C-2-acetone as probe molecule

^{13}C MAS NMR



Materials	δ_{13C}	$\Delta\delta_{13C}$
$CDCl_3$	205 ppm	0 ppm
SA/0	210 ppm	5 ppm
SA/10	213 ppm	8 ppm
H,Na-X	215 ppm	10 ppm
SA/70	216 ppm	11 ppm
H,Na-Y	220 ppm	15 ppm
ZSM-5	223 ppm	18 ppm
Lewis sites	230-240 ppm	25-35 ppm

J.F. Haw et al., Accounts of Chemical Research 29 (1996) 259.

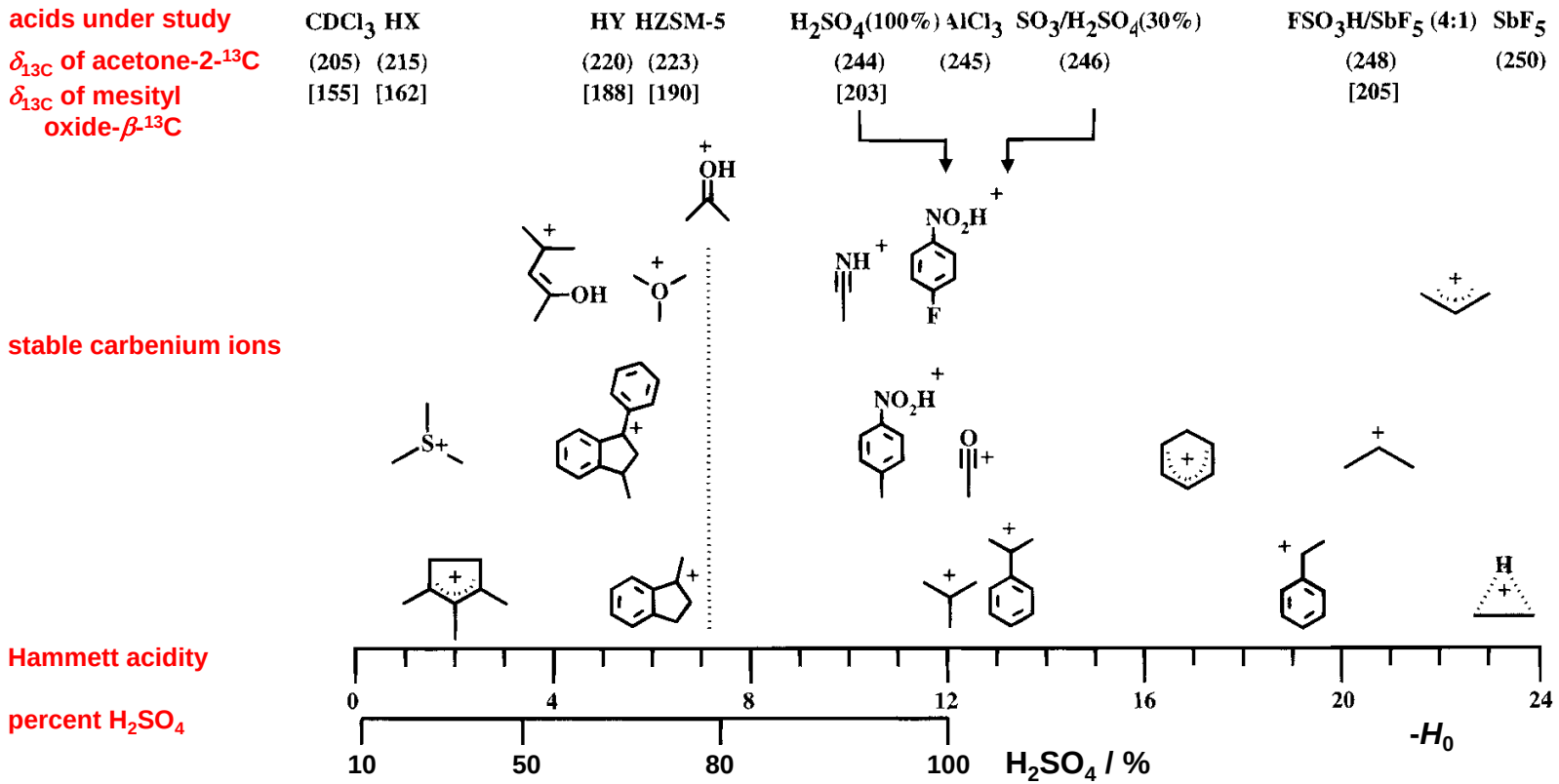
Lewis sites formed by steaming

Brønsted sites with different acid strengths (see Tab.)

Y. Jiang et a.l, Solid State Nucl. Magn. Reson., submitted.

III. Tailoring of surface sites

comparison of different acidity scales



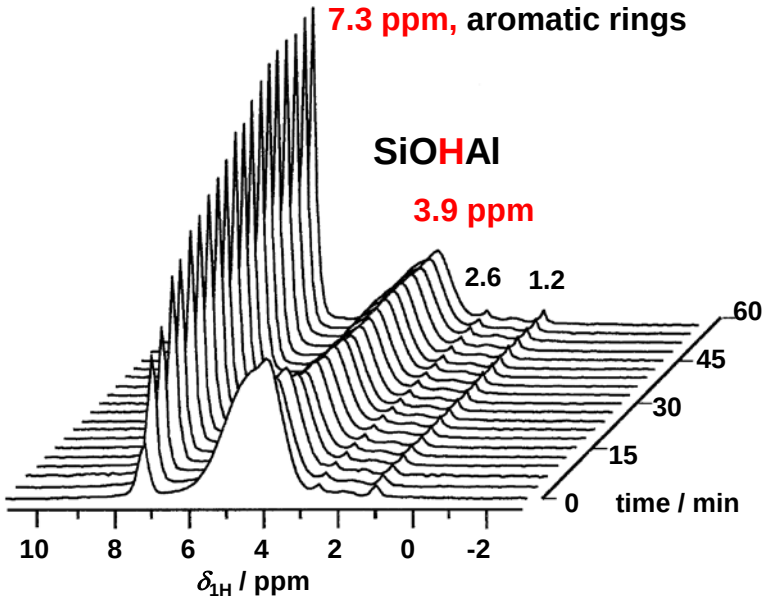
J.F. Haw et al., Acc. Chem. Res. 29 (1996) 259.

III. Tailoring of surface sites

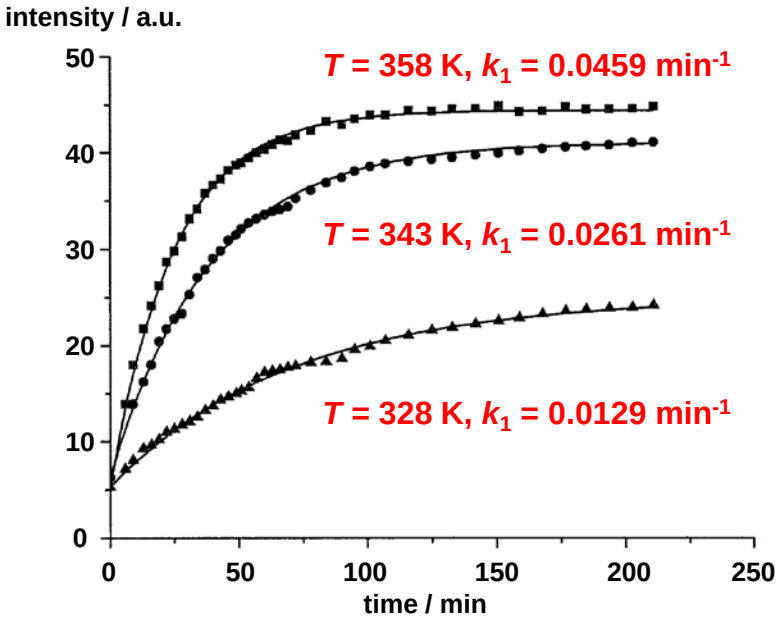
H/D exchange kinetics as an acidity scale

in situ **^{1}H VT/MAS NMR studies of H/D exchange on zeolite H,Na-Y loaded with ethylbenzene ($C_6D_5C_2H_5$)**

stack plot of ^{1}H MAS NMR spectra recorded at *T* = 358 K



H/D exchange rates at *T* = 328 - 358 K



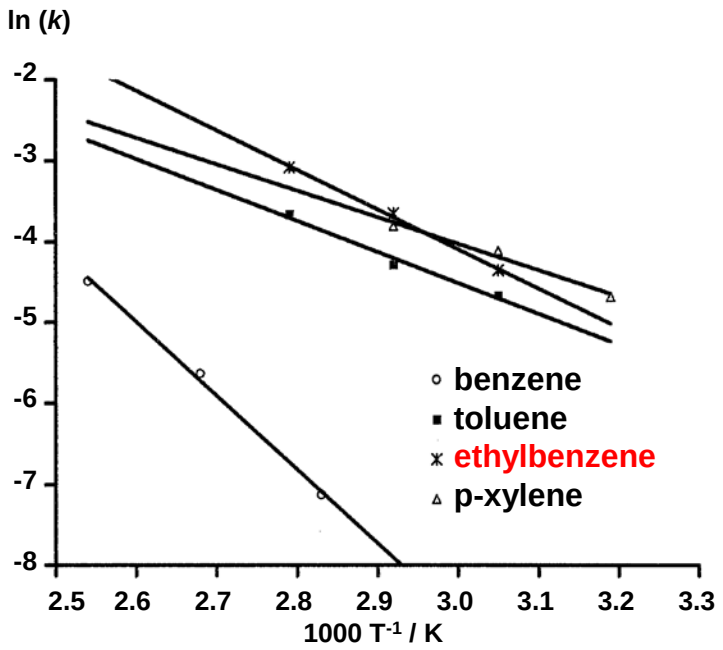
J. Huang et al., Microporous Mesoporous Mater. 99 (2007) 86.

III. Tailoring of surface sites

H/D exchange kinetics as an acidity scale

in situ **^{1}H VT/MAS NMR spectroscopy of deuterated aromatics on zeolites H,Na-Y (n_{Si}/n_{Al} = 2.7), 75La,Na-Y (n_{Si}/n_{Al} = 2.7), and H-ZSM-5 (n_{Si}/n_{Al} = 26)**

deuterated aromatics on zeolite 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	
	ethylbenzene	41	
	toluene	32	
	p-xylene	27	
H,Na-Y	benzene	76	5.1
La,Na-Y	benzene	67	5.7
H-ZSM-5	benzene	46	7.9

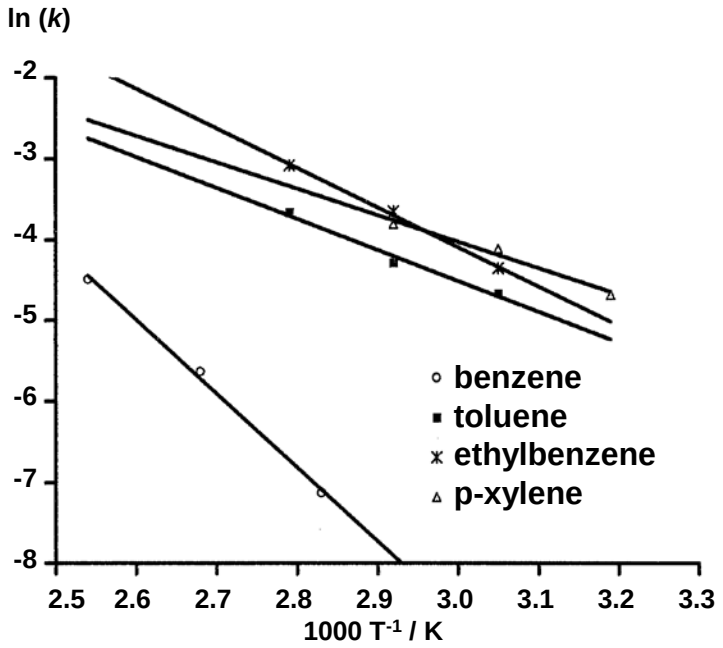
J. Huang et al., Microporous Mesoporous Mater. 99 (2007) 86.

III. Tailoring of surface sites

H/D exchange kinetics as an acidity scale

in situ **^{1}H VT/MAS NMR spectroscopy of deuterated aromatics on zeolites H,Na-Y (n_{Si}/n_{Al} = 2.7), 75La,Na-Y (n_{Si}/n_{Al} = 2.7), and H-ZSM-5 (n_{Si}/n_{Al} = 26)**

deuterated aromatics on zeolite 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
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	ethylbenzene	41	
	toluene	32	
	p-xylene	27	
H,Na-Y	benzene	76	5.1
La,Na-Y	benzene	67	5.7
H-ZSM-5	benzene	46	7.9

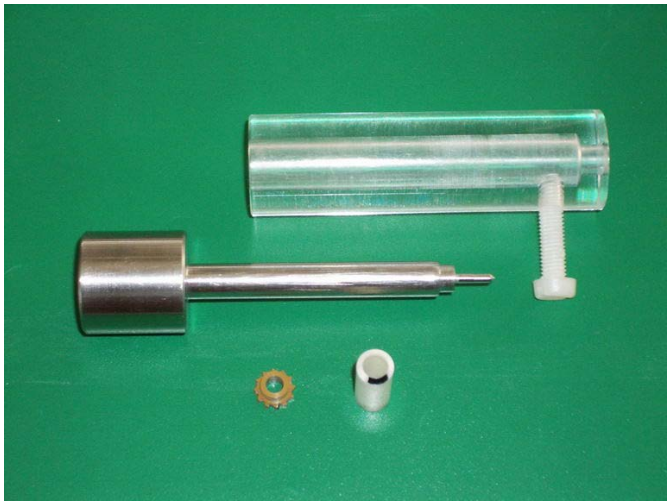
J. Huang et al., Microporous Mesoporous Mater. 99 (2007) 86.

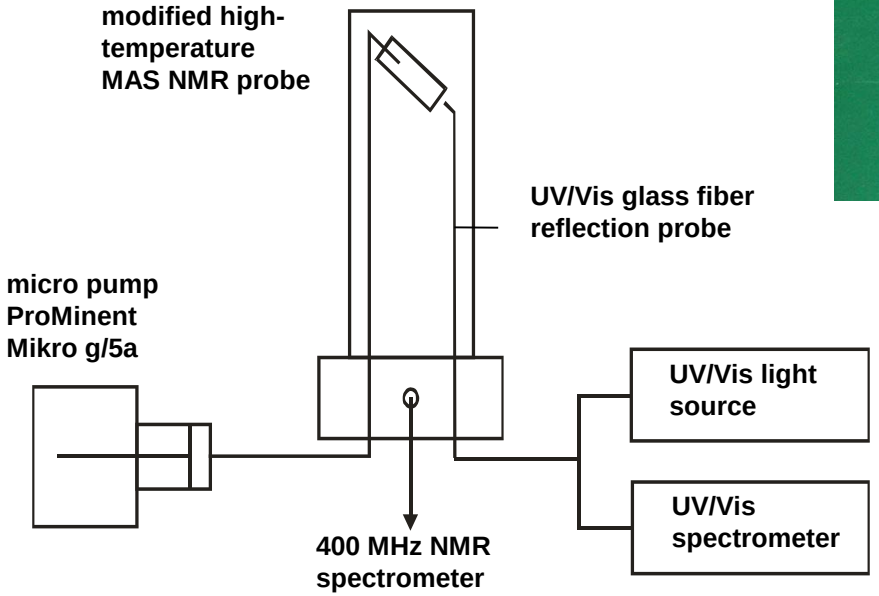
IV. Catalytic applications

IV. Catalytic applications

pulsed-flow MAS NMR-UV/Vis spectroscopy

installation of the injection technique and the glass fiber in the *in situ* MAS NMR probe



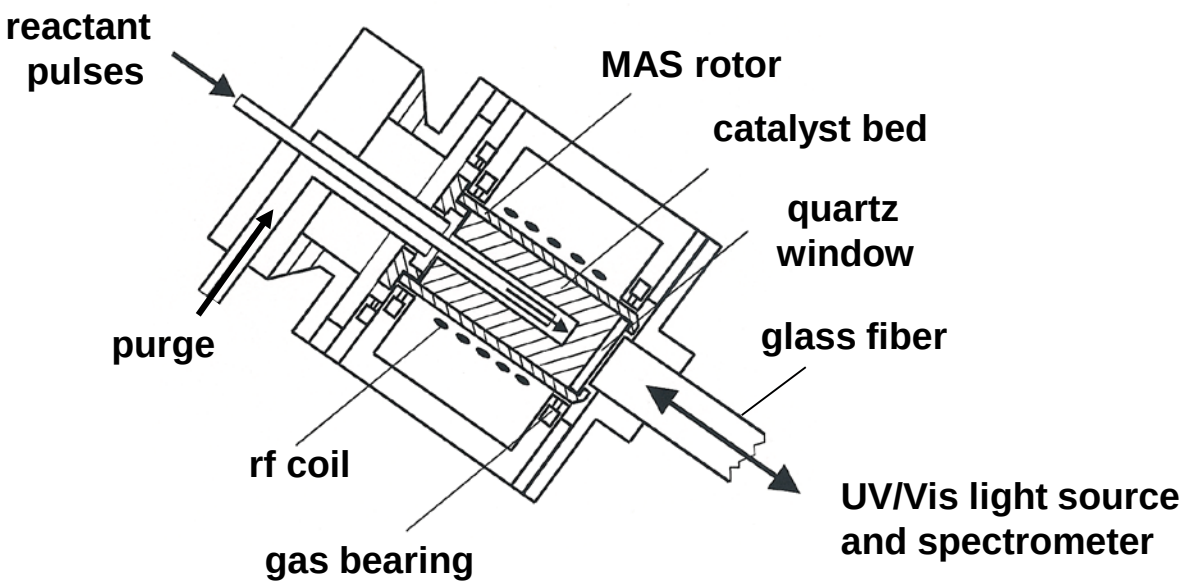


M. Hunger, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105.

IV. Catalytic applications

pulsed-flow MAS NMR-UV/Vis spectroscopy

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



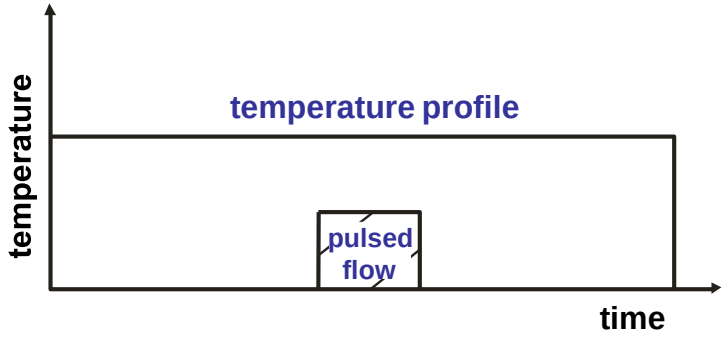
M. Hunger, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105.

IV. Catalytic applications

pulsed-flow MAS NMR-UV/Vis spectroscopy

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

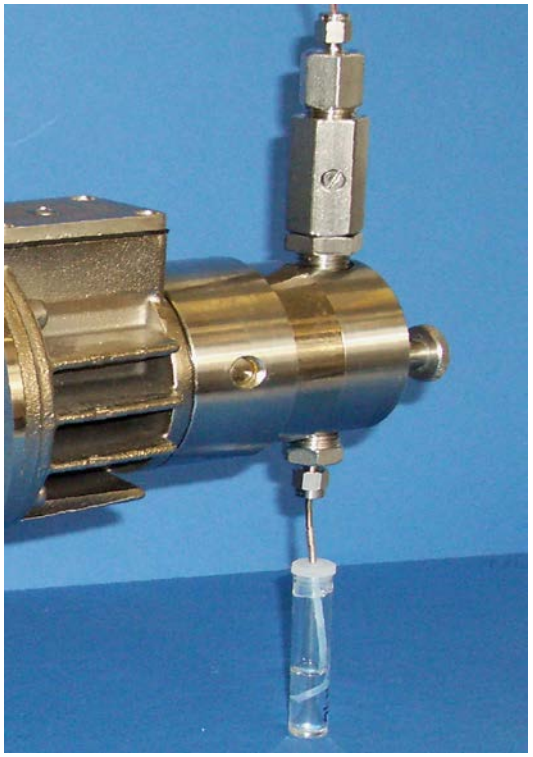
pulsed-flow experiment



pulsed-flow experiments:

- study of the time dependence of the conversion of reactants

- study of the isotopic exchange of reactants at high temperatures with well-defined starting time

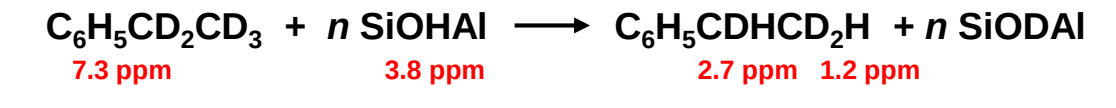


pump Mikro g/5 of Fa. ProMinent, Germany, for single pulses with volumes of 2 to 50 µl

IV. Catalytic applications

pulsed-flow MAS NMR-UV/Vis spectroscopy

side-chain H/D exchange of ethylbenzene on steamed zeolite deH,Na-Y/81.5

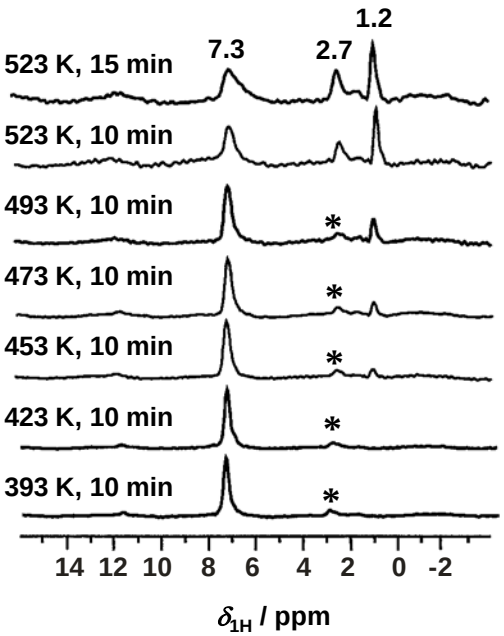


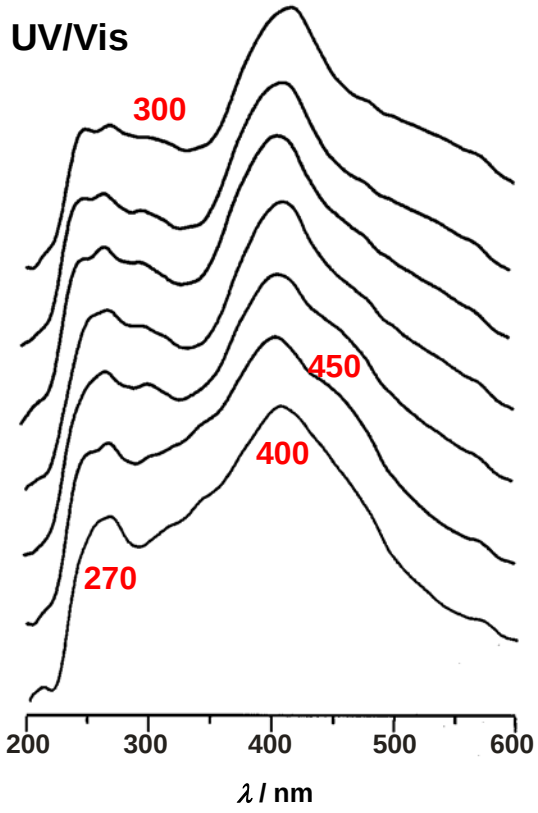
in situ ^{1}H VT/MAS NMR pulsed-flow experiments:

- 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)





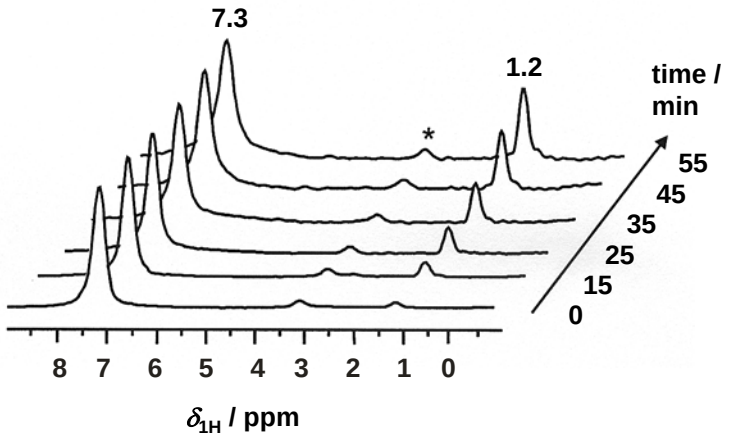
J. Huang etal., ChemPhysChem 9 (2008) 1107.

IV. Catalytic applications

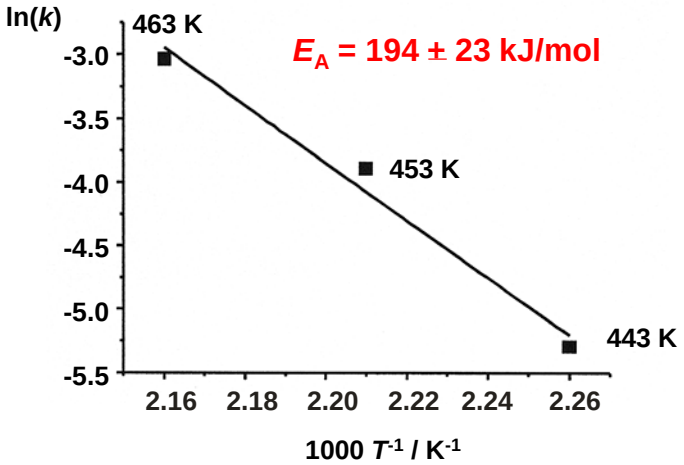
pulsed-flow MAS NMR-UV/Vis spectroscopy

study of the regioselective H/D exchange of the side-chain of $C_6H_5CD_2CD_3$ on dealuminated zeolite deH,Na-Y/81.5 (24.5 Al^{ex}/u.c, 10.9 SiOHAl /u.c)

^{1}H MAS NMR



Arrhenius plot



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

J. Huang etal., ChemPhysChem 9 (2008) 1107.

IV. Catalytic applications

pulsed-flow MAS NMR-UV/Vis spectroscopy

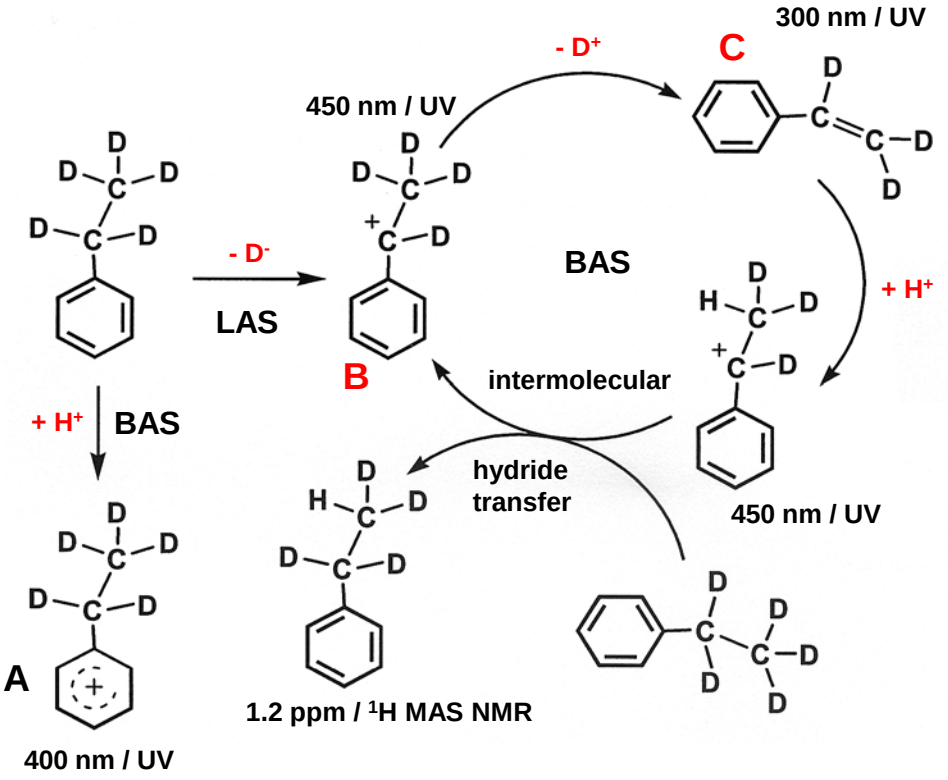
mechanism of the regioselective side-chain H/D exchange of ethylbenzene on steamed zeolite deH,Na-Y/81.5

^{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**



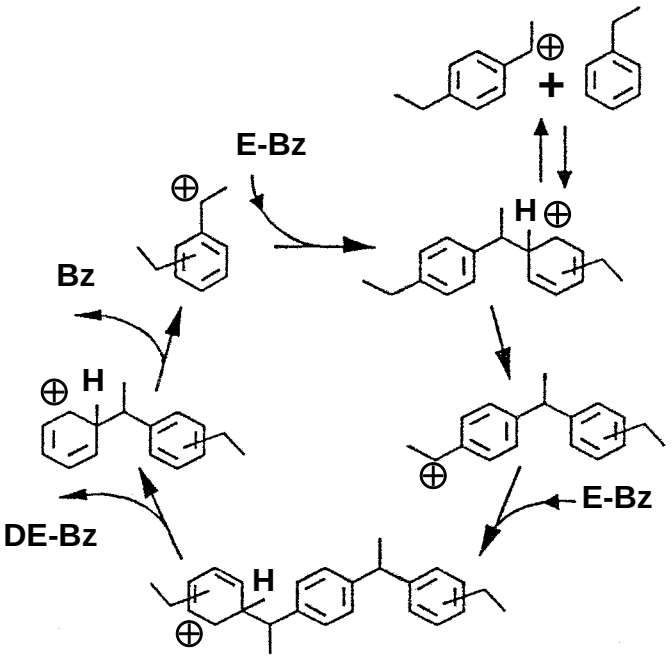
BAS: Broensted acid site **LAS: Lewis acid site**

J. Huang etal., ChemPhysChem 9 (2008) 1107.

IV. Catalytic applications

mechanisms of the ethylbenzene disproportionation

Streitwieser-Reif mechanism for the homogeneously catalyzed ethylbenzene disproportionation



suggested reaction mechanisms for the heterogeneously catalyzed reaction on zeolites:

- ***via*** **diphenylethane intermediates in large-pore zeolites**

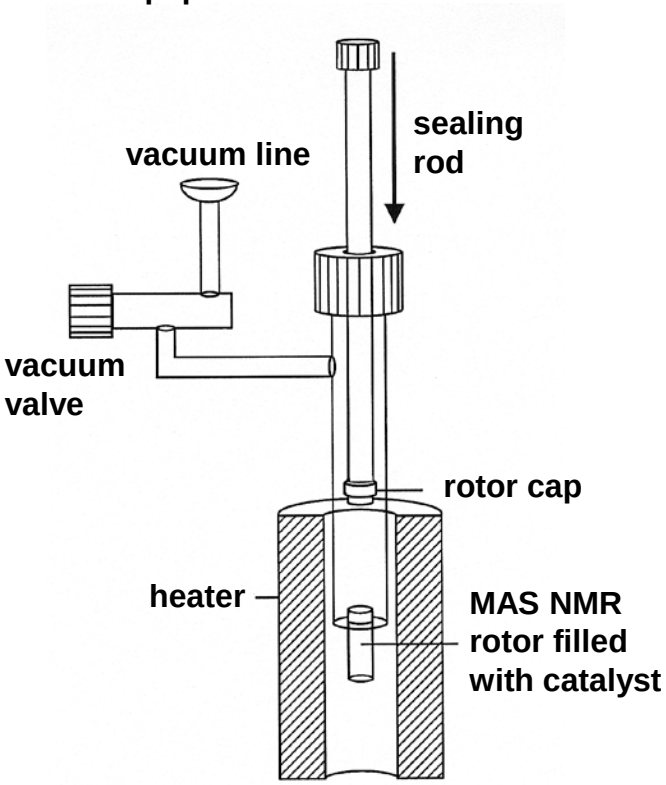
- **dealkylation/realkylation with free ethene or alkoxy species in medium-pore zeolites**

U. Weiß et al., Stud. Surf. Sci. Catal., Vol. 105, Elsevier, Amsterdam, 1997, p. 973.

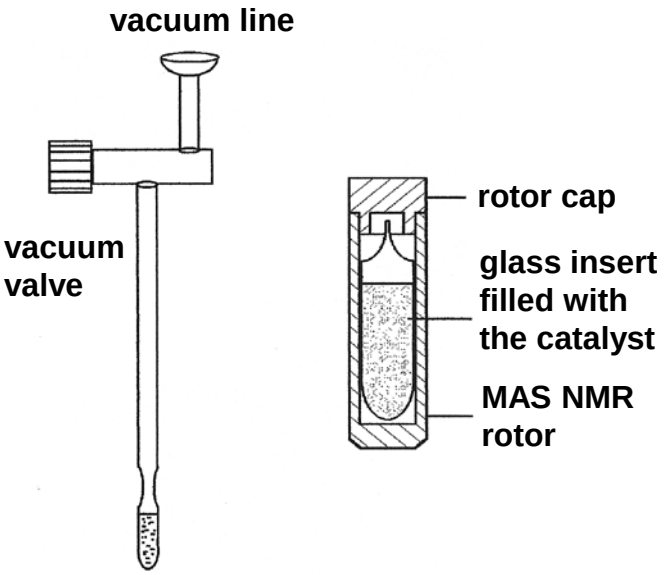
IV. Catalytic applications

preparation of sealed catalyst samples for MAS NMR studies under batch conditions

dehydration, loading, and sealing of the catalyst filled in an MAS NMR rotor inside a vacuum equipment



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



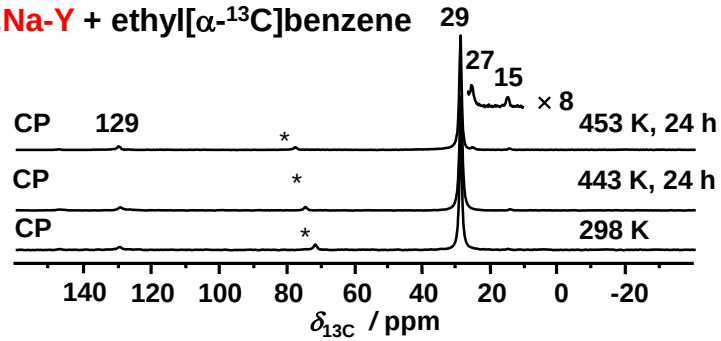
IV. Catalytic applications

mechanisms of the ethylbenzene disproportionation

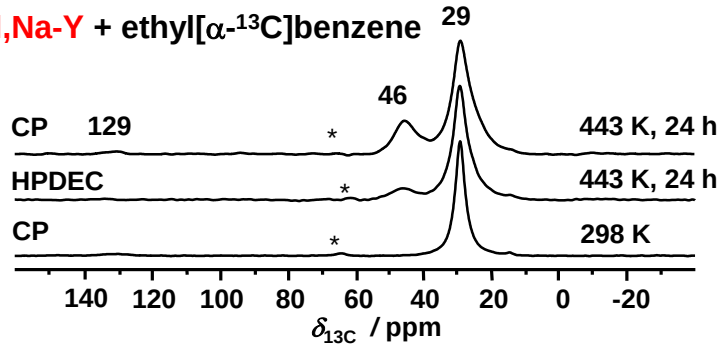
^{13}C MAS NMR investigation of the ethylbenzene conversion on large-pore zeolites H,Na-Y and Al,Na-Y

^{13}C MAS NMR

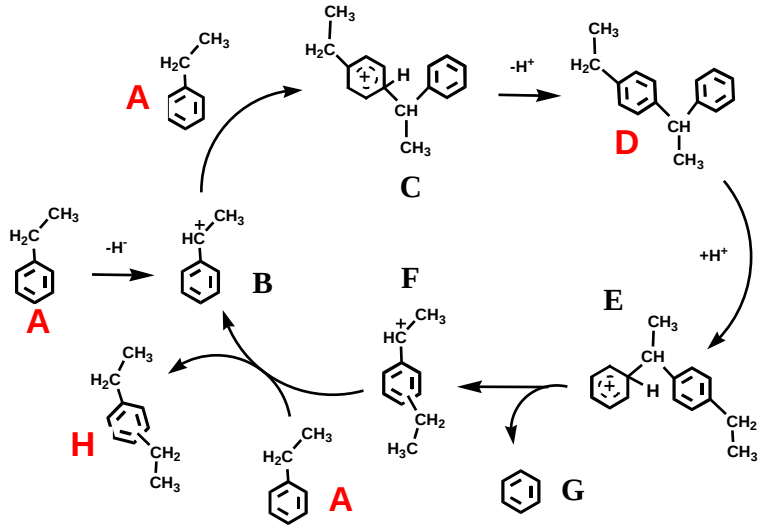
H,Na-Y + ethyl[α-^{13}C]benzene



Al,Na-Y + ethyl[α-^{13}C]benzene



reaction mechanism



assignment:

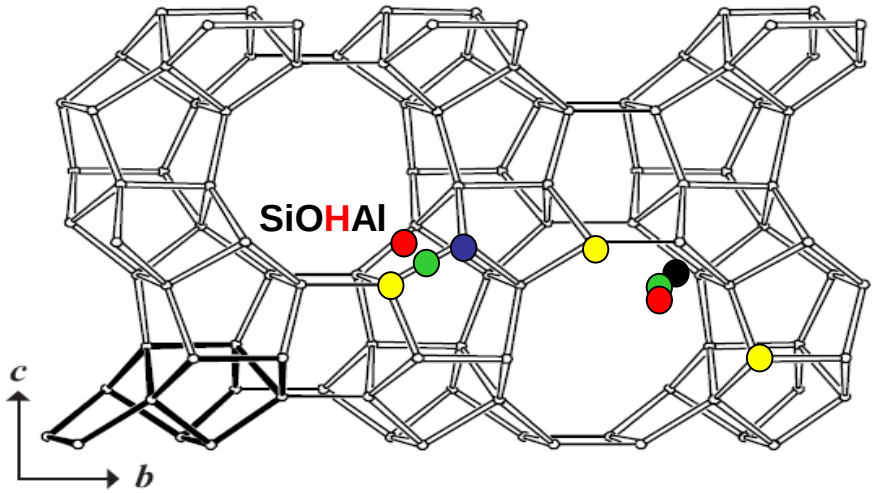
27 ppm	diethylbenzene (H)	46 ppm	diphenylethane (D)
29 ppm	ethylbenzene (A)	129 ppm	aromatic carbons

J. Huang et al., J. Am. Chem. Soc. 130 (2008) 12642.

IV. Catalytic applications

mechanisms of the ethylbenzene disproportionation

structure of medium-pore zeolite ZSM-5



$H^+_n[Al_nSi_{96-n}O_{192}]$

crossing intersections at interconnecting 10-ring channels

[100] 0.51 nm x 0.55 nm

[010] 0.53 nm x 0.56 nm

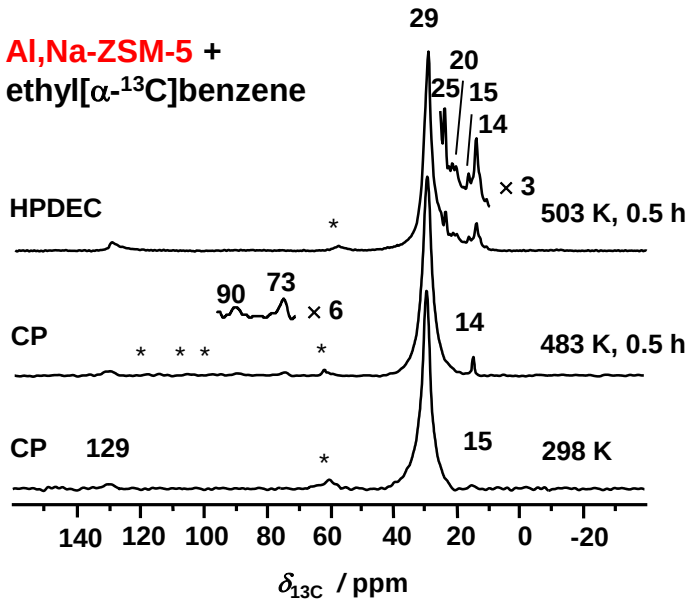
Al atom
Si atom
O atom
H atom
extra-framework cations (Na^+, Al^{3+} etc.)

IV. Catalytic applications

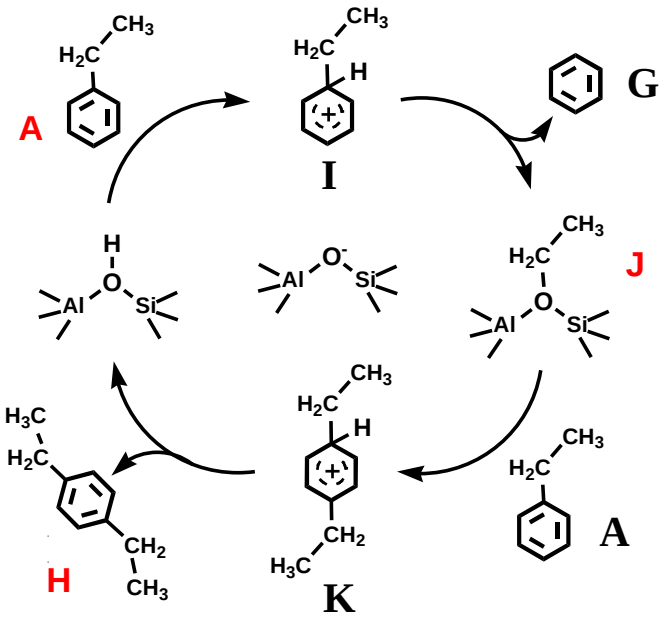
mechanisms of the ethylbenzene disproportionation

^{13}C MAS NMR investigation of the ethylbenzene conversion on medium-pore zeolite ZSM-5

^{13}C MAS NMR mechanism



reaction



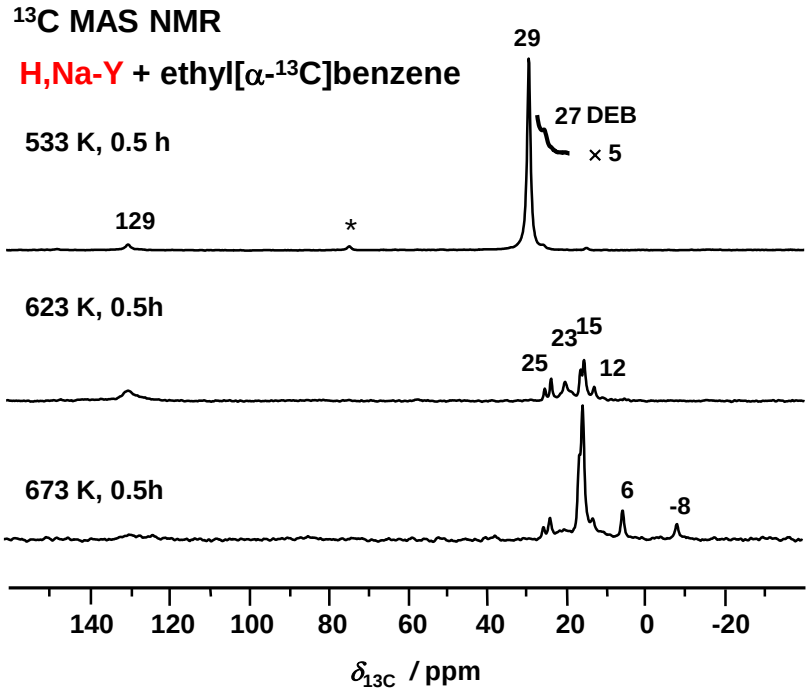
assignment:				
	25 ppm	**diethylbenzene (H)**	**73 ppm**	**surface ^{13}C-1-ethoxy groups (J)**
	29 ppm	**ethylbenzene (A)**	**90 ppm**	**oligomeric alkoxy groups**
			129 ppm	**aromatic carbons**

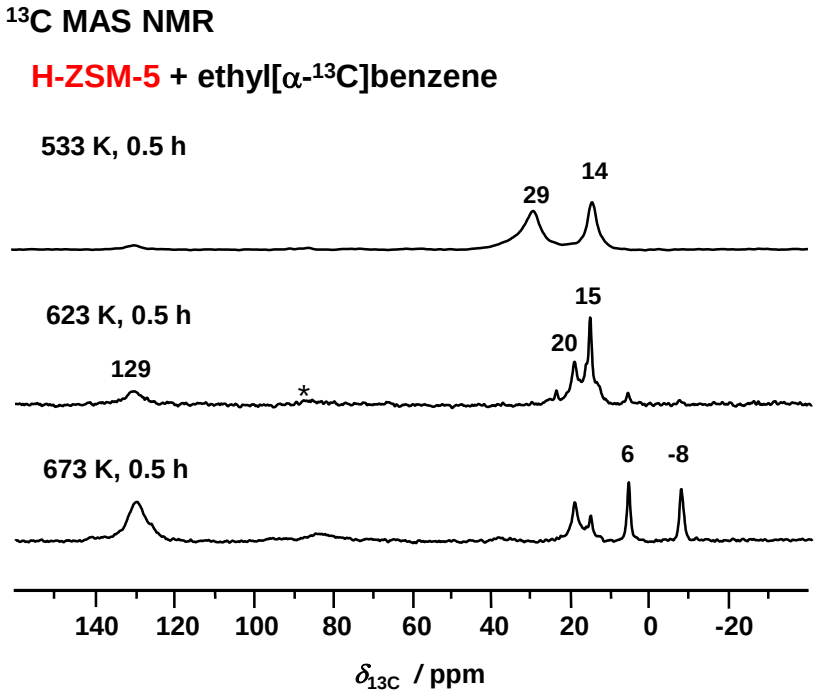
J. Huang et al., J. Am. Chem. Soc. 130 (2008) 12642.

IV. Catalytic applications

mechanisms of the ethylbenzene disproportionation

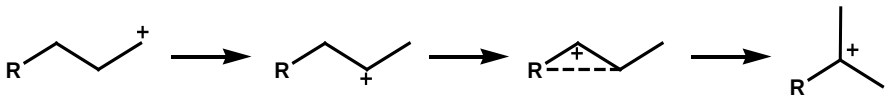
^{13}C MAS NMR investigation of the catalyst deactivation during ethylbenzene conversion

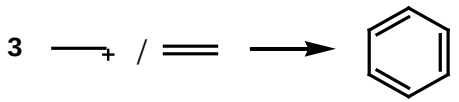




assignment:

-8 ppm	methane	23 ppm	butane
6 ppm	ethane	25 ppm	iso-alkanes
14 ppm	methyl of alkoxy	27 ppm	diethylbenzene
15 ppm	propane	29 ppm	ethylbenzene
20 ppm	alkylated aromatics	129 ppm	aromatic carbons





Y. Jiang et al., Catal. Today (2011) DOI: j.cattod.2010.10.024.

Summary

Solid-state NMR gives insight into the synthesis mechanisms of solid catalysts:

- nature and local structure of framework atoms, framework defects, and amorphous phases as demonstrated by application of solid-state ^{27}Al, ^{29}Si, ^{71}Ga NMR

Investigation of the routes for modifying solid catalysts:

- formation of extra-framework species, their coordination and location as well as quantitative studies of these sites

- properties of supported catalysts, interactions of the active compounds with the support

Characterization of Brønsted and Lewis acid sites:

- methods for determining the strength and activity of acid sites

- routes of their preparation and finding of suitable conditions for tuning their number, accessibility, and strength

Study of reaction mechanisms:

- reaction path of isotopically marked reactants under batch conditions

- *in situ* studies under continuous-flow and pulsed-flow condition, *e.g.*, for H/D exchange experiments at elevated temperatures

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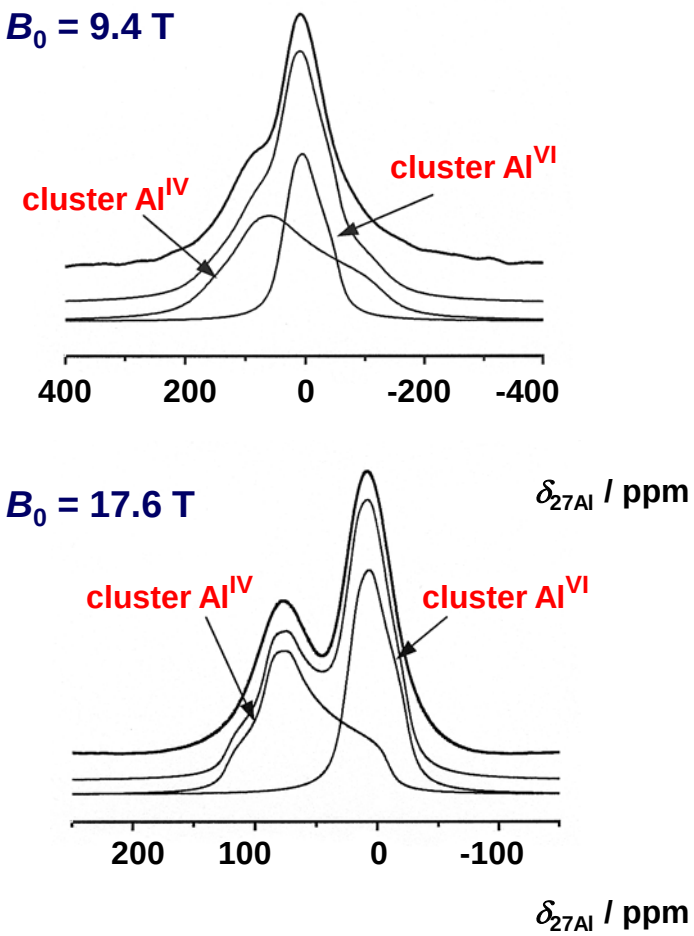
^{27}Al spin-echo NMR studies of reference materials

dehydrated γ-Al_2O_3

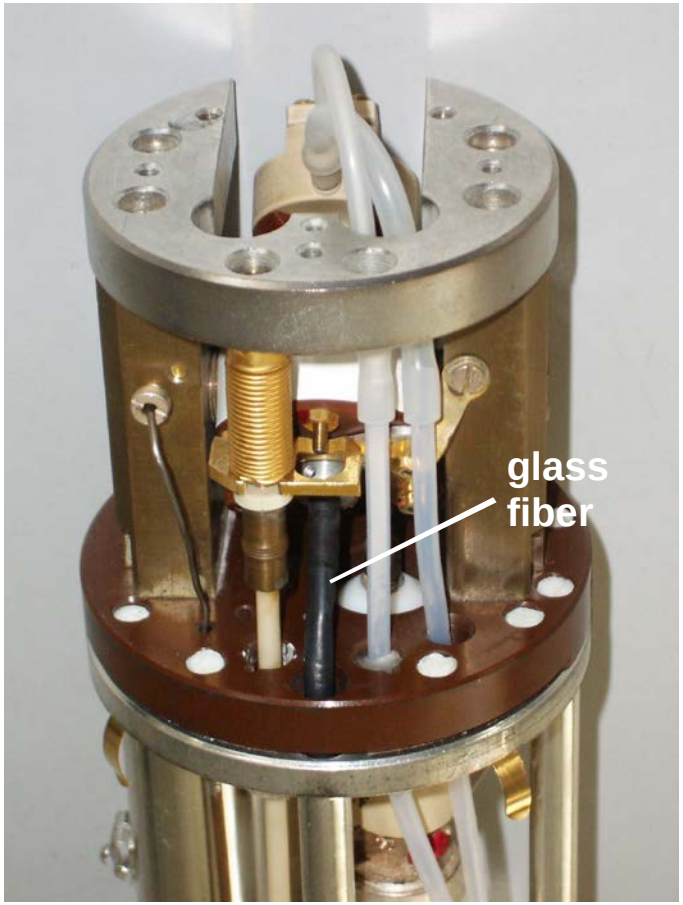


- **spectroscopic parameters of cluster Al^{IV}:**
  - ***QCC*** **= 8.5 MHz, η = 0.8**
  - **δ_{iso} = 68±5 ppm**
  - **I_{rel} = 60 %**

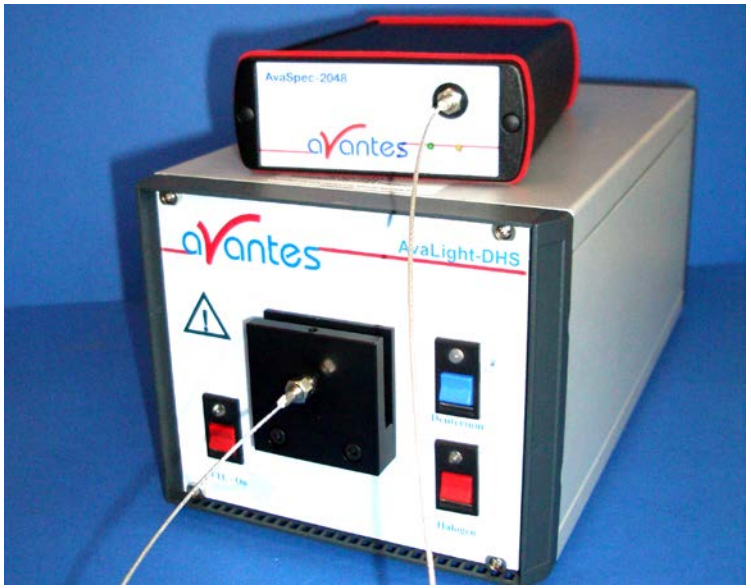
- **spectroscopic parameters of cluster Al^{VI}:**
  - ***QCC*** **= 5.5 MHz, η = 0.7**
  - **δ_{iso} = 12±5 ppm**
  - **I_{rel} = 40 %**

J. Jiao et al., Phys. Chem. Chem. Phys. 7 (2005) 3221.

Technique of in situ MAS NMR-UV/Vis spectroscopy



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, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105-127