In Situ Solid-State NMR Investigation of the Interaction and Conversion of Ethylbenzene on Acidic Zeolite Catalysts

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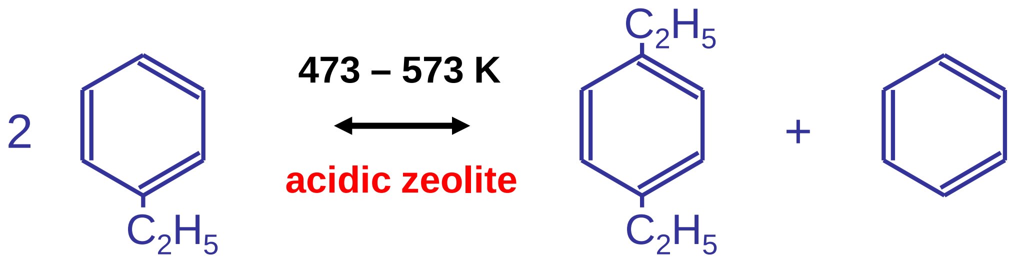
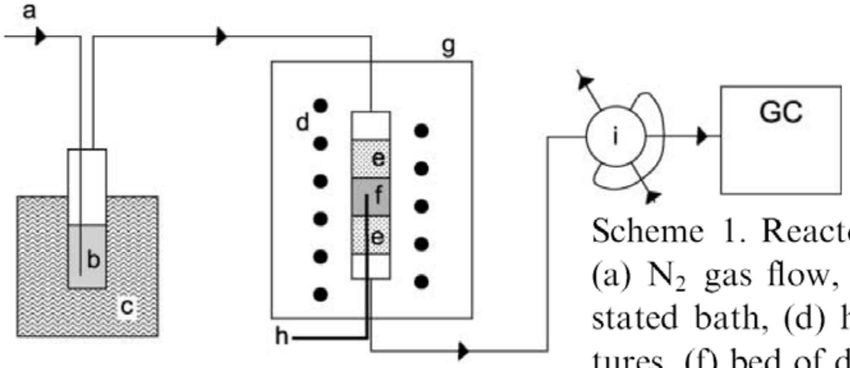
Importance of the ethylbenzene disproportionation



para-**diethylbenzene is intermediate for the formation of divinylbenzene (*p*-distyrene) acting as cross-linking agent of polystyrenes (G. Ertl et al., Handbook of Heterogeneous Catalysis, Vol. 7, VCH, 2008, p. 3184)**

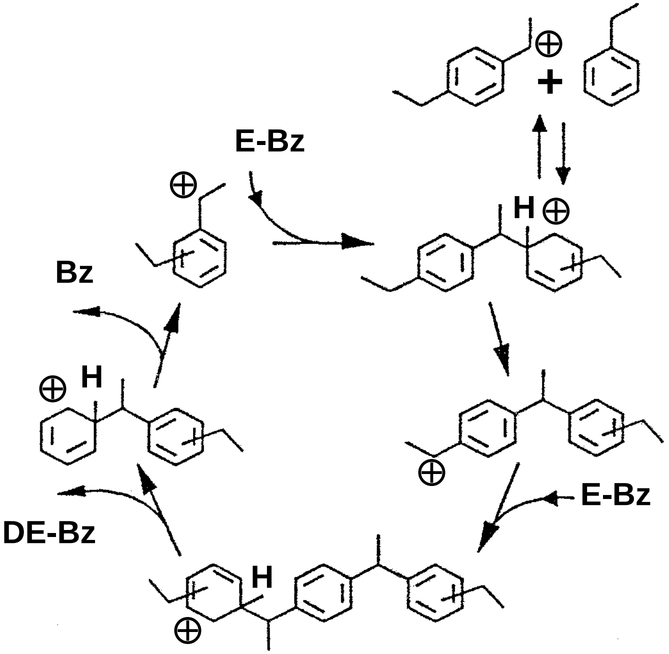
standard reaction of the International Zeolite Association for acidity characterization (D.E. De Vos et al., Microporous & Mesoporous Mater. 56 (2002) 185)



Scheme 1. Reactor setup for ethylbenzene disproportionation: (a) N_2 gas flow, (b) saturator with ethylbenzene, (c) thermostated bath, (d) heating coils for glass reactor, (e) inert structures, (f) bed of diluted catalyst, (g) oven, (h) thermocouple, (i) 6-way valve. Transfer lines between reactor and GC should be heated. Proper air circulation in the oven should be provided.

Suggested mechanisms of ethylbenzene disproportionation

Streitwieser-Reif mechanism for the homogeneously catalyzed reaction



suggested reaction mechanisms for the heterogeneously catalyzed reaction on zeolites:

- *via* diphenylethane intermediates in large-pore zeolites

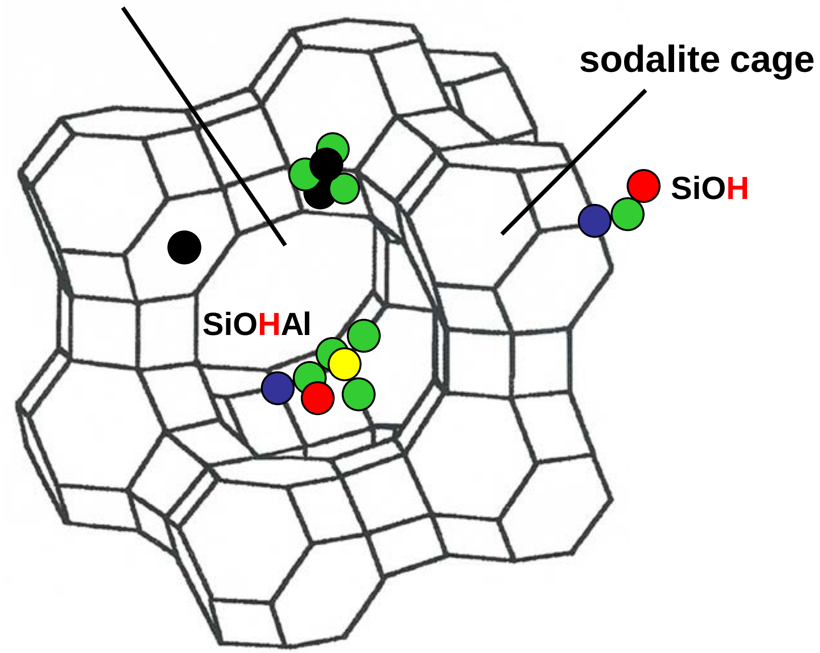
- dealkylation/realkylation with free ethene or alkoxy species in medium-pore zeolites

U. Weiß et al., Stud. Surf. Sci. Catal., Vol. 105, Elsevier, Amsterdam, 1997, p. 973-980.

Structure and acid sites of zeolite Y

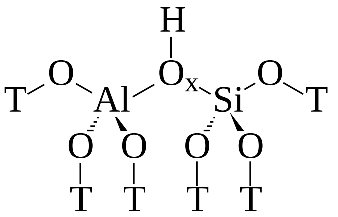
structure of zeolite Y (FAU, faujasite): **large-pore zeolite with 12-ring windows (diameter of 0.74 nm)**

supercage (free diameter of 1.23 nm)



🟡 **Al atom**
🔵 **Si atom**
🟢 **O atom**
🔴 **H atom**
⚫ **extra-framework Cations (Na^+, Al_3^+ etc.)**

Broensted acid sites:



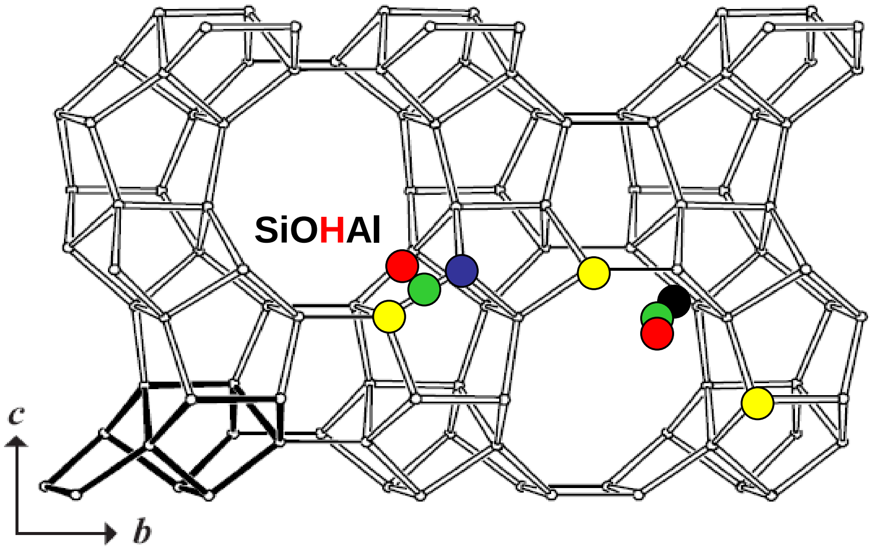
bridging OH group, Si(OH)Al

Lewis acid sites:

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

Structure and acid sites of zeolite ZSM-5

structure of zeolite ZSM-5 (MFI): **medium-pore zeolite with 10-ring pores**



🟡 **Al atom** 🟢 **O atom** ⚫ **extra-framework Cations (Na^+, Al_3^+ etc.)**

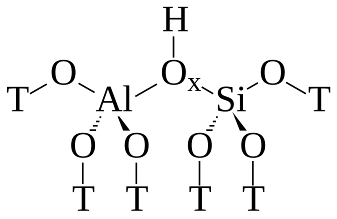
🔵 **Si atom** 🔴 **H atom**

crossing intersections at interconnecting 10-ring channels

[100] 0.51 nm x 0.55 nm

[010] 0.53 nm x 0.56 nm

Broensted acid sites:

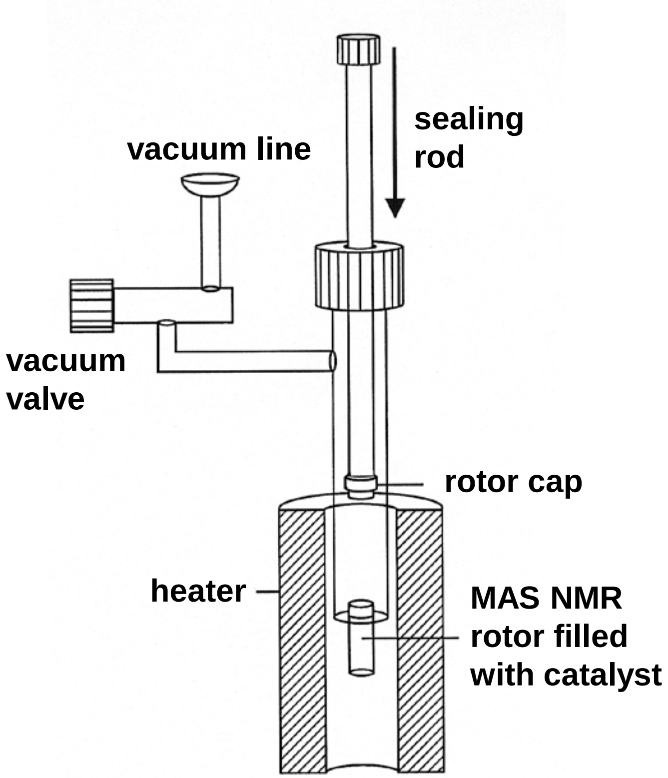


bridging OH groups, Si(OH)Al, with higher acid strength in comparision with zeolite Y

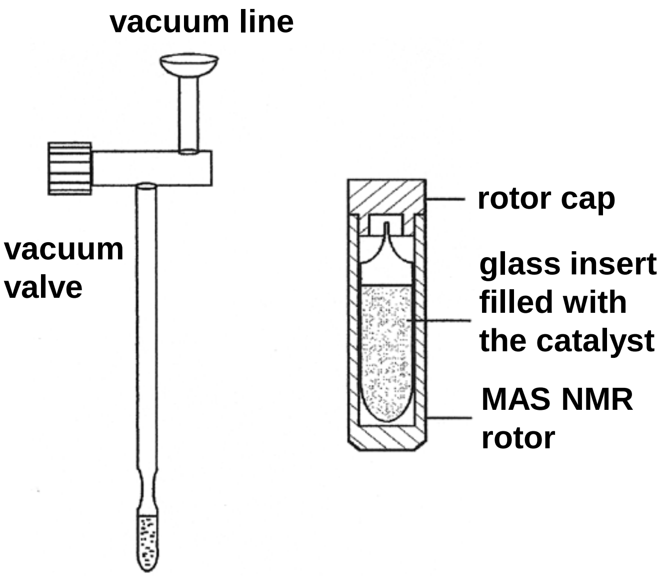
In situ solid-state NMR studies of the C_6-ring activation of aromatics adsorbed on acidic zeolites

Preparation of sealed catalyst samples for solid-state NMR studies under batch conditions

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



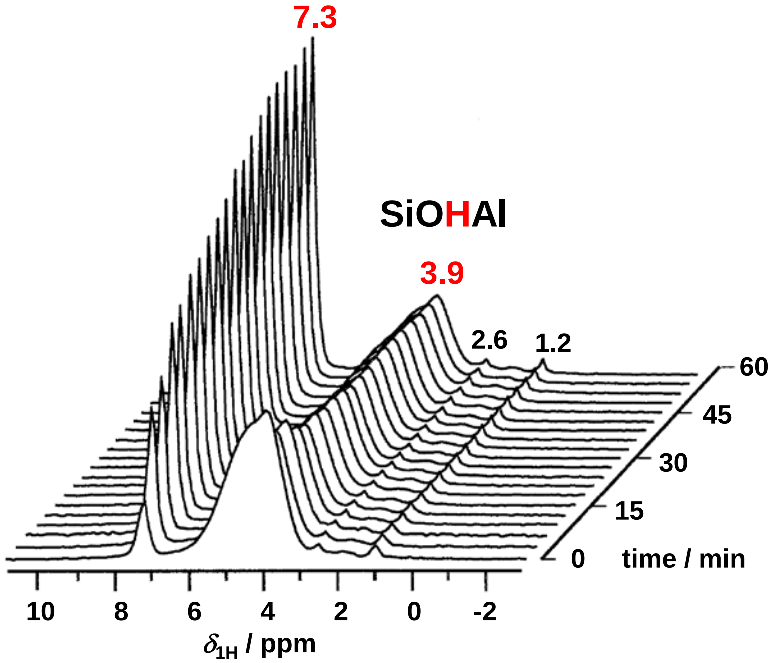
dehydration and loading of the catalyst inside the glass insert (e.g. commercial Wilmad MAS NMR inserts for 4 mm and 7 mm rotors)



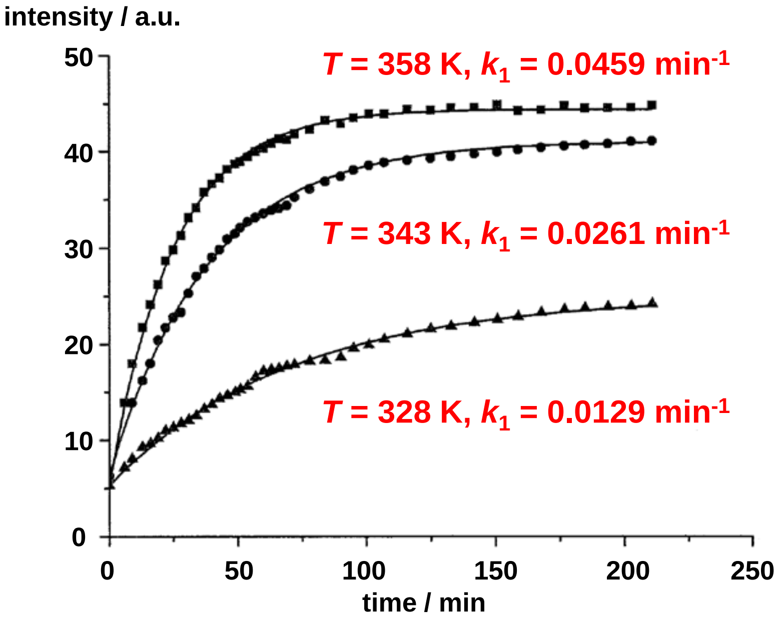
H/D exchange between aromatic deuterons and hydroxyl protons of bridging OH groups

^{1}H MAS NMR studies of zeolite H,Na-Y loaded with ethylbenzene ($C_6D_5C_2D_5$)

stack plot of spectra recorded at T = 358 K



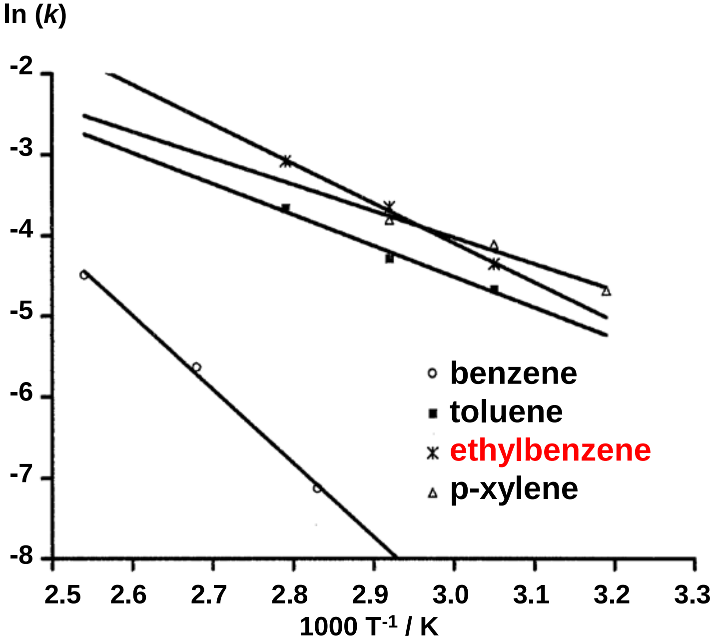
H/D exchange rates at T = 328 - 358 K



H/D exchange between aromatic deuterons and hydroxyl protons of bridging OH groups

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

deuterated aromatics on zeolite H,Na-Y

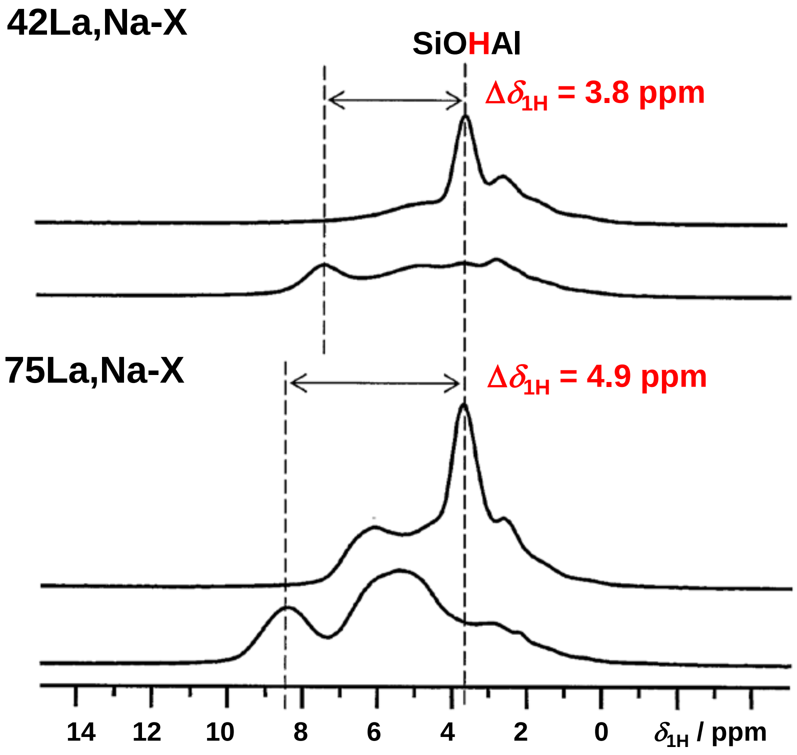


correlation of activation energies E_A of H/D exchange:

catalyst	molecule	E_A / kJ mol^{-1}
H,Na-Y	benzene	76
	ethylbenzene	41
	toluene	32
	p-xylene	27
H,Na-Y	benzene	76
La,Na-Y	benzene	67
H-ZSM-5	benzene	46

Characterization of acid strength via H-bond-induced low-field shift $\Delta\delta_{1H}$

^{1}H MAS NMR spectroscopy of acetonitrile-loaded Broensted acidic materials

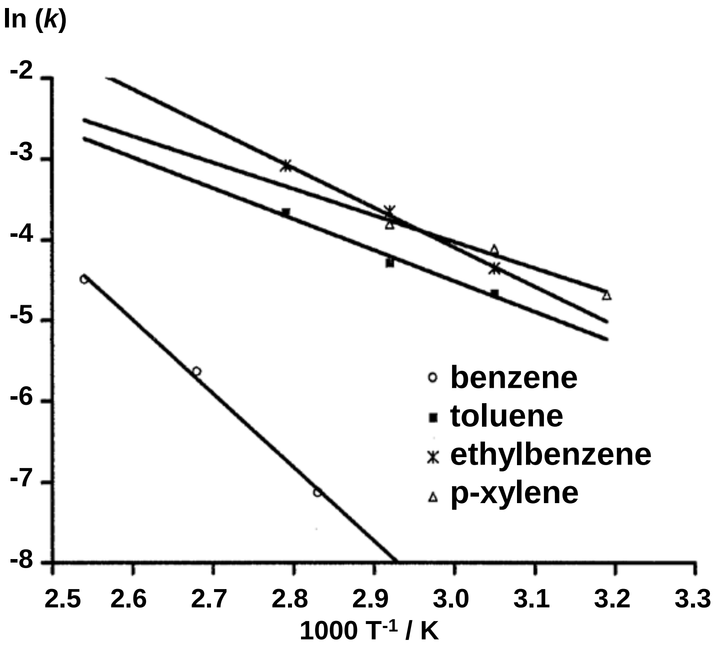


low-field shift $\Delta\delta_{1H}$	adsorbent and type of OH group
1.2 ppm	AlOH in MIL-53(Al)
3.6 ppm	H-X (Si/Al= 1.3)
3.8 ppm	42La,Na-X and 32Al,Na-X (Si/Al = 1.4)
4.9 ppm	75La,Na-X (S/Al = 1.4)
5.1 ppm	H-Y (Si/Al = 2.7)
5.3 ppm	34Al,Na-Y and 63Al,Na-Y (Si/Al = 2.7)
5.7 ppm	42La,Na-Y and 75La,Na-Y (Si/Al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

H/D exchange between aromatic deuterons and hydroxyl protons of bridging OH groups

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

deuterated aromatics on zeolite H,Na-Y



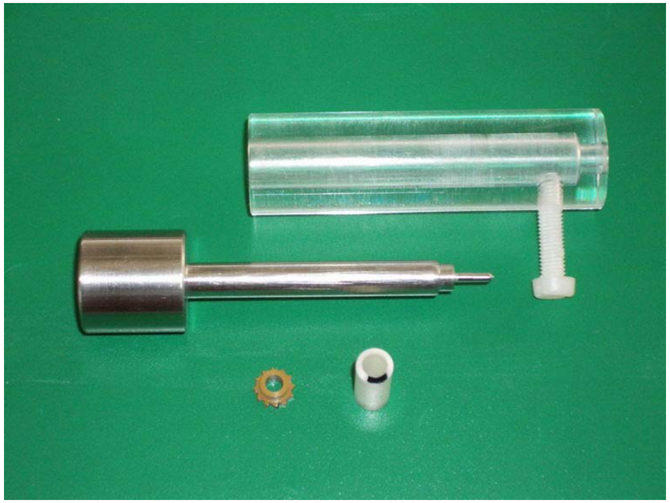
correlation of activation energies E_A of H/D exchange and low-field shifts $\Delta\delta_{1H}$ upon adsorption CD_3CN:

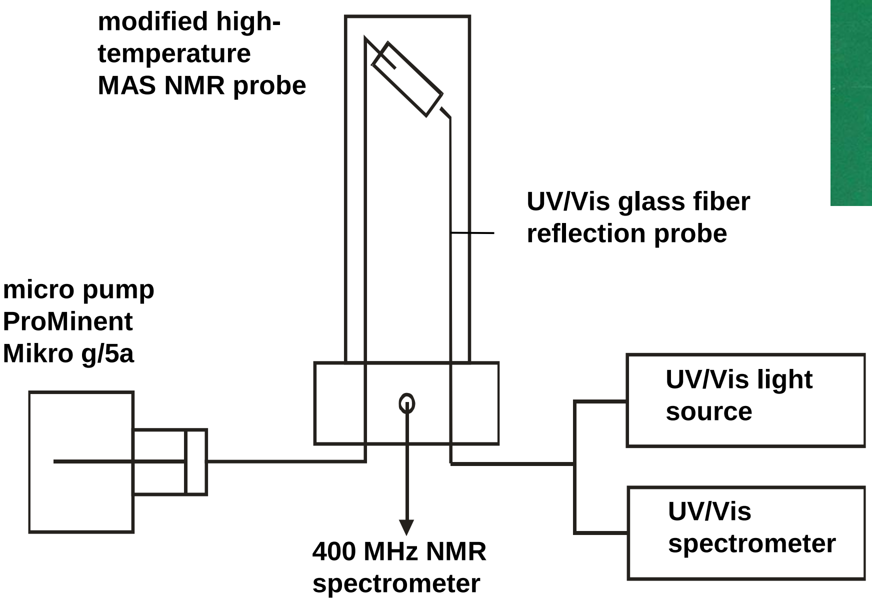
catalyst	molecule	E_A / kJ mol^{-1}	$\Delta\delta_{1H}$ / ppm
H,Na-Y	benzene	76	
	ethylbenzene	41	
	toluene	32	
	p-xylene	27	
H,Na-Y	benzene	76	5.1
La,Na-Y	benzene	67	5.7
H-ZSM-5	benzene	46	7.9

In situ solid-state NMR studies of the side-chain activation of alkylaromatics adsorbed on acidic zeolites

Pulsed-flow MAS NMR-UV/Vis spectroscopy

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





modified high-temperature MAS NMR probe

UV/Vis glass fiber reflection probe

micro pump ProMinent Mikro g/5a

UV/Vis light source

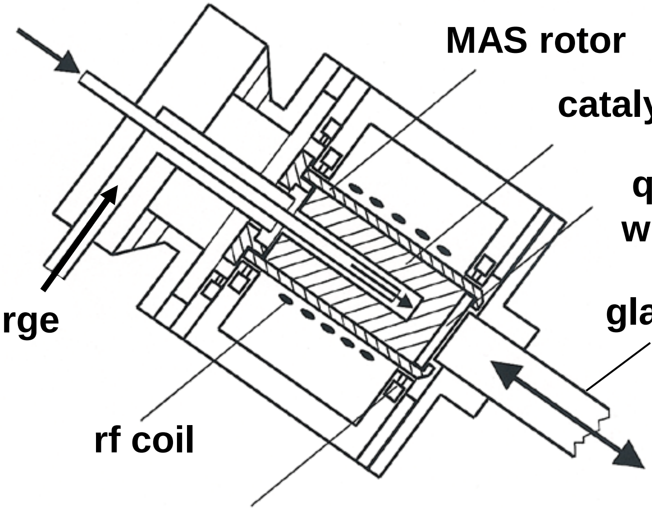
UV/Vis spectrometer

400 MHz NMR spectrometer

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

Technique of in situ 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



reactant pulses

MAS rotor

catalyst bed

quartz window

glass fiber

purge

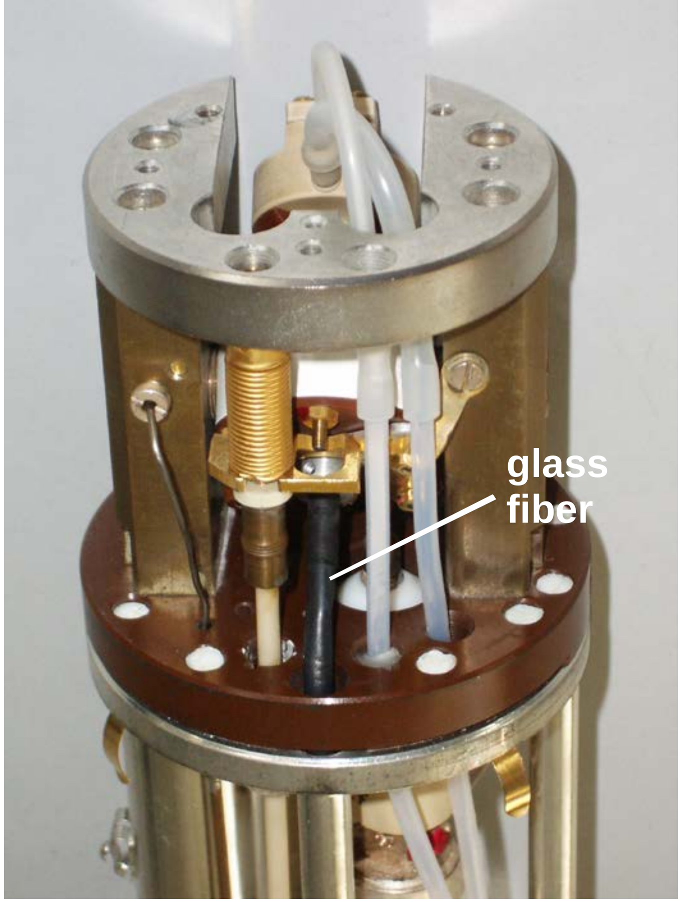
rf coil

gas bearing

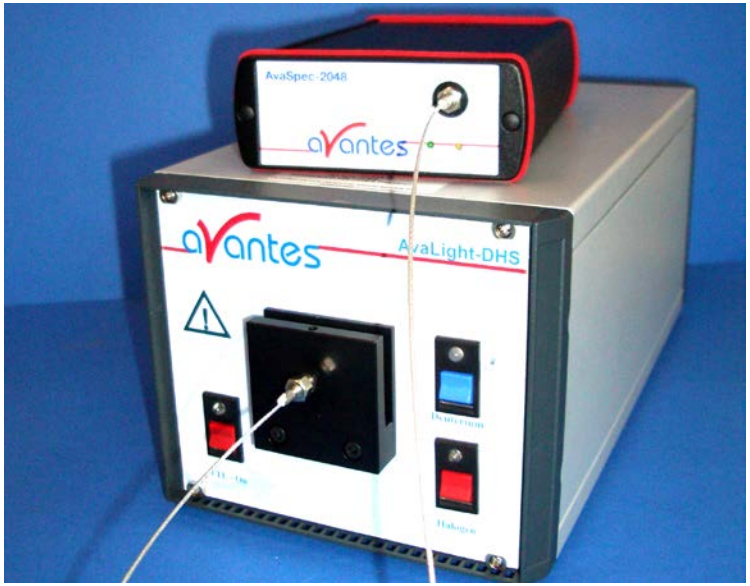
UV/Vis light source and spectrometer

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

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)

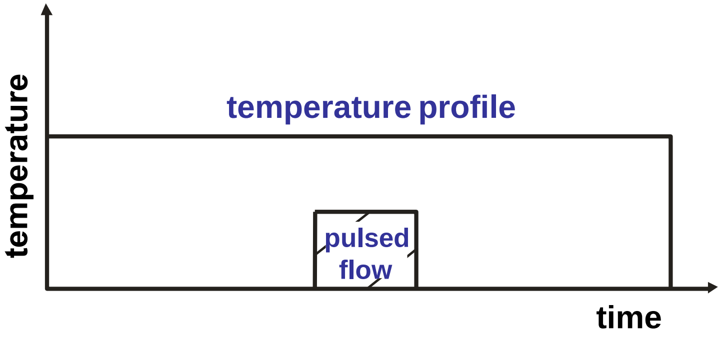


M. Hunger, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105-127

Pulsed-flow equipment

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

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

^{1}H MAS NMR pulsed-flow experiments:

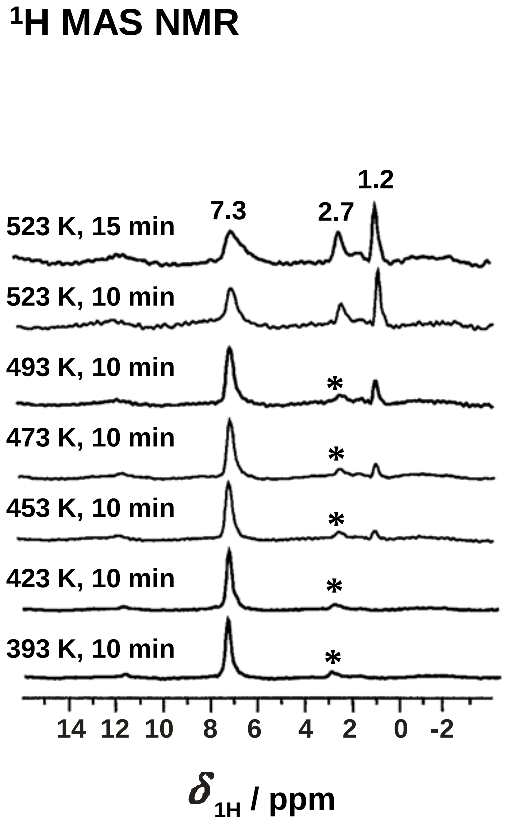
- steamed zeolite deH-Y (n_{Si}/n_{Al} = 5.4)
- pulses of 7.8 mg ethyl-*d*$_5$-benzene
- 32 scans per spectrum with repetition time of 10 s at 9.4 T
- sample spinning rate of *ca.* 2 kHz

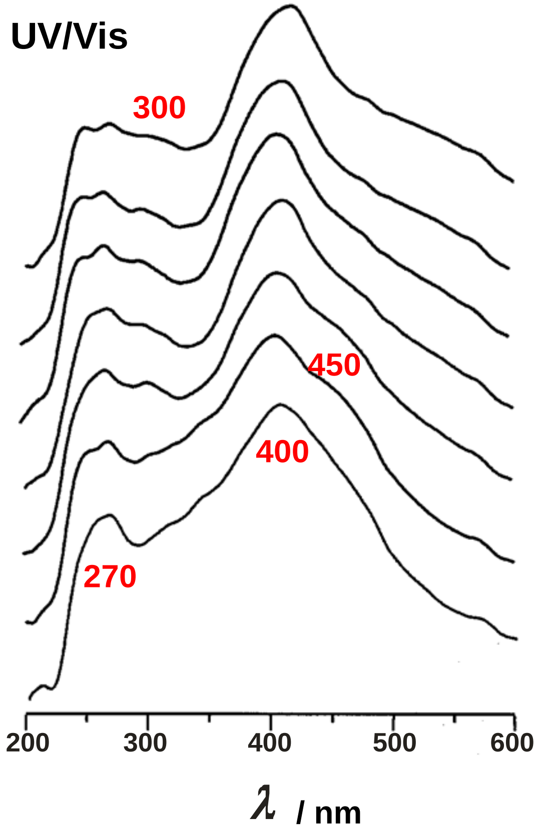
message:

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

$$C_6\textcolor{red}{H}_5CD_2CD_3 \;+\; n\;Si(O\textcolor{red}{H})Al \longleftrightarrow C_6H_5CD\textcolor{red}{H}CD_2\textcolor{red}{H} \;+\; n\;Si(OD)Al$$

7.3 ppm 3.8 ppm 2.7 ppm 1.2 ppm

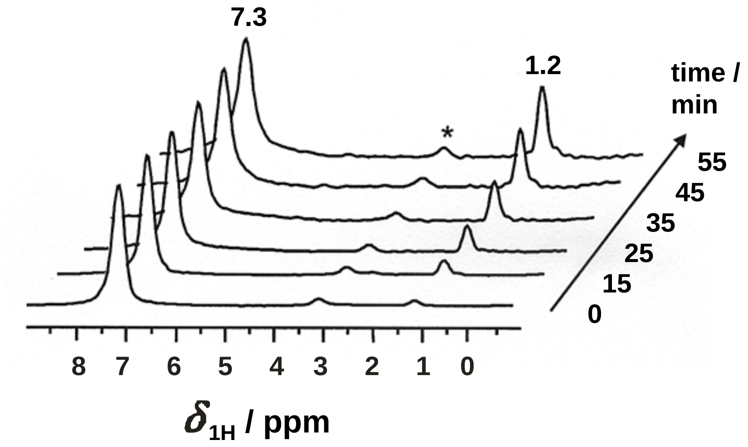




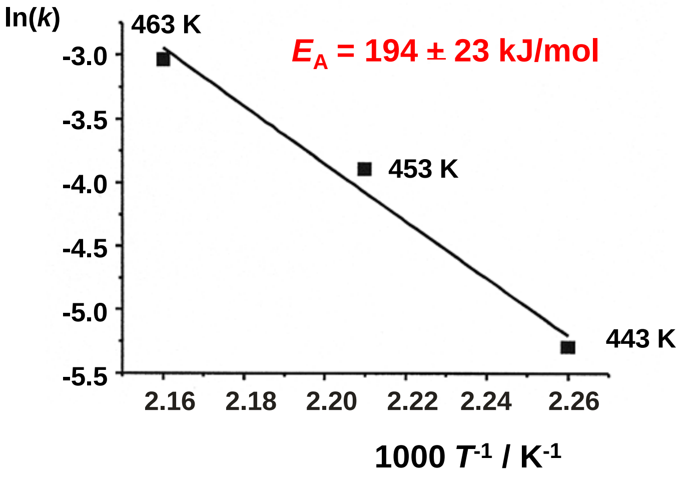
Study of the side-chain H/D exchange of ethylbenzene on dealuminated zeolite H-Y

in situ **pulsed-flow ^{1}H MAS NMR study of the regioselective H/D exchange of the side-chain of $C_6H_5CD_2CD_3$ on dealuminated zeolite deH-Y (Si/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**

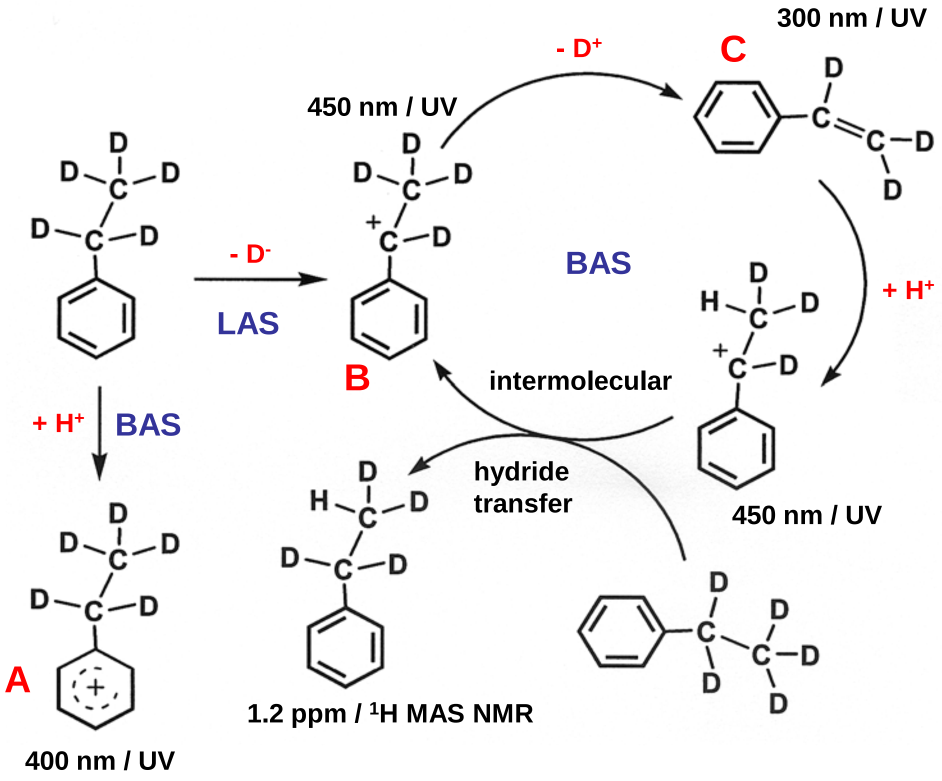
Mechanism of the regioselective side-chain H/D exchange of ethylbenzene on dealuminated zeolite H-Y

^{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**

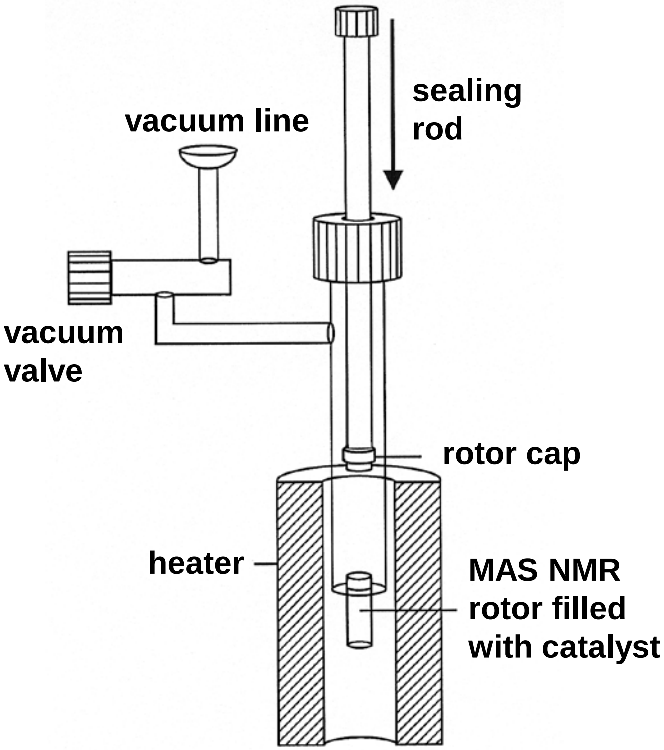


BAS: Broensted acid site **LAS: Lewis acid site**

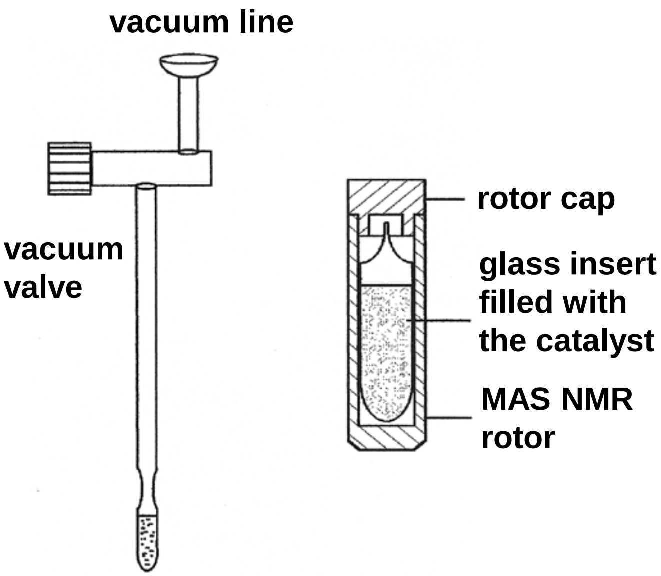
Solid-state NMR studies of the heterogeneously catalyzed conversion of ethylbenzene on acidic zeolites

Preparation of sealed catalyst samples for solid-state 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)

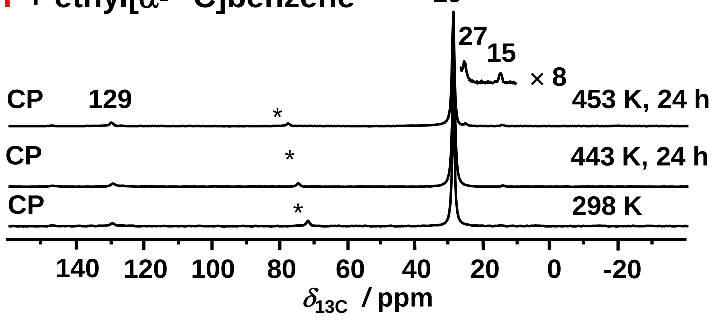


^{13}C MAS NMR study of the ethylbenzene conversion on zeolites H-Y and Al,Na-Y

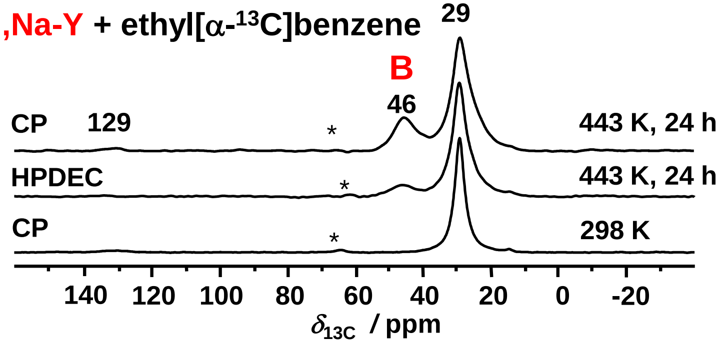
large-pore zeolite Y: supercages connected by 12-ring windows with a diameter of 0.71 nm

^{13}C MAS NMR

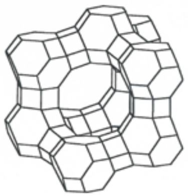
H-Y + ethyl[α-^{13}C]benzene

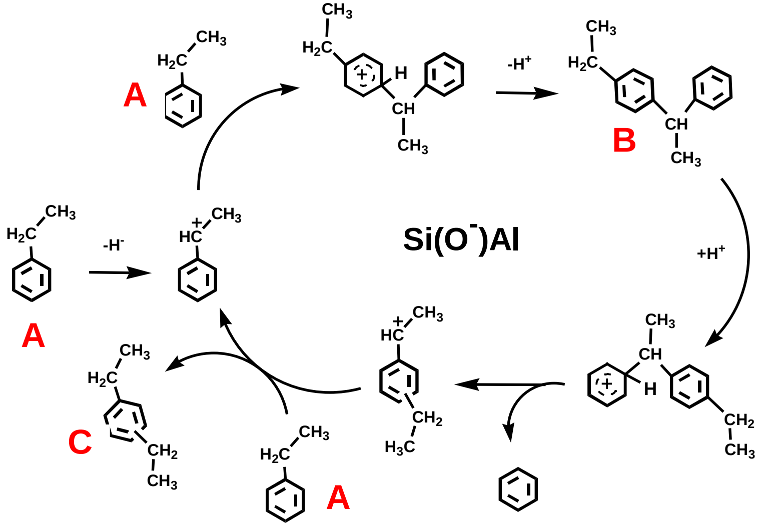


Al,Na-Y + ethyl[α-^{13}C]benzene



reaction mechanism:



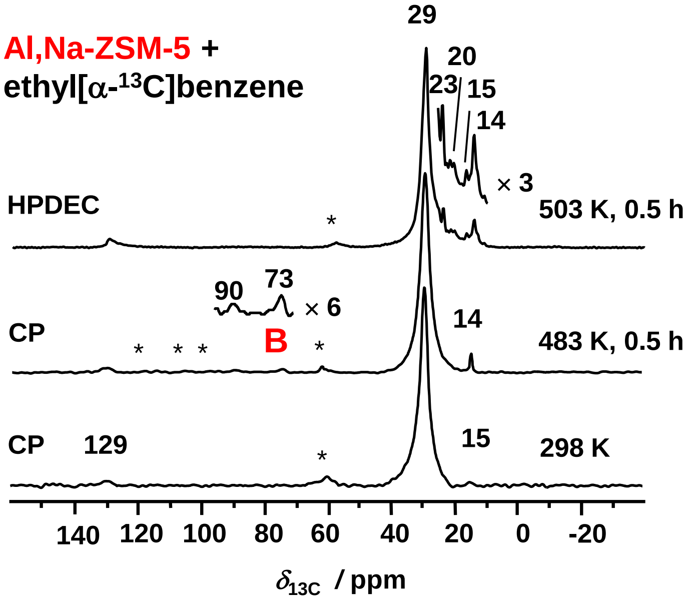


assignment:				
	27 ppm	diethylbenzene (C)	46 ppm	diphenylethane (B)
	29 ppm	ethylbenzene (A)	129 ppm	aromatic carbons

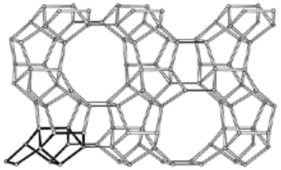
^{13}C MAS NMR study of the ethylbenzene conversion on zeolite Al,Na-ZSM-5

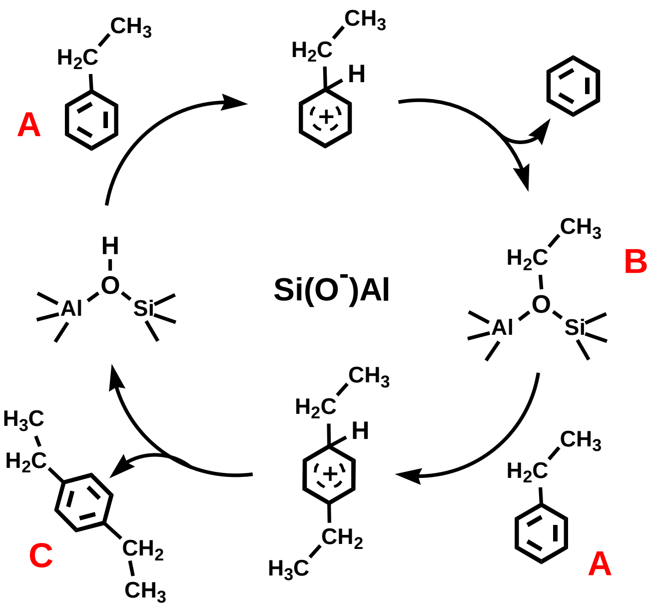
medium-pore zeolite ZSM-5: **10-ring pores with diameters of 0.51 to 0.56 nm**

^{13}C MAS NMR



reaction mechanism:





assignment:

23 ppm	diethylbenzene (C)	73 ppm	surface ^{13}C-1-ethoxy groups (B)
29 ppm	ethylbenzene (A)	90 ppm	oligomeric alkoxy groups
		129 ppm	aromatic carbons

Summary

Protonation/proton exchange of alkylaromatics on acidic zeolite catalysts:

- H/D exchange at the rings of alkylaromatics occurs already at 328 to 358 K and depends on the nature of the alkyl groups (+I effect)
- in the presence of Lewis acid sites, a regioselective H/D exchange at the side-chain of ethylbenzene via hydride abstraction and hydride transfer occurs

Reaction mechanisms on large- and medium-pore zeolites:

- ^{13}C MAS NMR signal at 46 ppm upon disproportionation of ethyl[α-^{13}C]benzene on large-pore zeolite Y (supercages, 12-ring windows) supports a mechanism *via* diphenylethane.
- ^{13}C MAS NMR signal at 73 ppm upon disproportionation of ethyl[α-^{13}C]benzene on medium-pore zeolite ZSM-5 (10-ring windows) supports a mechanism *via* dealkylation, ethoxy formation, and realkylation.

Experimental methods:

- pulsed-flow MAS NMR technique allows H/D exchange experiments at high temperatures with well-defined starting point.
- combination of *in situ* MAS NMR and *in situ* UV/Vis spectroscopy in one equipment gives complementary information on the systems under study.

Thanks to ….

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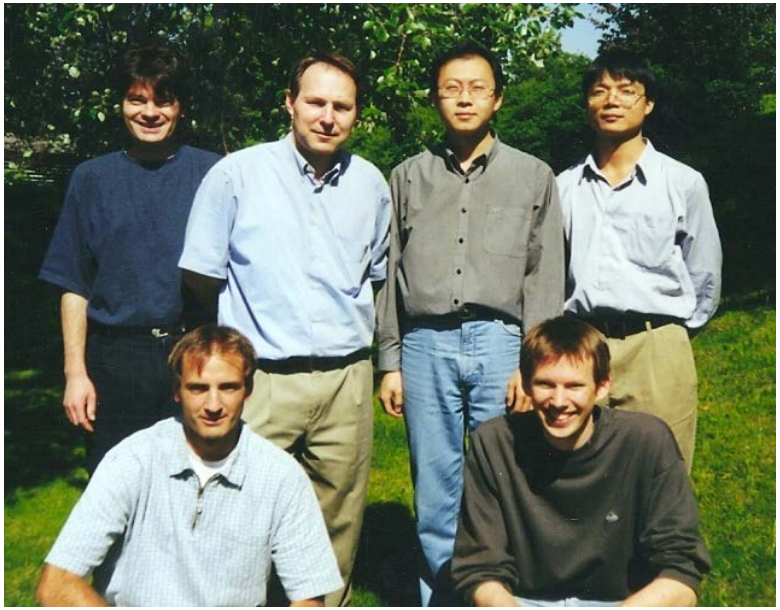
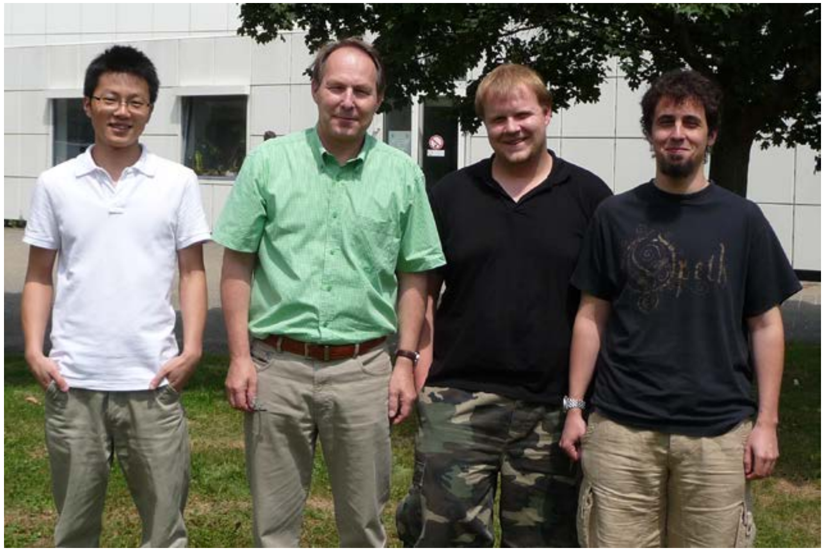




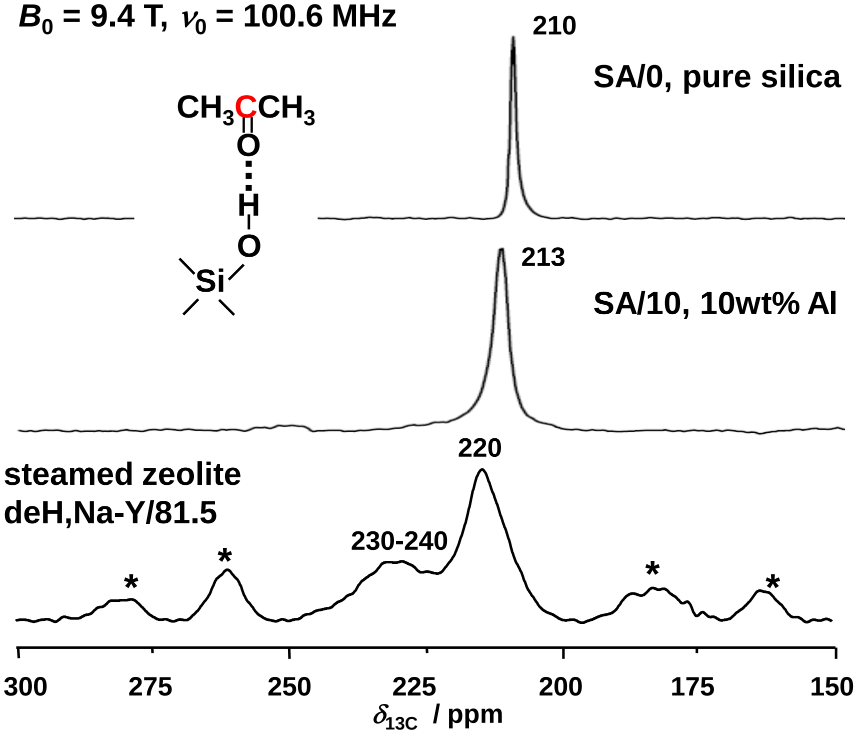
Preparation of dehydrated catalyst samples

vacuum line for dehydration of catalyst samples in glass tubes at elevated temperatures (often 673 K)

transfer of the dehydrated catalyst samples from glass tubes into MAS rotors inside a glove box (dry nitrogen)

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

^{13}C CPMAS NMR



Materials	δ_{13C}	□δ_{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.

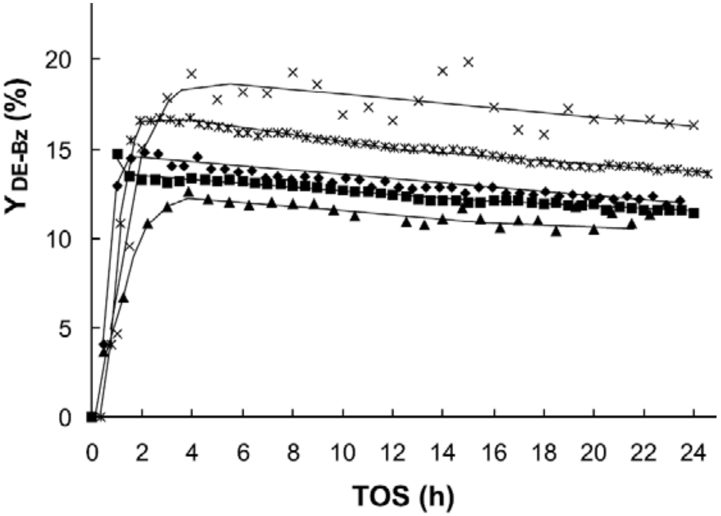
Lewis sites formed by steaming

Brønsted sites with different acid strengths (see Tab.)

Y. Jiang et al., Solid State Nucl. Magn. Reson. 39 (2011) 116-141.

Catalytic study of the ethylbenzene disproportionation over large-pore zeolites La,Na-Y

yield of diethylbenzene:



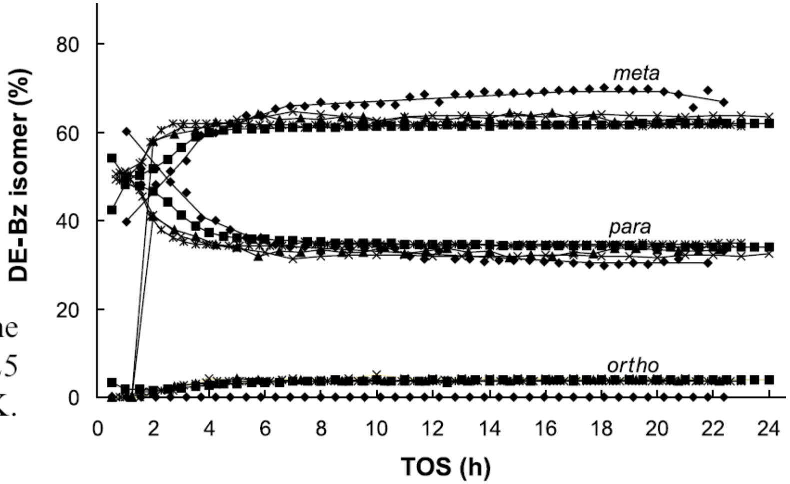
Yield of diethylbenzenes ($Y_{DE\text{-}Bz}$) as a function of time on stream. Data from L1 (◆), L2 (✱), L3 (▲), L4 (■) and L5 (×). Conditions: as in Fig. 1, but reaction temperature = 523 K.

L1 to L5: **data of five laboratories**

catalyst:

zeolite Na-Y with Si/Al = 2.4 exchanged in solution of $La(NO_3)_3$ until exchange degree of 72 %

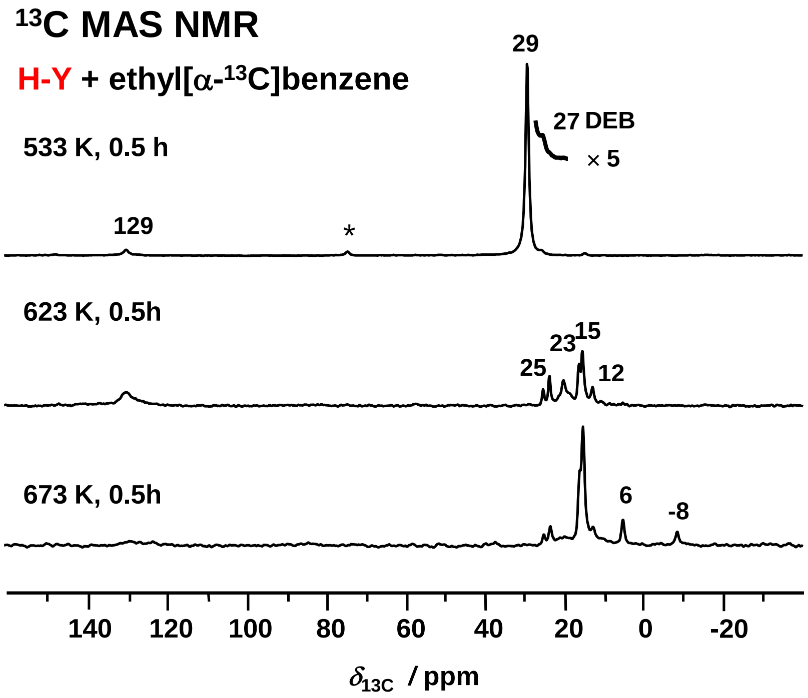
selectivities to *m*-, *p*- and *o*-diethylbenzene:



Selectivities to the diethylbenzene isomers (%) in the ethylbenzene disproportionation as a function of time on stream. Reaction temperature = 453 K.

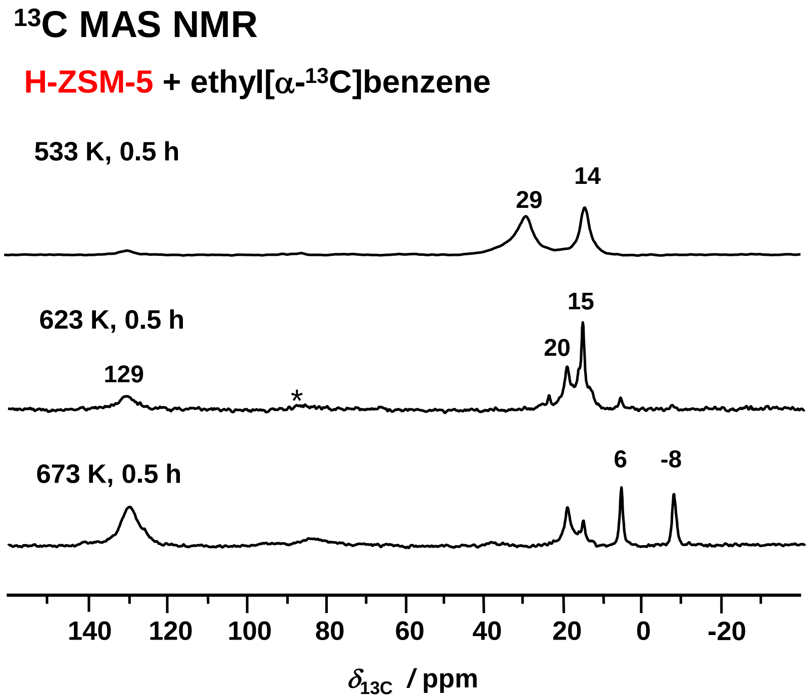
D.E. De Vos et al., Microporous & Mesoporous Mater. 56 (2002) 185.

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



^{13}C MAS NMR

H-Y + ethyl[α-^{13}C]benzene



^{13}C MAS NMR

H-ZSM-5 + ethyl[α-^{13}C]benzene

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