In Situ Solid-State NMR Investigation of the Reactivity of Ethylbenzene in Acidic Zeolites

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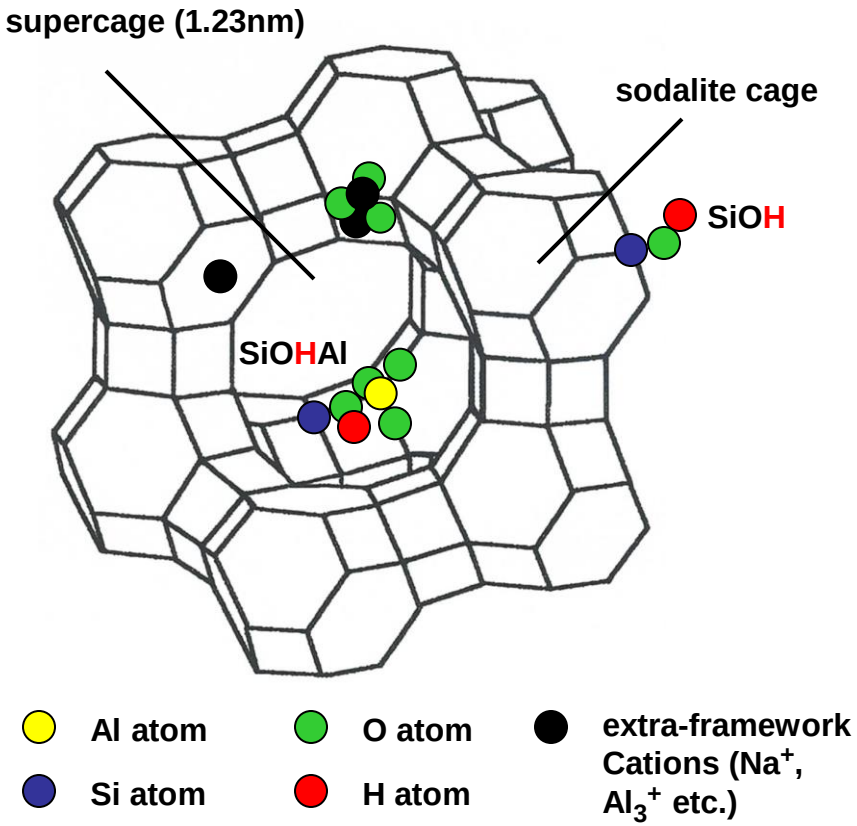
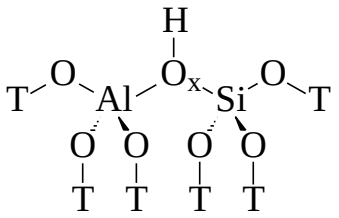
Broensted and Lewis acid sites in zeolites

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



Broensted acid sites:



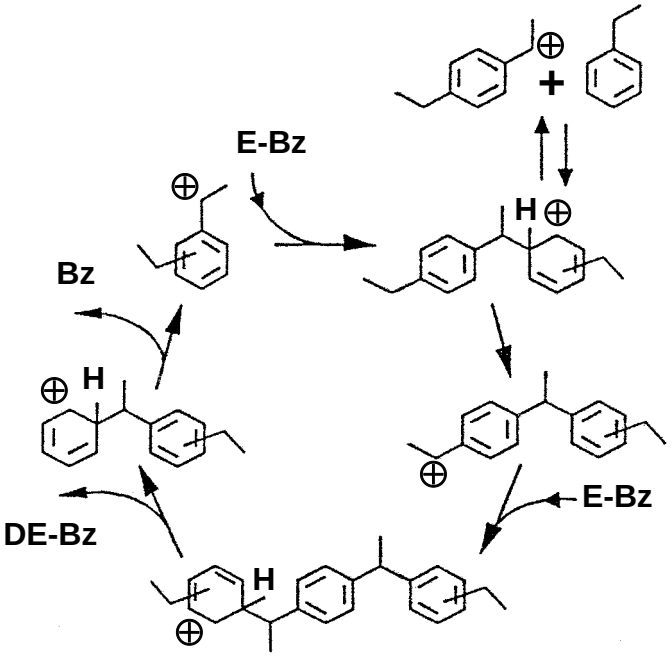
bridging OH group (SiOHAl)

Lewis acid sites:

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

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**

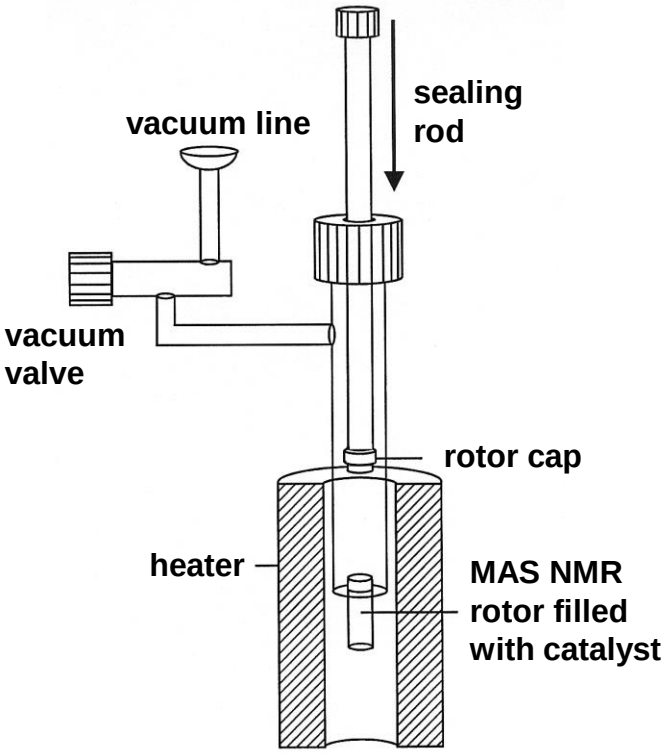
- **dealkylation/realkylation with free ethene or alkoxy species in medium-pore zeolites**

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

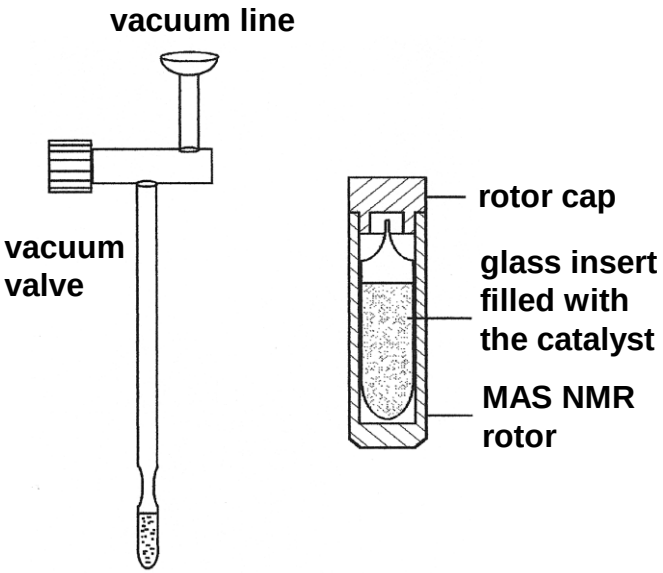
In situ solid-state NMR studies of the C_6-ring activation of aromatics adsorbed on acidic zeolites

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



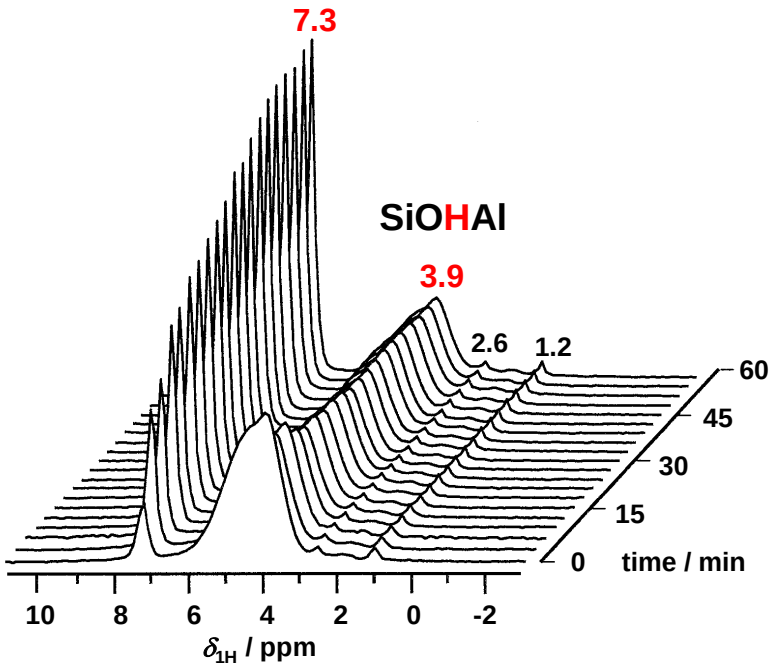
dehydration and loading of the catalyst inside the glass insert (e.g. commercial Wilmad MAS NMR inserts for 4 mm and 7 mm rotors)



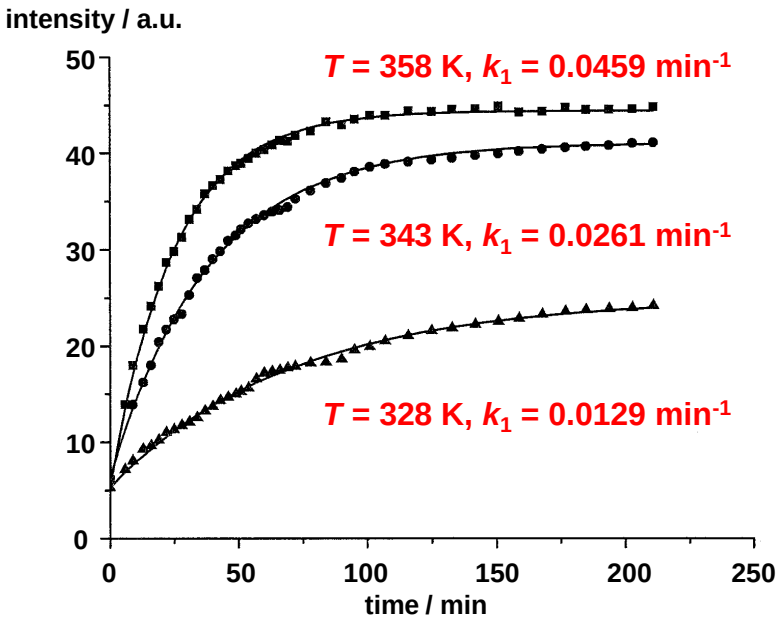
H/D exchange between aromatic deuterons and hydroxyl protons of bridging OH groups

^{1}H VT/MAS NMR studies of zeolite H,Na-Y loaded with ethylbenzene ($C_6D_5C_2H_5$)

stack plot of spectra recorded at *T* = 358 K



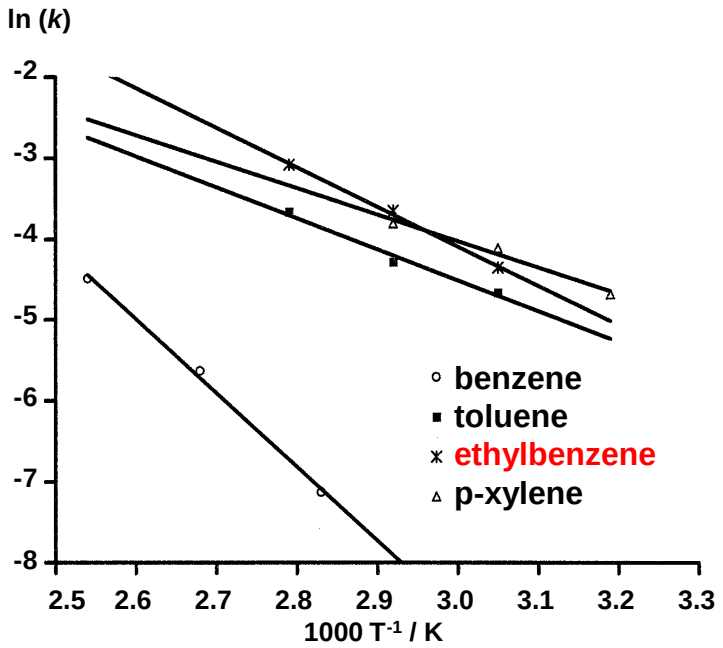
H/D exchange rates at *T* = 328 - 358 K



H/D exchange between aromatic rings and protons of surface OH groups

^{1}H VT/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

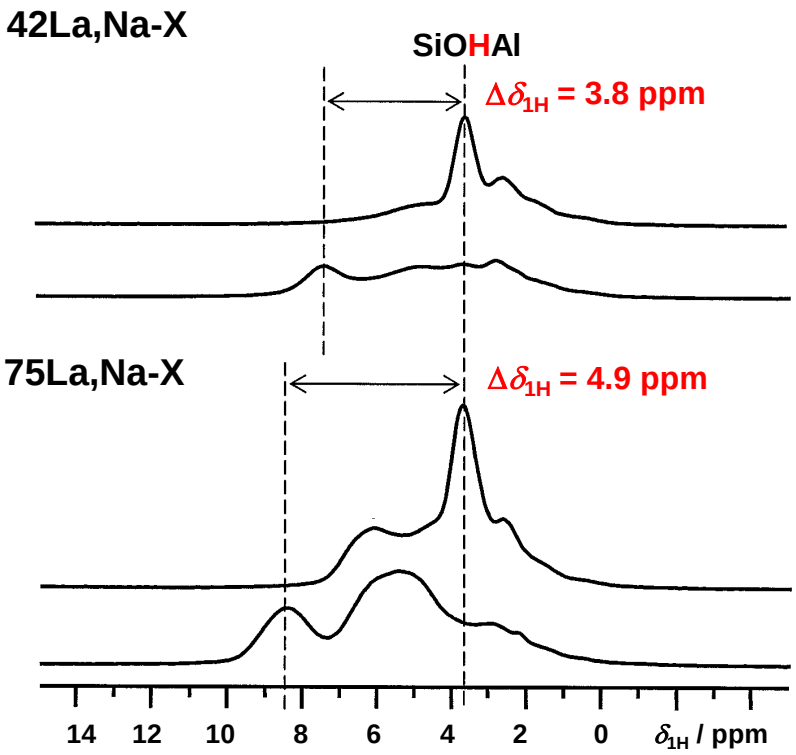


correlation of activation energies E_A of H/D exchange and low-field shifts $\Delta\delta_{1H}$ upon adsorption CD_3CN:

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

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 rings and protons of surface OH groups

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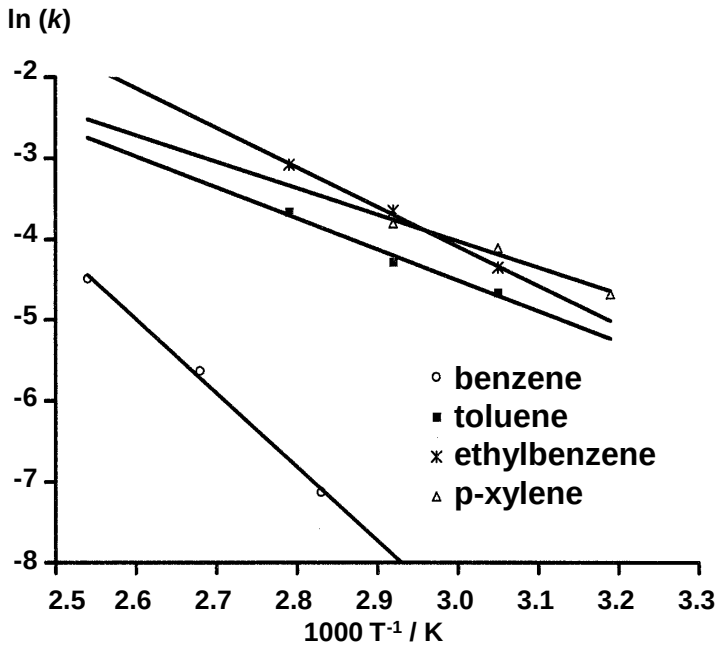
deuterated aromatics on zeolite H,Na-Y



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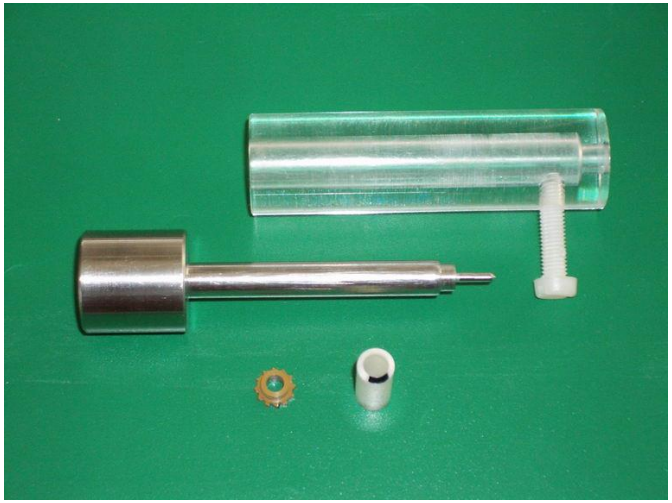
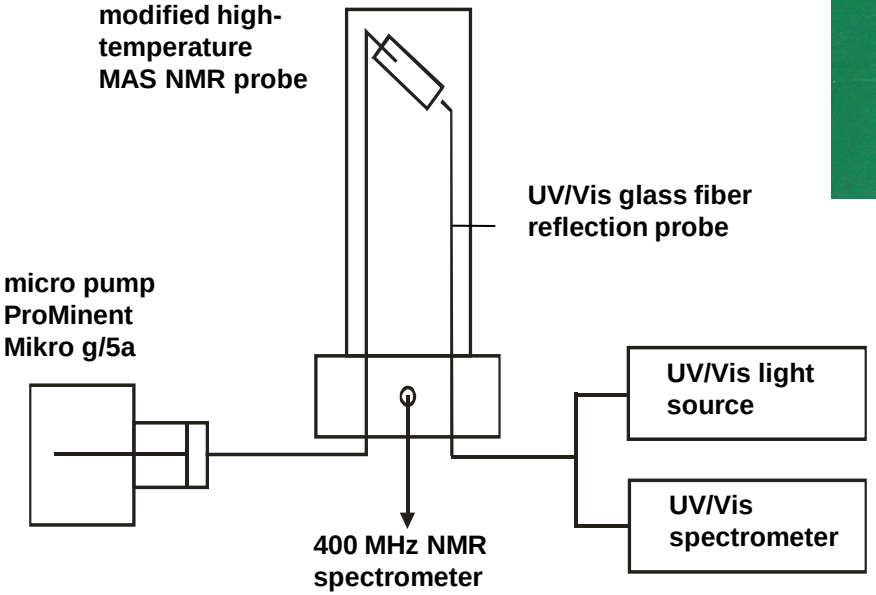
In situ solid-state NMR studies of the side-chain activation of alkylaromatics adsorbed on acidic zeolites

Pulsed-flow MAS NMR-UV/Vis spectroscopy

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

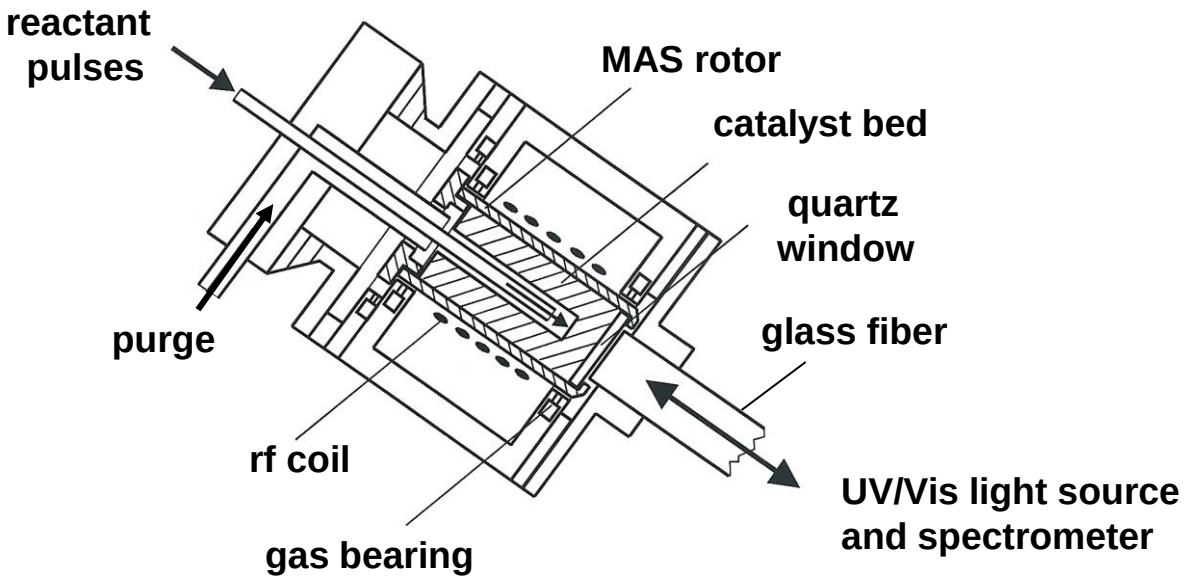




M. Hunger, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105-127

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



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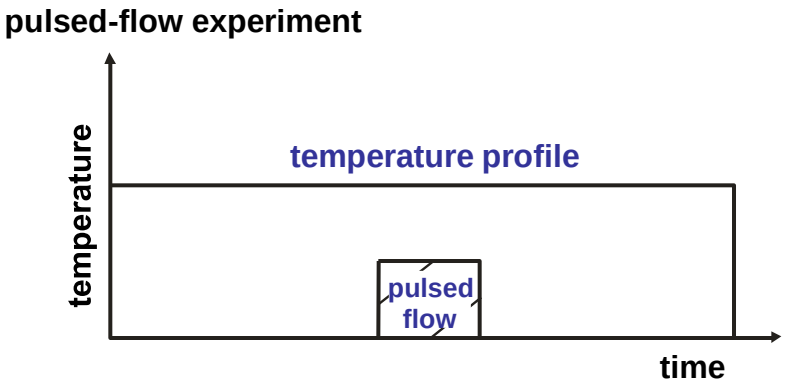
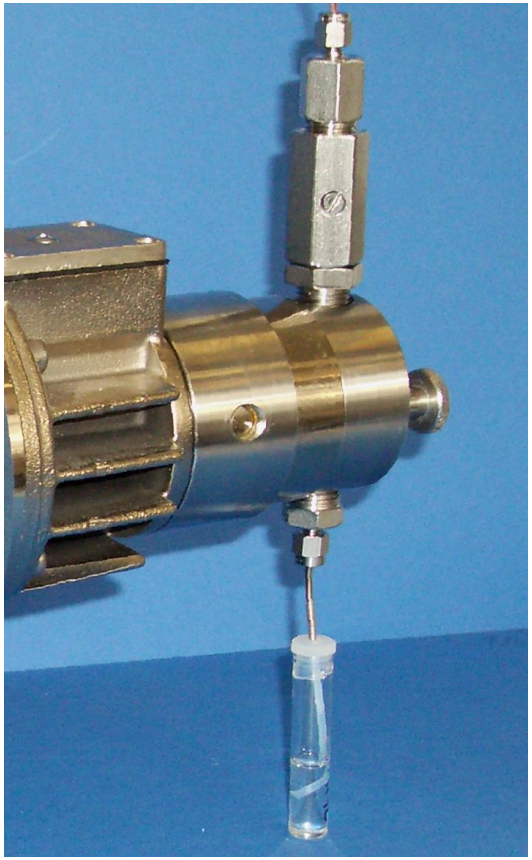
Pulsed-flow equipment

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





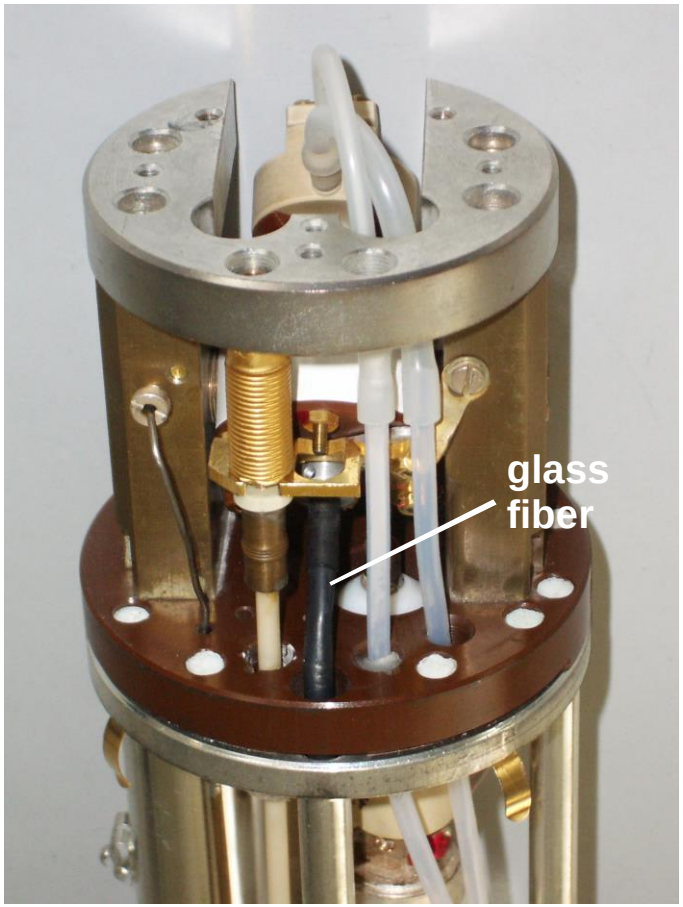
pulsed-flow experiments:

- 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

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)

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

^{1}H HT/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

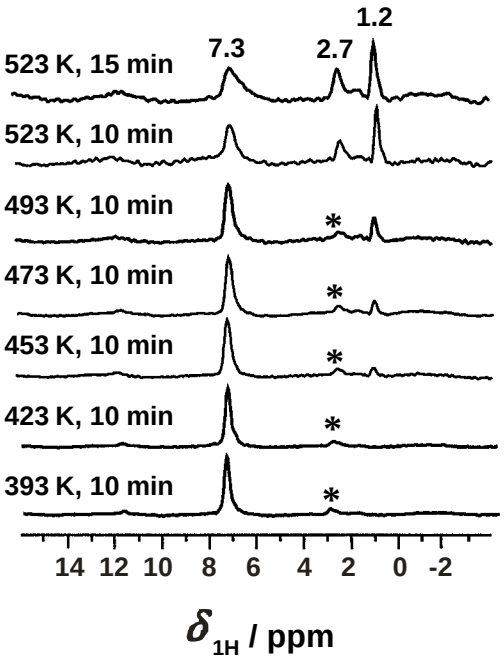
message:

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

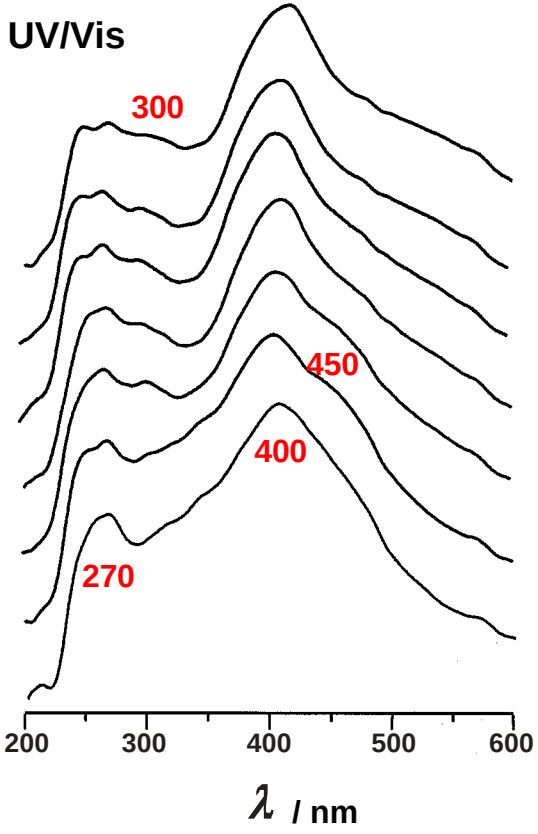
$C_6H_5CD_2CD_3$ + *n* SiOHAl ⟶ $C_6H_5CDHCD_2H$ + *n* SiODAl

7.3 ppm 3.8 ppm 2.7 ppm 1.2 ppm

^{1}H MAS NMR



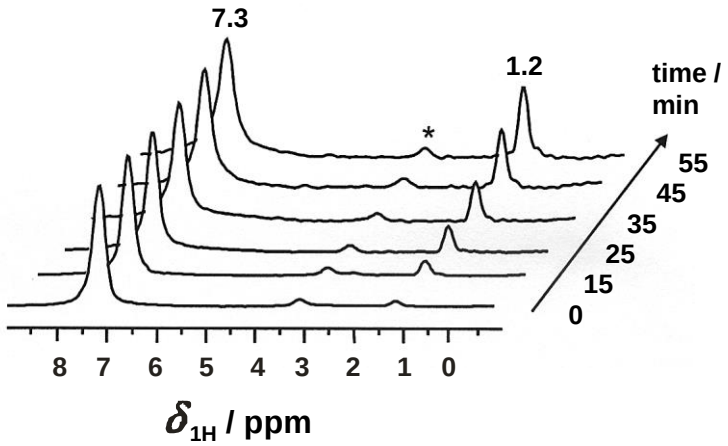
UV/Vis



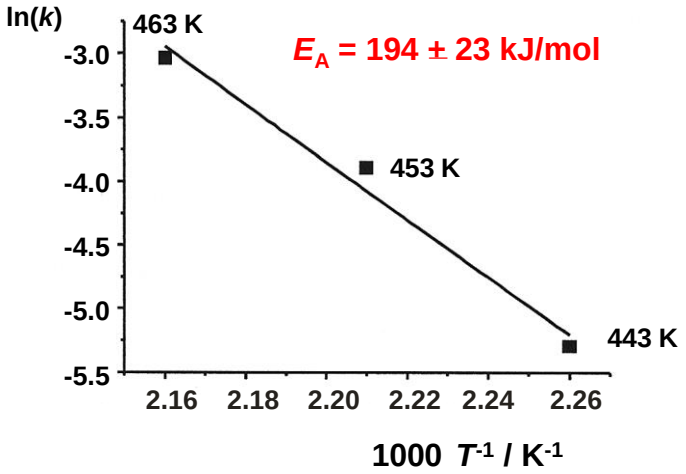
Study of the side-chain H/D exchange of ethylbenzene on dealuminated zeolite H-Y

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**

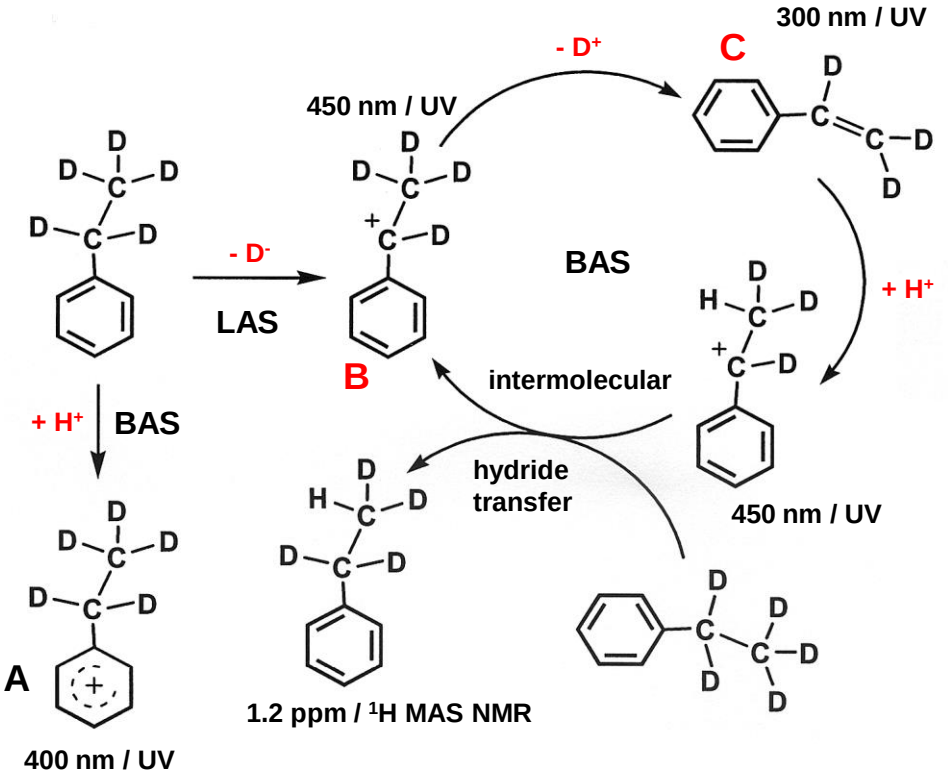
Mechanism of the regioselective side-chain H/D exchange of ethylbenzene on dealuminated zeolite H-Y

^{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**

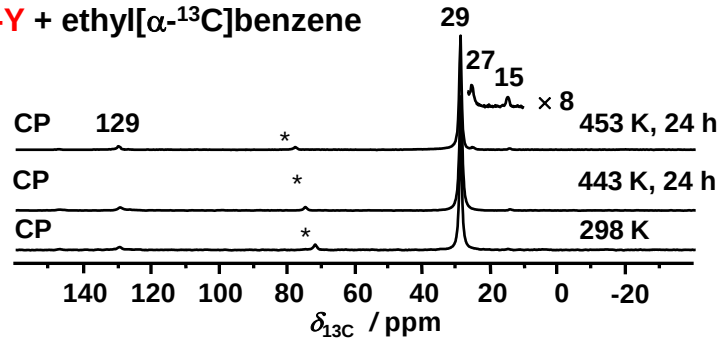
Solid-state NMR studies of the heterogeneously catalyzed conversion of ethylbenzene on acidic zeolites

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

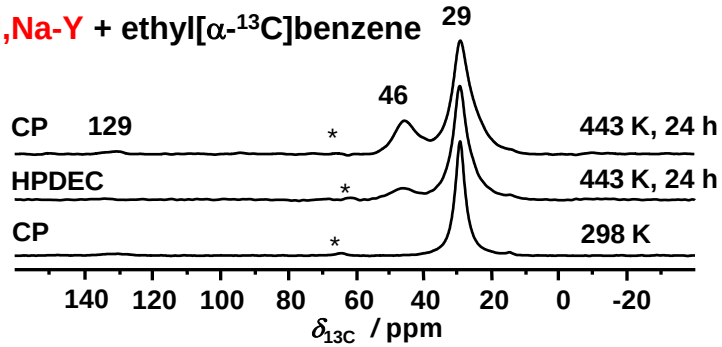
large-pore zeolite Y: 12-membered oxygen rings with diameter of 0.71 nm and supercages

^{13}C MAS NMR

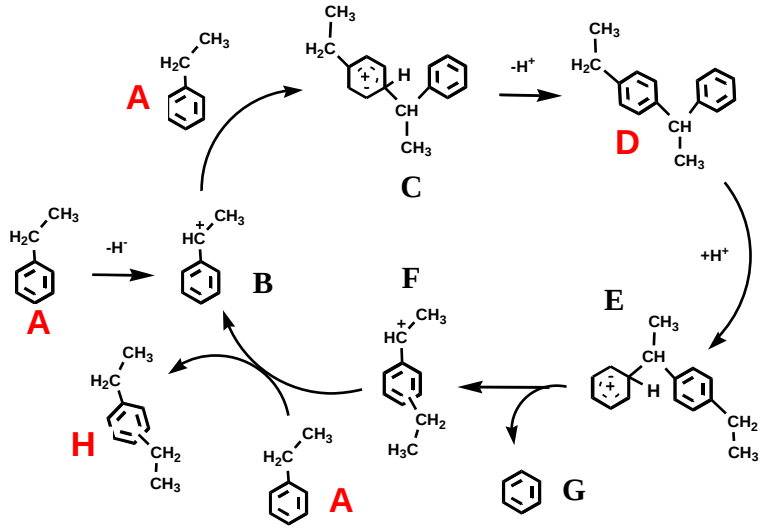
H-Y + ethyl[α-^{13}C]benzene



Al,Na-Y + ethyl[α-^{13}C]benzene



reaction mechanism

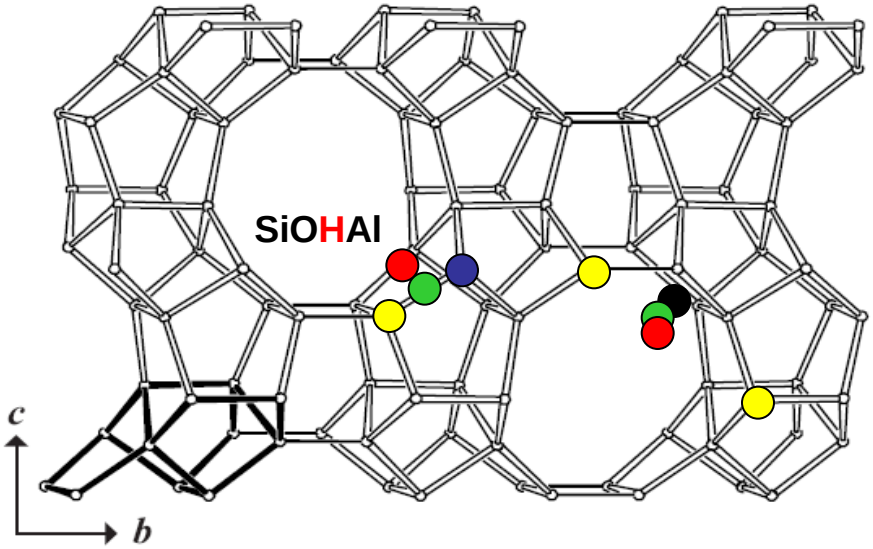


assignment:

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

Structure of medium-pore zeolite H-ZSM-5

structure-type MFI

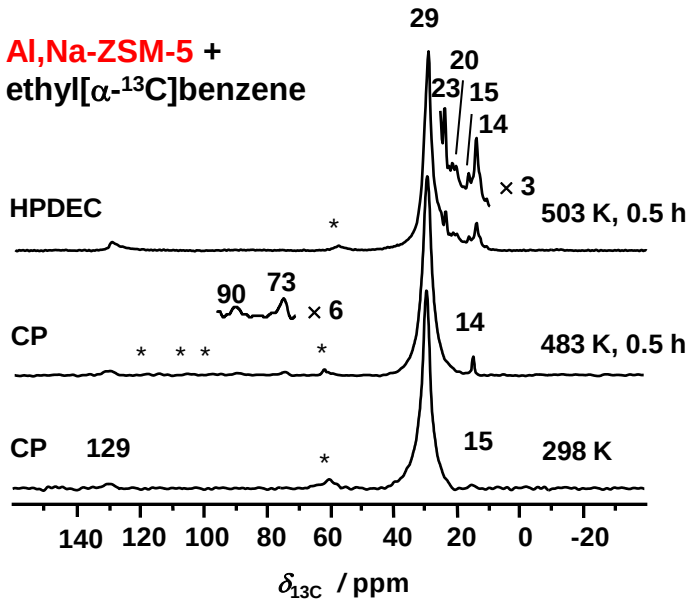


$H^+_n[Al_nSi_{96-n}O_{192}]$
crossing intersections at interconnecting 10-ring channels
[100] 0.51 nm x 0.55 nm
[010] 0.53 nm x 0.56 nm

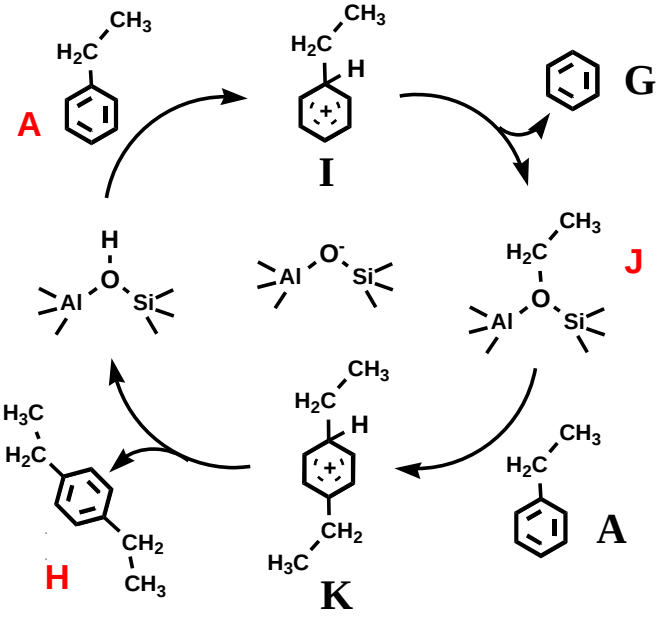
Al atom
Si atom
O atom
H atom
extra-framework Cations (Na^+, Al_3^+ etc.)

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

^{13}C MAS NMR

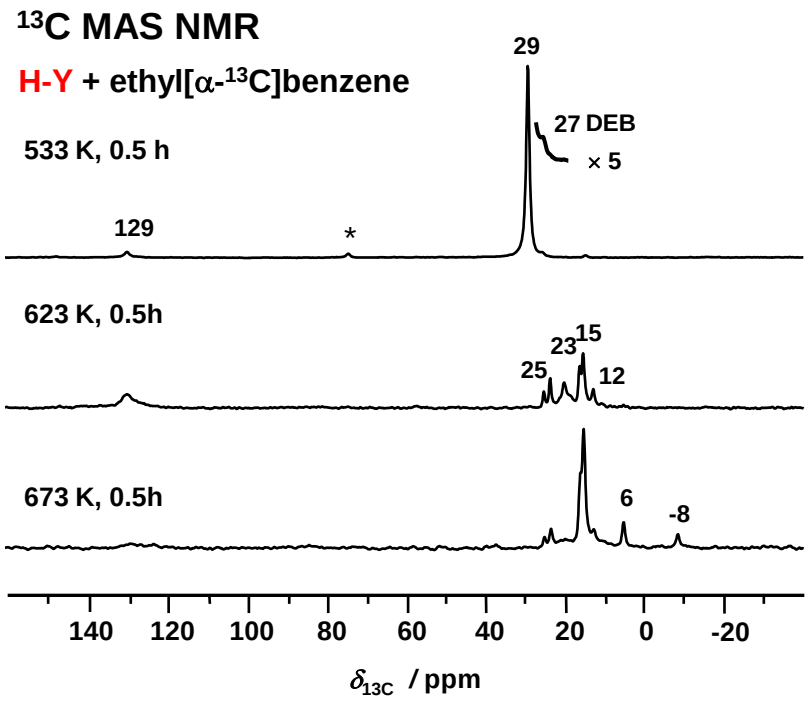


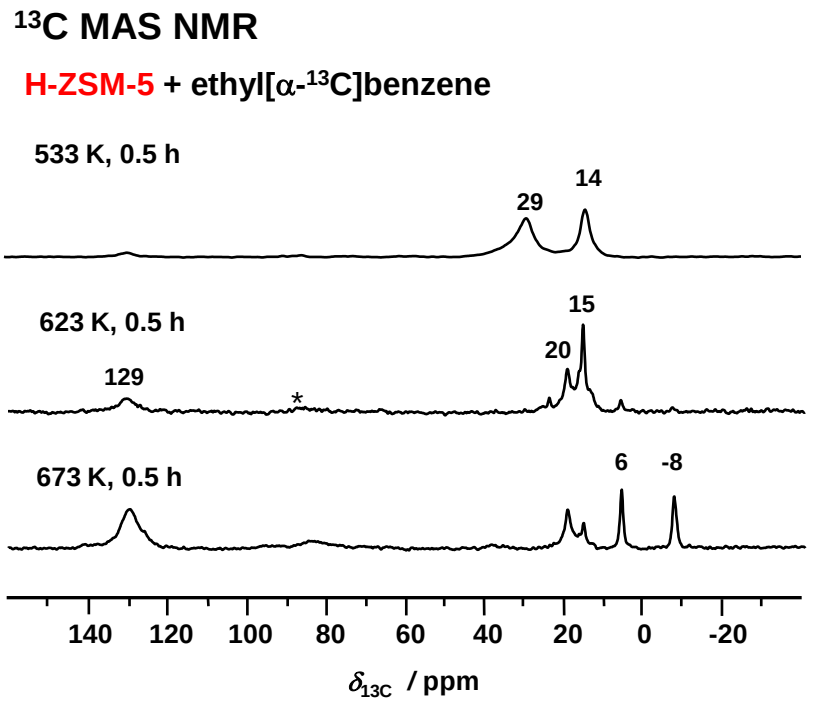
Reaction mechanism



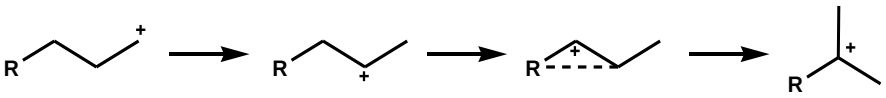
assignment:	**23 ppm**	**diethylbenzene (H)**	**73 ppm**	**surface ^{13}C-1-ethoxy groups (J)**
	29 ppm	**ethylbenzene (A)**	**90 ppm**	**oligomeric alkoxy groups**
			129 ppm	**aromatic carbons**

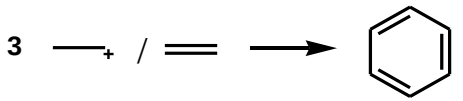
^{13}C MAS NMR investigation of the catalyst deactivation during ethylbenzene conversion





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





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 probe gives complementary information on the systems under study.

Thanks to ….

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Yean Sang Ooi

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