Characterization of acido-basic Zeolites

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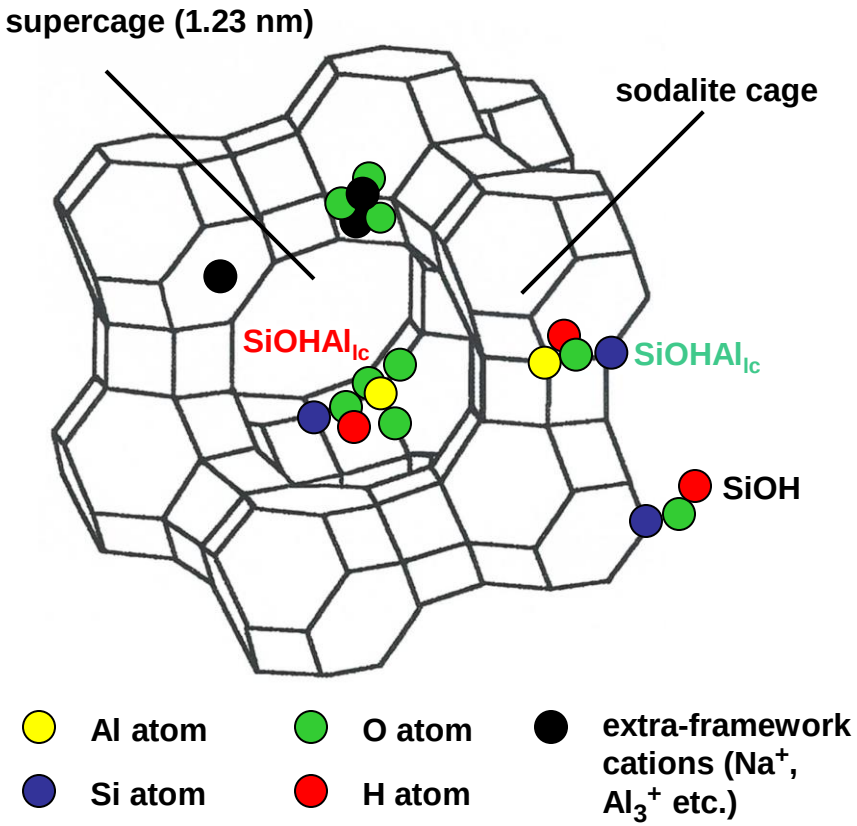
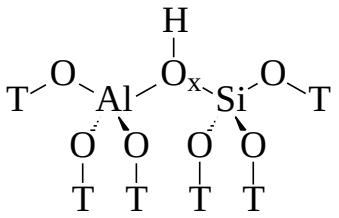
Nature of acid sites on zeolites

zeolite Y (FAU, faujasite): **supercages connected via 12-ring windows (0.74 nm)**



Brønsted acid sites:



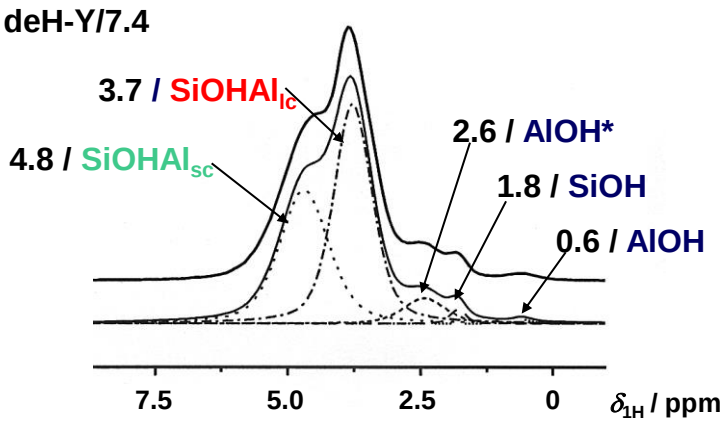
bridging OH group (SiOHAl)

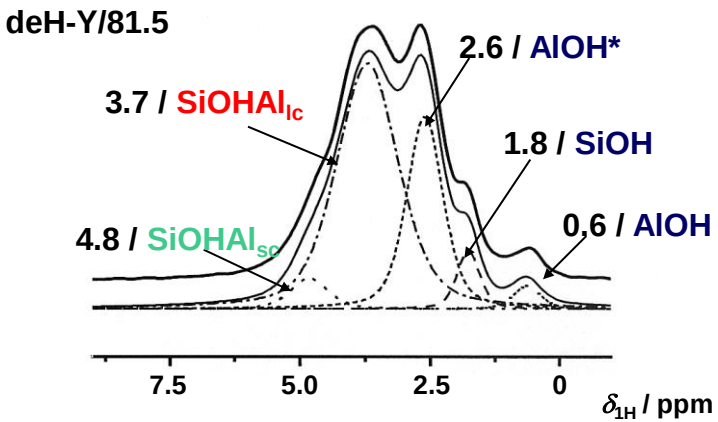
Lewis acid sites:

- **framework defects,**
- **extra-framework species (Al oxide clusters)**

Modification of Brønsted acid sites in zeolites *via* steaming

^{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 clusters:
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

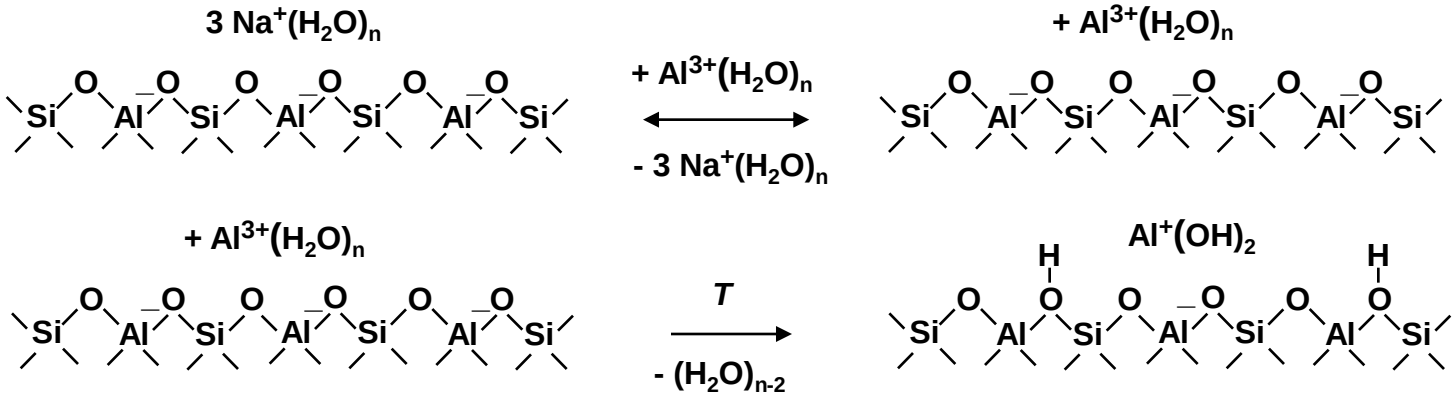
(hydrogen bonded SiOH and SiOHAl groups: 5.2 to 13 ppm)

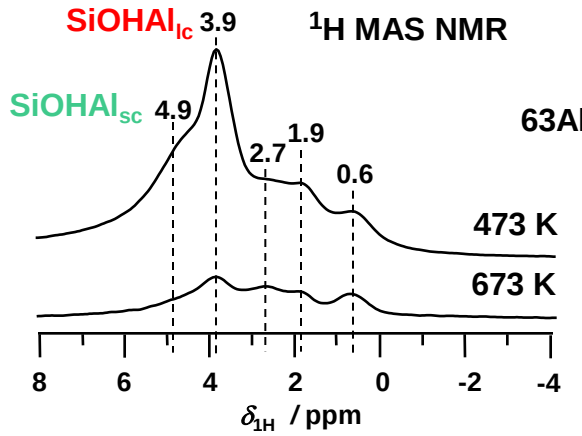
J. Jiao et al., J. Phys. Chem B. 108 (2004) 14305.

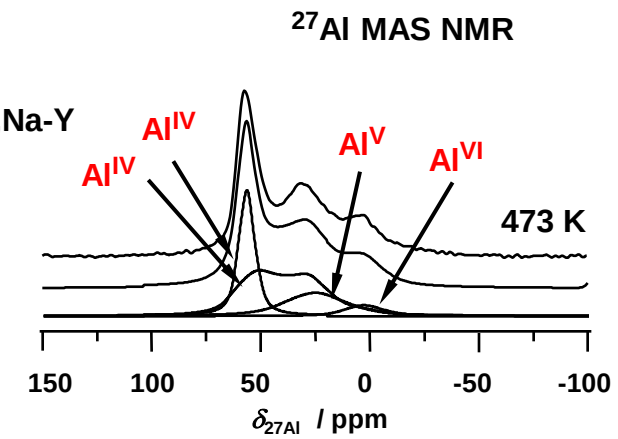
Preparation of Brønsted acid sites in zeolites *via* exchange with multivalent cations

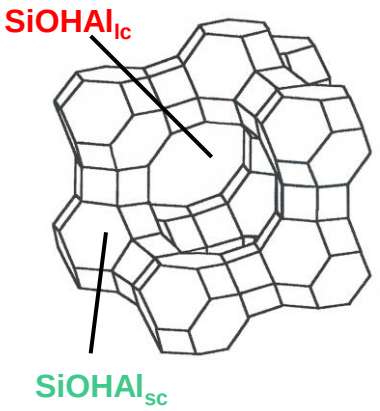
exchange of zeolite Na-Y (n_{Si}/n_{Al} = 2.7) in 0.1 M $Al(NO_3)_3$ solution

Hirschler Plank mechanism





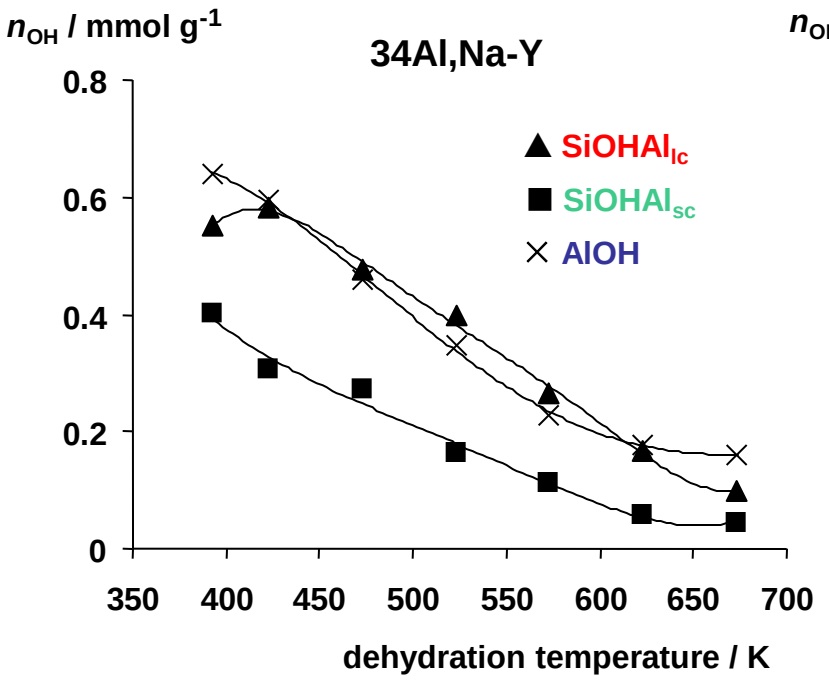


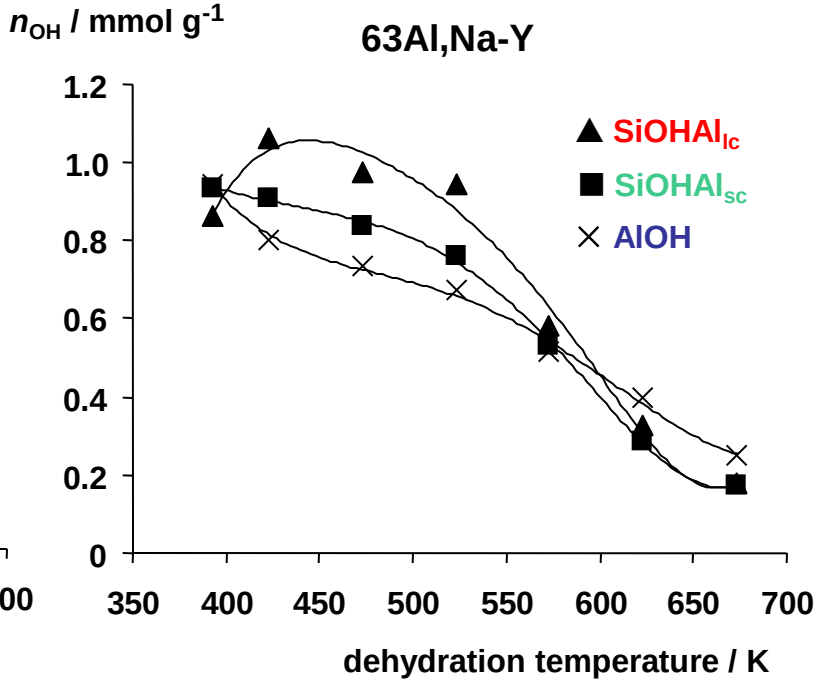


J. Huang et al., J. Phys. Chem. C 112 (2008) 3811.

Brønsted acid sites in zeolites prepared via exchange with multivalent cations (Al^{3+})

determination of the concentration of OH groups by evaluation of the ^{1}H MAS NMR intensities

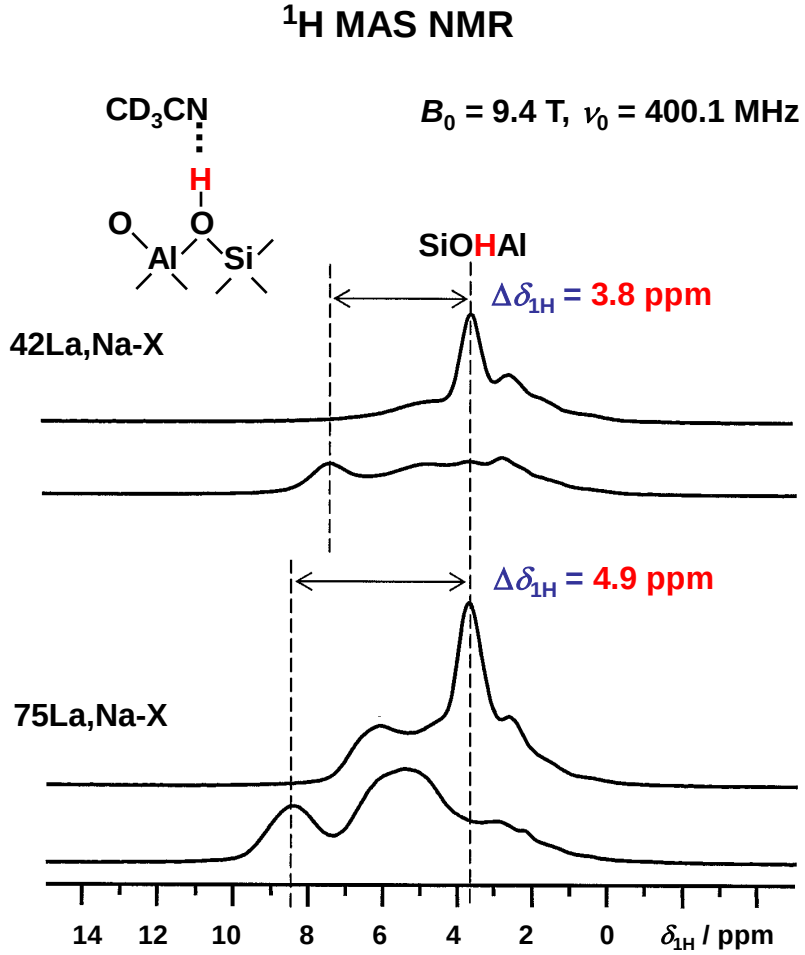




cation-exchange degree and dehydration temperature affect the number of Brønsted sites

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

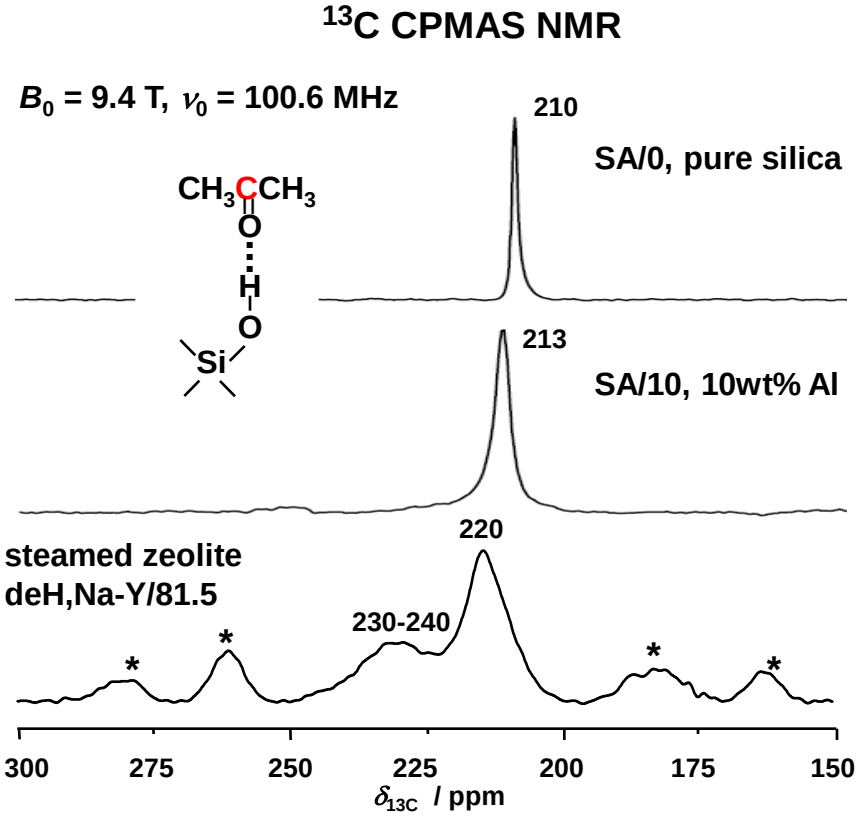
Characterization of the Brønsted acid strength *via* acetonitrile-induced low-field shift $\Delta\delta_{1H}$



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)

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

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



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.

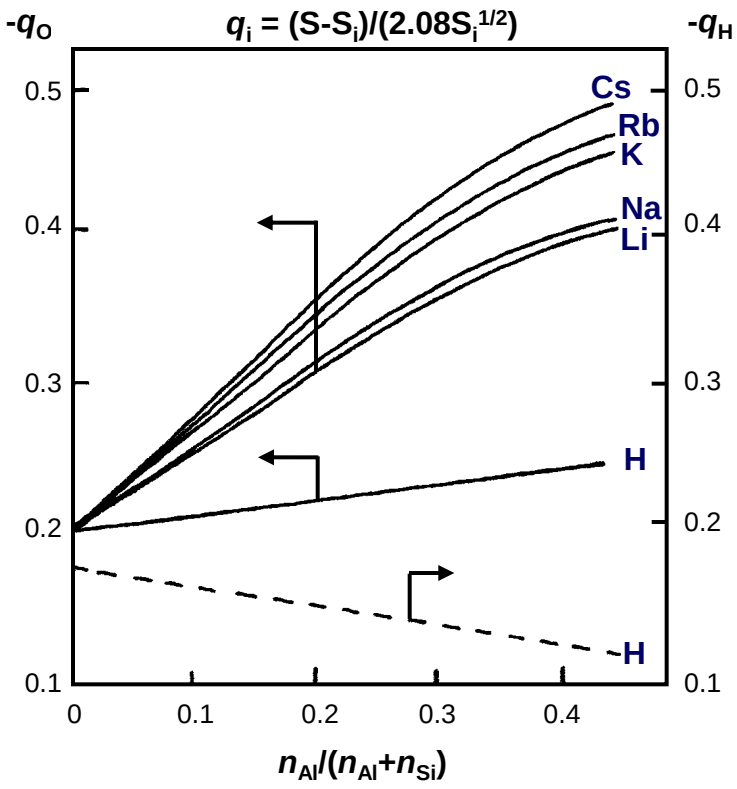
Lewis sites formed by steaming

Brønsted sites with different acid strengths (see Tab.)

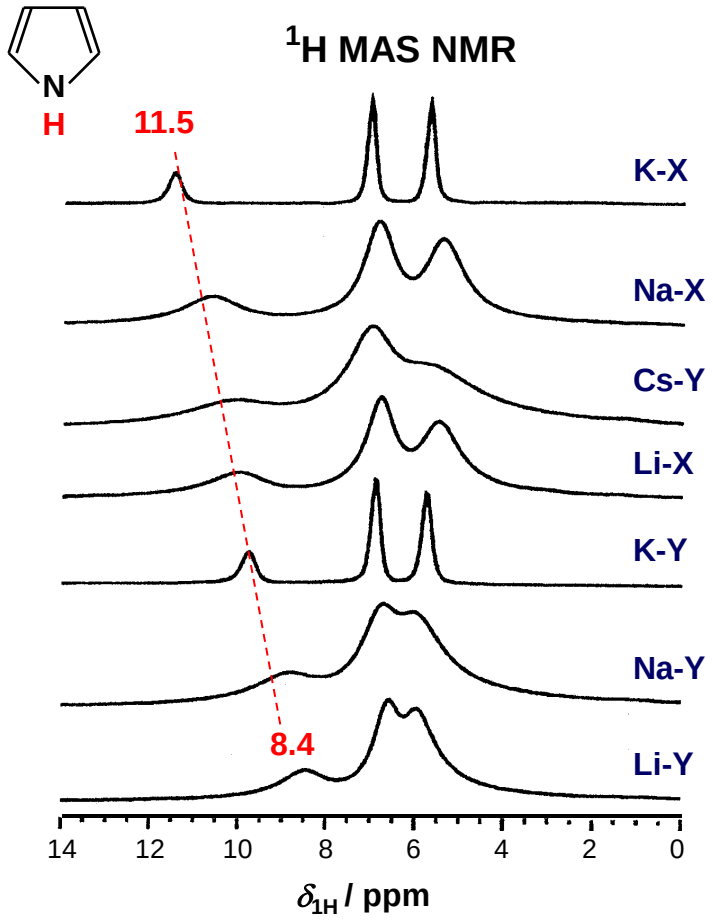
Y. Jiang et al., Solid State Nucl. Magn. Reson. 39 (2011) 116-141.
H. Fang et al., J. Phys. Chem. C 114 (2010) 12711-12718.

Characterization of base sites on zeolites *via* adsorption of pyrrole

partial charge on framework oxygens (left) and on hydroxyl protons (right) of zeolites



D. Barthomeuf, in: Acidity and Basicity of Solids, J. Fraissard et al. (eds.), Academic Publishers, 1994, p. 181.

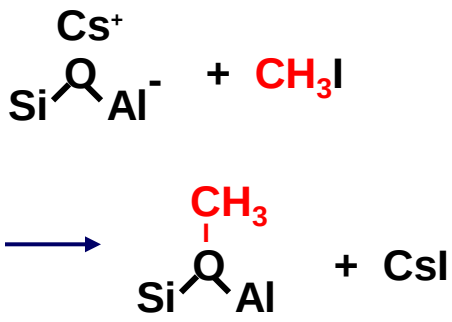


M. Sanchez-Sanchez, T. Blasco, Chem. Commun. (2000) 491.

Characterization of base sites on zeolites *via* methoxy groups

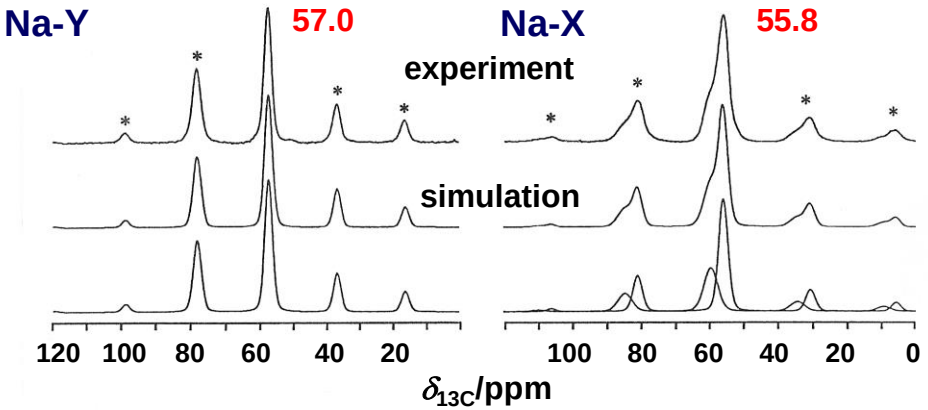
- ^{13}C MAS NMR spectroscopy of surface methoxy groups formed on basic oxygen atoms

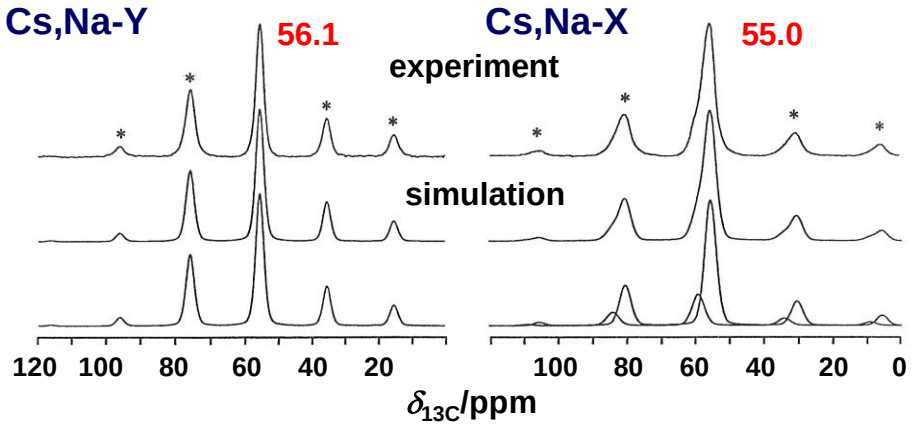
- conversion of CH_3I on basic zeolites:



→ signals at 54.3 to 59.2 ppm with a chemical shift anisotropy of ca. $\Delta\sigma$ = - 40 ppm

^{13}C MAS NMR





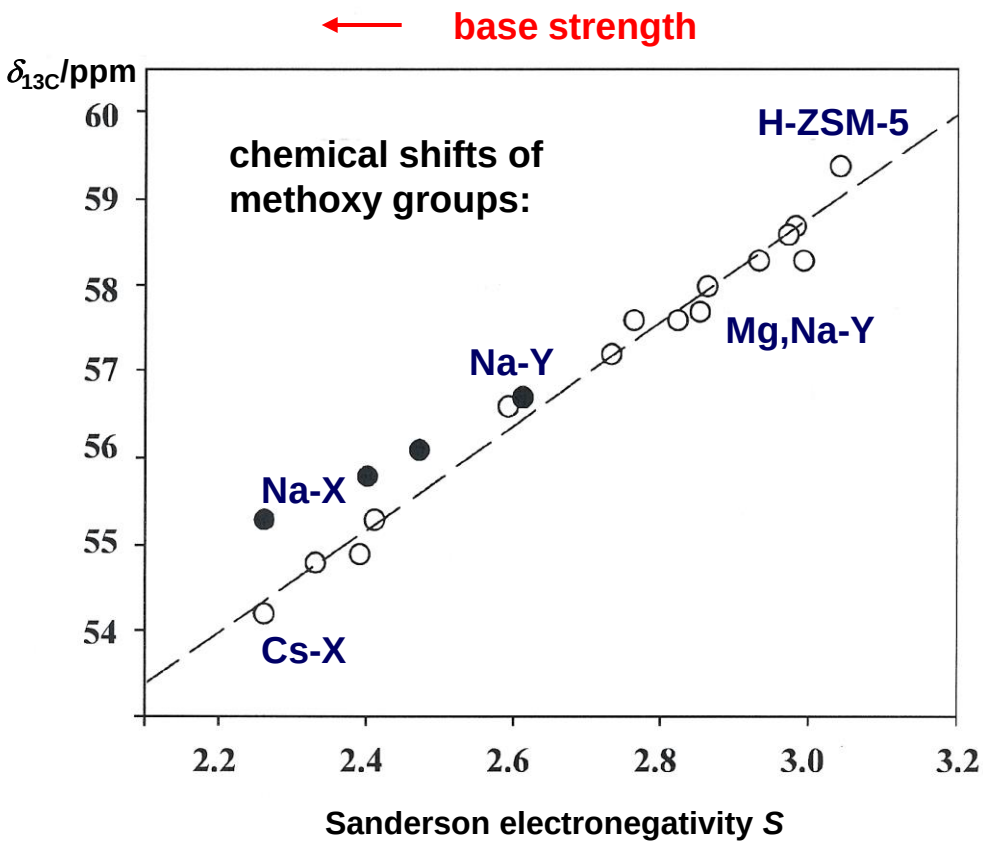
U. Schenk, PhD thesis, University of Stuttgart, 2001.

Characterization of base sites on zeolites *via* methoxy groups

- mean Sanderson electronegativity:

$$S = (S_{Al}{}^{k} S_{Si}{}^{l} S_{O}{}^{m} S_{Me}{}^{n})^{1/(k+l+m+n)}$$

→ decreasing ^{13}C NMR shift of surface methoxy groups with increasing base strength of the framework oxygen atoms



V. Bosacek et al., Z. Phys. Chem. 189 (1995) 241.

Recent studies on the preparation of Lewis acid sites on zeolites *via* introduction of framework metal atoms

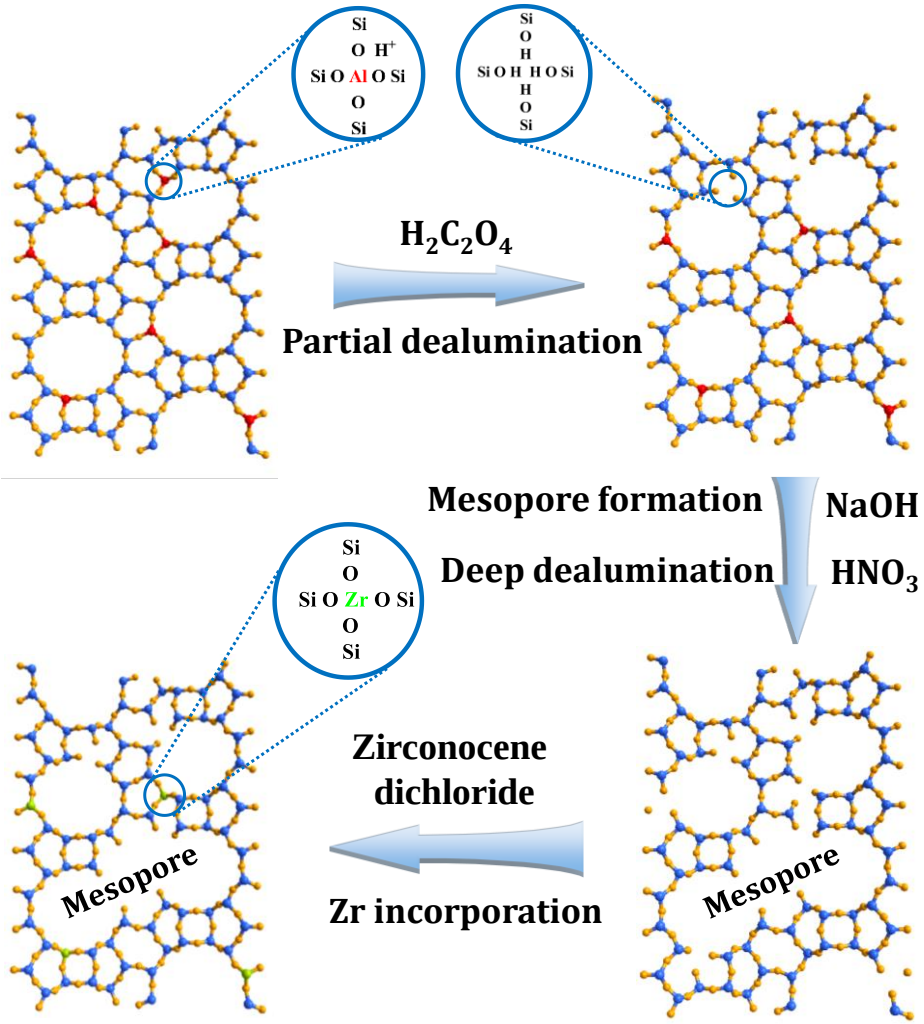
B. Tang, W. Dai, X. Sun, N. Guan, L. Li, M. Hunger, *A procedure for the preparation of Ti-Beta zeolites for catalytic epoxidation with hydrogen peroxide*, Green Chemistry **16** (2014) 2281-2291..

B. Tang, W. Dai, G. Wu., N. Guan., L. Li, M. Hunger, *Improved post-synthesis strategy to Sn-Beta zeolites as Lewis acid catalysts for the ring-open hydration of epoxides*, ACS Catal. **4** (2014) 2801-2810.

B. Tang, W. Dai, X. Sun, G. Wu, N. Guan, L. Li, M. Hunger, *Incorporation of cerium atoms into Al-free beta zeolite framework for catalytic application*, Chin. J. Catal. **36** (2015) 801-805.

B. Tang, W. Dai, X. Sun, G. Wu, N. Guan, M. Hunger, L. Li, *Mesoporous Zr-Beta zeolite prepared by post-synthesic strategy as a robust Lewis acid catalyst for the ring-opening aminolysis of epoxides*, Green Chem. **17** (2015) 1744-1755.

Recent study on the preparation of Lewis acid sites on zeolites *via* introduction of Zr atoms into zeolite Beta



B. Tang, W. Dai, X. Sun, G. Wu, N. Guan, M. Hunger, L. Li, Green Chem. 17 (2015) 1744-1755.

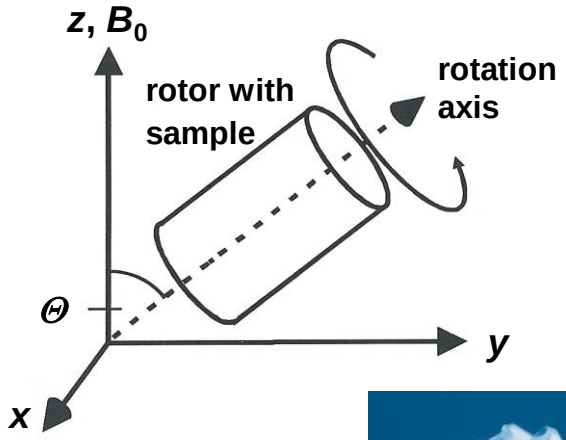
Techniques of solid-state NMR spectroscopy

spin *I* = 1/2 :

magic angle spinning (MAS)

$\nu_{CSA,\ DI,\ 1QI} = \mathcal{F}\ \{(3\cos^2\Theta - 1)/2\}$

→ $\Theta = 54.7^o$



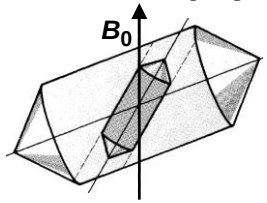
spin *I* = 3/2, 5/2 etc. :

double oriented rotation (DOR)

$\nu_{2QI} = \mathcal{F}\ \{(35\cos^4\Theta - 30\cos^2\Theta + 3)/8\}$

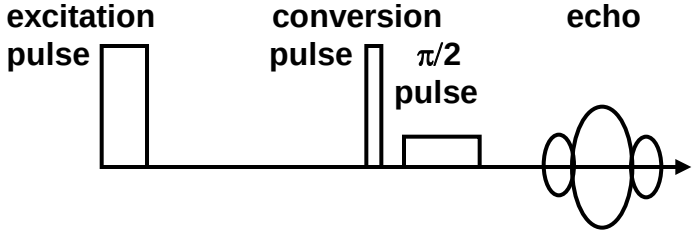
→ $\Theta = 30.6^o$

→ $\Theta = 70.1^o$



multiple-quantum MAS NMR (MQMAS)

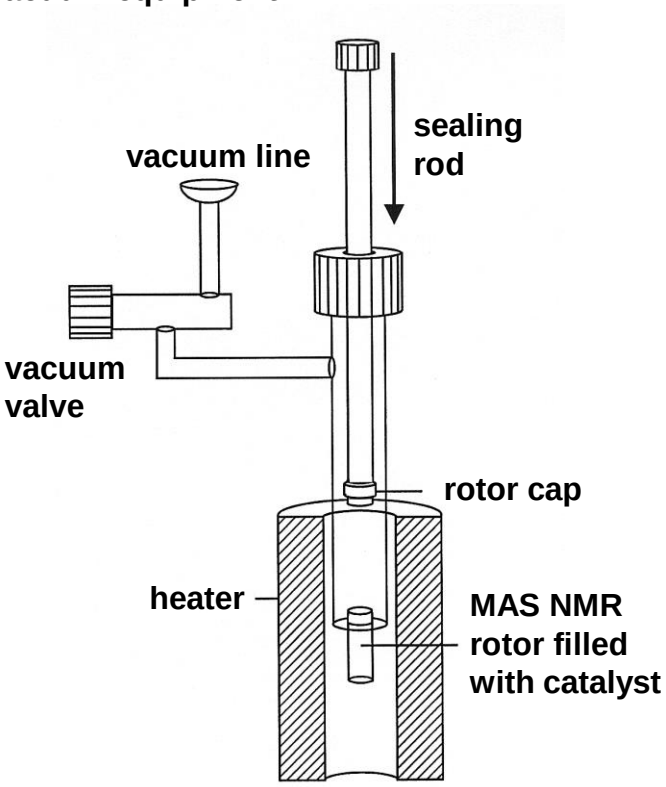
- excitation of three- and five-quantum transitions
- recording of a spin-echo free of anisotropic contributions



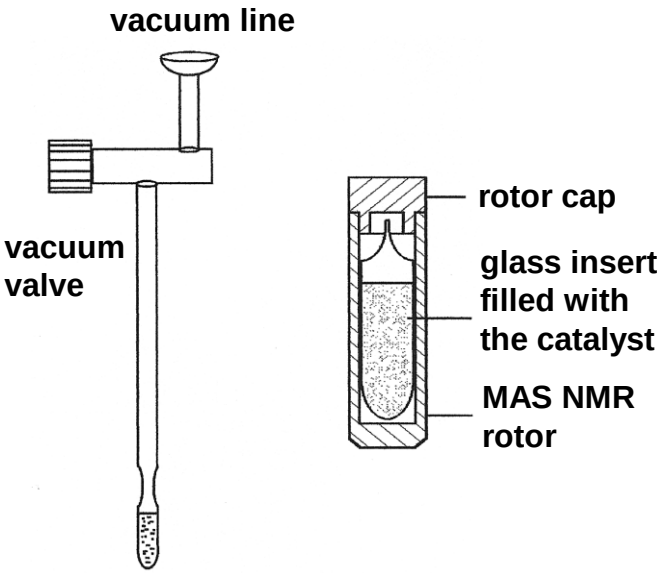
J. Amoureux et al., J. Magn. Reson A 123 (1996) 116

Preparation of samples for MAS NMR studies of activated solid catalysts

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)



M. Hunger et al., in: B.M. Weckhuysen (ed.), *In situ Spectroscopy of Catalysts*, American Scientific Publishers, Stevenson Ranch, California, 2004, p. 177-218.