Effect of Hydrothermal Treatments on the Acidity of Zeolites Y Investigated by Quantitative Solid-State NMR Spectroscopy

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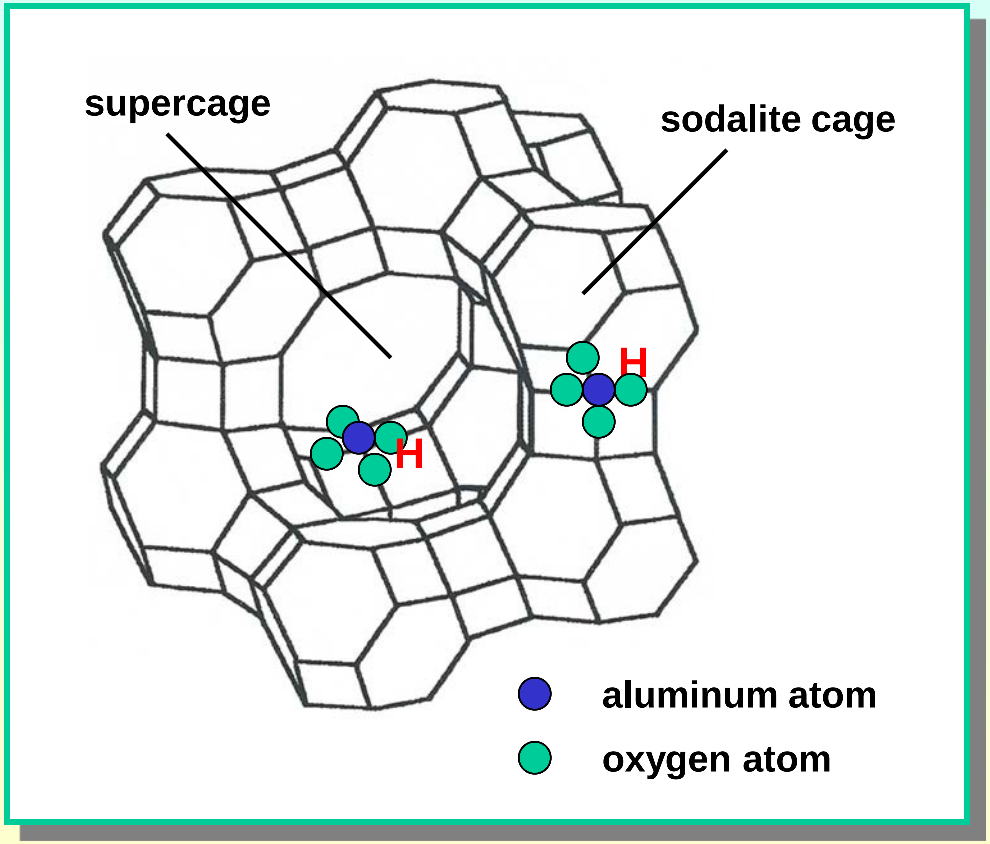
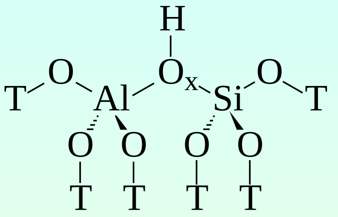
Hydrothermal Treatment of Zeolite Y

- **faujasite structure:**

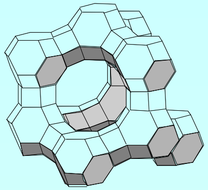


- **Broensted-acid sites:**



bridging OH group (SiOHAl)

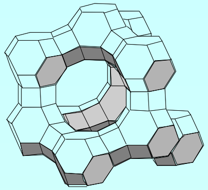
- **hydrothermal treatment:**
  - dealumination of the framework
  - formation of extra-framework species
  - dehydroxylation of SiOHAl groups
  - formation of defect sites (e.g. SiOH)



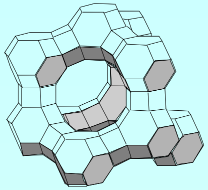
Aims of the Recent Study

Investigation of following topics:

- **advantages and limitations of NMR spectroscopy for the study of hydrothermally treated zeolites**
- **coordination change of framework aluminum atoms**
- **nature of extra-framework aluminum atoms formed by hydrothermal treatments**
- **healing of the zeolite framework**
- **quantitative determination of the hydroxyl coverage as a function of the hydrothermal treatment**



Sample Preparation and Experimental Techniques



Sample Preparation

commercial zeolite Na-Y (n_{Si}/n_{Al} = 2.6) $\xrightarrow[\text{exchange}]{\text{ammonium-}}$ NH_4-Y (exchange degree of 92 %)

hydrothermal treatment at 475°C

flowing nitrogen (100 ml/min)

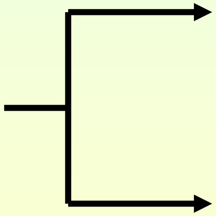
water pressures of 3.4 to 94.3 kPa

→

dealuminated zeolite H-Y

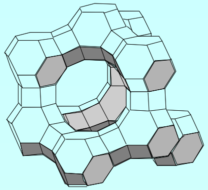
denoted as Y-*T*(475)

T: water bath temperature



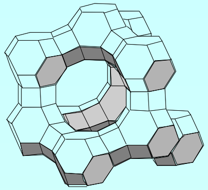
rehydrated samples were characterized by AES/ICP, XRD, ^{29}Si, ^{27}Al, and ^{1}H MAS NMR

non-hydrated samples were characterized by ^{29}Si and ^{1}H MAS NMR



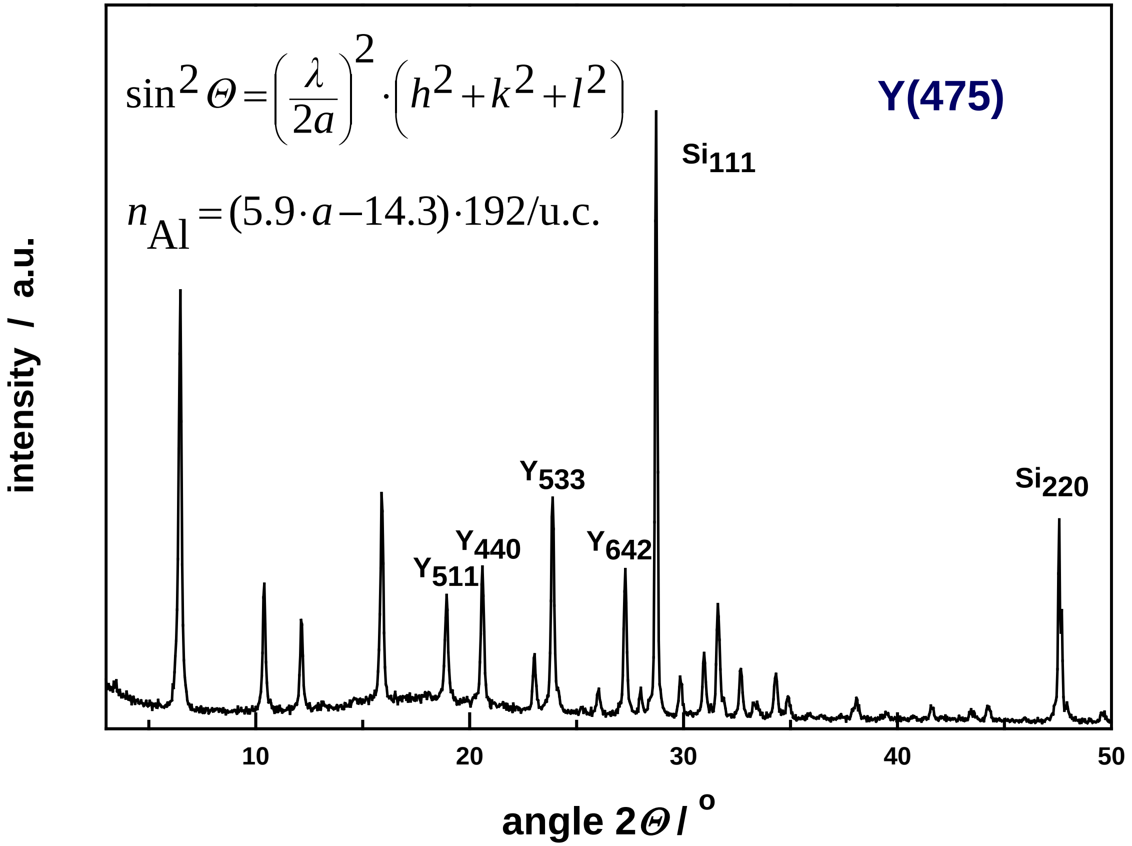
Experimental Techniques

- **XRD**: Siemens D5000, determination of the cell constant, application of an internal standard, calculation of of the framework aluminum content
- **^{29}Si MAS NMR:** MSL400 NMR spectrometer, determination of the framework n_{Si}/n_{Al} ratio of non-hydrated and hydrated samples
- **2D ^{27}Al 3QMAS NMR**: Avance 500WB NMR spectrometer, determination of the quadrupole parameter and coordination of framework and extra-framework aluminum atoms
- **1D ^{27}Al MAS NMR**: MSL400 NMR (and Avance 750WB NMR) spectrometer, investigation of the distribution of aluminum atoms
- **^{1}H MAS NMR**: MSL400 NMR spectrometer, quantitative determination of SiOH, AlOH, and SiOHAl groups of non-hydrated and dehydrated samples



Quantitative Investigation of Hydrothermally Treated and Rehydrated Zeolites H-Y

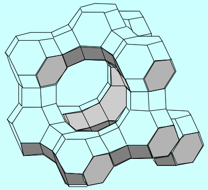
Determination of the Framework Aluminum Content by X-Ray Diffraction



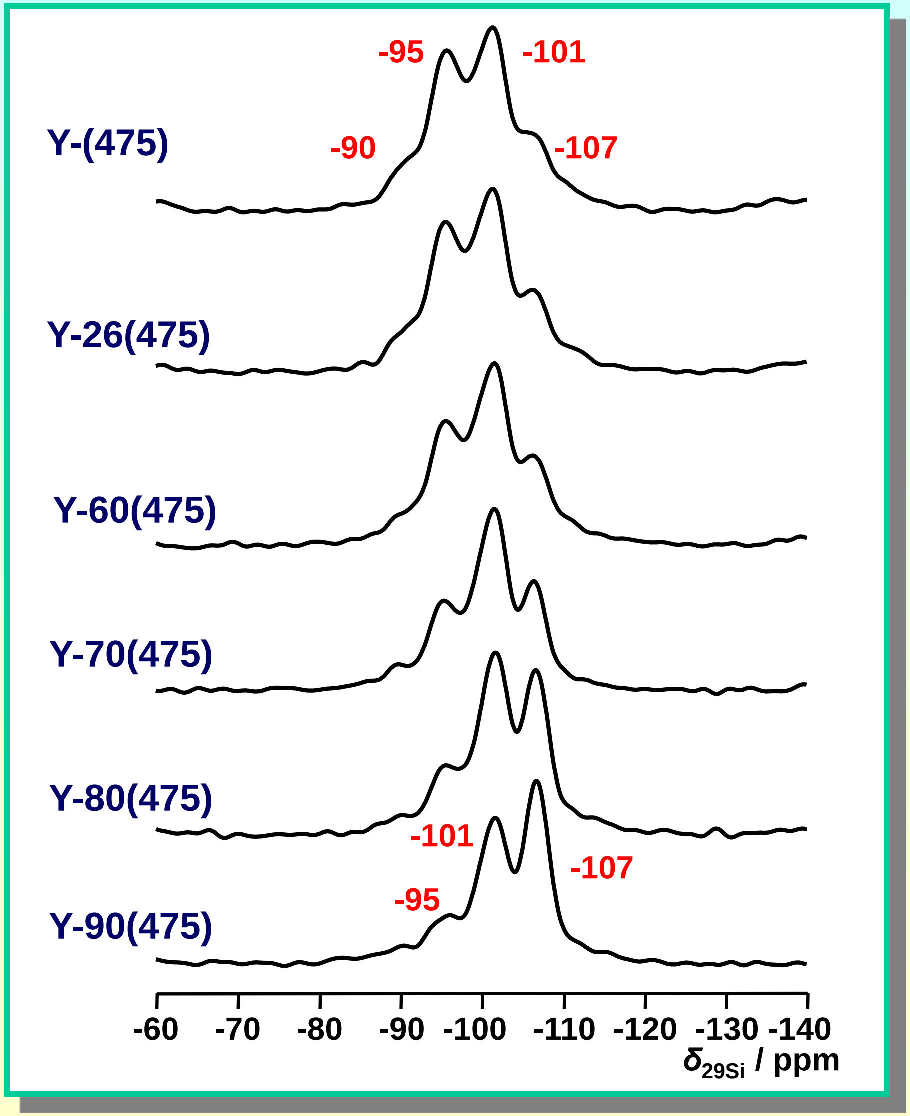
$$\sin^2\Theta = \left(\frac{\lambda}{2a}\right)^2 \cdot \left(h^2 + k^2 + l^2\right)$$

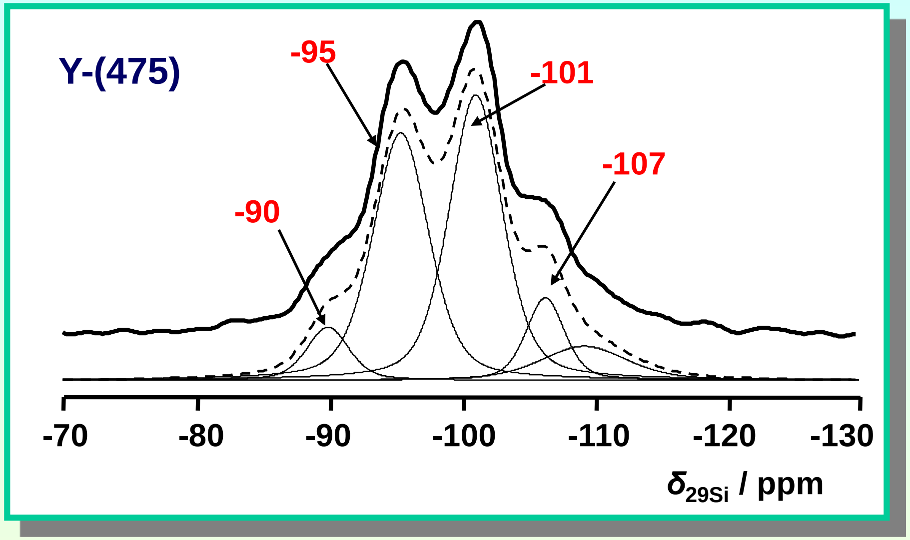
$$n_{\mathrm{Al}} = (5.9 \cdot a - 14.3) \cdot 192/\mathrm{u.c.}$$

H. Fichtner-Schmittler et al., Z. Phys. Chem. 271 (1990) 69-79



Determination of the Framework Aluminum Content by ^{29}Si MAS NMR



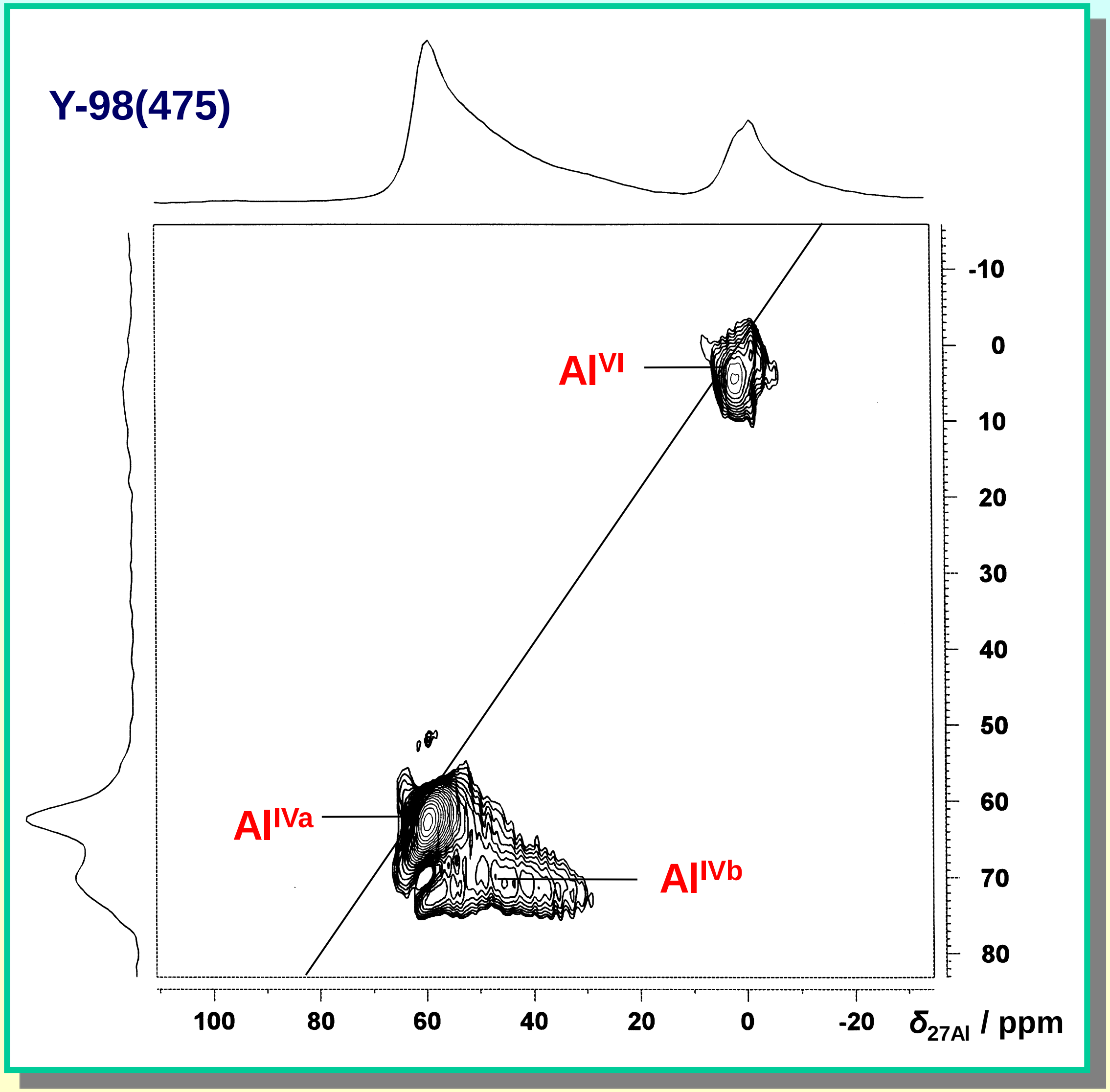


- signals of Q^4 silicon atoms:

-90 ppm	Si(1Si,3Al)
-95 ppm	Si(2Si,2Al)
-101 ppm	Si(3Si,1Al)
-107 ppm	Si(4Si)

$$n_{\mathrm{Si}} / n_{\mathrm{Al}} = \sum_{n=0}^{4} I_{\mathrm{Si}(n\mathrm{Al})} \Bigg/ \sum_{n=0}^{4} \frac{n}{4} \cdot I_{\mathrm{Si}(n\mathrm{Al})}$$

^{27}*Al MQMAS NMR Studies of Hydrated Zeolites Y*



- two signals of tetrahedrally coordinated aluminum species

  signal Al^{IVa}:

  δ_{iso}= 61.6 ppm

  ν_Q = 360 kHz

  signal Al^{IVb}:

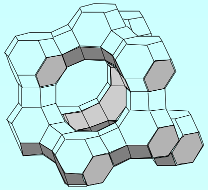
  δ_{iso}= 61.4 ppm

  ν_Q = 1005 kHz

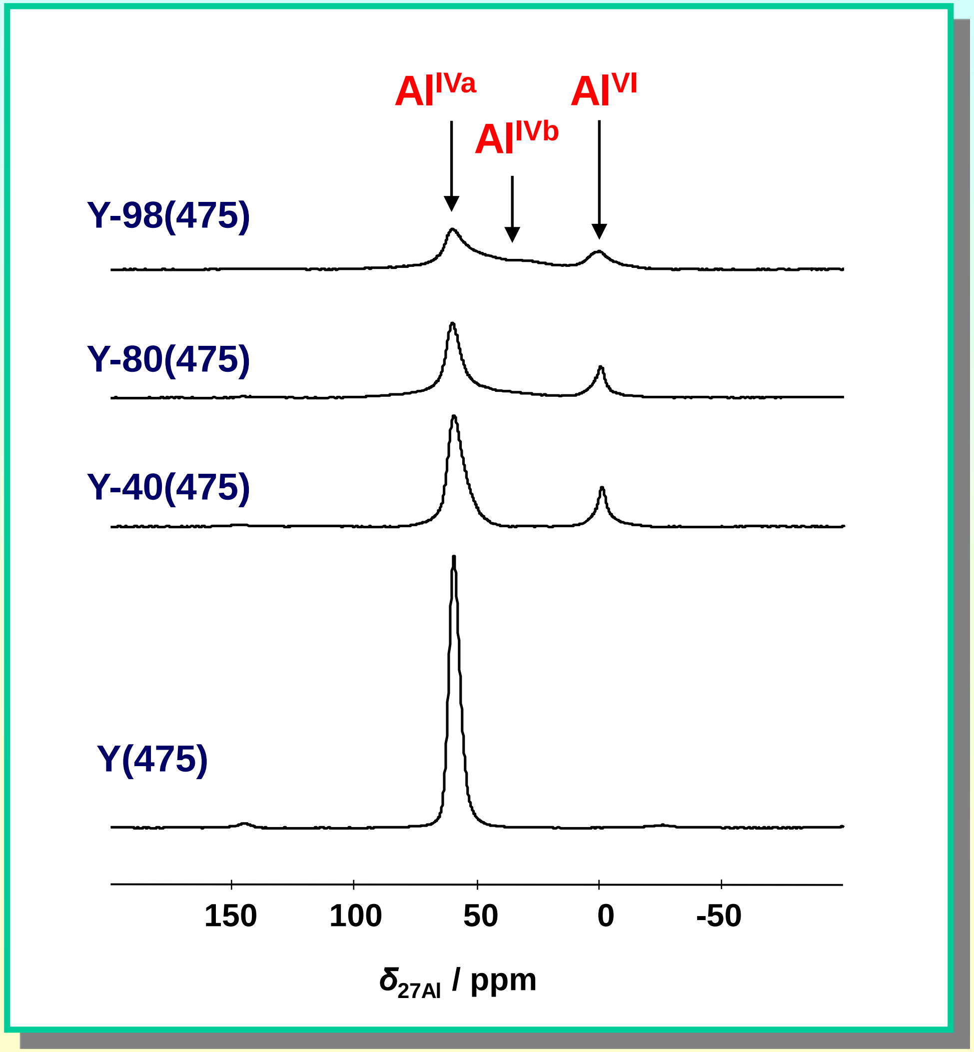
  signal Al^{VI}:

  δ_{iso}= 3.3 ppm

  ν_Q = 315 kHz

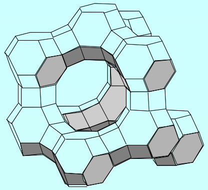


^{27}Al MAS NMR Studies of Hydrated Zeolites Y



- **total number of aluminum atoms obtained by AES/ICP**
- **simulation of the MAS NMR spectra using the quadrupole parameters obtained by MQMAS NMR**
- **correction of the relative intensities by the method of Massiot et al. ***

***: D. Massiot et al., J. Magn. Reson. 90 (1990) 231-242.**



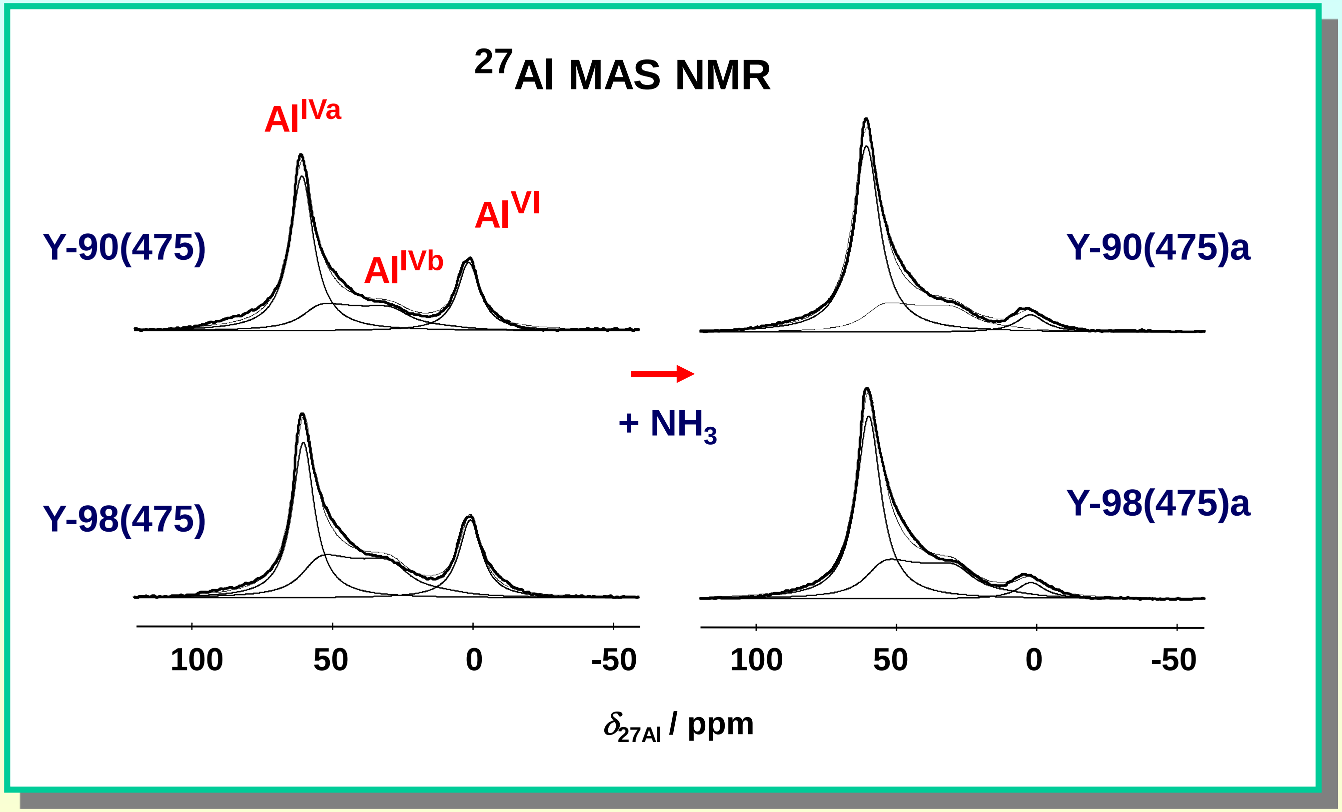
Comparison of Experimental Data

- **framework aluminum contents obtained by complementary methods (accuracy ± 5%):**

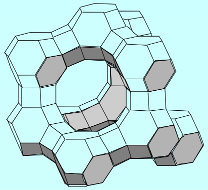
sample	**XRD**	**^{29}Si MAS NMR**	**^{27}Al MAS NMR**
	n_{Al} / u.c.	**n_{Al} / u.c.**	**n_{Al} / u.c.**
Y-(475)	**52.3**	**51.8**	**52.0**
Y-40(475)	**42.0**	**49.4**	**41.4**
Y-80(475)	**37.5**	**42.9**	**32.2**
Y-90(475)	**31.6**	**33.9**	**25.6**
Y-98(475)	**29.6**	**31.0**	**20.3**

→ **significant lower framework aluminum contents determined by ^{27}Al MAS NMR**

Effect of Ammonia Adsorption on Hydrothermally Treated Zeolites H-Y



→ **adsorption of ammonia causes a transformation of threefold to tetrahedrally coordinated aluminum**



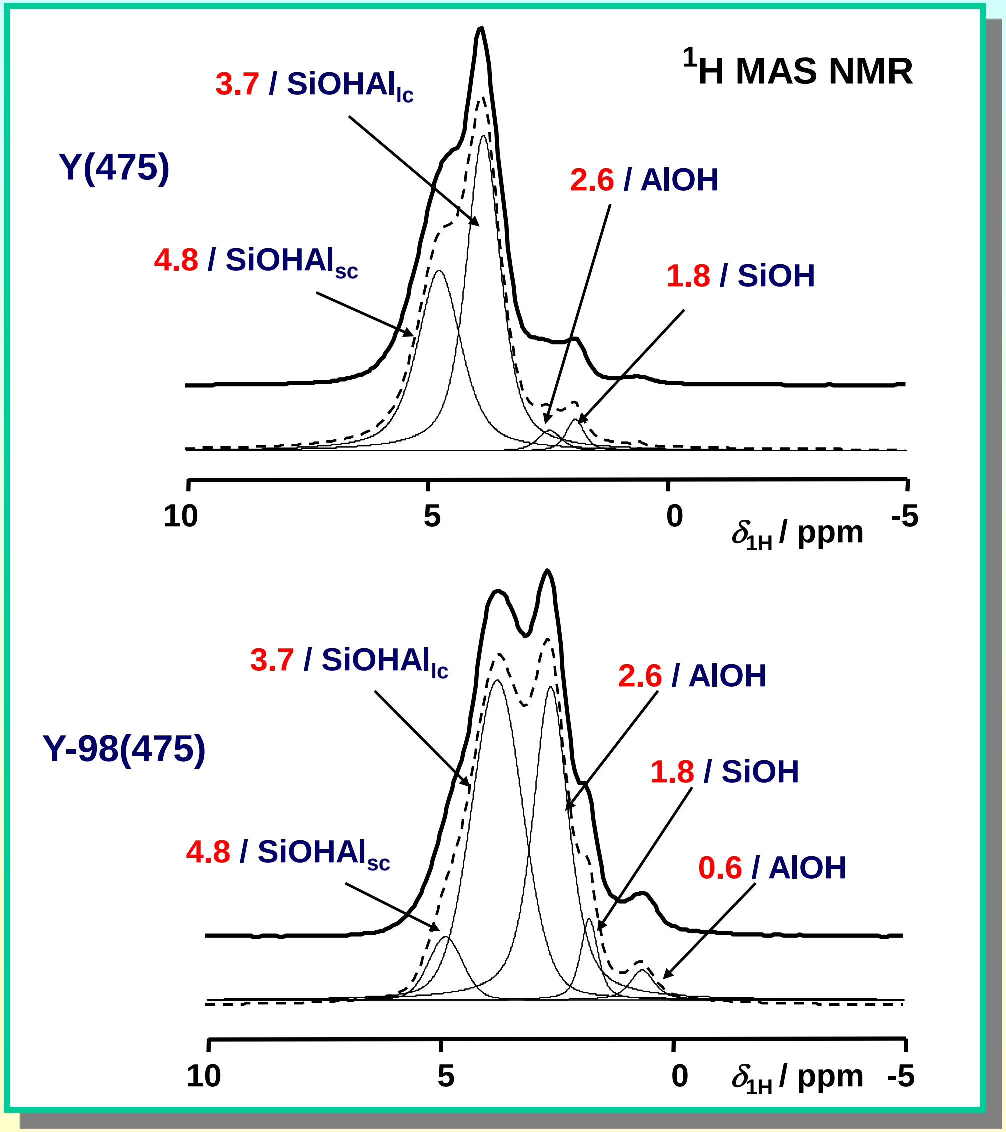
Comparison of Experimental Data

- framework aluminum contents obtained by complementary methods (accuracy ± 5%):

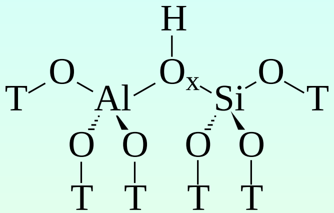
sample	XRD	^{29}Si MAS NMR	^{27}Al MAS NMR	^{27}Al MAS NMR
	n_{Al} / u.c.	n_{Al} / u.c.	n_{Al} / u.c.	n_{Al} / u.c.
				+ NH_3
Y-40(475)	42.0	49.4	41.4	49.8
Y-80(475)	37.5	42.9	32.2	39.3
Y-90(475)	31.6	33.9	25.6	32.4
Y-98(475)	29.6	31.0	20.3	28.2

→ comparable numbers of tetrahedrally coordinated framework aluminum atoms after loading of NH_3

Investigation of the Hydroxyl Coverage



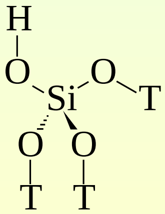
- **local structures of hydroxyl groups:**



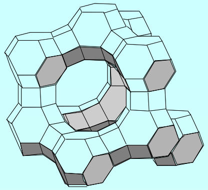
$SiOHAl_{lc}$: bridging OH groups in large cages (supercages), $x = 1$

$SiOHAl_{sc}$: bridging OH groups in sodalite cages, $x = 2$ and 3

SiOH: defect OH groups



AlOH: unknown

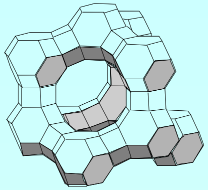


Comparison of Experimental Data

- numbers of aluminum atoms and hydroxyl groups determined by ^{27}Al MAS NMR and ^{1}H MAS NMR spectroscopy (accuracy ± 5%):

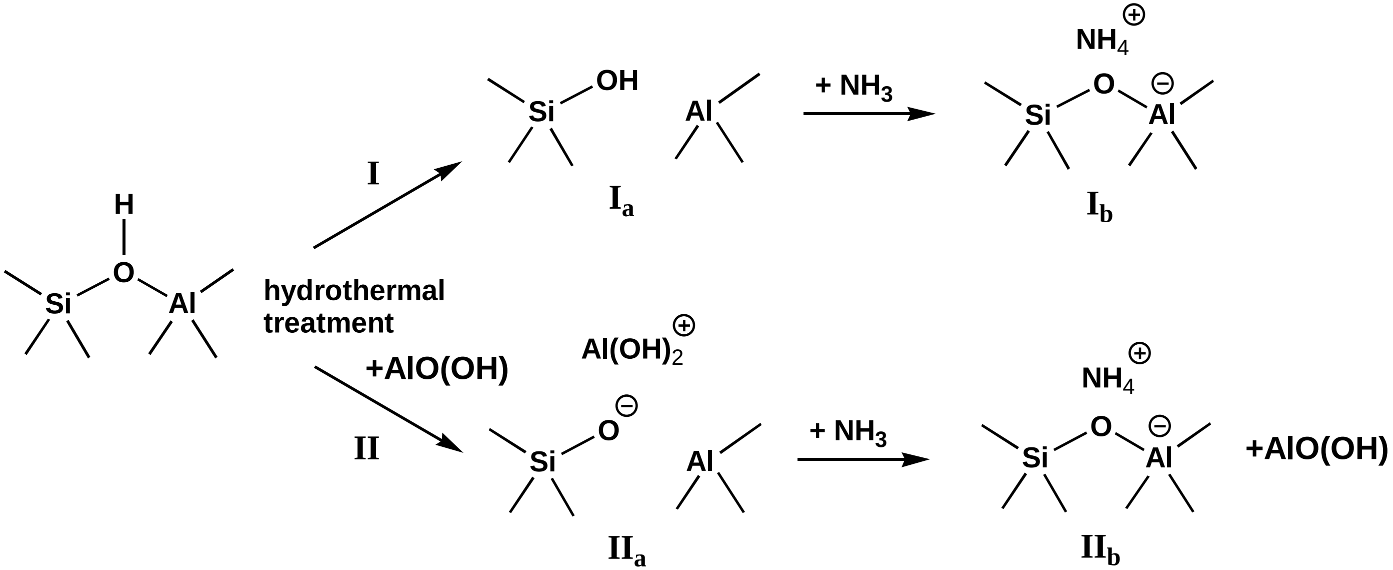
sample	Al^{IV} n_{Al} / u.c.	SiOHAl n_{OH} / u.c.	SiOH n_{OH} / u.c.	AlOH n_{OH} / u.c.
Y-80(475)	32.2	14.4	1.5	12.1
Y-80(475)a	39.3	22.8	1.1	11.4
Y-98(475)	20.3	18.5	2.0	15.6
Y-98(475)a	28.2	25.6	1.7	18.4
Y-98(475)w	24.7	19.9	4.1	11.1
Y-98(475)wa	30.6	30.2	1.3	13.8

→ coordination change is accompanied by a significant increase of the concentration of SiOHAl groups

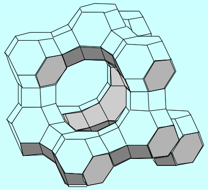


Reversible Coordination Change of Framework Aluminum Atoms

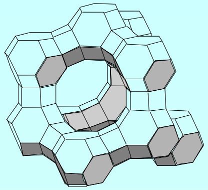
- **proposed mechanism:**



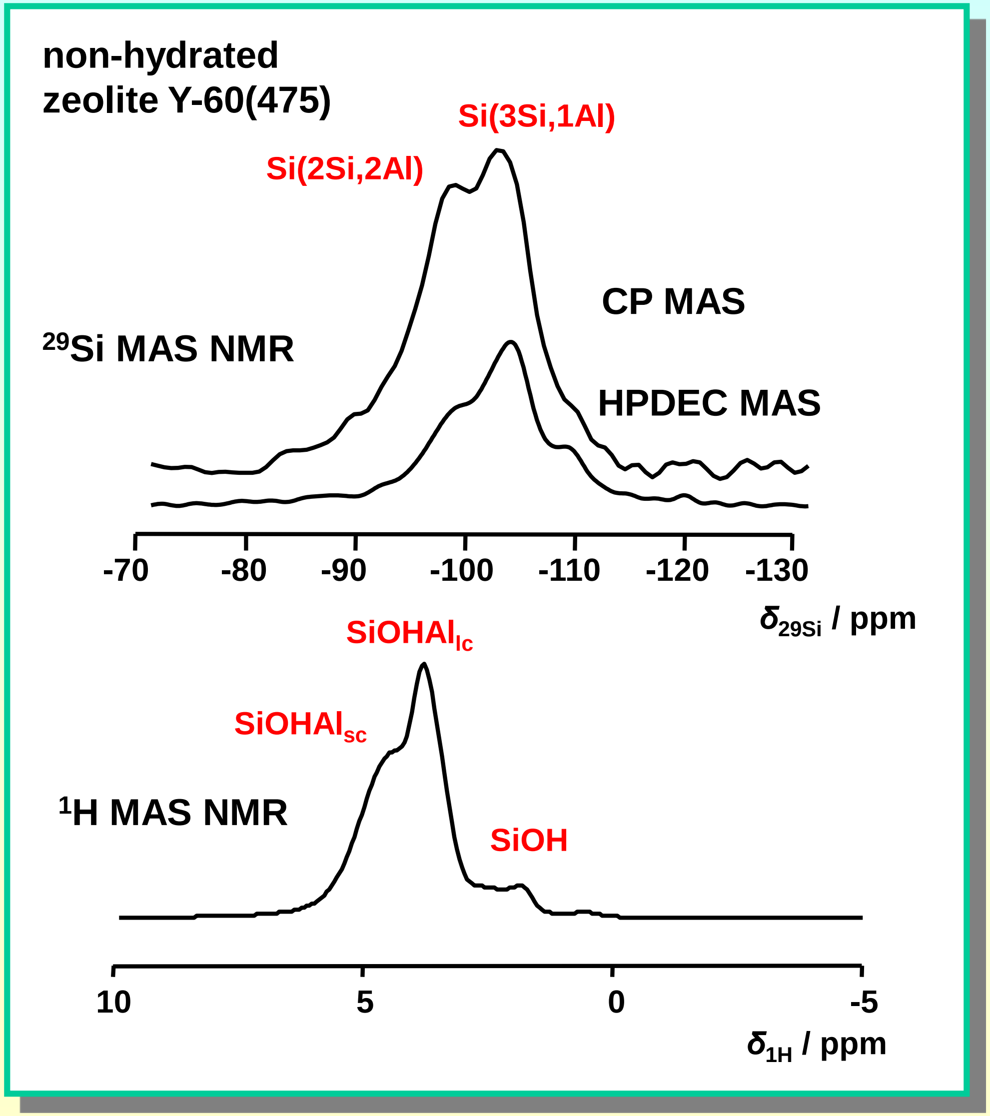
→ **pathway II may be the dominating mechanism of the coordination change of framework aluminum atoms in zeolites Y**

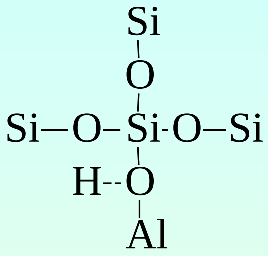


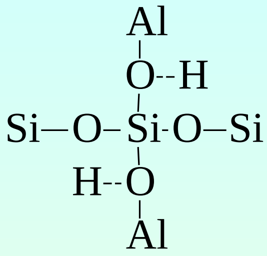
Quantitative Investigations of Steamed and Non-Hydrated Zeolites H-Y



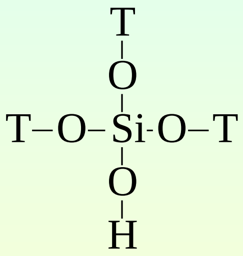
MAS NMR Studies of Non-Hydrated Zeolites H-Y





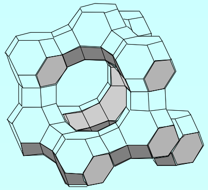


Q^4: Si(3Si,1Al) **Q^4: Si (2Si,2Al)**

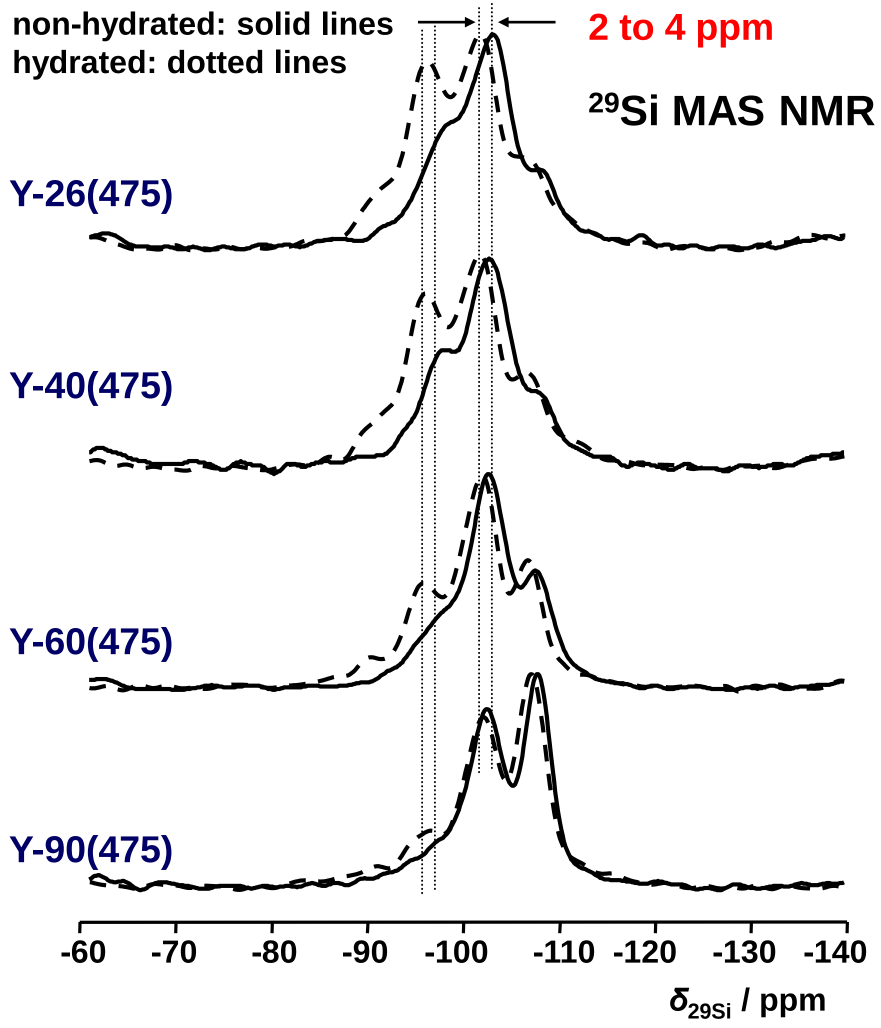


Q^3: Si(3T,1OH) with T: Si or Al

- **all ^{29}Si MAS NMR signals are due to Q^4 species**



Comparison of Hydrated and Non-Hydrated Zeolites H-Y

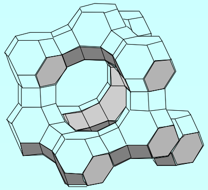


- **weak dealumination:**

  high-field shift of the ^{29}Si MAS NMR signals of non-hydrated samples by 2 to 4 ppm

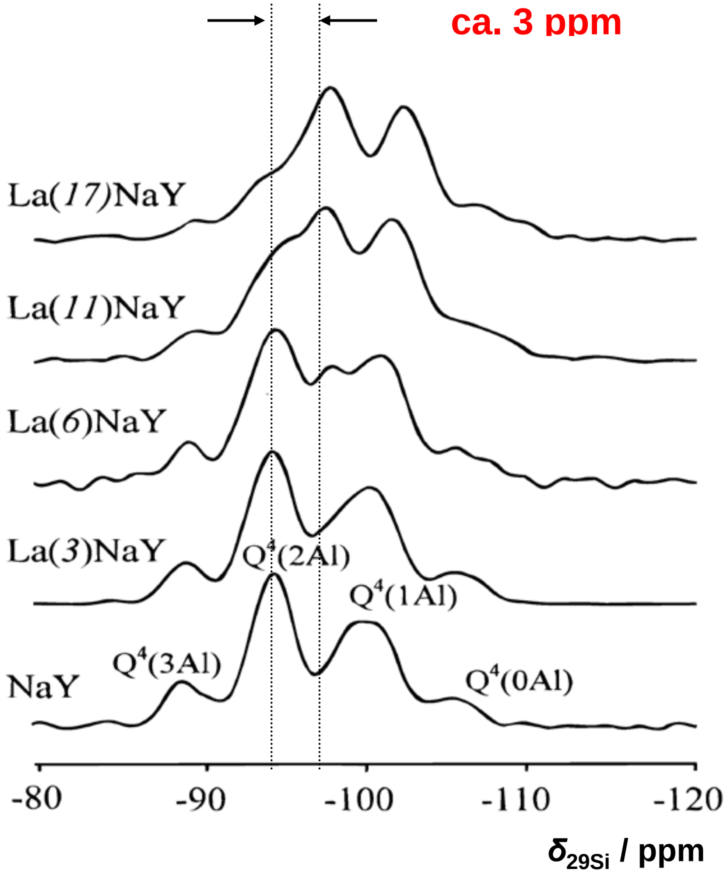
- **strong dealumination:**

  only small differences of the ^{29}Si MAS NMR signals of the Q^4 silicon species Si(2Si,2Al)



Effect of Multivalent Cations on the ^{29}Si MAS NMR Spectra of Zeolites Y

^{29}Si MAS NMR of lanthanum-exchanged zeolites Y *



- **zeolites La,Na-Y:**

  lanthanum cations induce a high-field shift of the ^{29}Si MAS NMR signals of by ca. 3 ppm

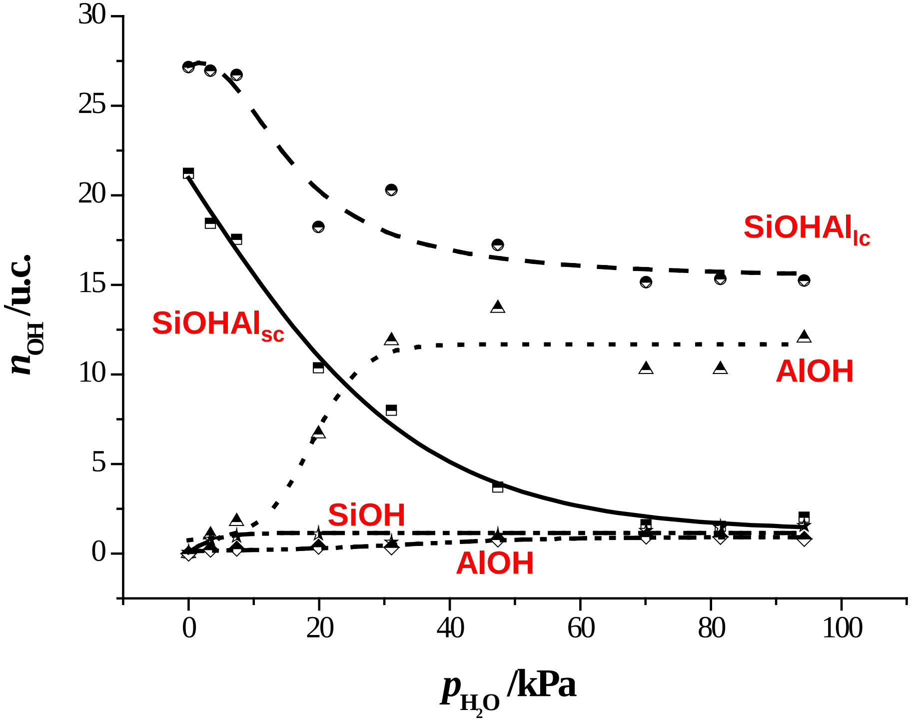
- **non-hydrated zeolites Y-*T*(475):**

  high-field shifts of the ^{29}Si MAS NMR signals of the Q^4 species may indicate the presence of cationic extra-aluminum species (Al^{3+}, $Al(OH)^{2+}$ …)

***: J.A. van Bokhoven et al., J. Phys. Chem. B 104 (2000) 6743-6754.**

Influence of the Hydrothermal Treatment on the Hydroxyl Coverage

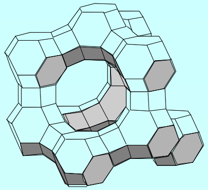
number of OH groups as a function of the water vapor pressure



- **weak treatment:**
  similar dehydroxylation of SiOHAl groups in supercages and sodalite cages

- **strong treatment:**
  stronger dehydroxylation of SiOHAl groups in sodalite cages, significant increase of AlOH groups at 2.6 ppm

- **whole range:**
  only weak formation of defect SiOH groups at 1.8 ppm and AlOH groups at 0.6 ppm



Comparison of Experimental Data

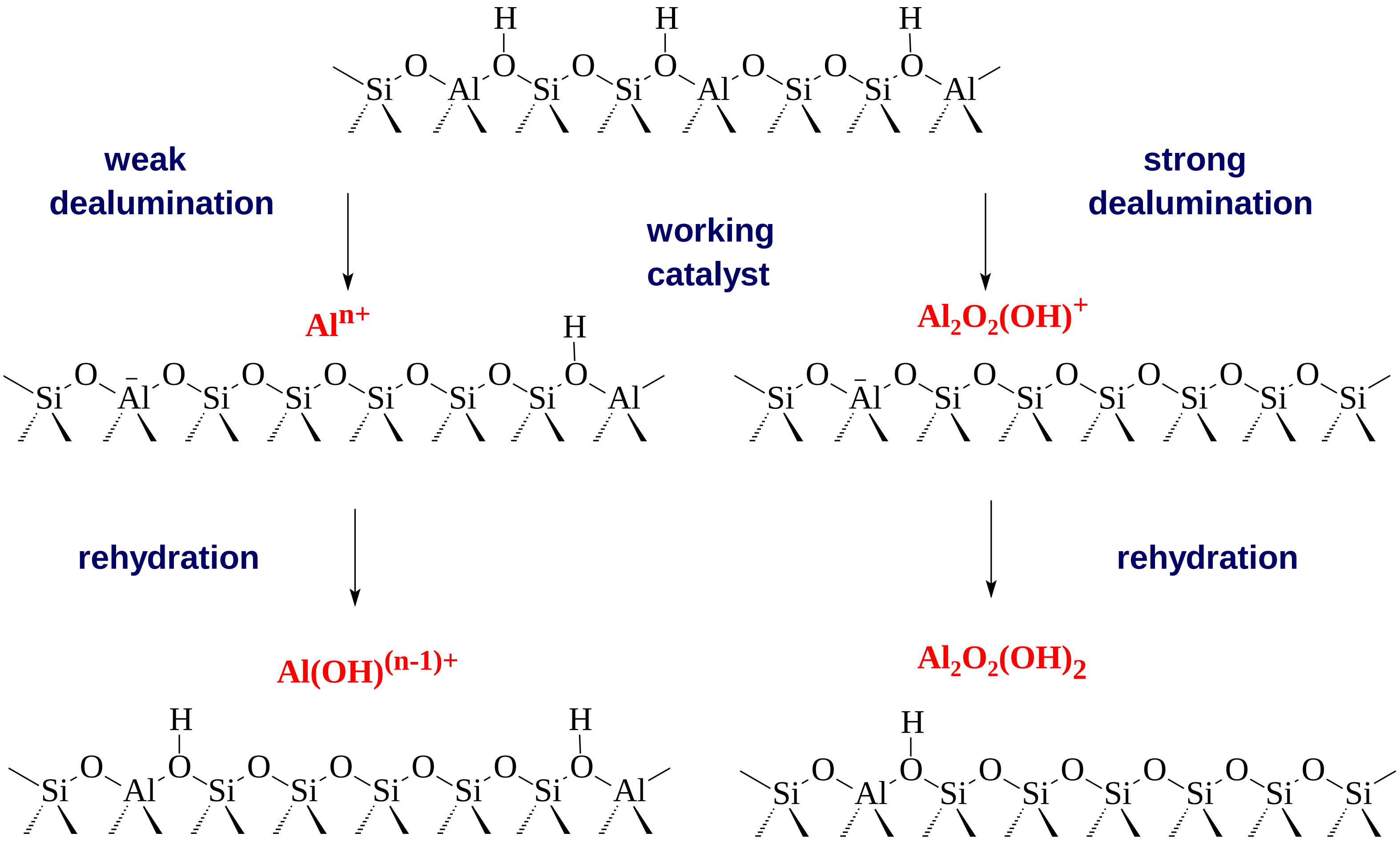
- mean charge per extra-framework aluminum atom in non-hydrated zeolites Y:

$$x = (n_{\text{framework Al}} - n_{\text{SiOHAl}} - n_{\text{Na}})/(n_{\text{extra-framework Al}})$$

sample	$n_{\text{framework Al}}$ /u.c.	$n_{\text{extra-framework Al}}$ /u.c.	n_{SiOHAl} /u.c.	x	n_{AlOH} /u.c.
Y-60(475)a	46.2	5.8	28.6	+2.3	6.7
Y-70(475)a	41.9	10.1	28.3	+0.9	11.9
Y-80(475)a	34.3	17.7	20.9	+0.5	13.7
Y-90(475)a	31.2	20.8	16.8	+0.5	10.3
Y-94(475)a	31.8	20.2	16.8	+0.5	10.3
Y-98(475)a	30.0	22.0	17.3	+0.4	12.0

strong dealumination: $\{n_{\text{Al}} : n_{\text{AlOH}} : n_{x\cdot\text{Al}}\}_{\text{extra}} \sim 2:1:1 \rightarrow \{[\text{Al}_2\text{O}_2(\text{OH})]^+\}_n$

Nature of Extra-Framework Aluminum



weak dealumination

working catalyst

strong dealumination

Al^{n+}

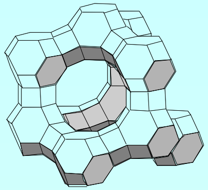
$Al_2O_2(OH)^+$

rehydration

rehydration

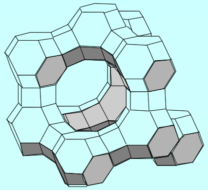
$Al(OH)^{(n-1)+}$

$Al_2O_2(OH)_2$



Summary

- low concentration of defect SiOH groups in strongly dealuminated zeolites supports a healing of the framework
- occurrence of highly charged extra-framework aluminum cations after weak hydrothermal treatment
- mean number of positive charges of extra-framework aluminum species decreases with increasing strength of the hydrothermal treatment
- hydrothermally induced formation of threefold coordinated framework alumium atoms which are transformed to tetrahedrally coordinated framework atoms by adsorption of ammonia
- concentration of bridging OH groups is effected by:
  - dealumination of the zeolite framework
  - coordination change of framework aluminum atoms
  - formation of cationic extra-framework aluminum species



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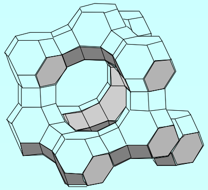


Dealumination of Zeolites

- **removal of aluminum from the zeolite framework was first reported in 1964 by *Barrer* and *Makki***

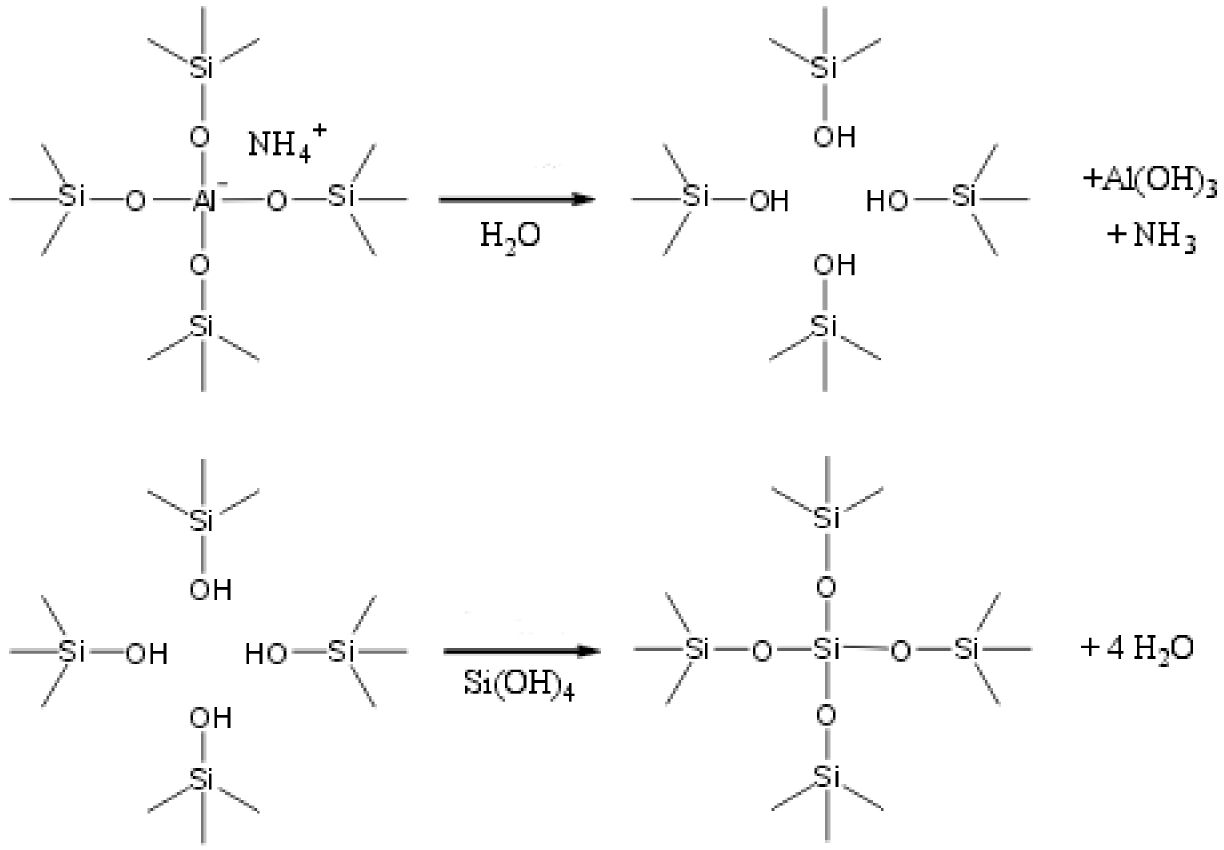
- **in 1967, *McDaniel* and *Maher* reported a method to increase the thermal stability of zeolite Y: Ultrastablilization procedure**

- **in 1980, *Lohse et al.* proposed a migration of silicon atoms leading to an occupation of empty tetrahedral sites and to a healing of the zeolite framework**

- **methods of dealumination:**
  - **dealumination with acids (HCl, HNO_3, H_4EDTA)**
  - **dealumination with silicon tetrachloride**
  - **hydrothermal treatment of the zeolite framework**

Proposed Dealumination Mechanisms I

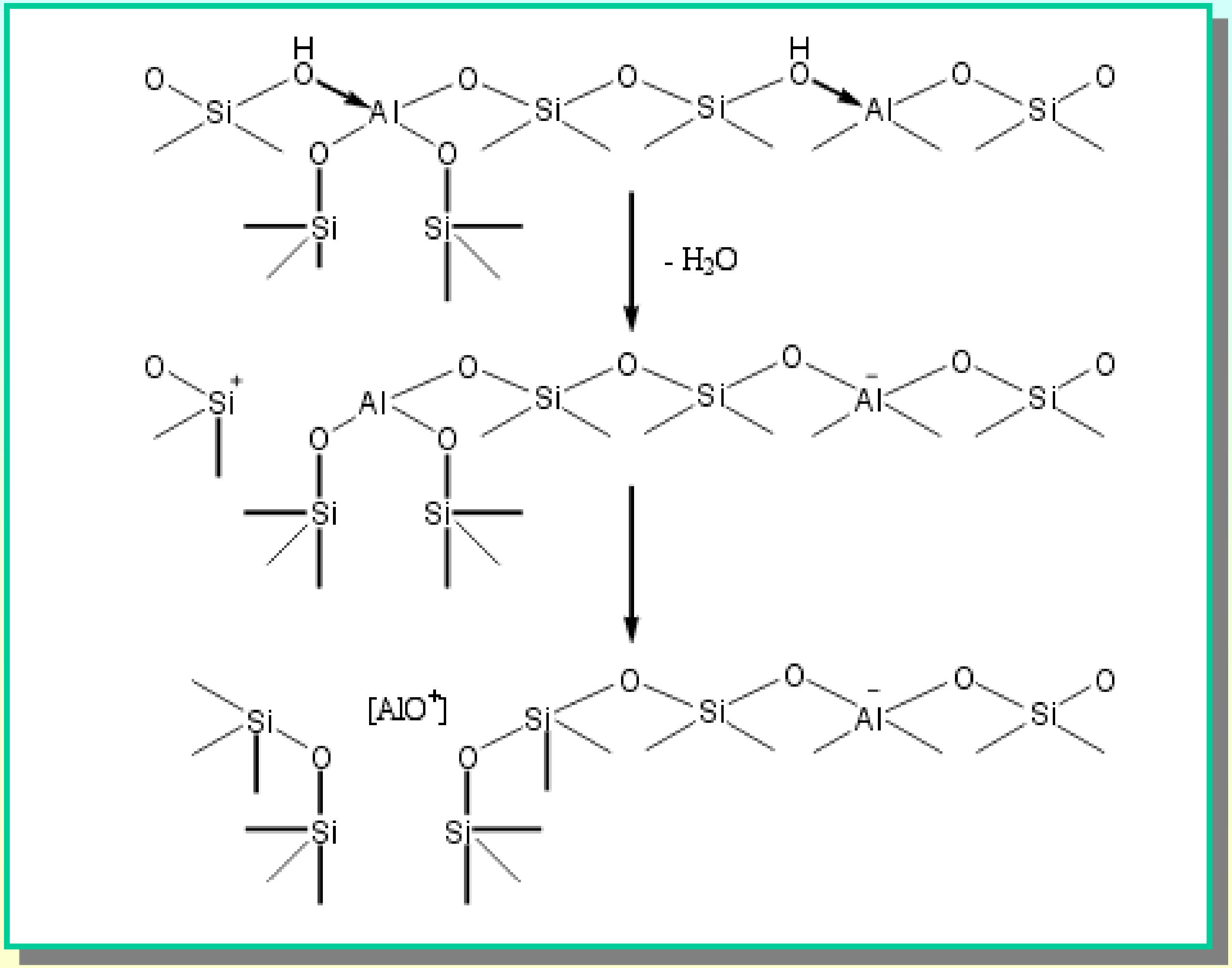
Kerr, 1974:



G.T. Kerr, in: W.M. Meier, J.B. Uytterhoeven (Eds.), Molecular Sieves, Advances in Chemistry Series, Vol. 121, American Chemical Society, Washington, 1974, p. 219-229.

Proposed Dealumination Mechanisms II

Kuehl, 1977:



G.H. Kuehl, J. Phys. Chem. Solids 38 (1977) 1259-1269.