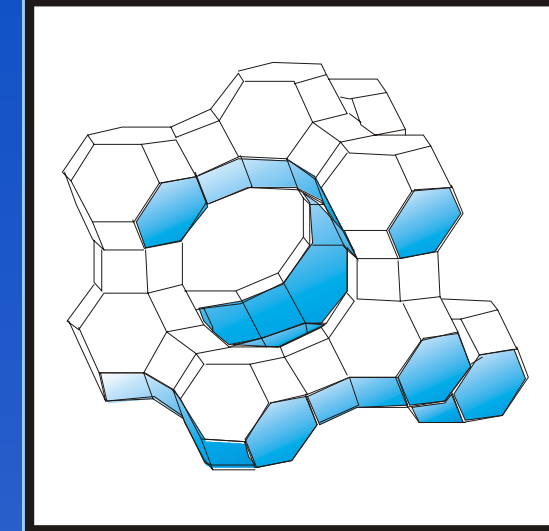


ELUCIDATING THE DEALUMINATION MECHANISM OF ZEOLITE H-Y BY SOLID-STATE NMR SPECTROSCOPY

S. Altwasser¹, J. Jiao¹, S. Steuernagel², J. Weitkamp¹ and M. Hunger¹

¹ Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany

² BRUKER BioSpin, D-76287 Rheinstetten, Germany



INTRODUCTION

Recent solid-state NMR investigations of steamed zeolites indicated that a coordination change of aluminum atoms from a tetrahedral (Al^{IV}) to an octahedral (Al^{VI}) coordination is not always accompanied by a dealumination of the framework. ²⁷Al MAS NMR spectra of steamed zeolites consist of signals at ca. 0 ppm due to octahedrally coordinated aluminum atoms, which were often assigned to extra-framework aluminum species. However, it was observed that adsorption of a strong base (ammonia, pyridine) leads to a partial transformation of Al^{VI} to Al^{IV} species [1]. Moreover, Wouters et al. [2] found an agreement between the framework n_{Si}/n_{Al} ratios of steamed zeolites H-Y determined by ²⁷Al MAS NMR and ²⁹Si MAS NMR spectroscopy only upon adsorption of ammonia. This indicates that octahedrally coordinated aluminum species may be formed in the zeolite framework caused, e.g., by an additional coordination of water molecules or an additional bonding of OH groups. In the literature, different models for a reversible change of the aluminum coordination were proposed, e.g., by Woolery et al. [3] and Wouters et al. [4,5]. It was the aim of the present work to reconsider the models of a reversible coordination change of framework aluminum atoms in steamed zeolites H-Y and to study the influence of this coordination change on the hydroxyl coverage.

EXPERIMENTAL PART

- Dealumination: Heating of 2 g of zeolite NH₄-Y (Degussa, $n_{Si}/n_{Al} = 2.7$) in a horizontal quartz glass tube under flowing N₂ to 753 K, calcination for 10 h and steaming with water loaded N₂ at 753 K → samples denoted deH-Y/x, where x stands for the temperature (in K) of the water bath used for loading the N₂ with water vapor.
- Washing of zeolites deH-Y/x with 0.16 M aqueous solution of HCl → samples denoted by 'w'.
- Ammonia loading: Activation at 723 K for 12 h at $p \leq 1.5$ Pa, loading with 5 kPa NH₃ for 1.5 h at room temperature → samples denoted by 'a'.
- ²⁷Al MQMAS NMR: Bruker Avance 500WB spectrometer, resonance frequency of 130.3 MHz, three-pulse-z-filter-sequence introduced by Amoureux et al. [6].
- ²⁷Al MAS NMR: Bruker Avance 750WB spectrometer, resonance frequency of 195.4 MHz, single-pulse excitation.
- ¹H MAS NMR: Bruker MSL 400 spectrometer, dehydrated samples, single-pulse excitation.

RESULTS AND DISCUSSION

- Study of a homologous series of steamed zeolites deH-Y/x with a systematically decreased amount of tetrahedrally coordinated framework aluminum atoms.
- XRD and ²⁹Si MAS NMR spectroscopy as two independent methods for determining the amount of framework aluminum atoms.
- ²⁷Al MQMAS NMR (Fig. 2) → isotropical chemical shifts and second order quadrupolar effect parameters of two signals of tetrahedrally coordinated Al species (Al^{IVa} and Al^{IVb}) and up to three different octahedrally coordinated aluminum species (Al^{VIa}, Al^{VIb} and Al^{VIc}).
- Simulation of the 1D ²⁷Al MAS NMR spectra (Fig. 2) with these quadrupolar parameters:
 - signal Al^{IVa}: framework Al, signal Al^{IVb}: tetrahedrally coordinated Al species in the vicinity of highly charged extra-framework aluminum species (Al^{VIa} and Al^{VIb}).
 - Al^{VIa} and Al^{VIb} species change their coordination after ammonia loading.
 - washing with aqueous HCl solution preferably removed Al^{VIc} species, which are not involved in the ammonia-induced coordination change.
 - Octahedrally coordinated Al atoms in the framework of steamed zeolites.
- Quantitative evaluation of ¹H MAS NMR spectra (Fig. 3) → adsorption of ammonia is accompanied by a significant increase in the amount of bridging OH groups.

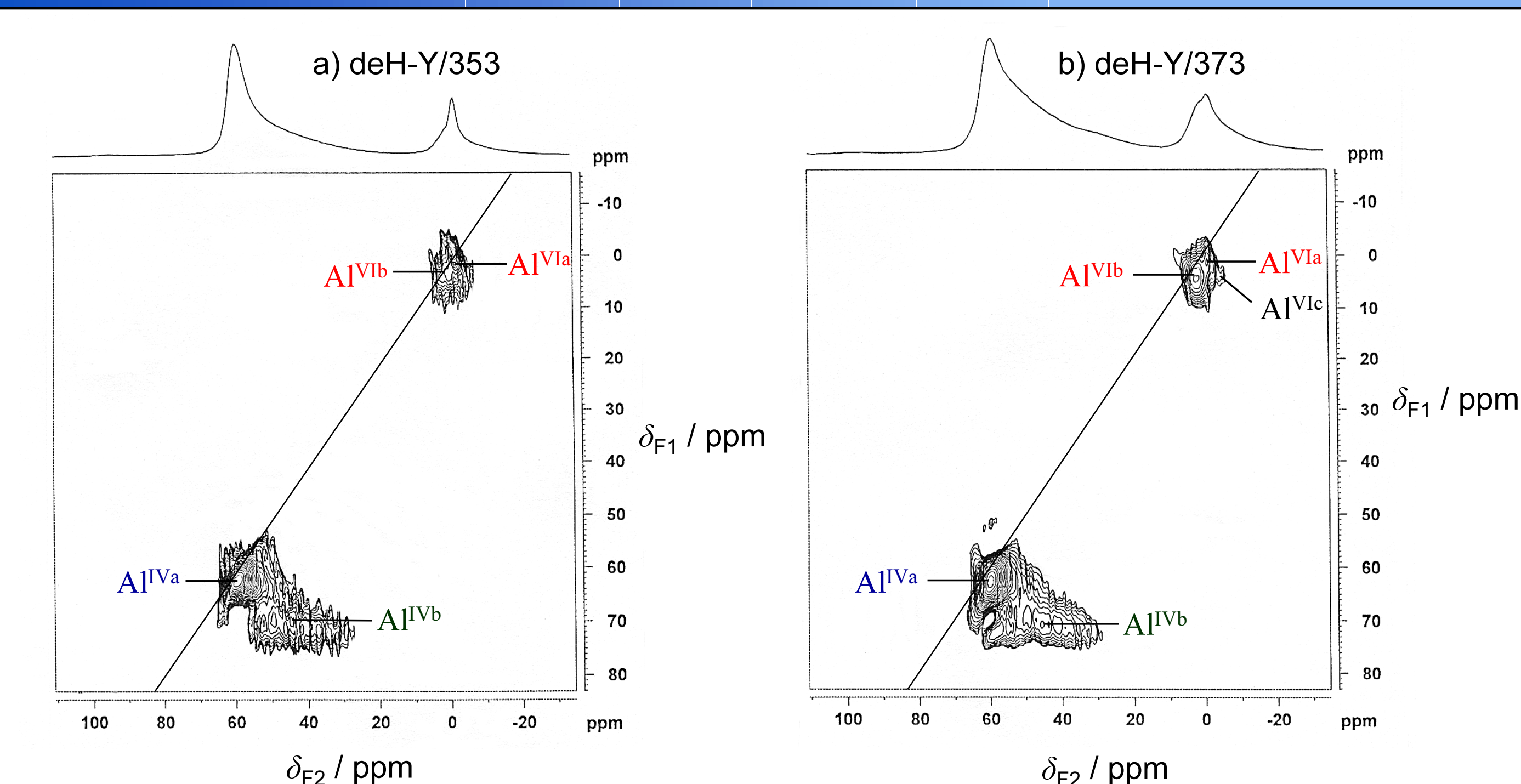


Figure 1: ²⁷Al MQMAS NMR spectra of the steamed zeolites deH-Y/353 (a) and deH-Y/371 (b) with framework n_{Si}/n_{Al} ratios of 3.5 and 5.2, respectively, recorded with a three-pulse-z-filter-sequence at a resonance frequency of 130.3 MHz.

SUMMARY

Steamed zeolites H-Y were investigated by XRD, ²⁹Si MAS NMR, ²⁷Al MQMAS NMR, high-field ²⁷Al MAS NMR, and ¹H MAS NMR spectroscopy. Upon adsorption of ammonia on the steamed materials, a reversible change of octahedrally coordinated to tetrahedrally coordinated aluminum atoms was found. Quantitative ²⁹Si, ²⁷Al, and ¹H MAS NMR measurements indicated that this coordination change is accompanied by the formation of bridging OH groups (SiOHAl) in the dehydrated materials, while only a weak decrease in the amount of silanol (SiOH) groups and no systematic change of AlOH groups occurred. Based on these results, a model for the reversible coordination change of Al

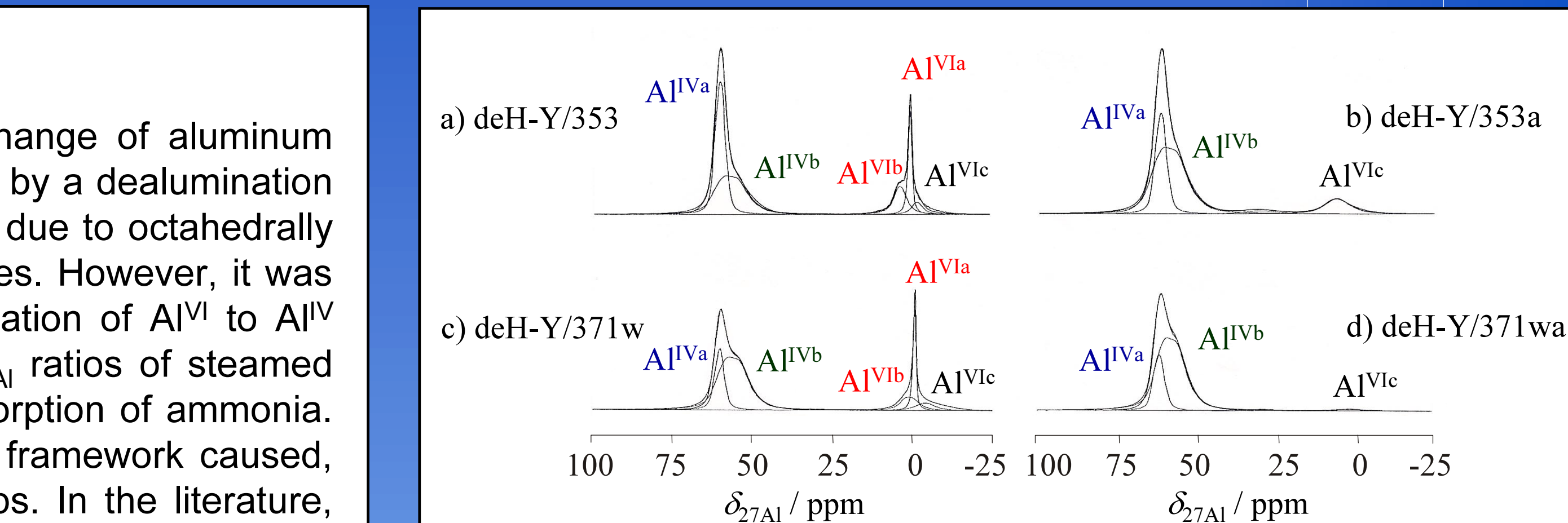


Figure 2: ²⁷Al MAS NMR spectra of the steamed zeolite deH-Y/353 recorded before (a) and after (b) ammonia treatment and of the steamed and washed zeolite deH-Y/371w before (c) and after (d) adsorption of ammonia. The spectra were obtained at a resonance frequency of 195.4 MHz.

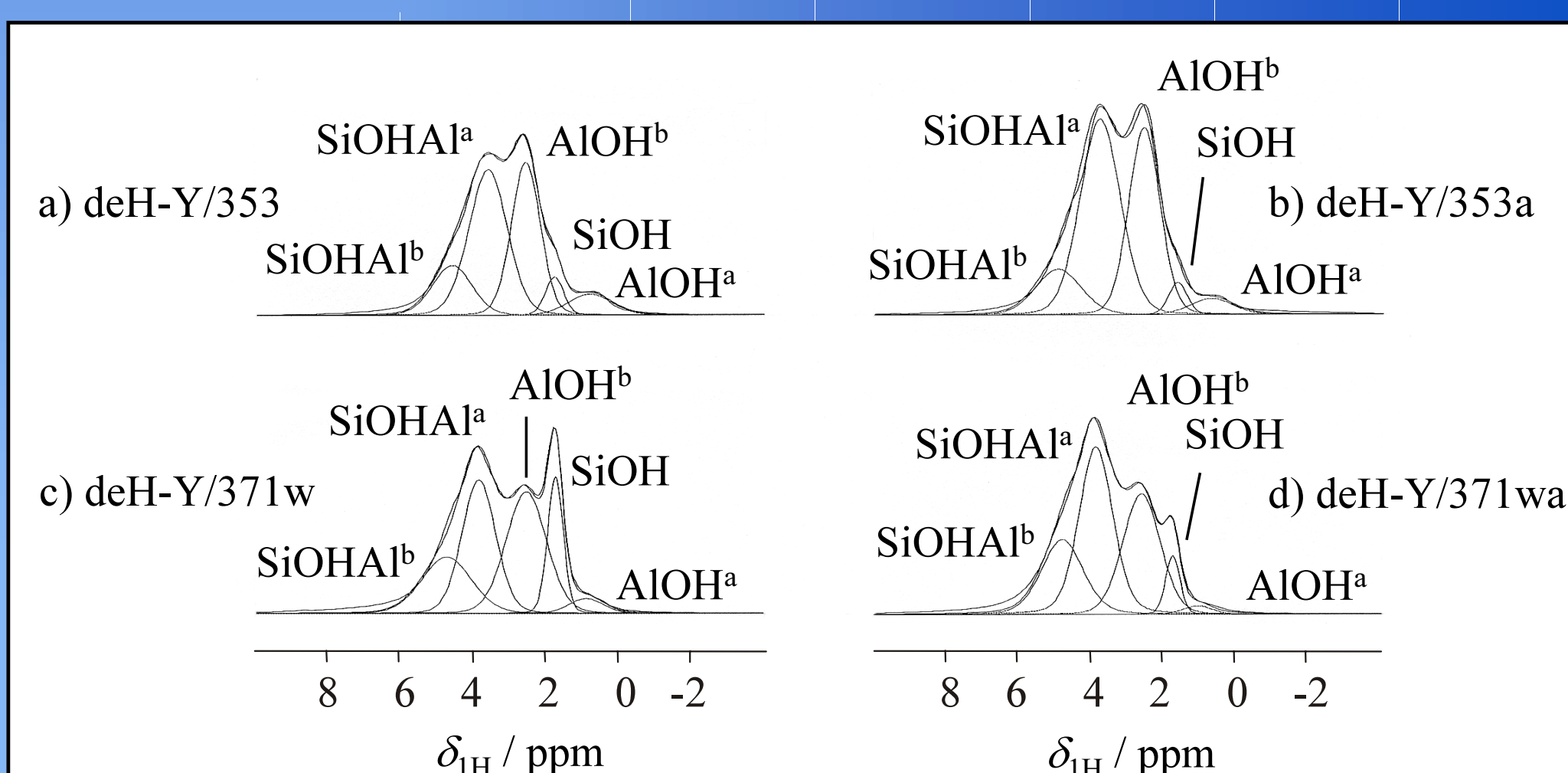
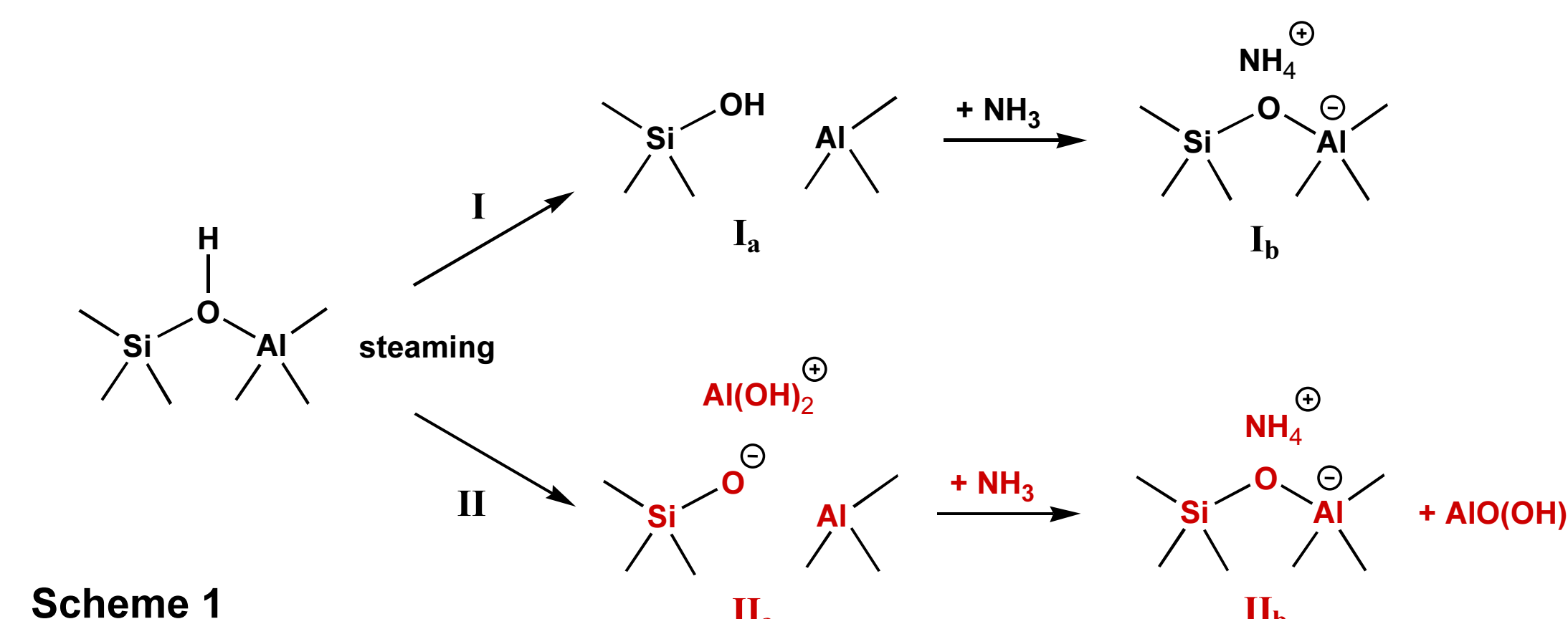


Figure 3: ¹H MAS NMR spectra of steamed zeolite deH-Y/353 (a, b) and steamed and washed zeolite deH-Y/371w (c, d) in the dehydrated state, recorded before (a, c) and after (b, d) adsorption of ammonia. The spectra were obtained at a resonance frequency of 400.1 MHz.

Coordination change of aluminum atoms in the framework of zeolites H-Y:



- Ammonia-induced formation of bridging OH groups is caused by the zeolite.
- Pathway I in scheme 1 was proposed by Woolery et al. [3] in first studies of a reversible coordination change of Al atoms → model is not supported by the present results.
- Proposal of a new mechanism: Pathway II in Scheme 1:
 - Rupture of the framework Si-O-Al bridge is induced by thermal treatment.
 - Extra-framework Al species coordinate at the SiO⁻ defect sites in the vicinity of threefold coordinated aluminum atoms (structure IIa).
 - After hydration IIa causes more than one signal of octahedrally coordinated Al atoms.

REFERENCES

- [1] Bourgeat-Lami, E., Massiani, P., Di Renzo, F., Espiau, P., Fajula, F., Appl. Catal., 72 (1991), 139-152.
- [2] Wouters, B.H., Chen, T.-H., Grobet, P.J., Proc. 12th International Zeolite Conference, Vol. 4 (1998), 2497-2502.
- [3] Woolery, G.L., Kuehl, G.H., Timken, H.C., Chester, A.W., Vartuli, J.C., Zeolites, 19 (1997), 288-296.
- [4] Wouters, B.H., Chen, T.-H., Grobet, P.J., J. Am. Chem. Soc., 120 (1998), 11419-11425.
- [5] Wouters, B.H., Chen, T.-H., Grobet, P.J., J. Phys. Chem. B, 105 (2001), 1135-1139.
- [6] Amoureux, J.P., Fernandez, C., Steuernagel, S., J. Magn. Reson. A, 123 (1996), 116-118.

ACKNOWLEDGEMENTS

Financial support by Deutsche Forschungsgemeinschaft, Volkswagenstiftung Hannover, Max-Buchner-Forschungsförderung, and Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dieter Freude and Thomas Loeser (University of Leipzig) for their support in recording high-field ²⁷Al MAS NMR spectra.

atoms in the framework of steamed zeolites H-Y is proposed assuming local structures consisting of threefold coordinated framework aluminum atoms with SiO⁻ defect sites in their vicinity. These SiO⁻ defect sites are coordinated to extra-framework aluminum species. After adsorption of ammonia at the threefold coordinated framework aluminum atoms, the SiO⁻ defect sites are healed to Si-O-Al⁺ bridges leading to a transformation of the threefold coordinated aluminum atoms to tetrahedrally coordinated atoms. Upon thermal decomposition of the ammonium ions formed at these Si-O-Al⁺ bridges, SiOHAl groups occur.