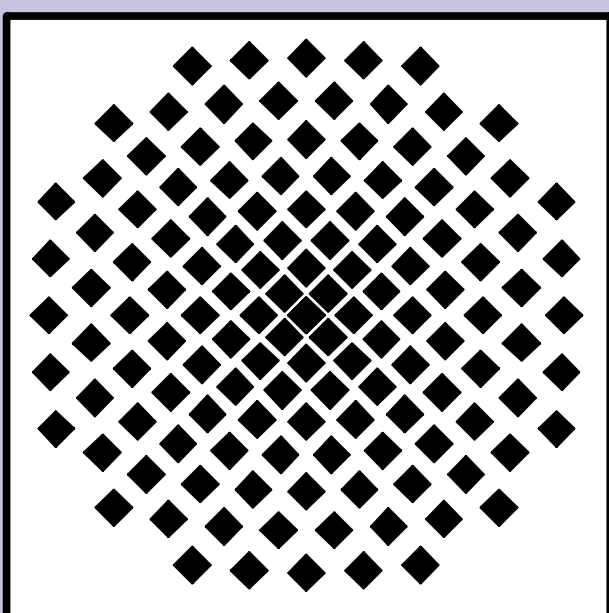
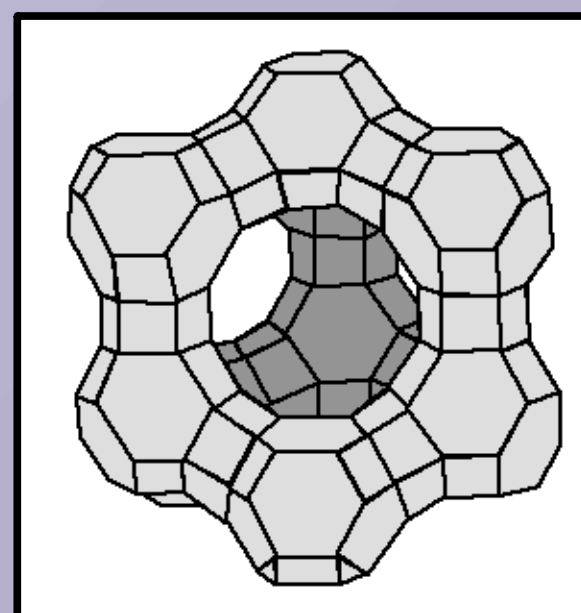




Effect of Water and Ammonia on H-SAPO-34 and H-SAPO-37 studied by *in situ* CF MAS NMR spectroscopy

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Introduction

Due to their acidic properties and shape-selectivity, microporous silicoaluminophosphates (SAPOs) find an increasing interest as solid catalysts in chemical technology [1-3]. The stability of rehydrated template-free silicoaluminophosphates shows substantial differences. In the case of H-SAPO-34, the presence of water influences the X-ray patterns indicating a strong loss of crystallinity which is completely restored after a dehydration at 823 K [4]. Briend et al. [5] explained the loss of crystallinity upon hydration of SAPO-34 by breaking Si-OH-Al bonds. Hydration of H-SAPO-37 at room temperature causes irreversible structural changes and leads to a material which is totally amorphous to X-ray diffraction. At temperatures of more than 345 K, template-free H-SAPO-37 exhibits a high stability towards hydration [6].

Experimental

Synthesis of SAPO-34 and SAPO-37:

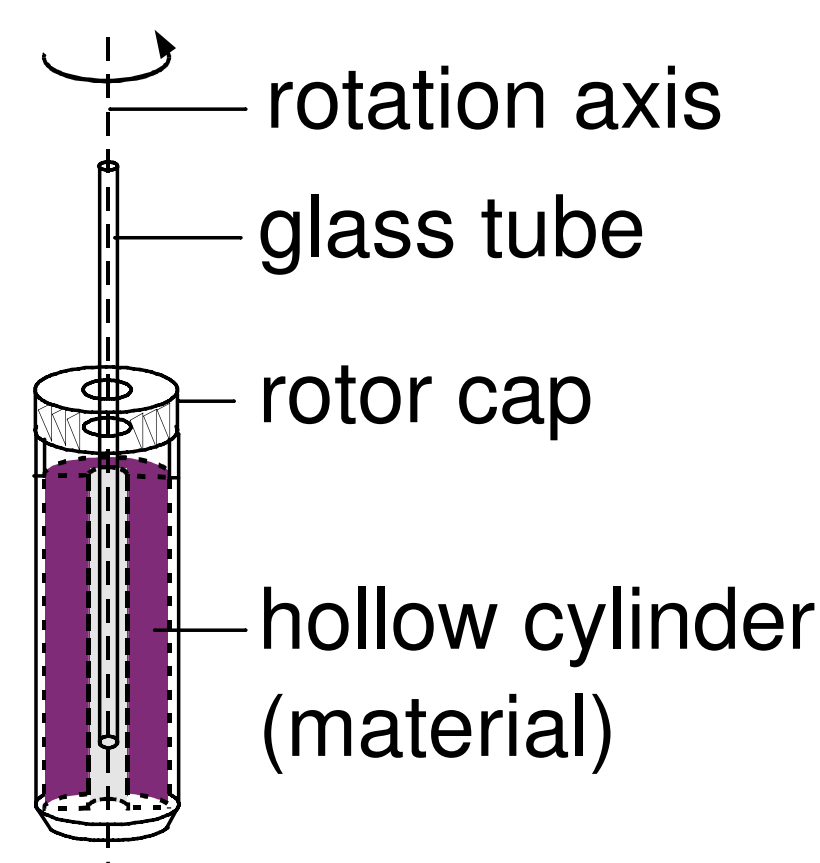
SAPO-34 was prepared according to a recipe for the synthesis of Ni-SAPO-34, omitting the nickel salt [8]. SAPO-37 was synthesized according to Ref. [9].

Characterization

Powder XRD patterns were obtained on a Siemens D5000 diffractometer ($\text{CuK}\alpha$ radiation). ^1H , ^{27}Al , ^{29}Si and ^{31}P MAS NMR measurements were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.13, 104.26, 79.49 and 161.98 MHz, respectively, with samples spinning rates of 4 kHz for ^{29}Si and 10 kHz for ^1H , ^{27}Al , and ^{31}P MAS NMR spectroscopy.

In situ solid-state NMR studies

The *in situ* MAS NMR investigations were carried out by applying a Bruker 4 mm MAS NMR probe modified with a gas injection system. A glass tube with an outer diameter of 1 mm was inserted into a 4 mm MAS NMR rotor via a hole in the rotor cap. Using a special tool, ca. 50 mg of the powder material was pressed to a hollow cylinder inside the MAS NMR rotor. The *in situ* CF MAS NMR experiment were carried out with a sample spinning rate of 10 kHz, single pulse $\pi/2$ and $\pi/12$ excitation, repetition times of 10 s and 500 ms, and 64 and 1200 accumulations for ^1H and ^{27}Al nuclei, respectively. During the *in situ* CF MAS NMR experiments, a flow of nitrogen ($\dot{V}(\text{N}_2) = 25$ or 50 ml/min) loaded with water ($p_{\text{H}_2\text{O}} = 2.3$ kPa, hydration) or mixed with ammonia ($\dot{V}(\text{NH}_3) = 0.2$ ml/min, ammoniation) or of dry nitrogen (deammoniation, dehydration) was injected into the spinning MAS NMR rotor.



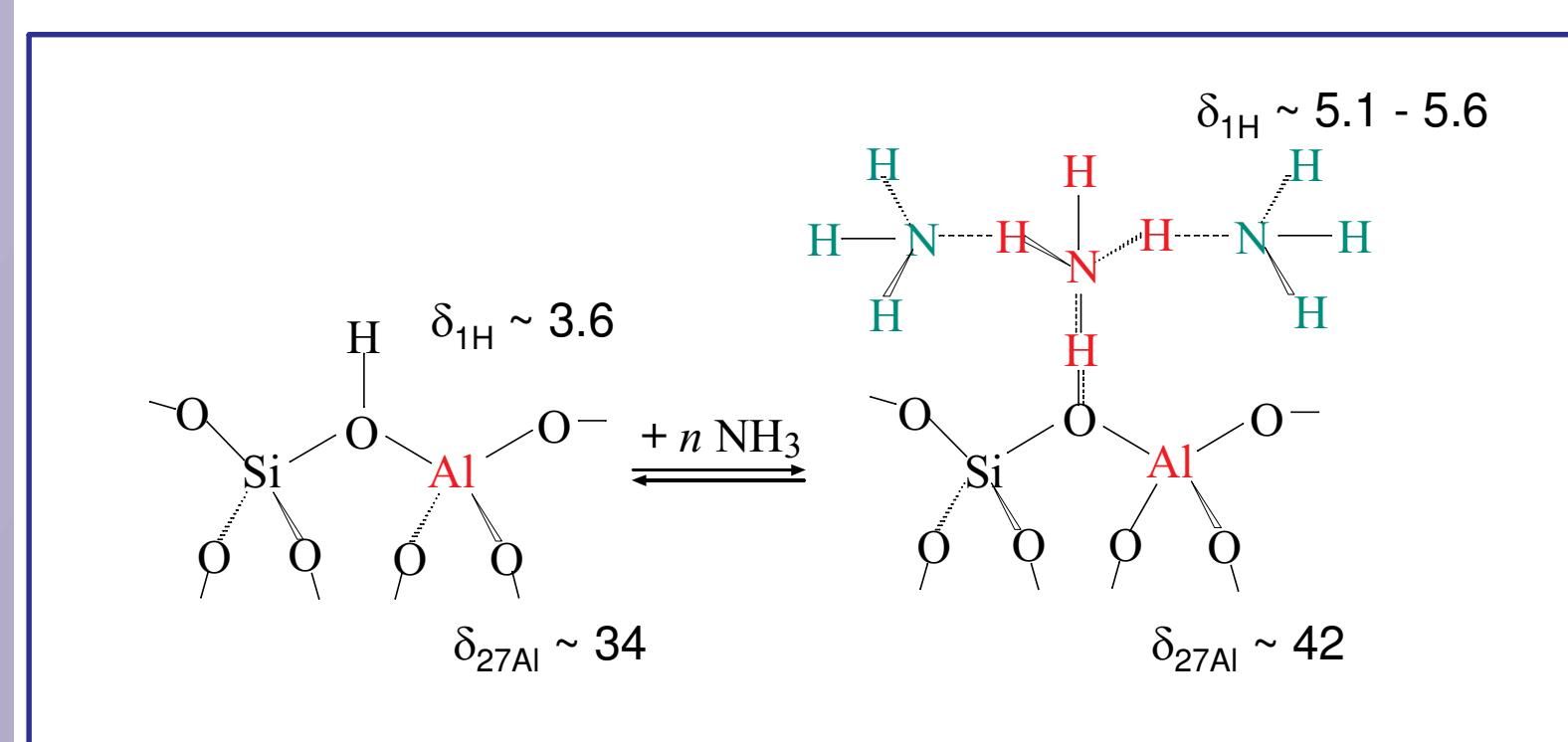
Vomscheid et al. [7] investigated the influence of ammonia on H-SAPO-34. Such an interaction takes place via the formation of Al^{IV} and Al^{VI} framework species and the breaking of Al-O-P bonds.

In the present work, modern *in situ* solid-state CF (CF: continuous-flow) MAS NMR spectroscopy was applied to investigate the framework changes or damages in H-SAPO-34 and H-SAPO-37 towards ammoniation/hydration followed by a deammoniation/dehydration. The investigations were performed to determine the primary adsorption sites of water and ammonia in silicoaluminophosphates and the variation of the aluminum coordination upon water and ammonia adsorption, the formation of framework defects and defect SiOH groups and the conditions of water and ammonia desorption.

Results and Discussion: Ammoniation

Two-step ammoniation of H-SAPO-37

1. ammoniation of SiOHAl groups



2. ammoniation of $\text{Al}(\text{OP})_4$ species

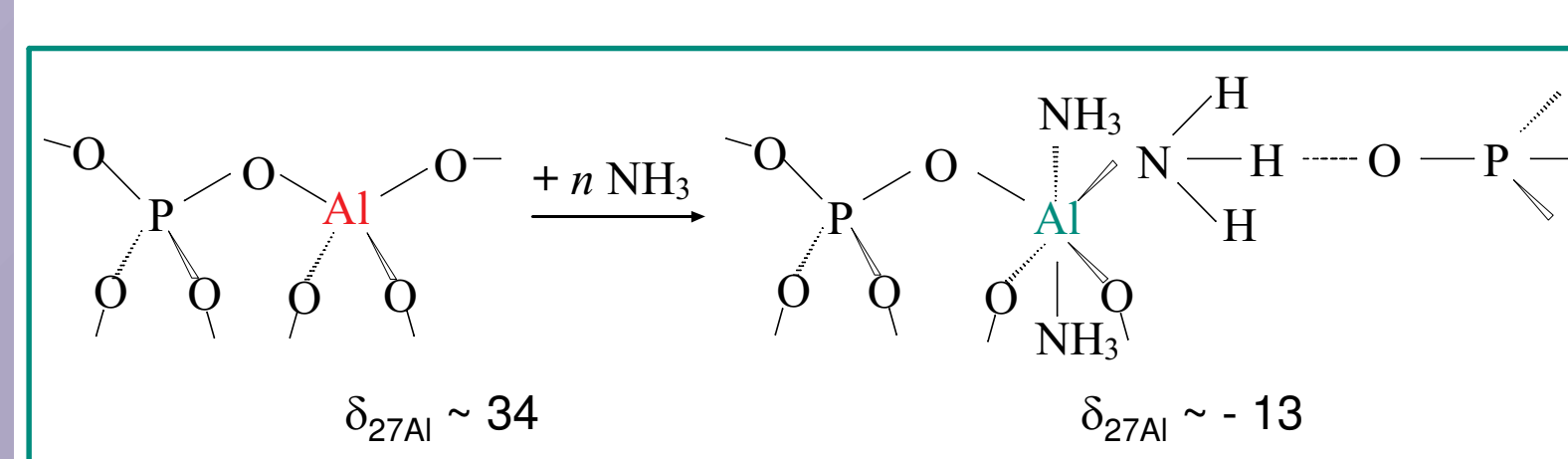
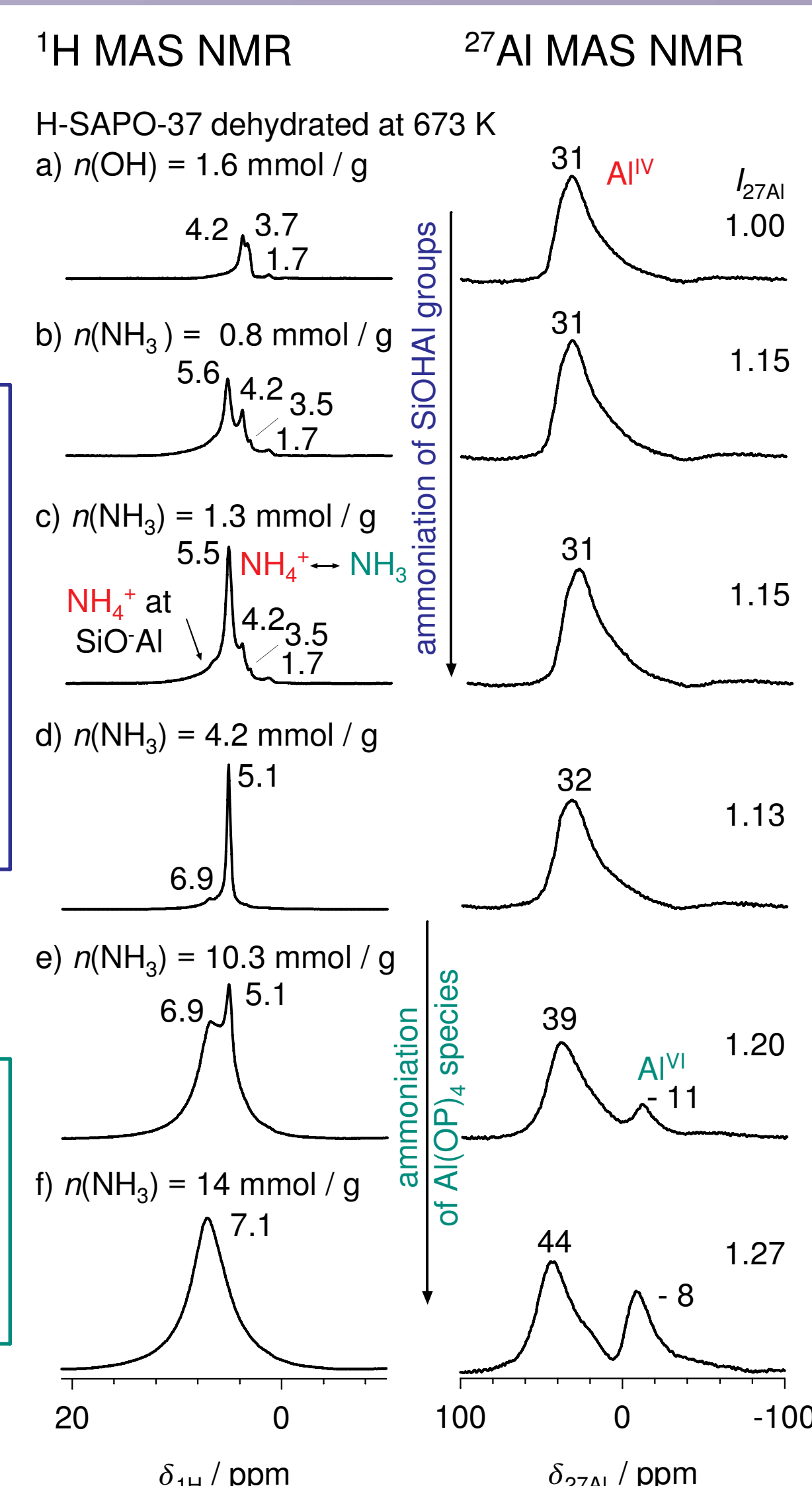


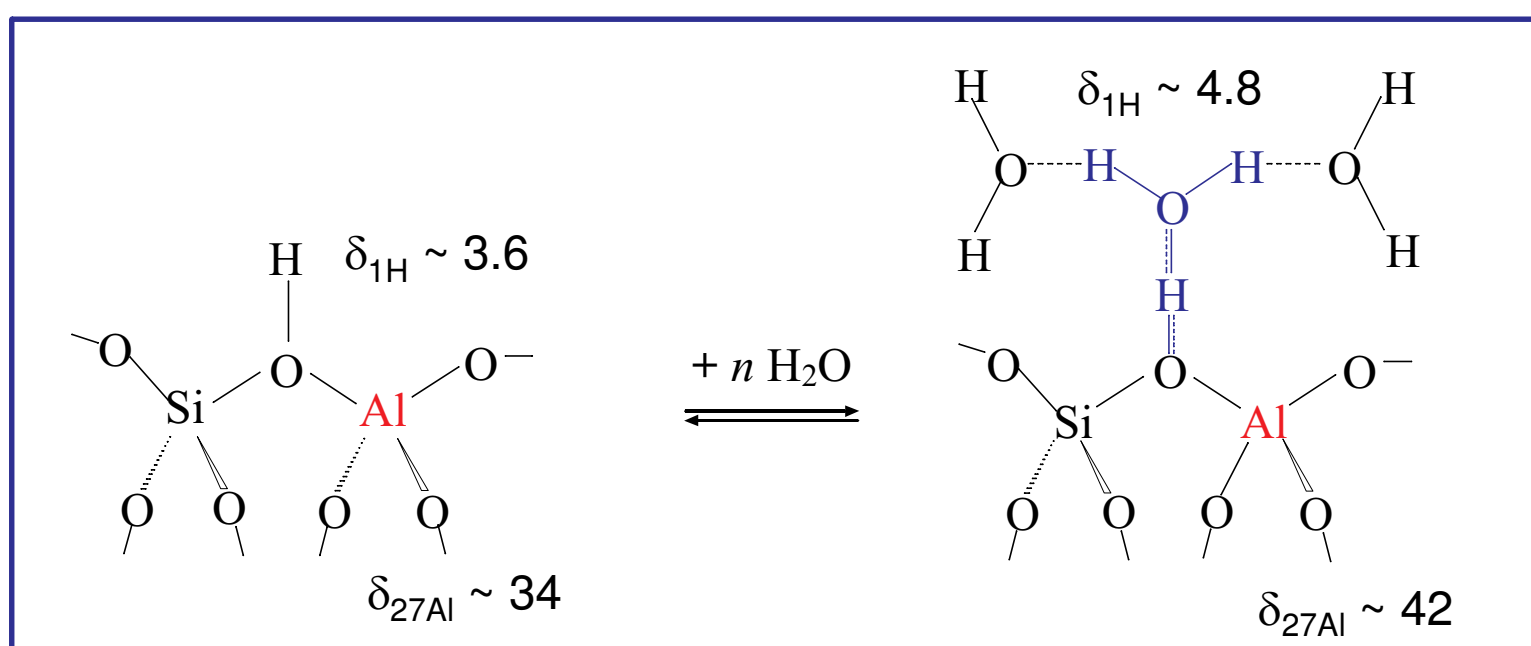
Fig. 4: Ammoniation of H-SAPO-37
left: reaction mechanisms, right: NMR spectra.



Results and Discussion: Hydration / Dehydration

Two-step hydration of H-SAPO-34

1. Hydration of SiOHAl groups



2. Hydration of $\text{Al}(\text{OP})_4$ species

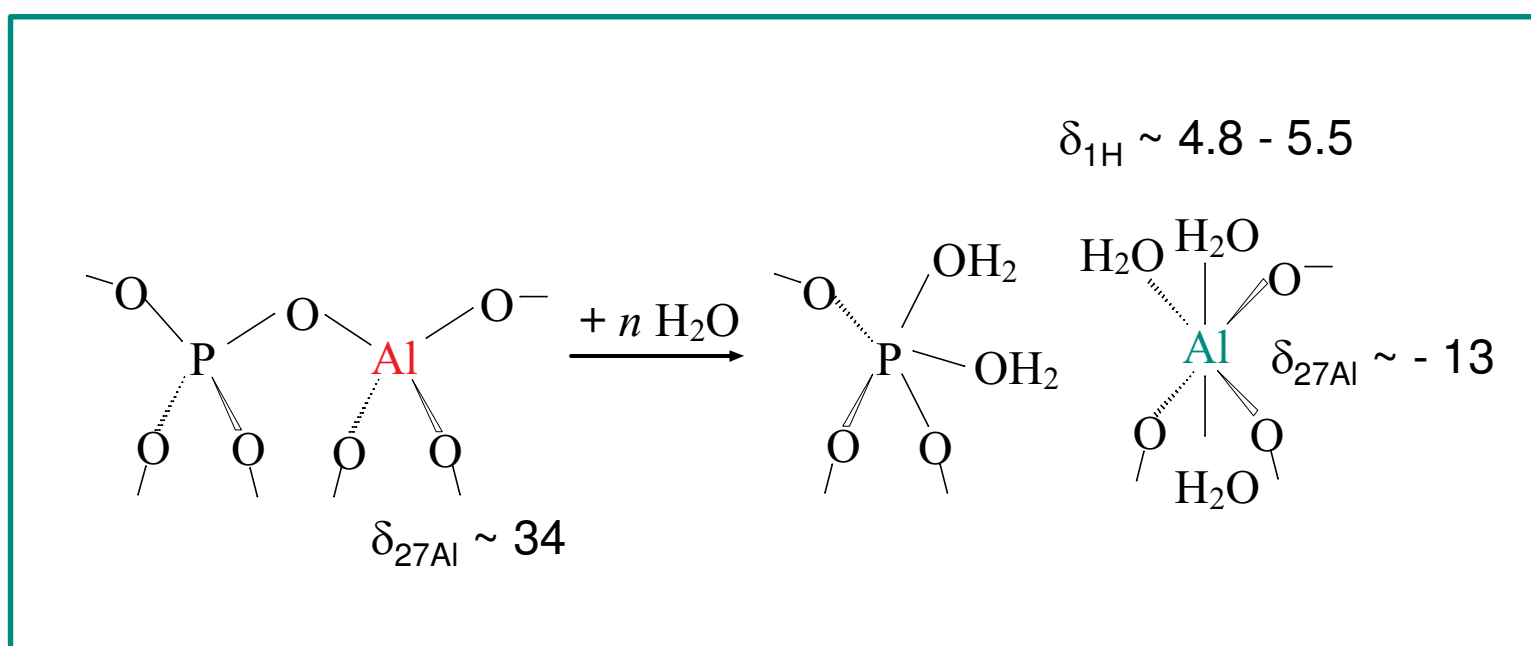
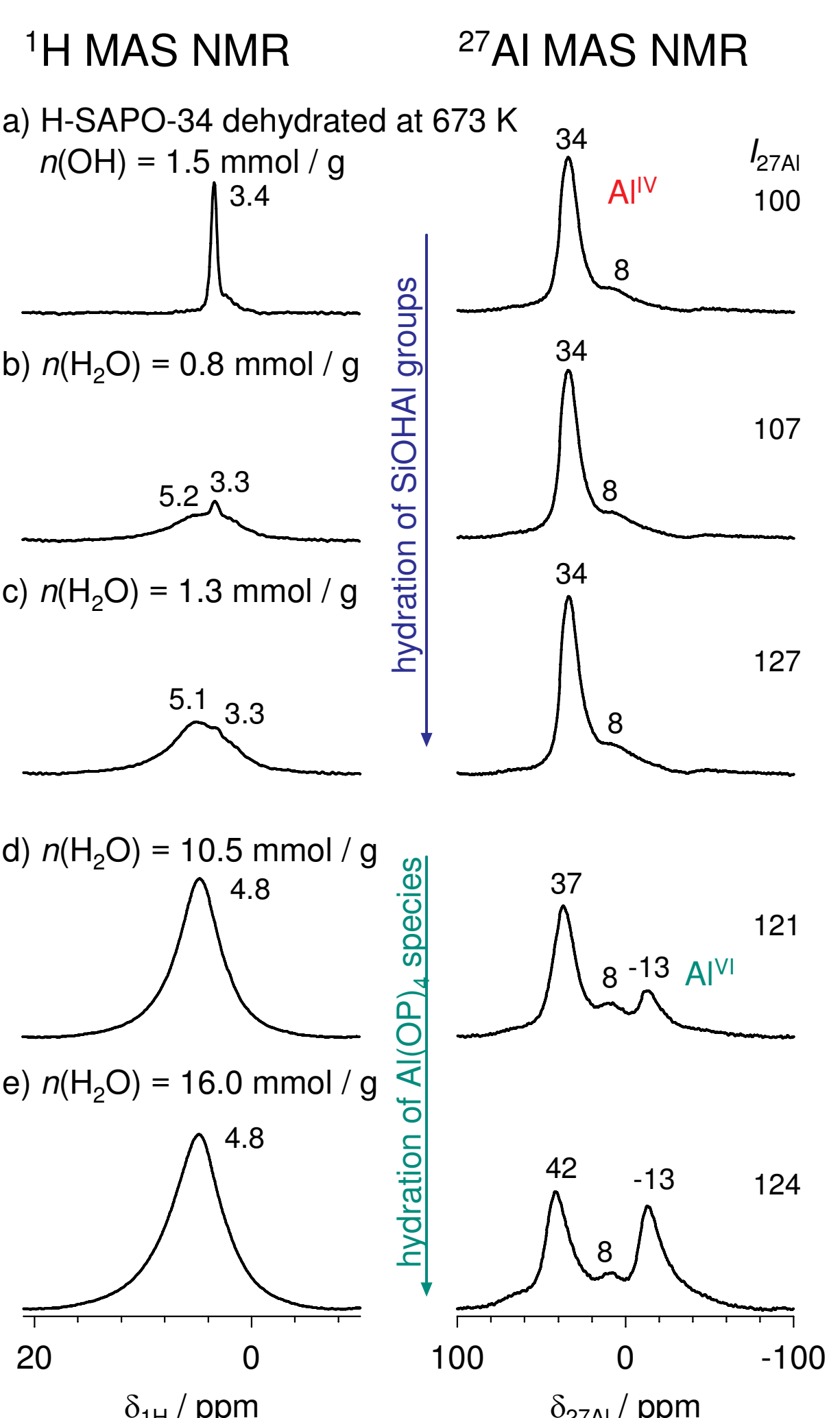


Fig. 1: Hydration of H-SAPO-34
left: reaction mechanisms, right: NMR spectra.



Dehydration of $\text{Al}(\text{OP})_x(\text{H}_2\text{O})_y$ species

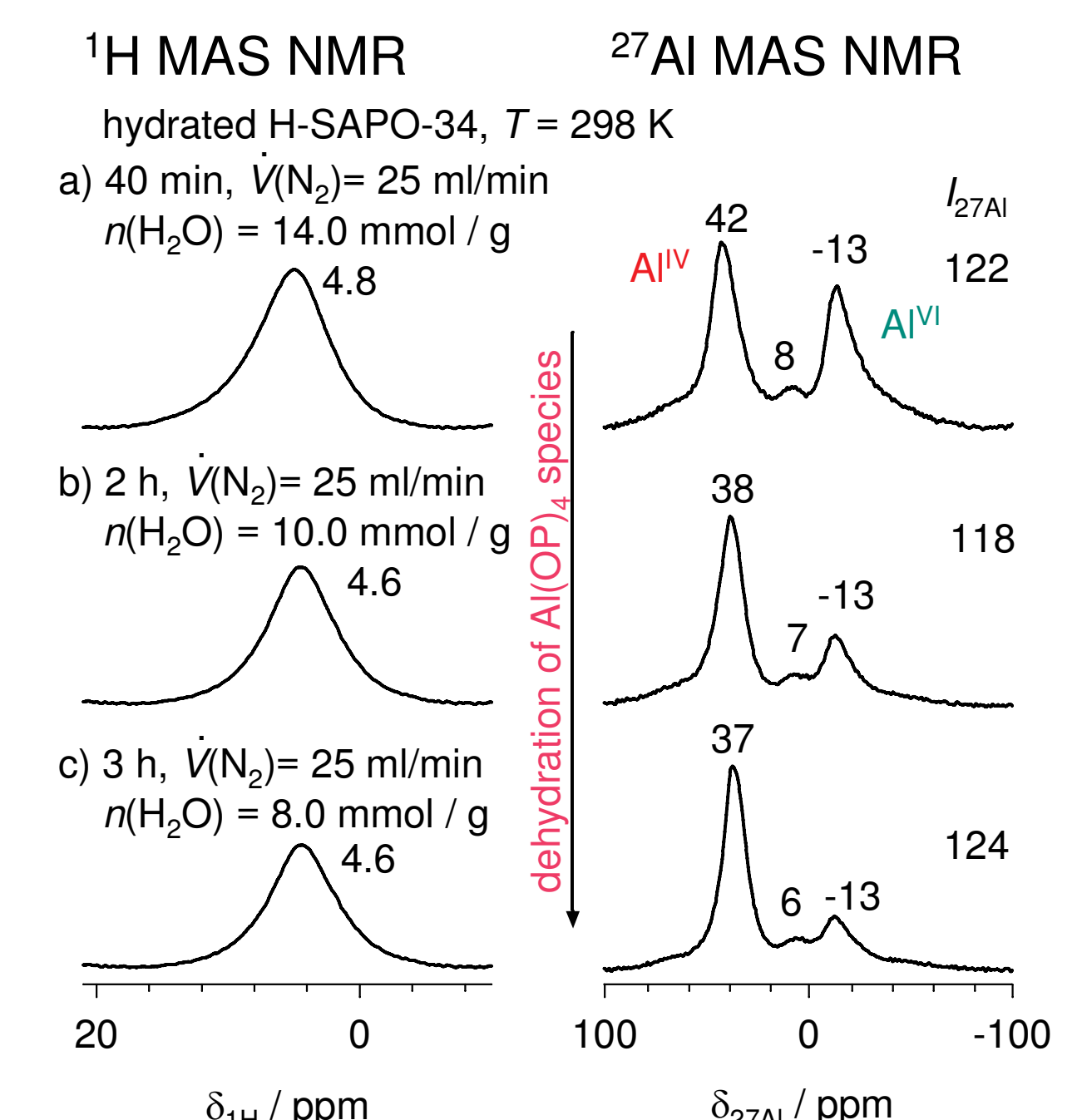


Fig. 2: Dehydration of SAPO-34 at 298 K with dry N_2 .

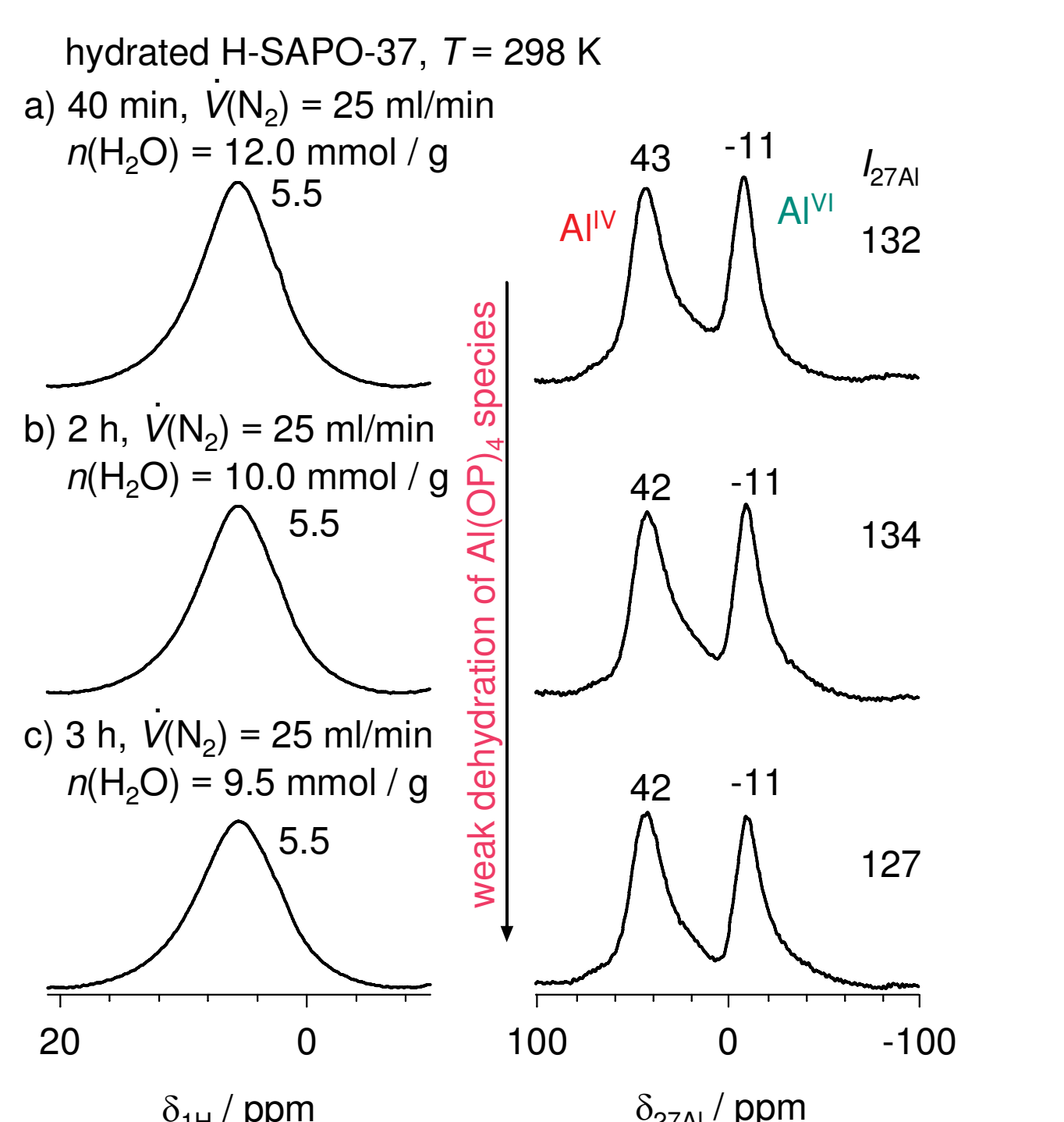


Fig. 3: Dehydration of SAPO-37 at 298 K with dry N_2 .

Hydration / Dehydration

- Preferred water adsorption at Brønsted acid sites (Fig. 1).
- For $n_{\text{H}_2\text{O}} > 3$, coordination of water molecules at aluminum species; appearance of octahedrally coordinated aluminum atoms in the ^{27}Al MAS NMR spectra (Fig. 1).
- SAPO-34, desorption of weakly physisorbed water molecules at room temperature (Fig. 2); no significant desorption of water molecules for SAPO-37 (Fig. 3).
- Dehydration of bridging OH groups requires higher temperatures. The stronger coordination of water in SAPO-37 indicates a hydrolysis of the H-SAPO-37 framework.
- No SiOH groups were detected; excluding the breakage of Si-O-Al bonds; indicating a preferred hydrolysis of P-O-Al bond.

Ammoniation / Deammoniation

- Ammonia adsorption at Brønsted acid sites (Fig. 4).
- For $n_{\text{NH}_3} > 3$, coordination of ammonia molecules at aluminum species; appearance of octahedrally coordinated aluminum atoms in the ^{27}Al MAS NMR spectra (Fig. 4).
- Deammoniation of $\text{Al}(\text{OP})_3(\text{NH}_3)_3$ species occurs at temperatures of $T > 373$ K.
- A subsequent hydration step appears mainly at $\text{Al}(\text{OP})_4$ -species.

The *in situ* CF MAS NMR spectroscopy is a suitable method to observe processes 'time-resolved', or subsequent steps of different treatments.

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