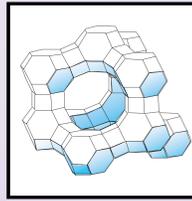


# NMR INVESTIGATIONS OF THE DRY-GEL-SYNTHESIS OF ZEOLITE BETA

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## INTRODUCTION

Zeolites are usually prepared via the hydrothermal synthesis method. Generally, an inhomogeneous gel, prepared from an aluminum and a silicon source, crystallizes in an autoclave at autogenous pressure and temperatures between 100 and 250 °C.

In 1990, Xu et al. [1] proposed a new method consisting of the conversion of a dry aluminosilicate gel by contact with water vapor and volatile amines to zeolite ZSM-5. This method is referred to as **vapor phase transport (VPT)** synthesis. Often, quaternary, non-volatile amines are used as templates. If the template is directly incorporated into the dry gel and only water is supplied from the gas phase, the method is referred to as **steam assisted conversion (SAC)** [2].

These procedures, summarized as **dry-gel-conversion**, have a number of advantages over the conventional hydrothermal crystallization.

- The dry-gel-synthesis of zeolites allows
- the preparation of zeolite membranes on a large number of supporting materials,
- the reduction of the consumption of the expensive structure directing agent,
- the reduction of the crystallization time,
- the variation of the chemical composition over a wide range,
- and a better insight into the formation mechanism of zeolites.

During the last years, much attention has been paid to the **isomorphous substitution of aluminum** in the zeolite framework. Ga-containing zeolites can be used as catalysts, e.g., in the alkylation, disproportionation and isomerization of aromatics [3].

In the present work, we present the detailed investigation of the crystallization process of a dry gel to zeolite [Ga]Beta and the characterization of the zeolites by different techniques of solid-state NMR spectroscopy.

## EXPERIMENTAL

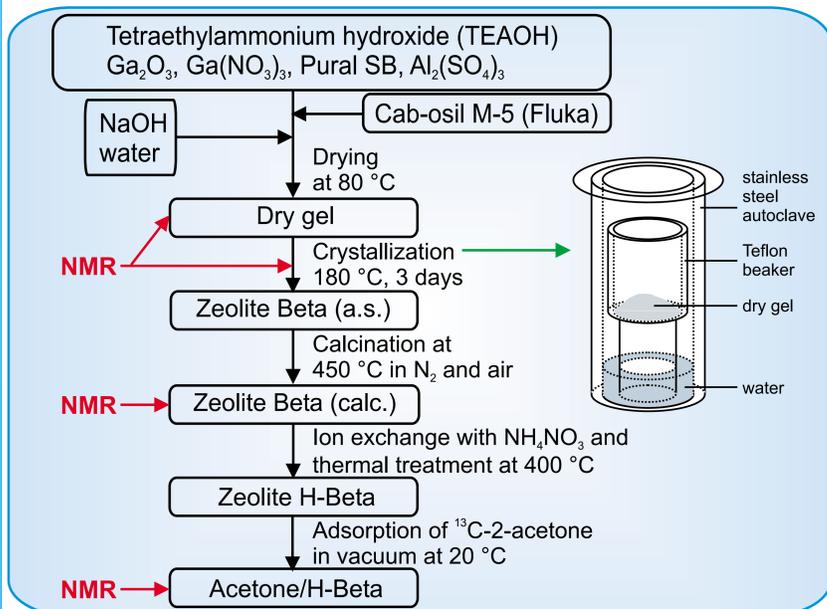


Fig. 1: Synthesis of Beta zeolites using the dry-gel-conversion method and modifications of the obtained materials.

Characterization of the synthesized materials was performed by X-ray powder diffractometry (XRD), chemical analysis (ICP-AES), scanning electron microscopy (SEM) and solid-state NMR spectroscopy.

**Solid-state NMR studies** were carried out on a Bruker MSL-400 spectrometer. <sup>1</sup>H, <sup>13</sup>C, <sup>27</sup>Al, <sup>29</sup>Si and <sup>71</sup>Ga MAS NMR experiments were performed at resonance frequencies of 400.13 MHz, 100.63 MHz, 104.23 MHz, 79.49 MHz and 122.03 MHz, respectively. All spectra were recorded after direct single-pulse excitation. High-power decoupling (HPDEC) was applied for <sup>13</sup>C and <sup>29</sup>Si MAS NMR spectroscopy. Tetramethylsilane (TMS) was used as an external chemical shift standard for <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si MAS NMR spectroscopy, a 0.5 M aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub> and a 1 M aqueous solution of Ga(NO<sub>3</sub>)<sub>3</sub> were applied for <sup>27</sup>Al and <sup>71</sup>Ga MAS NMR spectroscopy, respectively.

Tab. 1: Compositions of the dry gels and the as-synthesized, calcined and ammoniumion-exchanged Beta zeolites, determined by chemical analysis and NMR spectroscopy.

T source	$\frac{n_{Si}}{n_T}$ chem.	zeolite a.s.	zeolite calc.	zeolite calc.	zeolite NH <sub>4</sub>
		$\frac{n_{Si}}{n_T}$ chem.	$\frac{n_{Si}}{n_T}$ chem.	$\frac{n_{Si}}{n_T}$ NMR	$\frac{n_{Si}}{n_T}$ chem.
1 Ga(NO <sub>3</sub> ) <sub>3</sub>	37.6	37.1	37.8	37.8	31.8
2 Ga <sub>2</sub> O <sub>3</sub>	8.5	8.2	8.0	11.6	12.4
3 Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	34.0	36.3	35.7	-	36.6
4 Pural SB	12.6	12.4	11.9	-	11.8

- The zeolites [Al]- and [Ga]Beta synthesized by the dry-gel-method show the characteristic XRD patterns of hydrothermally prepared zeolites Beta and [Ga]Beta.
- The SEM images show crystallites of zeolites Beta with tetragonal shapes and a size of ca. 1 µm.

## RESULTS AND DISCUSSION

### NMR investigations of the dry-gel-synthesis

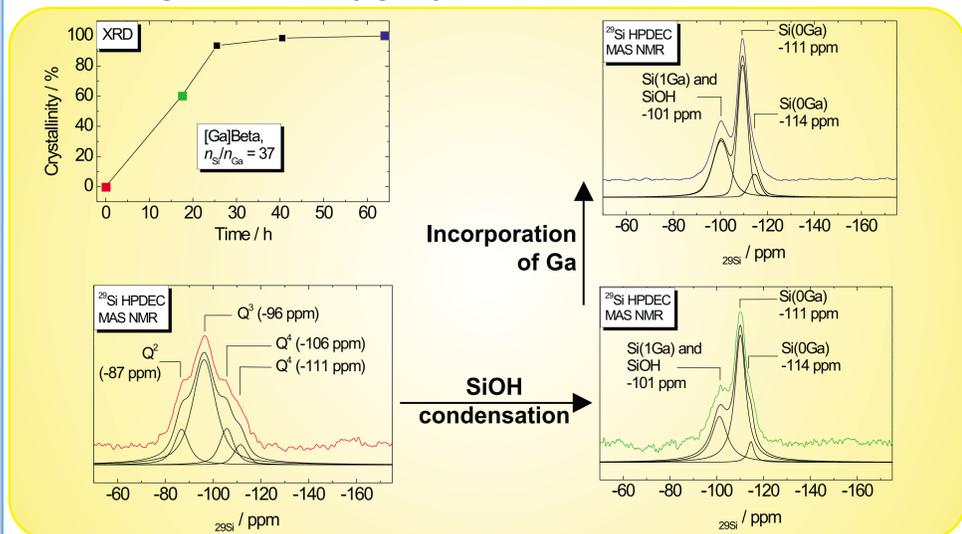


Fig. 2: Conversion process of a dry gallosilicate gel to zeolite [Ga]Beta, n<sub>Si</sub>/n<sub>Ga</sub> = 37.

### <sup>29</sup>Si HPDEC MAS NMR

- **0 h:** XRD-amorphous gel. The <sup>29</sup>Si HPDEC MAS NMR spectrum shows signals at -87 ppm (Q<sup>2</sup>), -96 ppm (Q<sup>3</sup>), -106 ppm and -111 ppm (Q<sup>4</sup> species).
- **17 h:** Crystallinity of 60 %. The corresponding <sup>29</sup>Si HPDEC MAS NMR spectrum reveals characteristic signals of Si(0Ga) species at -110 to -114 ppm. The line at -101 ppm is caused by a superposition of the signals of terminal SiOH groups and Si(1Ga) species.
- **65 h:** The crystallinity amounts to 100 %. The <sup>29</sup>Si HPDEC MAS NMR spectrum shows two signals at -110 to -114 and -101 ppm with a higher relative intensity of the signal at -101 ppm compared to the <sup>29</sup>Si HPDEC MAS NMR spectrum recorded after 17 h.

⇒ In the first period of the conversion of a dry gallosilicate gel to zeolite [Ga]Beta, a condensation of silanol species (Q<sup>2</sup>, Q<sup>3</sup>) to Q<sup>4</sup> species occurs. In the second period, the gallium is incorporated into the zeolite framework.

### <sup>71</sup>Ga MAS NMR

- The <sup>71</sup>Ga MAS NMR spectra recorded after **0 h** and **17 to 65 h** after the beginning of the crystallization consist of a single signal at 145 ppm and 150 ppm, respectively, which is assigned to tetrahedrally coordinated gallium species.
- The <sup>71</sup>Ga MAS NMR signals at 150 ppm indicate a more symmetric environment of the Ga-atoms (GaO<sub>4</sub> tetrahedra of the zeolite framework) compared to the disturbed fourfold coordination of the Ga-atoms in the amorphous gel.

### <sup>13</sup>C HPDEC MAS NMR

- The <sup>13</sup>C HPDEC MAS NMR spectra of all as-synthesized samples show two lines at 6.8 and 52.5 ppm. These lines are characteristic for the methyl and methylene groups of the template (tetraethylammonium cations) [5].
- The template is incorporated into the dry gel and remains unchanged in the channels and cages of the zeolite structure during the crystallization of the zeolite.

- The incorporation of aluminum and gallium into the framework of zeolite Beta was proved by <sup>1</sup>H, <sup>27</sup>Al, <sup>29</sup>Si HPDEC and <sup>71</sup>Ga MAS NMR spectroscopy [4].
- The <sup>71</sup>Ga MAS NMR spectrum of sample 2 after calcination shows a signal of octahedrally coordinated extra-framework gallium at -10 ppm (Tab. 1).
- A quantitative evaluation of the <sup>29</sup>Si HPDEC and <sup>1</sup>H MAS NMR spectra yields, that up to 30 % of the framework gallium was removed from their tetrahedrally coordinated framework positions upon calcination.

### <sup>13</sup>C HPDEC NMR characterization of acid sites

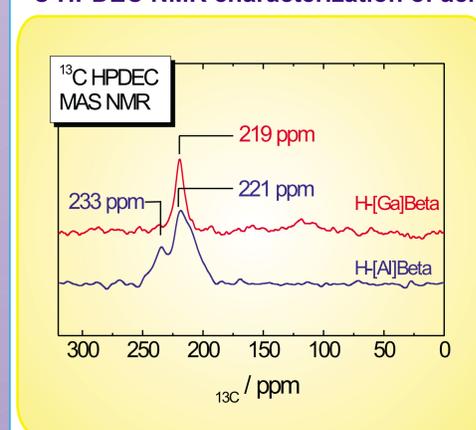


Fig. 4: <sup>13</sup>C HPDEC MAS NMR spectra of <sup>13</sup>C-2-acetone, adsorbed on zeolites H-[Ga]Beta (top) and H-[Al]Beta (bottom).

Tab. 2: Comparison of the <sup>13</sup>C MAS NMR chemical shift of <sup>13</sup>C-2-acetone, adsorbed on different zeolites.

Substrate	CDCl <sub>3</sub>	H-SAPO-34	HY	H-[Ga]Beta	H-[Al]Beta	H-ZSM-5
<sup>13</sup> C / ppm	205 <sup>[6]</sup>	217 <sup>[7]</sup>	218 <sup>[6]</sup>	219	221	223 <sup>[6]</sup>

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