

Characterization of hydrated gallium-containing catalysts by ^{71}Ga solid-state NMR

Spectroscopic background: ^{69}Ga and ^{71}Ga nuclei with a spin of $I = 3/2$, natural abundances of 60.4 % and 39.6 %, and sensitivities in comparison with ^1H nuclei (1.0) of 4.2×10^{-2} and 5.7×10^{-2} , respectively, are both suitable isotopes for solid-state NMR spectroscopy. Due to the quadrupole moments of $Q = 17.1 \times 10^{-30} \text{ m}^2$ for ^{69}Ga and $Q = 10.7 \times 10^{-30} \text{ m}^2$ for ^{71}Ga nuclei, the quadrupole coupling constants C_Q of gallium atoms at analogous structural sites are significantly lower for ^{71}Ga compared to ^{69}Ga nuclei. Therefore, the ^{71}Ga isotope is the preferred one for NMR studies of solids. For basic principles of solid-state NMR, see lectures “Solid-State NMR Spectroscopy” for Bachelor students or PhD seminars, accessible via the link “Lectures for Students”.

Because ^{71}Ga nuclei have similar NMR spectroscopic parameters like ^{27}Al nuclei, similar NMR line shapes occur for gallium and aluminum atoms incorporated at analogous framework sites in solids. Moreover, a **linear relationship between the ^{71}Ga and ^{27}Al chemical shifts** ($\delta_{^{71}\text{Ga}}$ and $\delta_{^{27}\text{Al}}$, respectively) of a series of structurally analogous aluminum- and gallium-containing compounds with exclusively oxygen in the first coordination sphere was found [1]:

$$\delta_{\text{Ga}} / \text{ppm} = 2.83 \cdot \delta_{\text{Al}} / \text{ppm} - 4.50 \quad (1)$$

Fig. 1, left-hand side, shows ^{71}Ga MAS NMR spectra of **gallium-containing zeolites ZSM-5**, recorded upon addition of gallium in the stage of gel formation during the synthesis of this material. These ^{71}Ga MAS NMR spectra were recorded at the resonance frequency of 183.0 MHz with a sample spinning rate of $\nu_{\text{rot}} = 8 \text{ kHz}$. In agreement with **Equ. (1)**, the ^{71}Ga MAS NMR signal of **tetrahedrally coordinated framework gallium (Ga(4Si))** appears at a resonance position of about $\delta_{^{71}\text{Ga}} = 159 \text{ ppm}$. Extensive dehydration leads to a strong broadening and disappearance of this signal in the ^{71}Ga MAS NMR spectrum, which agrees with the behaviour of framework aluminum signals in ^{27}Al MAS NMR spectroscopy. Steaming of the gallium-containing zeolite [Ga]ZSM-5 at 934 K for 3 h, 6 h, and 24 h results in the appearance of a signal of **octahedrally coordinated extra-framework gallium** species at about $\delta_{^{71}\text{Ga}} = 0 \text{ ppm}$ (**Fig. 1**, left, top).

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Due to the different quadrupole moments of the ^{69}Ga and ^{71}Ga isotopes, the quadrupole parameters of framework gallium atoms can be determined by their different second-order quadrupolar shifts [2]. By this method, quadrupole coupling constants of $C_Q = 3.0$ MHz for ^{69}Ga and $C_Q = 1.9$ MHz for gallium atoms located on tetrahedral framework (**Ga(4Si)**) positions in hydrated **gallium-containing [Ga]ZSM-5** have been calculated [2].

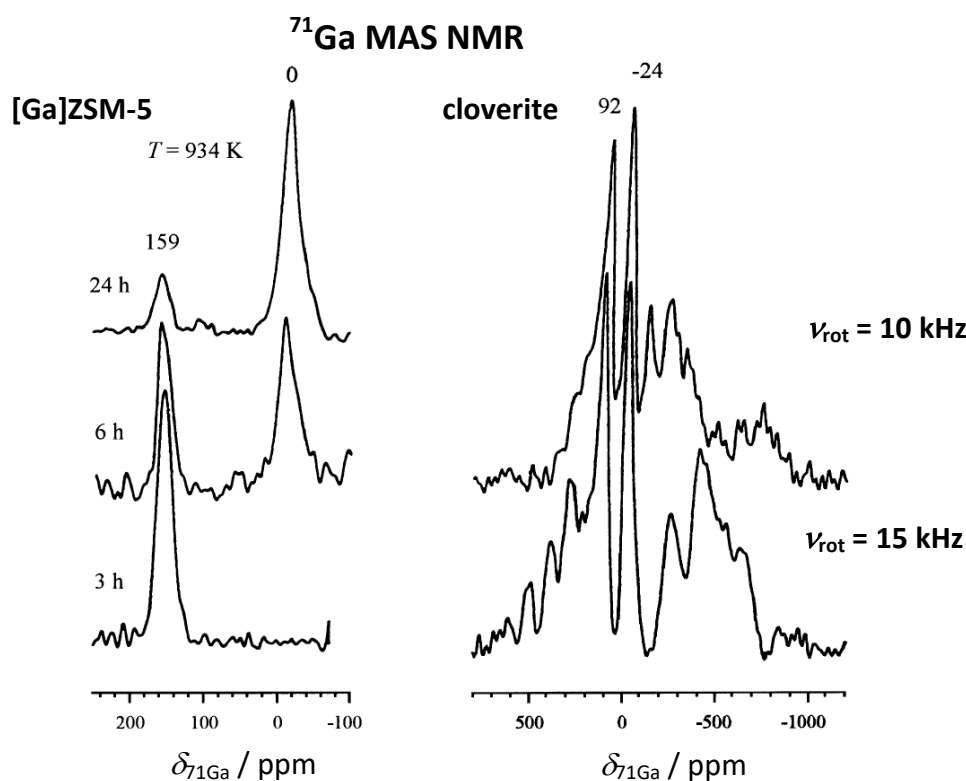


Fig. 1

Fig. 1, right-hand side, shows the ^{71}Ga MAS NMR spectra of an as-synthesized **gallophosphate-type zeolite cloverite** [3], which is an often investigated material with large 30 Å supercage [4-6]. In these spectra, two signals occur at chemical shifts of $\delta_{71\text{Ga}} = 92$ ppm and -24 ppm due to **penta-coordinated and octahedrally coordinated gallium atoms**, respectively. Both these gallium species are coordinated to one fluoride ion in the first coordination sphere. The octahedral gallium atoms are additionally coordinated with one additional water molecule. Considering the ^{27}Al MAS NMR signal of penta-coordinated aluminum atoms in the ^{27}Al MAS NMR spectra of aluminosilicate-type zeolites at the chemical shift of about $\delta_{27\text{Al}} = 30$ ppm (see Section “method 4”), **Equ. (1)** yields an estimated resonance position for penta-coordinated gallium atoms of about $\delta_{71\text{Ga}} = 80$ ppm. This estimation

was utilized for assigning the ^{71}Ga MAS NMR signal at $\delta_{71\text{Ga}} = 92$ ppm to penta-coordinated gallium atoms in the cloverite framework [3]. A comparison of spectra recorded with sample spinning rates of $\nu_{\text{rot}} = 10$ kHz and 15 kHz support the identification of the correct MAS NMR central lines. This method is required, because of the extraordinarily strong quadrupolar coupling of framework gallium atoms in cloverite. Using ^{71}Ga solid-state NMR spectroscopy without application of MAS, the ^{71}Ga quadrupole coupling constant of **gallium atoms in cloverite** was estimated to **$C_Q = 13$ MHz** [5].

Typical ^{71}Ga MAS NMR spectra of gallium incorporated into the framework of zeolite [Ga]Beta are shown in **Fig. 2** [7]. In this case, the incorporation of gallium into the zeolite framework during a dry-gel synthesis procedure was investigated. Before the ^{71}Ga solid-state NMR studies, all samples were hydrated with water vapour in a desiccator for 16 h. Starting with the fresh dry gel at the time 0 h (**Fig. 2b**), the stepwise formation of zeolite Beta and the incorporation of gallium atoms up to the synthesis time of 65 h (**Fig. 2e**) is demonstrated. For comparison, the ^{71}Ga MAS NMR spectrum of pure Ga_2O_3 is shown in **Fig. 2a**, which was the gallium source in this study [7].

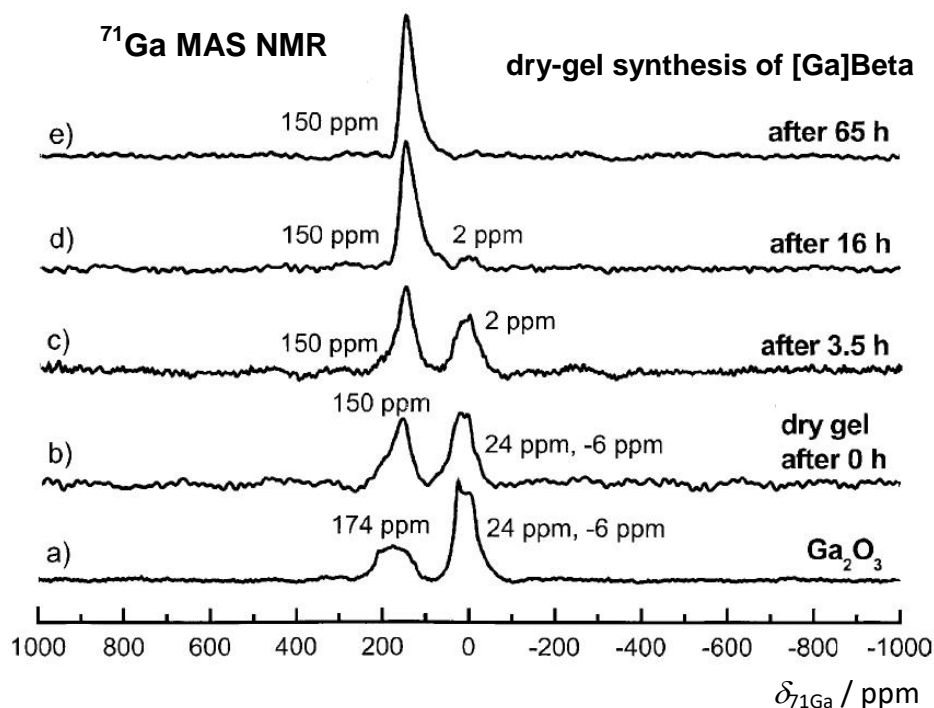


Fig. 2

The ^{71}Ga MAS NMR spectrum of Ga_2O_3 (**Fig. 2a**) consists of signals at $\delta_{71\text{Ga}} = -6$ to 24 ppm and 174 ppm due to **hexagonal and tetrahedrally coordinated gallium**
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species, respectively [8]. In the ^{71}Ga MAS NMR spectrum of the materials obtained at a synthesis time of 0 h (**Fig. 2b**), significant changes can be observed. The signal of octahedrally coordinated gallium loses intensity, while the signal of tetrahedrally coordinated gallium atoms is a superposition of a broad signal at $\delta_{71\text{Ga}} = 174$ ppm and a narrow signal at $\delta_{71\text{Ga}} = 150$ ppm (**Fig. 2b**). This observation indicates a dissolution of Ga_2O_3 during the preparation of the dry gel and the formation of gallium tetrahedra with a higher local symmetry. For increasing synthesis times, a systematic decrease of the signal of octahedrally coordinated gallium species at $\delta_{71\text{Ga}} = 2$ ppm occurs, while the intensity of the signal of tetrahedrally coordinated framework gallium species at $\delta_{71\text{Ga}} = 150$ ppm increases. After a synthesis time of 65 h (**Fig. 2e**), the ^{71}Ga MAS NMR spectrum consists of a signal at $\delta_{71\text{Ga}} = 150$ ppm, with a broad low-field shoulder, which hints to the transformation of most of the gallium atoms to **tetrahedrally coordinated gallium species in zeolite [Ga]Beta**. For clarifying the detailed nature of the ^{71}Ga MAS NMR signal at $\delta_{71\text{Ga}} = 150$ ppm in **Fig. 2e**, two-dimensional (2D) ^{71}Ga MQMAS NMR spectroscopy of the sample obtained after the synthesis time of 65 h was performed [7]. The corresponding spectrum in **Fig. 3** consists of $\text{Ga}^{\text{IV}}(1)$, $\text{Ga}^{\text{IV}}(2)$, and $\text{Ga}^{\text{IV}}(3)$ signals, due to three kinds of tetrahedrally coordinated gallium species. The large distance of the $\text{Ga}^{\text{IV}}(3)$

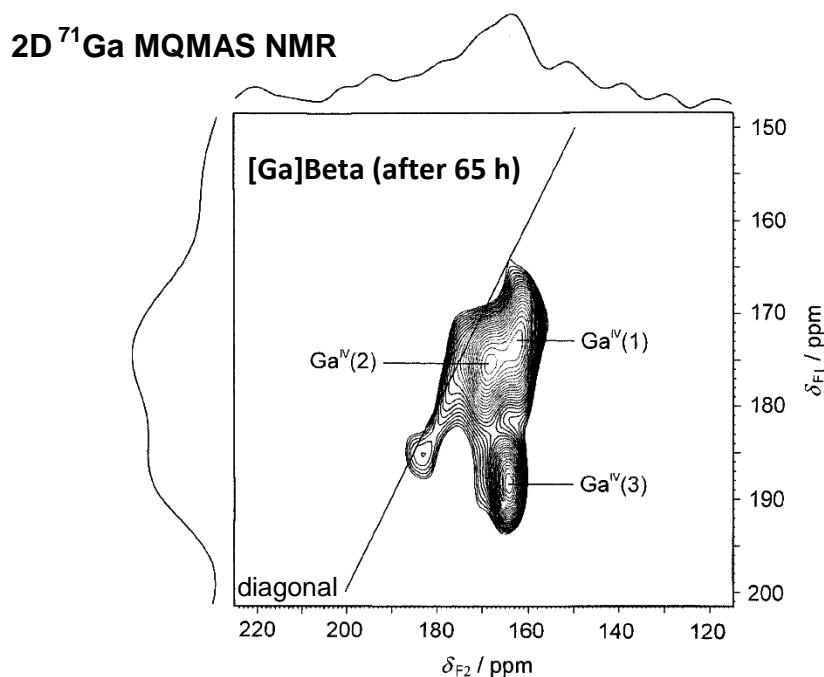


Fig. 3

signal from the diagonal corresponds to a high *SOQE* parameter (Second-Order Quadrupolar Effect parameter, similar to C_Q , see Refs. [2] and [9]) of the these gallium atoms of 4.7 MHz, which is close to the *SOQE* parameter observed for gallium atoms in oxidic species [10]. Therefore, the $\text{Ga}^{\text{IV}}(3)$ signal was assigned to extra-framework gallium species with a distorted tetrahedral oxygen coordination. Hence, the 2D ^{71}Ga MQMAS NMR spectrum in **Fig. 3** evidences the presence of tetrahedrally coordinated extra-framework gallium species in the final [Ga]Beta (after 65 h) material, which was not possible to identify by one-dimensional ^{71}Ga MAS NMR spectroscopy (**Fig. 2e**).

Catalyst preparation: For decreasing the quadrupolar interactions of the ^{71}Ga nuclei studied by the solid-state NMR methods described in the present section, the powder samples should be hydrated by contact with water vapour in a desiccator for at least 12 h.

^{71}Ga solid-state NMR studies: Due to the quadrupolar interactions of ^{71}Ga nuclei, their single pulse excitation should be performed by less than $\pi/4$ and most suitable by $\pi/8$ pulses. The ^{71}Ga MAS NMR and 2D ^{71}Ga MQMAS NMR spectra shown in Figs. 2 and 3 were recorded on an Avance 750 and an Avance 500 Bruker BioSpin spectrometer, at resonance frequencies of $\nu_0 = 228.8$ and 152.5 MHz, and with sample spinning rates of $\nu_{\text{rot}} = 33.5$ kHz (2 mm MAS NMR rotor) and 15 kHz (4 mm MAS NMR rotor), respectively. For obtaining the ^{71}Ga MAS NMR spectra, a single-pulse excitation of 0.75 μs and a repetition time of 500 ms were used. The 2D ^{71}Ga MQMAS experiment was carried out using the three-pulse sequence introduced by Amoureux et al. [11] with pulse lengths of 4.8 μs , 1.8 μs , and 17.5 μs , with an RF-field strength for excitation and conversion pulses of 110 kHz, a selective 90° pulse at an rf field corresponding to $\nu_{\text{ff}} = 7$ kHz, and using a repetition time of 500 ms. The chemical shifts are referenced to 1.0 M aqueous solution of $\text{Ga}(\text{NO}_3)_3$ ($\delta_{^{71}\text{Ga}} = 0$ ppm).

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