

Characterization of hydrated gallium-containing catalysts by $^{69/71}\text{Ga}$ 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, in these states, 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 [Ga]ZSM-5**, recorded upon addition of gallium in the stage of gel formation during the synthesis of these materials [2]. The ^{71}Ga MAS NMR spectra were recorded at the resonance frequency of $\nu_0 = 183.0 \text{ MHz}$ and with a sample spinning rate of $\nu_{\text{rot}} = 8 \text{ kHz}$. In agreement with **Eq. (1)** and Refs. [3] and [4], the ^{71}Ga MAS NMR signal of **tetrahedrally coordinated framework gallium (Ga(4OSi))** is assigned to a ^{71}Ga chemical shift value of **$\delta_{^{71}\text{Ga}} = 159 \text{ ppm}$** ($\delta_{^{27}\text{Al}}$ ca. 60 ppm). Extensive dehydration leads to a strong broadening and a disappearance of this signal in the ^{71}Ga MAS NMR spectrum. Steaming of the gallium-containing zeolite [Ga]ZSM-5 at $T = 934 \text{ K}$ for 3 h, 6 h, and 24 h and subsequent rehydration 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**) [2].

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 [3]. By this method, quadrupole coupling constants of $\mathbf{C_Q} = 3.0 \text{ MHz}$ for ^{69}Ga atoms and $\mathbf{C_Q} = 1.9 \text{ MHz}$ for ^{71}Ga atoms located on tetrahedral framework positions (Ga(4OSi)) in hydrated zeolite $[\text{Ga}]\text{ZSM-5}$ were determined [3].

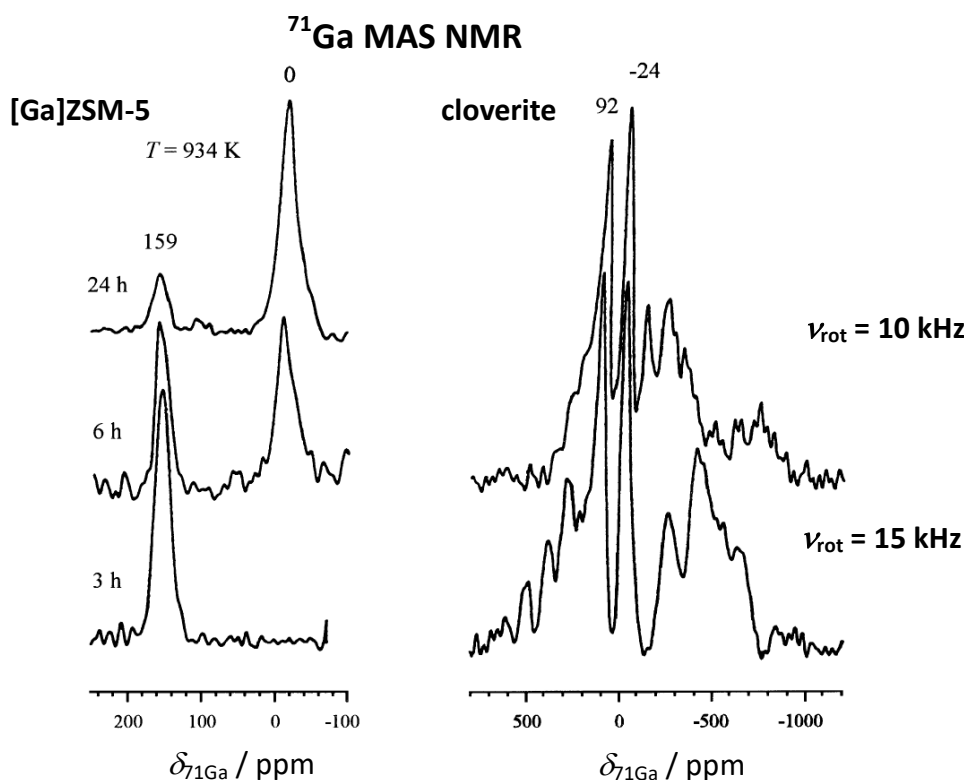


Fig. 1

Fig. 1, right-hand side, shows the ^{71}Ga MAS NMR spectra of an as-synthesized **gallophosphate-type zeolite cloverite** [5], which is an often investigated material with large 30 Å supercages [5, 6]. In these spectra, two signals occur at chemical shifts of $\delta_{71\text{Ga}} = -24 \text{ ppm}$ and 92 ppm due to **octahedrally coordinated and penta-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 water molecule. Because of the extraordinarily strong quadrupolar interactions of framework gallium atoms in cloverite, the identification of the MAS NMR central lines required a comparison of spectra recorded with sample spinning rates of $\nu_{\text{rot}} = 10 \text{ kHz}$ and 15 kHz . Using ^{71}Ga solid-state NMR spectroscopy without application of MAS, the quadrupole coupling constant of **^{71}Ga atoms in cloverite** was estimated to $\mathbf{C_Q} \cong 13 \text{ MHz}$ [6].

In **Fig. 2**, ^{71}Ga MAS NMR spectra of gallium incorporated into the framework of zeolite **[Ga]Beta** are shown [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 **[Ga]Beta** and the incorporation of gallium atoms up to the synthesis time of 65 h is demonstrated (**Fig. 2e**). 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]. This spectrum consists of signals at $\delta_{71\text{Ga}} = -6$ to 24 ppm and 174 ppm due to octahedrally and tetrahedrally coordinated gallium species, respectively [8].

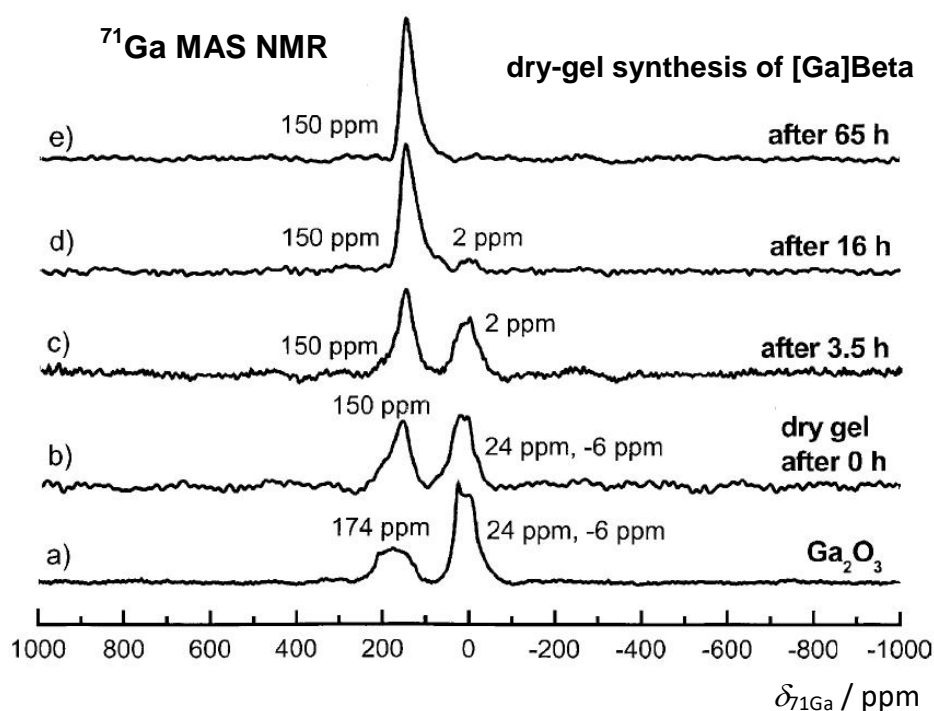


Fig. 2

The ^{71}Ga MAS NMR spectra of the dry-gel materials, obtained at synthesis times of 0 to 65 h (**Figs. 2b to 2e**), show significant changes. The signal of octahedrally coordinated gallium loses intensity, while the signals of tetrahedrally coordinated gallium atoms, which are a superposition of a broad signal at $\delta_{71\text{Ga}} = 174$ ppm and a narrow signal at $\delta_{71\text{Ga}} = 150$ ppm, increase. For increasing synthesis times, a systematic decrease and, finally, a disappearance of the signal of octahedrally coordinated gallium species at $\delta_{71\text{Ga}} = 2$ ppm is observed. This observation indicates dissolution of Ga_2O_3 during the dry-gel synthesis and the

formation of gallium tetrahedra with a higher local symmetry. After a synthesis time of 65 h (**Fig. 2e**), the ^{71}Ga MAS NMR spectrum consists of a signal at $\delta_{71\text{Ga}} = 150 \text{ ppm}$, 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 $\delta_{71\text{Ga}} = 150 \text{ ppm}$ 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 $\text{Ga}^{\text{IV}}(3)$

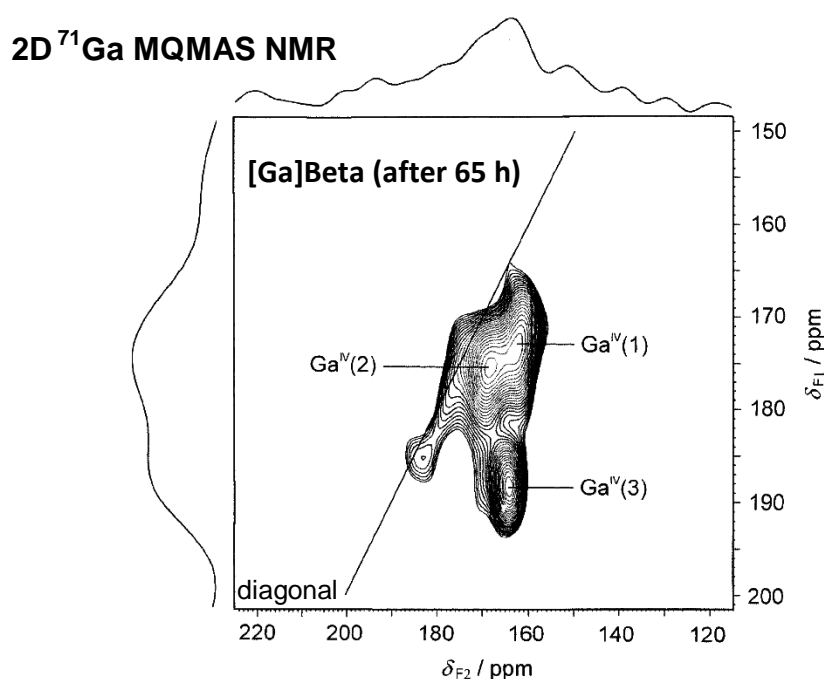


Fig. 3

signal from the diagonal corresponds to a high *SOQE* parameter (Second-Order Quadrupolar Effect parameter, see Refs. [2] and [9]) of these gallium atoms of 4.7 MHz, which is close to the *SOQE* parameter observed for gallium atoms in oxidic gallium 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 (65 h) **[Ga]Beta** zeolite, which was not possible to identify by one-dimensional ^{71}Ga MAS NMR spectroscopy (**Fig. 2e**).

Table 1 gives a survey on the ^{71}Ga solid-state NMR parameters of the above-mentioned zeolites and some additional materials.

Materials	Ga Species	C_Q / MHz	$\delta_{^{71}\text{Ga,obs}}$ / ppm	Refs.
hydrated [Ga]ZSM-5	$\text{Ga}^{\text{IV}}(4\text{OSi})$		150 - 155	[4]
hydrated [Ga]ZSM-5	$\text{Ga}^{\text{IV}}(4\text{OSi})$	1.9	159	[3]
steamed [Ga]ZSM-5	$\text{Ga}^{\text{IV}}(4\text{OSi})$		159	[2]
	$\text{Ga}^{\text{VI}}(x\text{OSi}, y\text{OGa})$		0	[2]
as-synthesized [Ga]Beta	$\text{Ga}^{\text{IV}}(4\text{OSi})$		150	[7]
hydrated [Ga]X	$\text{Ga}^{\text{IV}}(4\text{OSi})$		174	[8]
hydrated [Ga]Y	$\text{Ga}^{\text{IV}}(4\text{OSi})$	1.7	172	[8]
hydrated [Ga]sodalite	$\text{Ga}^{\text{IV}}(4\text{OSi})$	1.6	176	[8]
[Ga]natrolite	$\text{Ga}^{\text{IV}}(4\text{OSi})$	1.5	169	[8]
[Ga]cristoballite	$\text{Ga}^{\text{IV}}(4\text{OP})$	4.7	118	[10]
dehydrated $\beta\text{-Ga}_2\text{O}_3$	$\text{Ga}^{\text{IV}}(4\text{OGa})$	11.1	198	[11]
	$\text{Ga}^{\text{VI}}(6\text{OGa})$	8.3	25	[11]
[Ga]natrolite	$\text{Ga}^{\text{IV}}(4\text{OSi})$	1.5	169	[8]
[Ga]cristoballite	$\text{Ga}^{\text{IV}}(4\text{OP})$	4.7	118	[10]
dried cloverite		12.8 ± 2.1		[6]
as-synthesized cloverite	$\text{Ga}^{\text{VI}}(4\text{OP}, \text{F}, \text{H}_2\text{O})$		-24	[5]
	$\text{Ga}^{\text{V}}(4\text{OP}, \text{F})$		80	[5]
calcined cloverite	$\text{Ga}^{\text{V}}(4\text{OP}, \text{F})$		84	[5]

Table 1

The ^{71}Ga solid-state NMR parameters in **Table 1** and additional materials and their parameters summarized in Ref. [1] lead to the characteristic ^{51}Ga chemical shift ranges in **Fig. 4** (adapted from Fig. 2 in Ref. [1]).

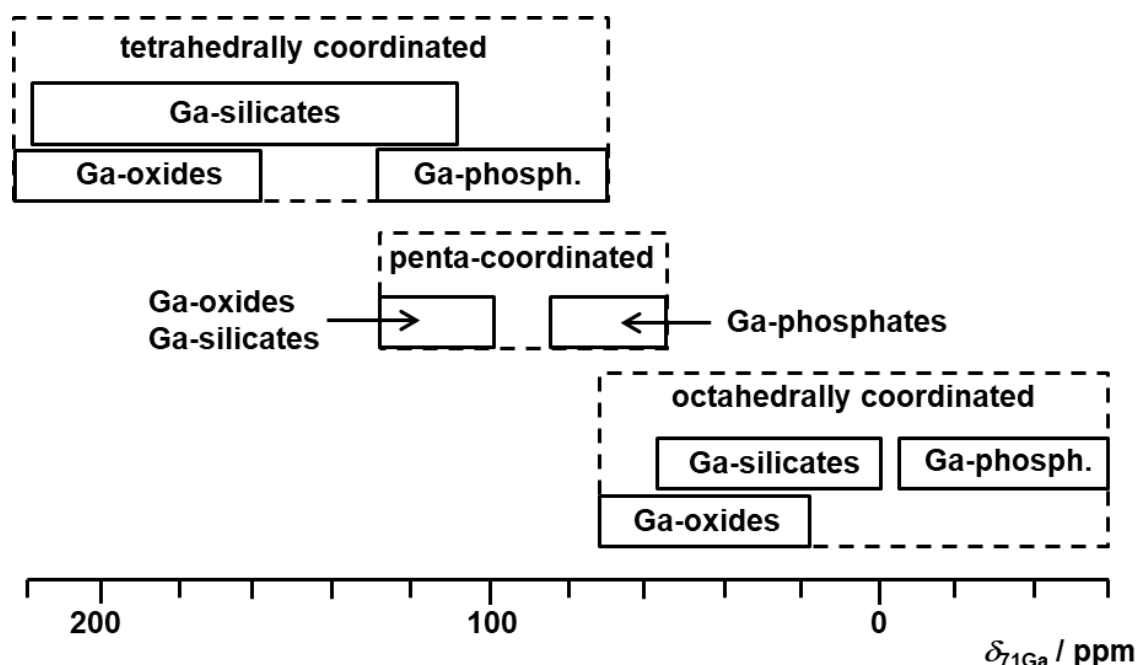


Fig. 4

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 were 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. [12] 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 $\nu_{\text{rf}} = 7$ 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).

References:

- [1] S.M. Bradley, R.F. Howe, R.A. Kydd, *Correlation between ^{27}Al and ^{71}Ga NMR chemical shifts*, Magn. Reson. Chem. 31 (1993) 883-886, DOI: 10.1002/mrc.1260311002.
- [2] C.R. Bayense, J.H.C. van Hooff, A.P.M. Kentgens, J.W. de Haan, L.J.M. van de Ven, *The removal of gallium from the lattice of MFI-gallosilicates as studied by ^{71}Ga M.A.S.-N.M.R. spectroscopy*, J. Chem. Soc. Chem. Commun. (1989) 1292-1293, DOI: 10.1039/c39890001292.
- [3] A.P.M. Kentgens, C.R. Bayense, J.H.C. van Hooff, J.W. de Haan, L.J.M. van de Ven, *A ^{69}Ga and ^{71}Ga MAS NMR study of the gallium analogue zeolite ZSM-5*, Chem. Phys. Lett. 176 (1991) 399-403, DOI: 10.1016/0009-2614(91)90051-A.
- [4] S.M. Bradley, R.T. Howe, *^{129}Xe nuclear magnetic resonance studies of H-Ga-MFI zeolites*, Microporous Mater. 4 (1995) 131-139, DOI: 10.1016/0927-6513(94)00089-E.
- [5] S.M. Bradley, R.F. Howe, J.V. Hanna, *^{71}Ga and ^{31}P MAS NMR spectroscopic studies of cloverite*, Solid State Nucl. Magn. Reson. 2 (1993) 37-46, DOI: 10.1016/0926-2040(93)90061-Q.
- [6] B. Zibrowius, M.W. Anderson, W. Schmidt, F.F. Schueth, A.E. Aliev, K.D.M. Harris, *Aspects of the characterization of cloverite by solid-state n.m.r. techniques*, Zeolites 13 (1993) 607-610, DOI: 10.1016/0144-2449(93)90131-L.
- [7] A. Arnold, S. Steuernagel, M. Hunger, J. Weitkamp, *Insight into the dry-gel synthesis of gallium-rich zeolite [Ga]Beta*, Microporous Mesoporous Mater. 62 (2003) 97-106, DOI: 10.1016/S1387-1811(03)00397-4.
- [8] H.K.C. Timken, E. Oldfield, *Solid-state gallium-69 and gallium-71 nuclear magnetic resonance spectroscopic studies of gallium analog zeolites and related systems*, J. Am. Chem. Soc. 109 (1987) 7669-7673, DOI: 10.1021/ja00259a015.
- [9] D. Freude, <https://www.dieter-freude.de/quad-nmr>.
- [10] D. Massiot, T. Vosegaard, N. Magneron, D. Trumeau, V. Montouillout, P. Berthet, T. Loiseau, B. Bujoli, *^{71}Ga NMR of reference Ga_{IV} , Ga_{V} , and Ga_{VI} compounds by MAS and QPASS, extension of gallium/aluminum NMR parameter correlation*, Solid State Nucl. Magn. Reson. 15 (1999) 159-169, DOI: 10.1016/S0926-2040(99)00053-3.
- [11] T. Vosegaard, I.P. Byriel, L. Binet, D. Massiot, H.J. Jakobsen, *Crystal structure by single-crystal NMR spectroscopy ^{71}Ga and ^{69}Ga single-crystal NMR of $\beta\text{-Ga}_2\text{O}_3$ twins*, J. Am. Chem. Soc. 120 (1998) 8184-8188, DOI: 10.1021/ja981666k.

- [12] J.P. Amoureux, C. Fernandez, S. Steuernagel, *Z-filtering in MQMAS NMR*, J. Magn. Reson. A 123 (1996) 116–118, DOI: 10.1006/jmra.1996.0221.