A 69Ga and 71Ga MAS NMR study of the gallium analog zeolite ZSM-5

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A $^{69}$Ga and $^{71}$Ga MAS NMR study of the gallium analogue zeolite ZSM-5

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$^{69}$Ga and $^{71}$Ga magic-angle-spinning (MAS) NMR spectra of a series of gallium analogue zeolites H-(Ga)ZSM-5, with varying Si/Ga ratios, were obtained at 14.1 and 7.1 T. The quadrupole coupling constant $e^2qQ/h$ was deduced from the shift difference of the centre of gravity of the $^{69}$Ga and $^{71}$Ga resonance. An analysis of the linewidth as a function of the magnetic field shows that the width is not only determined by the second-order quadrupolar broadening, but also by a distribution of chemical shifts. The values obtained for the quadrupole coupling constant and chemical shift distribution are compared to those found for $^{27}$Al in H-(Al)ZSM-5. It is argued that the observed differences are related to the different NMR properties of the isotopes, and do not point to any structural changes of the ZSM-5 lattice.

1. Introduction

Due to their interesting properties, zeolites isomorphously substituted with gallium have been studied extensively. With regard to the physical characterization of these zeolites, however, application of $^{69}$Ga and $^{71}$Ga MAS NMR is still quite rare. The capabilities of Ga MAS NMR for the study of zeolitic materials were first shown by Ione et al. [1]. Timken and Oldfield [2] applied Ga MAS NMR to a number of gallium analogue zeolites of the X, Y and sodalite type. They showed that it is advantageous to measure at high magnetic fields and use fast MAS in order to avoid overlapping spinning sidebands. By comparing the apparent shifts of the $^{69}$Ga and $^{71}$Ga line, estimates of the quadrupole coupling constants were calculated for the various zeolites. In a recent study of H-(Ga)ZSM-5 zeolites by $^{71}$Ga MAS NMR, we demonstrated the necessity of water equilibration of the samples, as in dry samples the lines are broadened beyond detection due to the large quadrupolar interaction even at 14.1 T [3]. Similar effects were observed in $^{27}$Al NMR studies of H-(Al)ZSM-5 zeolites [4,5]. Also in accordance with earlier $^{27}$Al NMR measurements [6] was the observation of octahedrally coordinated non-framework Ga in steam-treated gallosilicates equilibrated with acetylacetone.

The studies mentioned above show that $^{69}$Ga and $^{71}$Ga MAS NMR is a useful tool for the study of gallosilicates. In the present paper, the zeolite H-(Ga)ZSM-5 is studied by $^{69}$Ga and $^{71}$Ga MAS NMR at 14.1 and 7.1 T. The nature of the line broadening of the gallium resonances is determined and compared to the results found for $^{27}$Al NMR of H-(Al)ZSM-5.
2. Experimental

$^{69}\text{Ga}$ and $^{71}\text{Ga}$ NMR spectra were recorded on a Bruker AM 600 spectrometer at 144.04 and 183.02 MHz, respectively. A home-built probehead equipped with a 5 mm double-bearing magic-angle-spinning assembly from Doty Scientific was used. Typical spinning speeds of 9 kHz were employed. $^{71}\text{Ga}$ NMR spectra were obtained at 91.50 MHz on a Bruker CXP 300 spectrometer, using a 7 mm Bruker MAS probehead, with a spinning speed of 5 kHz. On both spectrometers, an excitation pulse of 2 $\mu$s with an rf field strength of approximately 50 kHz was used. Chemical shifts are referenced to an external Ga(NO$_3$)$_3$ solution. Preparation of the catalysts was carried out by a method based on Chen et al. [7].

3. Results and discussion

$^{71}\text{Ga}$ MAS NMR spectra at 14.1 T of the uncalcined TPA(Ga)ZSM-5 zeolite show one line at 155 ppm, with a width of 4.4 kHz. Peaks in this region are assigned to tetrahedrally coordinated gallium. Based on our earlier work [3], we assign this to framework gallium. After the usual pretreatments (calcination, ion-exchange, second calcination) to prepare the samples for catalytic use and full hydration of the sample, the line narrows to about 2.9 kHz and is now observed at 161 ppm. This change in linewidth and resonance position is assigned to a change in the quadrupolar interaction experienced by the framework gallium due to change of the counterion in the pores of the zeolite from the TPA$^+$ template to a H($H_2O$)$_n^+$ cluster in a fully hydrated H-(Ga)ZSM-5. The latter is believed to produce a much smaller field gradient at the site of the gallium due to its high mobility and delocalisation of the charge, as was also demonstrated in Al NMR experiments with aluminosilicates [4,5]. A decrease in quadrupolar interaction obviously narrows the line and the accompanying quadrupole-induced shift diminishes accordingly. The resonance (fig. 1a) has a typical asymmetric shape, a steep flank at low-field side and a more gradually sloping flank at the high-field side, which is also observed for aluminum in zeolites. This shape does not correspond to a second-order quadrupolar broadening, which results in a specific powder pattern whose shape depends on the asymmetry parameter $\eta$ [8]. This means that there must be other sources of line broadening, e.g. dipolar interactions or a distribution of quadrupolar coupling constants and/or chemical shifts from crystallographically different sites and/or lattice defects. This is supported by the fact that the $^{69}\text{Ga}$ resonance, which has the same typical shape (fig. 1b), is only 4 kHz wide. Based on the difference in Zeeman energy $\hbar\nu_0$ and quadrupole moment $Q$, one would expect a $^{69}\text{Ga}$ line to be 3.2 times broader than the corresponding $^{71}\text{Ga}$ line, if the second-order quadrupolar interaction were the only source of line broadening (table 1).

As was already pointed out by Timken and Oldfield [2], an estimate of the quadrupole coupling constant can be obtained from the difference in the apparent shift of the $^{69}\text{Ga}$ and $^{71}\text{Ga}$ isotopes, assuming, of course, that the above-mentioned distribution of quadrupole coupling constants is not very large. Due to their difference in quadrupole moment and Zeeman energy, $^{69}\text{Ga}$ and $^{71}\text{Ga}$ will experience a different quadrupolar-induced shift [9],
Table 1
NMR properties of $^{71}$Ga, $^{69}$Ga and $^{27}$Al, giving the spin, the resonance frequency at 2.35 T ($\omega$), the quadrupole moment ($Q$), and the Sternheimer anti-shielding factor for the s-state ions $M^{+}$ ($\gamma_m$).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spin</th>
<th>$\omega$ (MHz)</th>
<th>$Q$ ($10^{-24}$ cm$^2$)</th>
<th>$\gamma_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{71}$Ga</td>
<td>3/2</td>
<td>30.581</td>
<td>0.112</td>
<td>-9.50</td>
</tr>
<tr>
<td>$^{69}$Ga</td>
<td>3/2</td>
<td>24.069</td>
<td>0.178</td>
<td>-2.36</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>5/2</td>
<td>26.077</td>
<td>0.149</td>
<td>-1.90</td>
</tr>
</tbody>
</table>

$\delta_{CG}$(ppm) = $-\frac{4}{3} \times 10^3 (e^2 qQ/h \nu_0) \eta^2 (1 + \frac{1}{3} \eta^2)$.

With the quadrupolar moment $Q$ and the Zeeman energy $\nu_0$ known for both isotopes and assuming $\eta=0$, we can determine the field gradient $eq$ felt by the gallium in the lattice. It should be pointed out that this relation holds for the shift of the centre of gravity of the line, which is, with these asymmetric line shapes, not necessarily the highest point of the peak given by the spectrometer's peak-pick routine. Following this procedure for the resonances of H-$(Ga)ZSM-5$, we find a quadrupole coupling constant $(e^2 qQ/h)$ of 3.0 and 1.9 MHz for $^{69}$Ga and $^{71}$Ga, respectively (table 2). Using these parameters in a line-shape calculation, we obtain, again assuming $\eta=0$, a quadrupolar line broadening of 1900 Hz for $^{69}$Ga and 600 Hz for $^{71}$Ga, which is much less than the observed linewidths. It should be noted that the apparent linewidth does not vary greatly as a function of $\eta$.

In order to determine the origin of the additional broadening, a $^{71}$Ga MAS spectrum was obtained at 7.1 T (91.50 MHz). Now a 2600 Hz wide line was obtained at 157 ppm. That the linewidth hardly changes when the magnetic field is two times lower must mean that a distribution of chemical shifts is present. The increase of quadrupolar broadening when going to low field (7.1 T) is compensated by a decrease in frequency units of the chemical-shift distribution. As proton decoupling during acquisition has no effect on the gallium linewidth, we can rule out the influence of dipolar interactions between protons and gallium. Gallium–gallium dipolar interactions are very small because of the large average distance between gallium atoms in these samples. Even in samples with the highest gallium content (Si/Ga ≈ 11), the average gallium–gallium distance is still 8.8 Å which results in a negligible dipolar interaction. Moreover, the magic-angle-spinning would also average small dipolar interactions. In summary, we can conclude that the linewidth of the $^{69}$Ga and $^{71}$Ga resonance in H-$(Ga)ZSM-5$ can be analyzed as the sum of a chemical-shift distribution, due to crystallographically different sites and/or lattice defects, and second-order quadrupolar broadening due to an electric field gradient at the gallium sites. Obviously, this field gradient may also vary between different crystallographic sites, and will certainly be sensitive to lattice defects. Neglecting possible correlations between chemical shift and quadrupolar interactions, we can divide the gallium linewidth in a simple sum of chemical-shift distribution (linearly increasing with field strength) and quadrupolar interaction (inversely proportional to the field). From such an analysis, we obtain a quadrupole coupling constant of 3.5 and 2.2 MHz for $^{69}$Ga and $^{71}$Ga, respectively. If one considers the accuracy of the methods, this is in good agreement with the values determined from the quadrupole-induced shifts. A further conformation of these values was

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$\delta_\rho$ (T)</th>
<th>$\delta_{CG}$ (ppm)</th>
<th>Width (CSD + Q1) (Hz)</th>
<th>$e^2 qQ/h$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{69}$Ga</td>
<td>14.1</td>
<td>155.9</td>
<td>151.1</td>
<td>4000 (1650 + 2350)</td>
</tr>
<tr>
<td>$^{71}$Ga</td>
<td>14.1</td>
<td>161.1</td>
<td>159.2</td>
<td>2900 (2100 + 800)</td>
</tr>
<tr>
<td>$^{71}$Ga</td>
<td>7.1</td>
<td>157.1</td>
<td>150.6</td>
<td>2600 (1050 + 1550)</td>
</tr>
</tbody>
</table>

$^a$ Determined from the shift of the center of gravity. $^b$ Estimated from the linewidth.
obtained by a $^{71}\text{Ga}$ nutation spectrum which shows only one line at $2\omega_\text{rf}$. With an rf field strength of 60 kHz, this means that the quadrupole coupling constant $e^2 qQ/h$ must be bigger than 1.7 MHz.

The contribution of the distribution in chemical shifts to the linewidth amounts to about 12 ppm. A variation of the Si/Ga ratio from 60 to 11 did not give any variation of the calculated parameters. It should be noted, however, that the sample with the highest gallium content clearly shows the presence of a substantial amount of non-framework gallium (fig. 2). It cannot be excluded, however, that the samples with lower gallium contents contain NMR-invisible extra-lattice gallium. The quantitative aspects of Ga NMR of (Ga)ZSM-5 as a function of Si/Ga ratio and counterion effects are currently under investigation.

The large chemical-shift distribution of 12 ppm makes these samples favourable candidates for double-angle-rotation (DOR) or dynamic-angle-spinning (DAS) \cite{10,11} which completely averages second-order quadrupolar interactions, thus making it possible to observe crystallographically different gallium atoms. It should be noted that the spread in chemical shifts found in the $^{29}\text{Si}$ NMR spectra of dealuminated ZSM-5, showing well-resolved lines for silicon in crystallographically different sites, is only 7 ppm \cite{12}. In a 2D DAS experiment, one might even obtain the quadrupole coupling constants of the various sites \cite{11}.

Table 3 gives the linewidth of the $^{27}\text{Al}$ resonance in H–(Al)ZSM-5 as a function of field strength \cite{4}. Using the same linewidth analysis as described above, we find that the quadrupole coupling constant $(e^2 qQ/h)$ is approximately 800 kHz. Nutation NMR indicates that this coupling constant is probably even smaller \cite{5}. The distribution in chemical shifts amounts to about 6 ppm.

The question is, of course, how these numbers relate to those found for the two gallium isotopes. The observed quadrupole coupling constant of $^{27}\text{Al}$ is more than three times smaller than that found for $^{71}\text{Ga}$. This cannot be accounted for by the difference in quadrupole moment. However, one should also consider the contributions of the inner closed shells to the electric field gradient. The originally spherical symmetrical inner shells of electrons are polarized by the external field gradient and thus contribute to the field gradient at the nucleus; this is expressed in the Sternheimer shielding factor. In a pure ionic crystal lattice the shielding can be expressed as

$$\frac{69\text{Ga}}{100}$$

![Fig. 2. $^{69}\text{Ga}$ MAS NMR spectrum of H–(Ga)ZSM-5 (Si/Ga = 11) in which the presence of some non-framework gallium is clearly visible, as a broad resonance around 100 ppm.](image-url)
Table 3
Observed $^{27}$Al linewidths in H-(Al)ZSM-5 as a function of field strength. The approximate sum of the chemical-shift distribution and second-order quadrupolar broadening is given in parentheses.

<table>
<thead>
<tr>
<th>$B_0$ (T)</th>
<th>width (CSD+QI) (Hz)</th>
<th>$e^2Q/h$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>400 (100+300)</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>400 (300+100)</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>550 (500+60)</td>
<td>0.8</td>
</tr>
<tr>
<td>11.7</td>
<td>900 (830+40)</td>
<td></td>
</tr>
</tbody>
</table>

$e^2Q_{\text{den}} = (1-\gamma_\infty)e^2Q_{\text{ionic}},$

where $e^2Q_{\text{den}}$ is the experimental field gradient, and $e^2Q_{\text{ionic}}$ the field gradient due to the surrounding ionic charges. Using the shielding factors ($\gamma_\infty$) quoted for s-state ions Al$^{3+}$ and Ga$^{3+}$ (table 1) [13], we find that the external field gradients for aluminum and gallium are indeed of the same magnitude. The difference in chemical-shift distribution may be explained along these lines; the higher polarisability of the gallium electron cloud causes gallium to be more sensitive to structural changes than aluminum. This is expressed in the practically observed shift ranges, which are 1000 ppm for gallium and 400 ppm for aluminum. This is also reflected in the difference in chemical shift of octahedral and tetrahedral surrounding, which is approximately three times bigger for gallium as compared to aluminum. So far, however, insufficient Ga chemical-shift data have been collected to establish a correlation between the Ga and Al shift in solids.

4. Conclusion

In conclusion, we can say that gallium NMR is a suitable tool for studying gallosilicates. The existence of two isotopes with different Zeeman energies and quadrupole moments facilitates the determination of quadrupole coupling constants. Furthermore, the gallium chemical shift appears to be sensitive to structural changes, making Ga-NMR a good candidate for DOR and DAS studies. A comparison of the gallium NMR spectra of H-(Ga)ZSM-5 to those of aluminum in H-(Al)ZSM-5 shows that gallium is indeed incorporated in the ZSM-5 lattice. There are no indications that the observed differences of the chemical-shift distributions and the quadrupole coupling constants between Al and Ga are related to structural changes of the ZSM-5 lattice upon replacing Al by Ga. These differences can rather be related to the different NMR properties of the isotopes.

Acknowledgement

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