

The Removal of Gallium from the Lattice of MFI-Gallosilicates as studied by ^{71}Ga M.A.S.-N.M.R. Spectroscopy

Cees R. Bayense,^{*a} Jan H. C. van Hooff,^a Arno P. M. Kentgens,^b Jan W. de Haan,^a and Leo J. M. van de Ven^a

^a Eindhoven University of Technology, Laboratories of Inorganic Chemistry and Catalysis and of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b University of Nijmegen, Faculty of Science, SON/NWO HF-NMR Facility, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Solid state ^{71}Ga m.a.s.-n.m.r. spectroscopy on MFI-gallosilicates has shown evidence for the removal of tetrahedrally co-ordinated gallium from the zeolite lattice and the concomitant deposition of octahedrally co-ordinated gallium in the pores during steam treatment.

During the last decade much attention has been paid to the dealumination of zeolites by steam treatment.^{1,2} After such treatments, extra-framework aluminium species with different co-ordinations could be detected in the pores of the zeolite by ^{27}Al m.a.s.-n.m.r. spectroscopy.³ For certain catalytic uses gallosilicates proved to be more suitable than their aluminium analogues, e.g. in aromatization reactions.⁴ Therefore, investigation of the gallium co-ordination in these zeolites and their thermal and hydrothermal stabilities is appropriate.

In this work the results of solid state ^{71}Ga m.a.s.-n.m.r. spectroscopic measurements are presented, identifying the gallium species present in isomorphously substituted ZSM5 zeolites (all Al substituted by Ga in the stage of gel formation) after preparation and steam treatment for different durations. Preparation of the gallosilicates consisted of four steps: crystallization, removal of the template by calcination (3 h, 823 K), ion exchange ($\times 3$ with 2 M NH_4NO_3 solution, 1 h, 363 K), and a second calcination (3 h, 823 K). Steaming was carried out with the ammonium exchanged zeolites ($\text{Si/Ga} = 45$) at 923 K for 3, 6, 12, and 24 h. N.m.r. spectroscopic measurements were carried out on a Bruker AM600 n.m.r.

spectrometer (^{71}Ga frequency 183.0 MHz). Spectra were obtained using a single tuned probe equipped with a Doty double bearing m.a.s. assembly. Typical spinning speeds of ~ 8 kHz were employed.

With extensively dehydrated samples very broad gallium signals were observed. This is possibly due to the high quadrupolar interactions of the gallium. A similar effect was found in the case of ^{27}Al m.a.s.-n.m.r. spectroscopic measurements on aluminium zeolites, where the Al signal decreased during drying of the samples.⁵ In earlier work it was shown that in the case of ^{27}Al m.a.s.-n.m.r. spectra the line broadening due to electric asymmetry of the lattice-Al can be reduced by equilibration of the zeolite samples with water vapour at room temperature.⁵ Indeed, upon application of

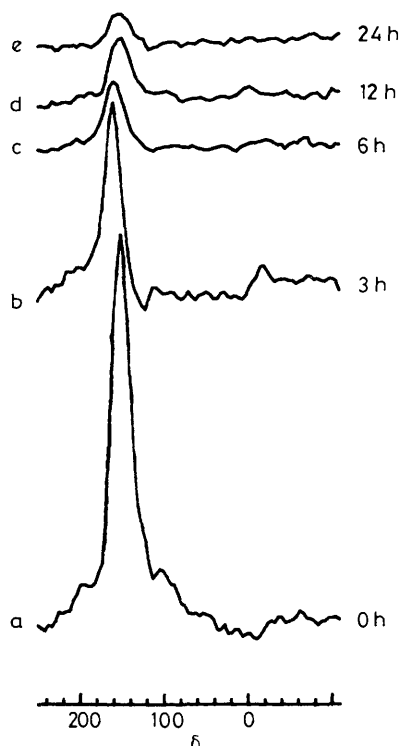


Figure 1. ^{71}Ga M.a.s.-n.m.r. spectra after various steaming times and water equilibration.

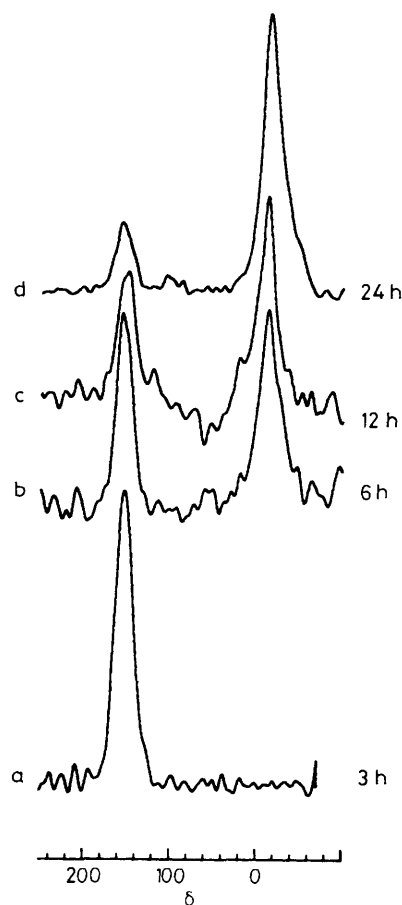


Figure 2. ^{71}Ga M.a.s.-n.m.r. spectra after various steaming times and acac equilibration.

this technique to the gallosilicates, a peak at about $\delta +159$ relative to the hexahydrated Ga^{3+} ion was observed (Figure 1a). This peak has been identified as a tetrahedral gallium species.⁶

The effect of steam treatment at 923 K for different times can be seen in Figure 1b—e. These spectra were recorded after water vapour equilibration of the samples at room temperature. From the decrease in the intensity of the signal at $\delta +159$, it is clear that during steaming a considerable loss of tetrahedral gallium occurred, although little or no signal at $\delta 0$ (from an octahedral gallium species) became visible after such pretreatment.

For aluminium zeolites, however, it is known that in certain cases detection of octahedral Al with m.a.s.-n.m.r. spectroscopy is improved after equilibration or impregnation of the samples with acetylacetone (acac).⁷ The spectra presented in Figure 2a—d were recorded after acac equilibration at room temperature. It is clear that a peak at $\delta 0$ appears in the spectrum with increasing intensity with steaming time, while the peak at $\delta +159$ decreases. These results should be regarded as qualitative rather than quantitative, but they strongly support the idea of the transition of lattice gallium to extra-lattice gallium upon steaming at 923 K. Because the octahedral gallium species was detected only after acac treatment, the measurement of the unsteamed sample (Figure 1a) was repeated after equilibration with acac. This resulted in the same spectrum as was found after equilibration with water.

It can thus be concluded that almost no octahedral gallium was present in the unsteamed zeolite.

More work on the presence of gallium in gallosilicates with various Si/Ga ratios and gallo-aluminosilicates is in progress.

The authors thank G. Nachtegaal of the SON/NWO HF-NMR facility at the University of Nijmegen for her help with recording the spectra on the 600 MHz spectrometer and the Netherlands Organization of Scientific Research (N.W.O.) for financial support and for support of the n.m.r. facility.

Received, 17th March 1989; Com. 9/01171D

References

- 1 J. Klinowski, J. M. Thomas, C. A. Fyfe, G. C. Gobbi, and J. S. Hartman, *Inorg. Chem.*, 1983, **22**, 63.
- 2 T. H. Fleisch, B. L. Meyers, G. J. Ray, H. B. Hall, and C. L. Marshall, *J. Catal.*, 1986, **99**, 117.
- 3 J. Sanz, V. Fornes, and A. Corma, *J. Chem. Soc., Faraday Trans. I*, 1988, **84(9)**, 3113.
- 4 H. Kitagawa, Y. Sendoda, and Y. Ono, *J. Catal.*, 1986, **101**, 12.
- 5 A. P. M. Kentgens, K. F. M. G. J. Scholle, and W. S. Veeman, *J. Phys. Chem.*, 1983, **87**, 4357.
- 6 H. K. C. Timken and E. Oldfield, *J. Am. Chem. Soc.*, 1987, **109**, 7669.
- 7 D. Freude, T. Fröhlich, H. Pfeifer, and G. Scheler, *Zeolites*, 1983, **3**, 171.