29Si N.M. R longitudinal relaxation times in ZSM-5 zeolites


Published in:
Journal of the Chemical Society, Chemical Communications

DOI:
10.1039/c39850000214

Published: 01/01/1985

Citation for published version (APA):
The presence of Pr₄N⁺ templates causes an increase of $T_1$ for $^{29}$Si nuclei in ZSM-5 zeolites of more than one order of magnitude, and relatively small changes in zeolite structure are important; due care is required in extracting quantitative data from $^{29}$Si magic angle spinning n.m.r. spectra of zeolites.

In many cases relative numbers of differently positioned Si atoms in zeolites, e.g. the series of Si($n$Al), $n = 0-4$, have been analysed by $^{29}$Si n.m.r. spectroscopy. In order to be quantitatively reliable, these measurements must be carried out by pulse excitation with sufficiently long interval times. Some, but not all, papers report precautions against taking too short interval times. Usually, pulse delays of 1—10 s are used, and ca. 5 s seems to be the rule for ZSM-5 type zeolites. Cross-polarization (c.p.) spectra may be obtained in cases where organic material (templates or other) are occluded in
the zeolite channels. Little or nothing is known about the possibly different c.p. characteristics caused by different sorbates and/or by crystallographic sites. Nevertheless, in some cases even c.p. magic angle spinning (m.a.s.) n.m.r. data are used, along with pulsed spectra, in order to obtain quantitative results. As yet, no systematic study of \(^{29}\text{Si}\) n.m.r. \(T_1\) values for zeolites has been presented to our knowledge. Some values for ZSM-39 were reported recently. The necessity to produce systematic results was also indicated recently, with reference to the rather large \(T_1\) values obtained recently with tetrapropylammonium hydroxide as the template. Some values for ZSM-39 were reported recently.4 Rather the influence of possibly small structural differences within zeolites will be emphasized.

The present communication presents a series of \(T_1\) measurements on a number of ZSM-5 zeolites, including silicalite, with and without templates or sorbates. No attempts were made, at the present stage, to distinguish crystallographically distinct sites.4 Rather the influence of possibly small structural differences within zeolites will be emphasized.

The zeolites were prepared by standard procedures,7 mostly with tetrapropylammonium hydroxide as the template. Organic material was removed by calcination at 550 °C. Organic sorbates were introduced to the H+-form of this zeolite (sample 7). These latter two effects are thought to arise from the uptake of water, conceivably via dipolar interactions between \(^{29}\text{Si}\) nuclei and protons of water and/or lattice changes, e.g. relocations of residual sodium within the framework.11 Lattice modifications have also been mentioned as a background of sorbate-induced chemical shift changes.8 Some similar sorbates, as well as Me,\(\text{N}^+\) (with Cl\(^-\) as counter ion) and NH\(_3\), were also included in the present study. With the single exception of NH\(_3\) on ZSM-5, all sorbates lowered the \(T_1\) values of \(^{29}\text{Si}\) (Table 1).

This apparent contrast with conclusions reached by West6 could well be connected with the differences in \(^{29}\text{Si}\) n.m.r. chemical shift dispersions (vide supra) and suggest that relatively small changes in structural parameters (e.g. orthorhombic versus monoclinic symmetry) among the zeolite atoms can have large effects on \(^{29}\text{Si}\) n.m.r. parameters: shifts as well as \(T_1\) values.

Further research on this point, including different calcination temperatures, is in progress. The mode of adsorption is probably of importance as indicated by the different effects of cyclohexene and benzene on silicalite or benzene on silicalite and on ZSM-5. The sorption mode can be followed by means of \(^{13}\text{C}\) c.p. m.a.s. n.m.r. (linewidths) and \(^{29}\text{Si}\) c.p. m.a.s. n.m.r. (optimal c.p. times; Table 1) measurements.

For the H+-ZSM-5 samples the \(T_1\) values do not depend systematically on Si/Al ratios. We tentatively ascribe the very large differences in \(T_1\) values between zeolites as-synthesized (with Pr\(_4\)N\(^+\)) and the corresponding calcined samples to a combination of noticeable steric interaction of the templates on the zeolite framework and the possibility of thermally induced dislocations upon high temperature treatment as described before by Wu and co-workers.11 Framework distortion by NH\(_3\)+ of zeolite-p has been found recently, based on X-ray diffraction.12 Structural constraints imposed by the zeolites on the Pr\(_4\)N\(^+\) moieties have been mentioned13 or stated14 before and we now surmise that the opposite effect is partially responsible for the \(T_1\) variation in \(^{29}\text{Si}\) n.m.r. spectra. Further work on the elucidation of the relaxation mechanism(s) is obviously required. Our present results and those of others5,6 indicate with certainty, however, that due care should be taken in all cases where cross-polarized and/or pulse-excited \(^{29}\text{Si}\) m.a.s. n.m.r. spectra of zeolites are compared for quantitative purposes.1 The same is true for studies where changes in the zeolite framework, e.g. as a consequence of reacting sorbates, are analysed by \(^{29}\text{Si}\) n.m.r. spectroscopy.

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**Table 1.** Relaxation times (\(T_1/s\)) and optimal cross-polarization times (\(t_{c.p.}/ms\)) for the \(^{29}\text{Si}(\text{OSi})_4\) resonance of ZSM-5 zeolites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>(T_1)</th>
<th>(t_{c.p.})</th>
<th>(H_2O)'</th>
<th>Cyclohexene</th>
<th>Benzene</th>
<th>NH(_3)</th>
<th>Me,(\text{N}^+)</th>
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<tbody>
<tr>
<td>1</td>
<td>5000</td>
<td>145.1</td>
<td>8</td>
<td>6.5</td>
<td>6.0</td>
<td>2.0</td>
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<td>3.1</td>
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<td>170</td>
<td>57.6</td>
<td>7</td>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
<td>34</td>
<td>45.7</td>
<td>5</td>
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<tr>
<td>5</td>
<td>33</td>
<td>2.6</td>
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<tr>
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<td>16</td>
<td>119.9</td>
<td>6</td>
<td>7.2</td>
<td>4.5</td>
<td>3.6</td>
<td>13</td>
<td>7.2</td>
</tr>
</tbody>
</table>

\(^a\) Template is Pr\(_4\)N\(^+\). \(^b\) Template is hexane-1.6-diol. \(^c\) Non-single-exponential behaviour. \(^d\) After exposure to air. \(^e\) Calcined form for Si/Al = 5000. \(^f\) By exposure to air. \(^g\) After drying at 400 °C. \(^h\) No cross-polarization observed.
We thank C. W. R. Engelen for the preparation of some samples. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Received, 17th September 1984; Com. 1310

References