

^{29}Si N.M.R. Longitudinal Relaxation Times in ZSM-5 Zeolites

Leo J. M. van de Ven,^{a*} Jos G. Post,^b Jan H. C. van Hooff,^b and Jan W. de Haan^a

^a *Laboratory of Instrumental Analysis, and* ^b *Laboratory of Inorganic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands*

The presence of Pr_4N^+ 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 $\text{Si}(n\text{Al})$, $n = 0-4$, 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,¹ 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.² Cross-polarization (c.p.) spectra may be obtained in cases where organic material (templates or other) are occluded in

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.

Sample	As-synthesized ^a		Calced at 550 °C	H ⁺ -ZSM-5 ^c with sorbate									
	Si/Al	T_1		$t_{c.p.}$	T_1	H ₂ O ^f		Cyclohexene		Benzene		NH ₃	Me ₄ N ⁺
						T_1	$t_{c.p.}$	T_1	$t_{c.p.}$	T_1	$t_{c.p.}$		
1	5000	145.1	8	6.5 ^c	6.0 ^c	2.0	5	3.1 ^c	30	4.9 ^h	—		
2	170	57.6 ^c	7	—	—	—	—	—	—	—	—		
3	75	—	—	—	5.2	—	—	—	—	—	—		
4	34	45.7 ^c	5	—	—	—	—	—	—	—	—		
5	33	2.6 ^b	—	—	—	—	—	—	—	—	—		
6	25	—	—	—	5.6	—	—	—	—	—	—		
7	16	119.9	6	7.2 ^c 5.3 ^{cd}	4.5 5.5 ^{cg}	—	—	3.6 ^c	13	7.2 ^{ch}	3.1 ^c		

^a Template is Pr₄N⁺. ^b Template is hexane-1,6-diol. ^c Non-single-exponential behaviour. ^d After exposure to air. ^e Calced form for Si/Al = 5000. ^f By exposure to air. ^g After drying at 400 °C. ^h No cross-polarization observed.

the zeolite channels. Little or nothing is known about the possibly different c.p. characteristics caused by different sorbates and/or by different 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.³ As yet, no systematic study of ^{29}Si n.m.r. T_1 values for zeolites has been presented to our knowledge. Some values for ZSM-39 were reported recently.⁴ The necessity to produce systematic results was also indicated recently,⁵ with reference to the rather large T_1 values obtained earlier for kaolinites.⁶

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 between 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⁺-ZSM-5 zeolites *via* a vacuum line after evacuation. ^{29}Si M.a.s. n.m.r. spectra were obtained at 59.63 MHz on a Bruker CXP-300 spectrometer using *ca.* 4 kHz m.a.s. rotation.

For the zeolites studied here, the ^{29}Si n.m.r. spectrum consists largely of (superimposed) Si(OSi)₄ resonances. The silicalite spectrum shows nine distinguishable lines but its resolution is slightly worse than those reported earlier for similar calcination temperatures.^{8,9} The relative intensities of the individual lines, however, are the same. After calcination at 800 °C the usual picture was obtained. The influence of benzene sorbate on the ^{29}Si n.m.r. shifts was also different from that reported earlier^{5,8} but the presence of organic sorbates was established unequivocally by means of ^{29}Si and ^{13}C c.p. m.a.s. n.m.r. experiments.

T_1 Values were obtained *via* inversion–recovery experiments with typically 10–30 different delay times. Results are summarized in Table 1. The very large influence on T_1 of the presence of Pr₄N⁺ is evident; the Si/Al ratio does not seem of importance for this major effect. (The two values of 46 and 58 s were obtained from samples with a higher Na⁺ content.) On the other hand, T_1 was 2.6 s with hexane-1,6-diol.¹⁰ (In this respect, hexanediol acts as a template; *vide infra*.) Calcination causes T_1 to drop to 7.2 s (Si/Al = 16) or 6.5 s (Si/Al = 5000) while subsequent exposure to air causes further reduction for the T_1 of the Si/Al = 16 zeolite. A similar result was obtained

with 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}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 Me₄N⁺ (with Cl⁻ as counter ion) and NH₃, were also included in the present study. With the single exception of NH₃ on ZSM-5, all sorbates lowered the T_1 values of ^{29}Si (Table 1).

This apparent contrast with conclusions reached by West⁵ could well be connected with the differences in ^{29}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}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}C c.p. m.a.s. n.m.r. (linewidths) and ^{29}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 (^{29}Si) 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 Pr₄N⁺) and the corresponding calced 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 NH₄⁺ of zeolite-p has been found recently, based on X-ray diffraction.¹² Structural constraints imposed by the zeolites on the Pr₄N⁺ 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}Si n.m.r. spectra. Further work on the elucidation of the relaxation mechanism(s) is obviously required. Our present results and those of others^{4,5} indicate with certainty, however, that due care should be taken in all cases where cross-polarized and/or pulse-excited ^{29}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}Si n.m.r. spectroscopy.

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

- 1 E. Lippmaa, M. Mägi, A. Samoson, M. Tarmak, and G. Engelhardt, *J. Am. Chem. Soc.*, 1981, **103**, 4992, and earlier papers of this group.
 - 2 C. A. Fyfe, G. C. Gobbi, J. Klinowski, J. M. Thomas, and S. Ramdas, *Nature (London)*, 1982, **296**, 530.
 - 3 J. B. Nagy, Z. Gabelica, E. G. Derouane, and P. A. Jacobs, *Chem. Lett.*, 1983, 2003.
 - 4 J. B. Higgins, D. E. Woessner, J. C. Trewella, and J. L. Schlenker, *Zeolites*, 1984, **4**, 112.
 - 5 G. W. West, *Aust. J. Chem.*, 1984, **37**, 455.
 - 6 P. F. Barron, R. L. Frost, and J. O. Skjemstad, *J. Chem. Soc., Chem. Commun.*, 1983, 581.
 - 7 E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, and R. M. Kirchner, *Nature (London)*, 1978, **271**, 512.
 - 8 C. A. Fyfe, G. J. Kennedy, C. T. De Schutter, and G. T. Kokotailo, *J. Chem. Soc., Chem. Commun.*, 1984, 541.
 - 9 C. A. Fyfe, G. C. Gobbi, and G. J. Kennedy, *Chem. Lett.*, 1983, 1551.
 - 10 B. N. Lok, T. R. Cannan, and C. A. Messina, *Zeolites*, 1983, **3**, 282.
 - 11 E. L. Wu, S. L. Lawton, D. H. Olson, A. C. Rohrman, and G. T. Kokotailo, *J. Phys. Chem.*, 1979, **83**, 2777.
 - 12 L. B. McCusker, *Zeolites*, 1984, **4**, 51.
 - 13 G. Boxhoorn, R. A. van Santen, W. A. van Erp, G. R. Hays, R. Huis, and A. D. H. Clague, *J. Chem. Soc., Chem. Commun.*, 1982, 264.
 - 14 J. B. Nagy, Z. Gabelica, and E. G. Derouane, *Zeolites*, 1983, **3**, 43.
-