

## The Origin of $^{29}\text{Si}$ Spin-Lattice Relaxation in Zeolites: a Means of Rapid Acquisition of N.M.R. Spectra and of probing Internal Sites in Microporous Catalysts

Jacek Klinowski,\* T. Adrian Carpenter, and John M. Thomas

*Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.*

The paramagnetic oxygen molecule is the dominant source of  $^{29}\text{Si}$  spin-lattice relaxation in zeolites with intracrystalline water playing a much smaller part; n.m.r. signals corresponding to crystallographically non-equivalent sites relax at different rates in the vicinity of sorbed oxygen.

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$^{29}\text{Si}$  Spin-lattice relaxation times,  $T_1$ , in crystalline aluminosilicates, particularly zeolites, are relatively short in comparison with those for  $^{13}\text{C}$  in organic solids.  $^{29}\text{Si}$  Magic-angle-spinning (m.a.s.) n.m.r. spectra of zeolites are normally composed<sup>1-3</sup> of up to five signals corresponding to  $\text{Si}(n\text{Al})$  structural units where  $n$ , which can be 0, 1, 2, 3, and 4, is the number of

aluminium atoms linked, *via* bridging oxygens, to the central silicon atom. Farlee *et al.*<sup>4</sup> measured  $T_1$  values of 5–30 s in various zeolites and found that, for a given zeolite,  $T_1$  of a silicon atom in an  $\text{Si}(n\text{Al})$  unit varies little with  $n$ , and is also insensitive to a change in the Si/Al ratio. This indicates that relaxation is not affected by the presence of  $^{27}\text{Al}$  and also

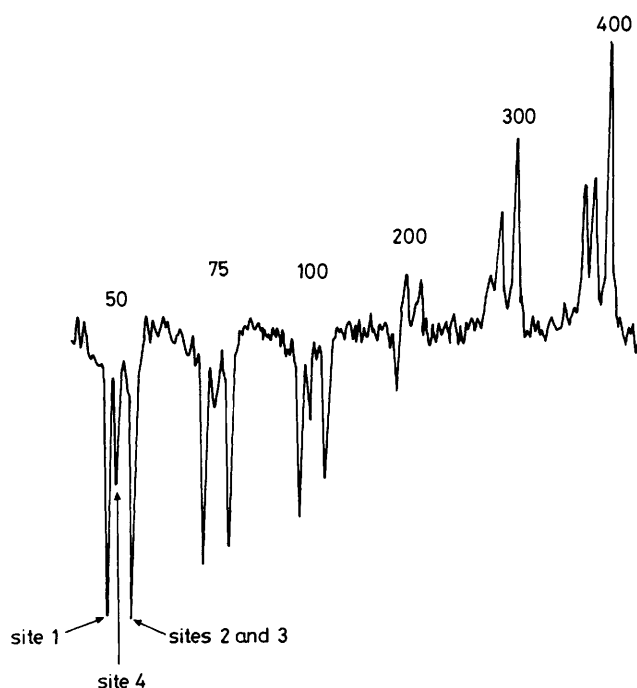
**Table 1.** Spin-lattice relaxation times,  $T_1$  (in seconds), at room temperature for various zeolites under the atmospheres of argon and oxygen at 1 atm pressure. Relaxation times were determined for the various  $^{29}\text{Si}$  n.m.r. signals by the saturation recovery method (following 30 saturating pulses of 4.50  $\mu\text{s}$  duration) at 79.5 MHz using a Bruker MSL-400 spectrometer with a double-bearing magic-angle-spinning probehead. 64 Scans were accumulated for each value of  $\tau$ .

Sample	Argon	Oxygen		
Na-A	57	14.09		
Na-A (dehydrated)	111.3	1.05		
Ca-A (dehydrated)	180	0.70		
Silicalite (dehydrated)	255	1.05	2.65	1.37
		1.36	2.63	1.29
		1.18	2.50	1.31
		1.24	3.20	1.28
		1.08	4.37	1.69
Dealuminated mordenite	236.4	0.399		
	209.6	0.261		
	225.0	0.270		
Dealuminated mordenite (dehydrated)	609	0.487		
	1349	0.284		
	892	0.380		

explains why short recycle times used by most workers (typically *ca.* 5 s, *i.e.* much shorter than  $5T_1$ ) still give quantitatively reliable spectra. It is often assumed that spin-lattice relaxation in zeolites is controlled by spin diffusion from paramagnetic centres. However, this mechanism is likely to be very inefficient in view of the large distance between neighbouring silicons (separated by oxygens and often aluminiums), the relatively low abundance of  $^{29}\text{Si}$ , and the 'detuning' influence of  $^{27}\text{Al}$  in this energy-conserving process. Also, the 'impurity' hypothesis cannot explain why  $T_1$  for synthetic zeolites with very low levels of paramagnetic remains short nor, especially, why, upon rendering a zeolite amorphous  $T_1$  increases by orders of magnitude<sup>5</sup> while the concentration of paramagnetic component remains constant.

Cookson and Smith<sup>6</sup> recently reported that atmospheric oxygen has a very large effect on  $T_1$  of  $^{29}\text{Si}$  nuclei in silicalite (the highly siliceous form of ZSM-5). Values measured in a stationary sample were 1.35 s under oxygen, 6.1 s under air, and 230 s under nitrogen. We have examined the various contributions to  $T_1$  and here report that the paramagnetic oxygen molecule is indeed the principal factor. Values of  $T_1$  measured under different atmospheres are cited, and we draw attention to some important implications for n.m.r. studies of zeolitic catalysts in particular and silicates in general.

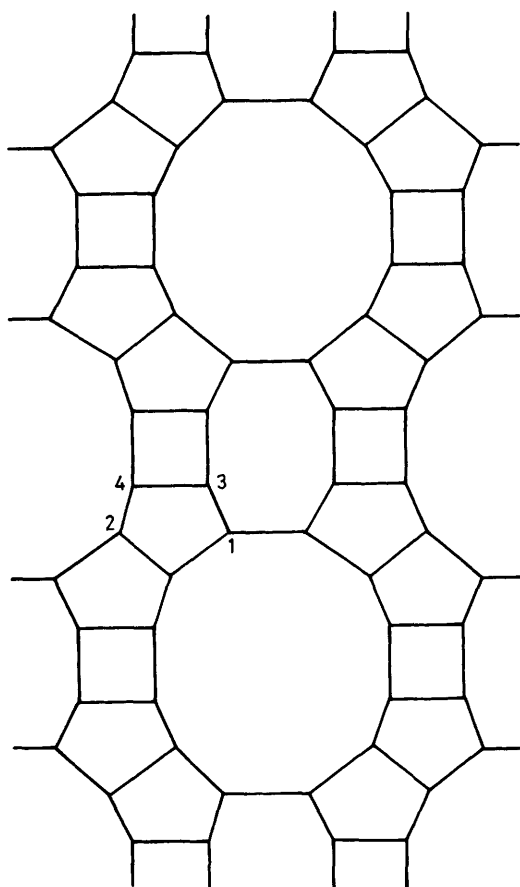
Apart from oxygen, the following have to be considered as possible contributors to  $T_1$ : (i) framework and non-framework aluminium, (ii) the charge-balancing cations, and (iii) zeolitic water. To assess the role of each of these factors we have measured  $T_1$  of four samples: zeolite Na-A (Si/Al = 1.00); zeolite Ca-A (Si/Al = 1.00); hydrothermally dealuminated mordenite (with framework Si/Al >100, but containing considerable amounts of extra-framework Al so that overall Si/Al  $\approx$  5); and silicalite which contained no detectable aluminium and thus no exchangeable cations.  $T_1$  was measured under oxygen and under argon (which does not possess a naturally-occurring n.m.r.-active isotope capable of



**Figure 1.** A series of inversion-recovery  $T_1$  spectra for  $^{29}\text{Si}$  in dealuminated mordenite under the atmosphere of oxygen (1 atm pressure). Signals corresponding to the various crystallographically non-equivalent sites for silicon<sup>8</sup> are indicated together with the values of  $\tau$  (in ms) for each spectrum.

affecting the relaxation of  $^{29}\text{Si}$ ) using saturation recovery and inversion recovery methods with magic-angle-spinning. Both methods gave similar results. When more than one  $^{29}\text{Si}$  signal was present in the spectrum,  $T_1$  was measured for each. Zeolite samples were contained in sealed capsules made from high purity quartz glass.<sup>7</sup> The capsule was filled with zeolite powder, connected to an evacuable gas-handling line which had provisions for heat treatment of the sample. Spin-lattice relaxation time of silicon in the capsule itself (*ca.* 2 h) is so long in comparison with that in the sample, that it contributes no detectable n.m.r. signal. After pumping and/or heating the sample, oxygen or argon were admitted as required, and the capsule was sealed and placed inside a cylindrical n.m.r. rotor capable of spinning at 4 kHz. To assess the role of water, samples were prepared in two different ways before oxygen or argon were admitted: 'wet' samples were pumped at room temperature for 1 h (this treatment does not remove zeolite water, most of which can be displaced only by pumping a sample heated to 400  $^{\circ}\text{C}$ ), whereas 'dehydrated' samples were made by evacuation (to  $10^{-5}$  Torr) and heating to 500  $^{\circ}\text{C}$  for 24 h.

A single-exponential expression could always be fitted to the data to obtain  $T_1$ . From the results (Table 1) it is apparent that the influence of oxygen on relaxation is dramatic: for mordenite,  $T_1$  of all three signals is reduced by more than three orders of magnitude in comparison with the value under argon. On the other hand, water plays a secondary role in relaxation: in zeolite Na-A under argon dehydration increases  $T_1$  by a factor of 2, and in mordenite under argon by a factor of 3–6. Most of the decrease in  $T_1$  occurs on substituting air for argon. For example,  $T_1$  for the three signals in mordenite in air is 2.13, 1.09, and 1.32 s respectively. The nature of the charge-balancing cation (compare Na-A and Ca-A), the



**Figure 2.** The structure of mordenite viewed along [001].<sup>12,13</sup> The four kinds of crystallographic sites are indicated. Their relative populations (16:16:8:8 per unit cell respectively) are not reflected in this projection.

framework Si/Al ratio, or the presence of extra-framework aluminium does not appear to have a clear effect on relaxation. Neither do paramagnetic impurities:  $T_1$  for the commercial samples of zeolite A and mordenite is similar to that in silicalite prepared from ultrapure materials in Teflon vessels. Finally, relaxation times of crystallographically non-equivalent silicon atoms in mordenite and silicalite differ considerably within the same sample. An example is given in Figure 1 which shows a series of inversion recovery spectra for dealuminated mordenite under oxygen. The three signals, shown inverted in the first spectrum on the left and known<sup>8</sup> to correspond to sites 1, 4, and (2 + 3) in the zeolitic framework (Figure 2) clearly recover at different rates. For  $\tau = 200$  ms the signal corresponding to site 1 (at the entrance to side pockets in the structure of mordenite) is still negative, while the other two, which relax faster, are already positive. It is likely that this effect is related to the location of extra-framework debris produced on dealumination which may 'block' this site to oxygen and/or to the different affinity of the various sites for oxygen. It is impossible at this stage to interpret the large differences (extreme values are 1.05 and 4.37 s under  $O_2$ ) for  $T_1$  in the various sites<sup>9</sup> in silicalite, as the structure of this material is not sufficiently well known.

Our results offer a ready explanation why  $T_1$  increases so dramatically when the zeolite is made amorphous and why relaxation in compact silicates (such as crystalline quartz<sup>10</sup>) and glasses is so slow. It is simply that most silicon atoms in such samples are inaccessible to oxygen. It also seems likely that the significant lengthening of  $T_1$  on addition to zeolites of various organic materials<sup>11</sup> is due to the displacement of oxygen from the intracrystalline space by the guest molecules. We think that reports<sup>4</sup> of a major influence of dehydration of the zeolite on  $^{29}\text{Si}$   $T_1$  stem from the failure to separate the effect of *dehydration* and *evacuation*. There is however, evidence<sup>14</sup> that water incorporated into a vitreous silicate can exert a quite appreciable influence upon the relaxation of  $^{29}\text{Si}$  nuclei.

Our results offer a means of rapid acquisition of  $^{29}\text{Si}$  n.m.r. spectra of zeolites and possibly other 'open' materials such as clays. In some cases, for spectra recorded under oxygen,  $T_1$  is reduced by a factor of 100 in comparison with air; the acquisition time for the same signal-to-noise ratio is therefore reduced by a factor of 10. Secondly, a new, quantitatively reliable method suggests itself for the study of *surfaces* of amorphous silicas, silica-aluminas, and silicate glasses. This method will be free from the disadvantages of cross-polarization which does not readily produce quantitative results. Finally, by careful control of the partial pressure of oxygen, or by using another, bulkier, paramagnetic molecule, radical or cluster ion (e.g.<sup>15</sup>  $\text{Na}_4^{3+}$ ), site-selective spectra might readily be obtained from a variety of materials.

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## References

- (a) E. Lippmaa, M. Mägi, A. Samoson, M. Tarmak, and G. Engelhardt, *J. Am. Chem. Soc.*, 1982, **102**, 4889; (b) S. Ramdas, J. M. Thomas, J. Klinowski, C. A. Fyfe, and J. S. Hartman, *Nature (London)*, 1981, **292**, 228.
- J. Klinowski, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1984, **16**, 237.
- J. M. Thomas and J. Klinowski, *Adv. Catal.*, 1985, **33**, 199.
- R. D. Farlee, D. R. Corbin, and A. J. Vega, 25th Rocky Mountain Conf., Denver, August, 1983; R. D. Farlee and D. R. Corbin, 1984 Intl. Chem. Congr. Pacific Basin Societies, Honolulu, December 1984.
- J. Klinowski and J. M. Thomas, unpublished.
- D. J. Cookson and B. E. Smith, *J. Magn. Reson.*, 1985, **63**, 217.
- T. A. Carpenter, J. Klinowski, D. T. B. Tennakoon, C. J. Smith, and D. C. Edwards, *J. Magn. Reson.*, to be submitted.
- J. M. Thomas, J. Klinowski, S. Ramdas, B. K. Hunter, and D. T. B. Tennakoon, *Chem. Phys. Lett.*, 1983, **102**, 158.
- C. A. Fyfe, G. C. Gobbi, J. Klinowski, J. M. Thomas, and S. Ramdas, *Nature (London)*, 1982, **296**, 530.
- T. A. Carpenter, J. Klinowski, and J. M. Thomas, unpublished.
- G. W. West, *Aust. J. Chem.*, 1984, **37**, 455.
- W. M. Meier, *Z. Kristallogr.*, 1961, **115**, 439.
- W. M. Meier and D. H. Olson, 'Atlas of Zeolite Structure Types,' Juris Druck, Zürich, 1978.
- L. F. Gladden, T. A. Carpenter, and S. R. Elliott, *Philos. Mag.*, 1986, **B53**, L81.
- P. P. Edwards, M. R. Harrison, J. Klinowski, S. Ramdas, J. M. Thomas, D. C. Johnson, and C. J. Page, *J. Chem. Soc., Chem. Commun.*, 1984, 982.