

The Effect of Sorbates on the High-Resolution ^{29}Si N.M.R. Spectra of Silicalite

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Abstract

The ^{29}Si n.m.r. spectrum from silicalite which consists of nine specific peaks is changed substantially when ethanol, propan-1-ol, n-decane, or especially benzene is present in the channel system.

The ^{29}Si resonance line from calcined silicalite consists of nine separate peaks which, it is claimed, arise from the crystallographically non-equivalent tetrahedral silicon atoms, each joined by oxygen bridges to four other silicon atoms.¹ It has been suggested that the three high-field peaks are associated with silicon atoms in four-membered rings.²

The present work indicates that significant changes occur in the position and the intensity of these peaks when organic molecules are present in the channel system. Some shifts are similar in magnitude to those observed in zeolites³ when the environment of the silicon in the aluminosilicate structure is changed. The effects of sorbed molecules should be considered when assigning peaks to specific structural units.

Experimental

The silicalite ($\text{Si}/\text{Al} > 4400$) was prepared by conventional means from tetrapropylammonium bromide and Aerosil 200 as a silica source, and was calcined in air at 500°C for 16 h. Organic molecules were introduced into the channel system by adding excess liquid to the calcined sample and this material, in the form of a stiff paste, was placed in a Delrin or zirconia spinner. The specimen dried quickly and high-speed rotation outside the spectrometer removed the excess liquid. The amount of sorbate was not measured except for the benzene sample. In this case approximately 10 wt % benzene was sorbed which corresponds to about eight benzene molecules per unit cell. The same amount of silicalite was used for all samples. A Bruker CXP-200 spectrometer operating at 39.76 MHz was used and mostly the repetition time was 5 s. In each case 600 free induction decays were accumulated and the specimen was spun at c. 3 kHz. A line-broadening of 5 Hz was used and the vertical scales of the spectra were adjusted so that the integrated intensity (i.e. the area under the curve) was the same for the five samples. The chemical shifts are given in parts per million from tetramethylsilane. The spectra were calibrated by using the line from NaA (Linde 4A) zeolite, taken to be -89.5 ppm from tetramethylsilane.

¹ Fyfe, C. A., Gobbi, G. C., Klinowski, J., Thomas, J. M., and Ramdas, S., *Nature (London)*, 1982, **296**, 530.

² Nagy, J. B., Gabelica, Z., Derouane, E. G., and Jacobs, P. A., *Chem. Lett.*, 1982, 2003.

³ Lippmaa, E., Magi, M., Samosan, A., Tarmak, M., and Engelhardt, G., *J. Am. Chem. Soc.*, 1981, **103**, 4992.

Results and Discussion

Fig 1 shows the spectra from calcined silicalite, and from this material with the addition of ethanol, propan-1-ol, n-decane, or benzene. They were plotted in this way to emphasize the variation in lineshape; the actual intensities of *A*, *B*, *C*, *D*, *E* were in the ratio 1 : 0.42 : 0.4 : 0.45 : 1 even though the silicon content was the same for each sample. This saturation effect was significantly reduced by increasing the repetition time; this gives a clear indication that the presence of some organic molecules in the channels increases the spin-lattice relaxation time T_1 . The lineshapes, however, were not altered so that it is quite valid to compare the spectra shown in Fig. 1. The original spectrum was obtained again after the treated samples were heated at 500°C for 2 h. The spectra from silicalite mixed with water or 1,3,5-trimethylbenzene were very similar to that from the calcined sample. There was a slight broadening of the peaks in the spectrum from the sample containing water, and a slight shift to higher field (increased shielding) for the complete spectrum from the sample containing trimethylbenzene.

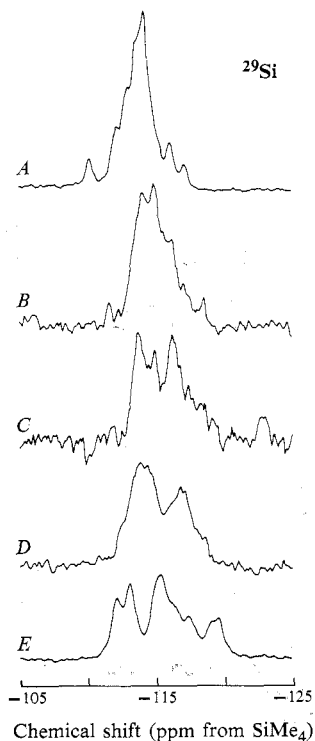


Fig. 1. The effect of sorbed organic molecules on the high-resolution ^{29}Si n.m.r. spectra of silicalite at 39.76 MHz:
A, as calcined;
B, mixed with ethanol;
C, mixed with propan-1-ol;
D, mixed with n-decane;
E, mixed with benzene.

The chemical shifts of the nine individual peaks in the spectrum from calcined silicalite were -109.8 , -111.9 , -112.6 , -113.2 , -113.8 , -114.5 , -115.0 , -115.8 and -116.9 ppm. The peaks at -114.5 and -115.0 were quite clear when no line broadening was used to obtain the spectrum. A detailed correlation between the peaks from the treated samples with those from the calcined is not possible at this stage but some general comments can be made. The spin-lattice relaxation times are increased in some of the treated samples. Benzene has no additional effect (there

is a slight effect of saturation for both the calcined and benzene samples) but the effect of ethanol, propanol, and decane is quite significant and accurate measurements of T_1 are required. There is clearly an overall shift to higher field values and this increase in shielding is most pronounced for the sample containing benzene where a substantial fraction of the silicon atoms have a chemical shift around -119 ppm. The low field peak at -109.8 ppm in the calcined sample is not observed in any of the treated samples, and there is a general decrease in intensity and a possible shift in position of the main line at -113.8 ppm when organic molecules are present in the channel system. Water, which can enter the channels, and trimethylbenzene, which cannot enter, cause no major changes in the spectrum. The ethanol spectrum shows two main peaks at -113.7 and -114.6 ppm and smaller peaks at -111.4 , -116.1 , -116.8 and -118.4 ppm. In propan-1-ol a peak is still observed at -114.6 ppm and the larger low field peak is now at -113.4 ppm. The main change however is the appearance of a large peak at -115.9 ppm, the intensity of which has increased at the expense of the lower field peaks when compared with the spectrum from the ethanol sample. The spectrum from the *n*-decane sample is similar to that from the propan-1-ol sample. The two main peaks, at -113.6 and -116.5 ppm with shoulders at -112.0 and -118.4 ppm, seem to be generally broader so that fine structure is not so evident. A small peak at -118.4 ppm in the alcohol and the decane samples represents the most shielded silicons in these systems.

Peaks occur in the spectrum from the benzene sample at -111.8 , -112.9 , -115.1 , -115.9 , -117.0 , -118.8 and -119.4 ppm, and four of them (viz. -111.8 , -112.9 , -115.9 , -117.0 ppm) are in a similar position to four peaks in the calcined sample. The main peak at -113.8 ppm in the calcined sample has been replaced by a broad peak at -115.1 ppm and two peaks at -119 ppm and this suggests that roughly one-third of the silicon atoms are unaffected by the benzene molecules while quite significant and varied shielding is imposed on the remaining two-thirds.

In summary, this work demonstrates that a variety of organic molecules in the silicalite channel system cause significant changes to the ^{29}Si n.m.r. spectrum. These changes are similar in magnitude to those associated with different structural units and care need be taken to eliminate the effects of sorbed molecules when assigning these spectra to specific sites in the silicalite structure.

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