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MULTITECHNIQUE ANALYSIS OF THE LATTICE STRUCTURES OF HIGHLY SILICEOUS ZEOLITES

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ABSTRACT

The combined use of high-resolution solid state NMR techniques (both 1D and 2D) with synchrotron-based powder x-ray diffraction studies yields detailed information on the lattice structures of highly siliceous zeolites. The two methods are complementary, the former probing short range ordering and structures while the latter is sensitive to long range orderings and periodicities.

INTRODUCTION

Structural investigations of zeolites are hindered by two factors. Firstly, although they are highly crystalline, they are usually microcrystalline with dimensions of the order of microns precluding the straightforward application of single crystal diffraction techniques. Secondly, the distribution of Si and Al over the T-sites in the lattice is often disordered in nature and only an average structure can be obtained. Although the data from powder refinements can be greatly improved by the use of synchrotron X-ray sources and Rietveld analysis techniques¹ and single crystal investigations of microcrystallites may also be possible using synchrotron X-ray sources in the future,² at present combined information from a variety of techniques is necessary to deduce the lattice structures of these materials. In this regard, high-resolution solid-state NMR spectroscopy has emerged in recent years as an important complementary technique to diffraction investigations,³ reflecting as it does local environments and short range orderings compared with the long range orderings and periodicities to which diffraction techniques are most sensitive. In the present work we present several examples of the combined use of these techniques in the investigation of the lattice structures of highly siliceous analogs of zeolites.

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In the ^{29}Si MAS NMR spectra of highly siliceous zeolites, sharp resonances are observed whose numbers and relative intensities reflect the numbers and relative populations of the crystallographically inequivalent sites in the unit cell and whose frequencies (chemical shifts) reflect the local geometries of the T sites.⁴ The amount of information which can be obtained from these spectra depends ultimately on the resolution of the spectra and we have paid careful attention to the important factors determining the spectral linewidths. By careful hydrothermal treatment which effects both aluminium removal and the healing of lattice defects and by optimizing all of the spectroscopic variables in the NMR experiment it is possible to obtain ultra-high resolution ^{29}Si MAS NMR spectra where the linewidths of the resonances in some cases approach those of solution spectra. As an example of improvements which can be achieved by these procedures, the ^{29}Si MAS NMR spectrum of zeolite ZSM-5 at ambient temperature is shown in Figure 1. The linewidths are $\sim 6\text{ Hz}$ ($\sim 0.07\text{ ppm}$) which makes it possible to resolve between 20 and 22 of the 24 expected resonances depending on the exact temperature and confirms the monoclinic symmetry of the crystal structure.⁵ Excellent resolution has also been achieved with samples of zeolites Y, A, beta, mordenite, ZSM-11, ZSM-12, KZ-2 and others.

Figure 1. ^{29}Si MAS NMR spectrum of highly crystalline ZSM-5, 0.0 Hz linebroadening.

RESULTS AND DISCUSSION

This improved resolution when combined with synchrotron x-ray powder data gives quite detailed information on the lattice structures. For example, the ^{29}Si MAS NMR spectrum of zeolite ZSM-12 (Figure 2A) shows seven narrow resonances of exactly equal intensity indicating seven symmetrically inequivalent silicon atoms in the unit cell.⁶ This is in general agreement with the structure proposed by La Pierre et al.⁷ However, synchrotron x-ray data collected on exactly the same sample indicate a doubling of the c-parameter from 12.16Å to 24.33Å, the others being unaffected. Since the NMR experiment unambiguously showed that there was a maximum number of 7 symmetrically inequivalent Si sites per unit cell, only space group C2/c remained for the refinement of the structure. (Figure 2B) Assuming this

Figure 2.a. ^{29}Si MAS NMR spectrum of highly siliceous Zeolite ZSM-12, 0.0Hz linebroadening.
b. Projection of the ZSM-12 framework along [010].

space group symmetry, the structure refined to an R factor of ~ 5.4% with all bond lengths and angles within reasonable limits.⁸ In the case of ZSM-5, the increased resolution makes it possible to detect and to quantify changes in the lattice structure induced by temperature and sorbed organic molecules (Figure 3).⁹ In both cases, there is an induced phase transition from monoclinic (24 T-sites) to orthorhombic (12T-sites). In the case of temperature variation there is a relatively sharp transition over a few degrees between 355 K and 359 K. The addition of p-xylene however, causes a

Figure 3. Effect of temperature and sorbed organics on the ^{29}Si MAS NMR spectrum of zeolite ASM-5. A. 393K B. 298K, 10 μL p-xylene/250 mg. C. 298K, 35 μL pyridine/250 mg D. 298K, 20 μL acetylacetone/250 mg.

gradual increase in the proportion of orthorhombic form present, both phases co-existing and highly ordered. The change is complete when approximately 1.6 molecules per unit cell have been sorbed. By ensuring that the experimental data are quantitatively reliable and by permutating the combined effects of temperature and sorbed p-xylene, concentration. A complete three dimensional phase diagram can be constructed as shown in Figure 4.9. The lower planar area shows the relatively limited regime where the monoclinic form is stable while the upper area corresponds to the stability range of the orthorhombic form for this sorbate. Similar experiments can be carried out with other sorbates. It is now possible to use the NMR data to choose the exact conditions under which x-ray data will be most informative. Thus synchrotron x-ray powder data have been collected at the points on the phase diagram indicated by arrows.¹⁰ The high temperature form with no sorbed p-xylene refines to $R = 5\%$ in the space group $Pnma$ with appropriate bond lengths and angles. The other data sets are currently under refinement.

Figure 4. A three-dimensional surface of the crystallographic phase relationship between the concentration of p-xylene (increasing left to right) and temperature (increasing front to back). The vertical axis gives sites in the unit cell) phase present. The solid line going left to right shows the effect of increasing p-xylene concentration upon the crystal symmetry at ambient temperature. The near vertical solid line at 355 K shows the effect of temperature on an unloaded ZSM-5 sample. The solid circles are selected experimental results from the MAS NMR data, and the dotted curves joining them show variation with p-xylene concentration at constant temperature (left to right) and variation with temperature at constant p-xylene concentration (front to back). (B) A two-dimensional projection of part A as indicated showing the relationship of the orthorhombic and monoclinic crystallographic phases with varying temperature and concentration of p-xylene.

Further information on the nature of the interaction and improved diffraction data can be obtained from NMR investigations of the effect of substituting the methyl groups in p-xylene with chlorine atoms which are known from physical organic chemistry to have identical steric interactions but differ in all other aspects. Figure 5 shows that the ^{29}Si MAS NMR spectra of ZSM-5 loaded with p-xylene, p-chlorotoluene and p-dichlorobenzene are almost identical indicating that, at least for hydrocarbons, the substrate-lattice interactions are based on size and shape alone.¹¹ Confirmation of this conclusion comes from the fact that the three-dimensional phase diagrams for p-xylene and p-dichlorobenzene are identical when the concentrations are expressed in molecules/unit cell. These data may now be used as a justification for using the p-dichlorobenzene system as an exact model for the p-xylene/ZSM-5 structure and synchrotron x-ray data have been collected on this system. The advantage of the former system is that the p-dichlorobenzene sorbate makes a much larger contribution

Figure 5. ^{29}Si MAS NMR spectra obtained at 79.6 MHz of highly siliceous ZSM-5 with A p-xylene (10 μl /250 mg zeolite, B p-chlorotoluene (10 μl /250 mg zeolite); C. p-dichlorobenzene (10 mg/250 gm zeolite).

to the overall scattering due to the substantial electron density on the chlorine atoms. This refinement is in progress and when complete should provide the most detailed structural information on the nature of the host/guest interactions which induce the phase-transition of the lattice.¹⁰

Other structural investigations may be complicated by temperature induced phase transitions. Thus, Figure 6 shows the variable temperature ^{29}Si MAS NMR spectra of a pure sample of zeolite ZSM-11 synthesized free of any intergrowths of ZSM-5 in our laboratory.¹² Narrow resonances are observed in all of the spectra indicating a high degree of crystallinity and local order. The postulated lattice structure space group has seven inequivalent sites of relative proportions 1:1:2:2:2:2:2.¹³

Figure 6. ^{29}Si MAS NMR spectra (79.6 MHz) of zeolite ZSM-11 recorded at the temperatures indicated. Each spectrum is the result of 720 scans with a delay time of 10S.

Inspection of Figure 6 shows that there are too many resonances in the room temperature (293K) spectrum and in fact the system is in an intermediate state between two limiting structures at ambient. Using the data of Figure 6 as our guide, synchrotron powder x-ray data have been obtained in the high and low temperature limits. Data obtained at 373K refined smoothly ($R=4.4\%$) in the tetragonal space group $I4m2$ yielding the postulated structure with reasonable values for all bond lengths and angles.¹³ Refinement of the low temperature limiting structure is currently in progress.⁹ The relative intensities of the limiting high temperature spectrum are in exact agreement with the postulated structure while those of the low temperature form indicate a lowering of the symmetry of the lattice with a basic structural unit which still contains a total of twelve T-sites.

In high-resolution NMR studies in solution, two dimensional NMR spectroscopy has made it possible to detect two dimensional connectivities between bonded atoms from the through-bond interactions between the nuclei.¹⁴ In principle, at least, it should be possible to carry out such measurements in the solid-state and probe the bonding within a zeolite lattice. We have recently extended our NMR investigations of these systems by showing for the first time that three-dimensional lattice connectivities can be established using two-dimensional solid-state NMR techniques.¹⁵

In order to test the validity and reliability of the experiments, a system of known structure (zeolite ZSM-39) was chosen and synthesized in the completely siliceous form from SiO_2 enriched in ^{29}Si to approximately 80%.

The ZSM-39 high temperature structure (space group $Fd3$) contains three crystallographically inequivalent sites T_1 , T_2 , and T_3 with relative proportions 8:32:96 and is shown schematically in Figure 7.^{16,17} At room

Figure 7. Schematic representation of the lattice structure of ZSM-39. The three T-sites T_1 , T_2 and T_3 are shown circled and the nature of the attached T atoms indicated.

temperature, the symmetry is lower and the degeneracy of the T_3 site is lifted, giving three resonances of intensities 32:32:32. The solid state ^{29}Si MAS NMR spectrum shown at the top of Figure 8 clearly reflects the asymmetric unit in the lattice, the assignments of the resonances being unambiguous from the known site occupancies. In the present work we will interpret the interactions as being, to a first approximation, between the three sites T_1 , T_2 , and T_3 . From the structure shown in Figure 7, it can be seen that there are direct Si-O-Si connections between T_1 and T_2 and also between T_2 and T_3 but none between T_1 and T_3 .

Figure 8. ^{29}Si MAS NMR spectrum of the ^{29}Si enriched sample of ZSM-39 used in the 2D NMR experiments.

Figure 9 shows the result of a ^{29}Si 2D NMR spin diffusion experiment¹⁸ carried out using the parameters given in the figure caption. The attraction of this experiment, analogous to the NOESY technique in solution lies in the strong dependence of the interaction on the through-space internuclear distance ($1/r^6$ if there is motion and $1/r^3$ if there is not). Because of the large differences in internuclear distance between "directly" connected silicons and others further removed ($\sim 3 \text{ \AA}$ for $^{29}\text{Si-O-}^{29}\text{Si}$ vs $\sim 5.5 \text{ \AA}$ for $^{29}\text{Si-O-Si-O-}^{29}\text{Si}$) it was hoped that they would be clearly differentiated. Figure 8 shows that the expected connectivities T_1T_2 and T_2T_3 are clearly observed while that between T_1 and T_3 is not seen. Although this result is encouraging and certainly merits further investigations, we feel that some caution should be used in the interpretation of data of this type as the theoretical description of the interactions involves additional contributions from non-distance dependent parameters, namely the chemical shift anisotropies and the isotropic shift differences of the interacting nuclei

whose importance is difficult to estimate.¹⁹ Further experiments on systems of known structure will be needed to properly establish whether experiments of this type are reliable probes of lattice connectivities in these systems.

Figure 9. Contour plot of ^{29}Si 2D-spin diffusion experiment on ZSM-39 with 128 experiments, 8 scans in each experiment, sweepwidth of 5 kHz and 256 data points collected during acquisition. The fixed delay during which spin diffusion occurs was 10 sec., the spinning rate 2 kHz and the total time for the experiment approximately 6 hours. Sine bell squared apodization was used and the plot has been symmetrized.

An alternative and more reliable and unambiguous method is the COSY technique²⁰ which relies on the scalar couplings between the interacting nuclei which operate through the bonding electrons. ^{29}Si -O- ^{29}Si connectivities within the reference molecule Q8M8 have recently been demonstrated by Benn et al.²¹ The results of a 2D COSY experiment on the ZSM-39 sample are presented in Figure 10. The sequence was identical to that used in solution studies except that the initial preparation step was a

cross-polarization sequence²² and the experiment was carried out using the conditions given in the figure caption. Again, the connectivities T_1T_2 and T_2T_3 are exactly those expected and in this case the result is quite unambiguous.¹⁵

Figure 10. Contour and stacked plots of a 2D COSY experiment on ZSM-39 at 373K. 128 Experiments, 64 scans in each experiment, 5 kHz sweepwidth, 256 data points on acquisition and a fixed delay of 5 m.sec. Sine bell apodization was used and the data are presented without symmetrization or smoothing. The total experimental time was approximately 23 hours.

Although the two dimensional experiments described above are very time consuming and demanding in terms of both sample preparation and spectroscopy, they greatly extend the potential of the technique in the investigation of zeolite lattice structures and provide information not obtainable by other means. Further work in this area is in progress including the development of an experimental protocol to obtain such data on natural abundance samples.

Thus, considerable insight into the structures of zeolites can be obtained by the combined use of solid state NMR and diffraction techniques. The two are complementary in nature and should always be used together preferably on the same sample to obtain the maximum information.

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REFERENCES

- 1a. McCusker, L.B.; Baerlocher, C. Proc. Sixth Int. Conf. Zeolites, Reno, 1983.
- b. Rietveld, H.M., J. Appl. Cryst., 1969, 2, 65.
2. Eisenberg, P.; Newman, J.B.; Leonowicz, M.E.; Vaughan, D.E.W. Nature, 1984, 309, 45.
3. Englehardt, G.; Michel, D., High Resolution Solid State NMR of Zeolites and Related Systems, John Wiley & Sons, (1987).
- 4a. Fyfe, C.A.; Gobbi, G.C.; Murphy, W.J.; Ozubko, R.S., and Slack, D.A., Chem. Lett. 1983, 1547.
- b. Fyfe, C.A.; Gobbi, G.C.; Murphy, W.J.; Ozubko, R.S., and Slack, D.A., J. Am. Chem. Soc. 1984, 106, 4435.
5. Fyfe, C.A., O'Brien, J.H.; and Strobl, H., Nature, 1987, 363, 6110.
6. Fyfe, C.A.; Strobl, H.; Kokotailo, G.T.; Pasztor, C.T.; Barlow, G.E.; Bradley, S.; Zeolites, 1988, 8, 132.
7. LaPierre, R.B. et al Zeolites 1985, 5, 346.
8. Gies, H.; Marler, B; Fyfe, C.A.; Kokotailo, G.T., Cox, D.E. unpublished results.
9. Fyfe, C.A.; Strobl, H., Kokotailo, G.T.; Kennedy, G.J.; and Barlow, G.E., J. Am. Chem. Soc. 1988, 110, 3373.
10. Gies, J.; Fyfe, C.A.; Strobl, H.; Kokotailo, G.T.; Feng, Y.; Cox, D.E.; Unpublished results.
11. Fyfe, C.A.; Gies, H.; Kokotailo, G.T.; Pasztor, C.; Strobl, H.; Cox, D.E., Can. J. Chem. (1988), 66, 1942.

- 12a. Fyfe, C.A.; Kokotailo, G.T.; Kennedy, G.J.; and De Schutter, C.T., J. Chem. Soc. Chem. Commun. 1985, 306.
- b. Fyfe, C.A.; Gies, H.; Kokotailo, G.T.; Pasztor, C.; Strobl, H.; Cox, D.E., J. Amer. Chem. Soc. (In press).
Kokotailo, G.T.; Chu, P.; Lawton, S.L., and Meier, W.M., Nature, 1978 275, 119.
- 14a. Benn, R. and Gunther, J., "Modern Pulse Methods in High Resolution NMR Spectroscopy", Angew. Chem. Int. Ed. Engl. 22, 250 (1983).
- b. Bax, A., "Two Dimensional Nuclear Magnetic Resonance in Liquids", Delft University Press (1982).
- c. Delorme, A.E., "Modern NMR Techniques for Chemistry Research", Pergamon Press (1987).
- d. Sanders, J. And Hunter, B., "Modern NMR Spectroscopy, A guide for Chemists", Oxford University Press (1987).
15. Fyfe, C.A.; Gies, H.; Geng, Y.; submitted.
16. Schlenker, J.L., Dwyer, F.G., Jenkins, E.E., Rohrbaugh, W.J. Kokotailo, G.T.; and Meier, W.M., Nature, 1981, 294, 340.
17. Gies, H.; Liebau, F.; Gerke, H.; Angew. Chem., 1982, 94, 214. Gies, H.; Z. Kristallogr., 1984, 167, 73.
18. Szeverenyi, N.M.; Sullivan, M.J.; Maciel, G.E.; J. Mag. Res., 1982, 47, 462.
- 19a. Vanderhart, D.L.; J. Mag. Res., 1987, 72, 13.
- b. Kubo, A.; McDowell, C.A.; J. Chem. Soc. Farad. Trans I, 1988, 84, (In press).
20. Muller, L.; Kumar, A.; Ernst, R.R.; J. Chem. Phys., 1975, 63, 5490.
21. Benn, R.; Grandey, H.; Brevard, C.; Pagelot, A.; J. Chem. Soc. Chem. Commun., 1988, 102.
22. Pines, A.; Gibby, M.G.; Waugh, J.S.; Chem. Phys. Lett., 1972, 15, 273.