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^{29}Si MAS NMR Studies of a High Silica Form of the Novel Molecular Sieve: MCM-22

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Abstract: MCM-22 is a new molecular sieve that contains unique structural features. ^{29}Si MAS NMR studies of a highly siliceous MCM-22 prepared by the hydrothermal treatment of a [B]MCM-22 are presented and discussed in light of the proposed framework topology. The structural information obtained from this NMR investigation is complementary to and consistent with the structure proposed from X-ray diffraction measurements. The major conclusions of this present work are that MCM-22 contains at least one *buried* T-site in its framework structure that is not accessible to a channel wall and that the NMR data favor the orthorhombic form of the proposed structure.

Introduction

Molecular sieves are microporous framework structures of tetrahedral (T) atoms (such as Si, Al, P, and B) interconnected in three dimensions through oxygen atoms.[1] The dimensions of the pore structures give them unique size and shape selectivity resulting in widespread commercial use in the petrochemical and refining industries as sorbents and catalysts.[2] Although they are highly crystalline materials, their inherently small crystal size precludes the use of single-crystal diffraction techniques for structural elucidation. Structural characterization of molecular sieve crystals is usually carried out with the use of powder diffraction techniques combined with Rietveld refinement techniques.

High-resolution solid-state NMR spectroscopy is recognized as an important and sometimes indispensible complementary technique to traditional diffraction methods.[3] NMR is sensitive to short-range ordering, local geometries, and local symmetry, whereas diffraction studies average much longer range periodicities and ordering. For example, the ^{29}Si MAS NMR spectra of low Si/Al ratio molecular sieves are comprised of several resonances corresponding to the five possible first coordination sphere environments for a silicon atom in the framework (i.e. Si(4Al), Si(3Al,1Si), Si(2Al)(2Si), Si(1Al)(3Si), and Si(4Si)). Except for the few cases of completely ordered, low Si/Al ratio materials, this microdistribution of framework T atoms cannot be obtained from the average framework structures determined by X-ray methods. For the case of completely siliceous systems a more direct relationship exists between the ^{29}Si MAS NMR spectra and the framework structure. The removal of Al (or any other framework atom) to produce a completely siliceous framework generates a perfectly ordered lattice in which each silicon atom has the same local environment, Si(4Si). Thus, for structures with more than one crystallographic site, a series of much sharper resonances is observed whose numbers and intensities *directly* reflect the numbers and relative occupancies of crystallographic inequivalent T atoms in the unit cell of the framework. Thus, the ^{29}Si MAS NMR spectra of highly siliceous molecular sieves can be used as a very sensitive probe of the unit cell contents at the atomic level. In addition, it has been demonstrated by Fyfe et al.[4−11] that two-dimensional ^{29}Si MAS NMR experiments can be used to determine T−O−T connectivities in highly siliceous zeolites.

MCM-22 is a new molecular sieve[12] with unique and unusual structural characteristics.[13] The recent presentation of its framework topology,[13] which included detailed structural drawings derived from high-resolution electron micrographs and synchrotron X-ray diffraction powder data, has shown MCM-22 to be comprised of two independent pore systems, both accessible through 10-membered rings. One of these pore systems is defined by two-dimensional, sinusoidal channels. The other consists of large supercages whose inner free diameter, 7.1 Å, is defined by 12-membered rings with inner height of 18.2 Å. The novelty of the MCM-22 framework is further underscored by the presence of a very unusual T−O−T chain passing through the center of a modified dodecasil-1H (DOH) [$4^35^66^3$] cage resulting in a framework tetrahedral atom being "buried" inside the cage.

^{29}Si MAS NMR experiments on highly siliceous MCM-22 are of fundamental interest because they can provide complementary structural information to that determined by diffraction techniques. Of particular relevance and importance in the characterization of this new framework material is the direct determination of subtle structural features with NMR such as local symmetry, the minimum number of independent T sites per unit cell, their relative populations, and the accessibility of these T sites to channel walls. These structural features can be studied in highly siliceous, crystalline samples.

In this contribution we report the preparation of a highly siliceous MCM-22 and its characterization with high-resolution

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^{29}Si MAS NMR. The structural information obtained from this NMR investigation is complementary to and consistent with the structure proposed from X-ray diffraction measurements and provides further insight into the local geometries of this unique material. The NMR data (i.e. number of peaks, individual peak intensities, and chemical shifts) favor the orthorhombic form of the proposed structure. The NMR data also show that MCM-22 contains one "buried" T site in its framework structure, as previously proposed from the refinement of the X-ray diffraction data, that is not accessible to a channel wall.

Experimental Section

Sample Preparation. The boroaluminosilicate version of MCM-22 used in this study was synthesized as previously described.[12] Highly siliceous MCM-22 was prepared by the hydrothermal treatment of the parent MCM-22 that had been calcined at 538 °C (1000 °F) for 16 h to remove the organic directing agent. The dealumination/deboronation was carried out using the same basic procedure that has been used previously to successfully dealuminate many other zeolites.[14-16] A 0.5 g sample of the parent was refluxed overnight in 100 mL of 2 M NH_4Cl, filtered, washed with 500 mL of water, and then dried at 100 °C for 1 h. Approximately 0.25 g of this washed sample was placed inside a quartz tube in a vertical tube furnace. The temperature was then ramped at 5 °C/min to a final temperature of 850 °C where it was held for 8 days. The furnace was then turned off and allowed to return back to room temperature. Air saturated with water at atmospheric pressure was passed through the quartz tube and over the zeolite sample throughout the course of this heating cycle. The structural integrity of the sample is of paramount importance for these NMR experiments in order to optimize spectral resolution. XRD analysis of the steamed sample confirmed that it retained the framework topology of MCM-22 and had not suffered any loss in crystallinity.

NMR Procedures. ^{29}Si MAS NMR spectra were obtained on a Bruker AM-500 spectrometer at 99.35 MHz with ~4.5 kHz spinning speed, 5 μs excitation pulses ($\pi/2 = 8$ μs), and a 60 s recycle time. The ^{29}Si chemical shifts were referenced to TMS using a secondary standard of high silica sodalite at $\delta = -117.42$ ppm. The magic angle was accurately adjusted prior to data acquisition using KBr that had been added directly to the samples.[17] The spin−lattice relaxation time characteristics of MCM-22 were investigated with a progressive saturation $(90-\tau)_n$ technique.[18]

Discussion

Shown in Figure 1 are the ^{29}Si MAS NMR spectra of this highly siliceous MCM-22 sample and the H^+ form of the corresponding starting material. The spectrum of the parent is comprised of several overlapping resonances arising from the combined effects of crystallographic site inequivalence and the number of nearest neighbor aluminum or boron atoms on the ^{29}Si chemical shifts. The improved resolution in the steamed sample is due to removal of the effect of the distribution of nearest neighbor atoms on the observed chemical shifts. Since the framework T sites of the steamed sample are now completely occupied by Si, the observed spectrum is now due to crystallographic inequivalent framework atoms. The high level of spectral resolution in the steamed sample indicates that there are at least seven peaks corresponding to crystallographically distinct T sites. The area under each of these resonances directly relates to the population of the corresponding T site(s). The relative areas of these peaks can be obtained by deconvoluting the experimental spectrum in terms of overlapping Lorentzian lines.

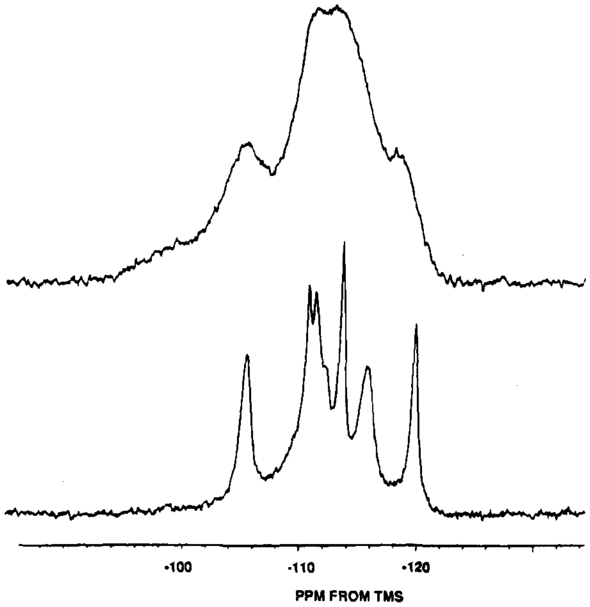

Figure 1. ^{29}Si MAS NMR spectra of H-MCM-22 (top) and siliceous MCM-22 (bottom).

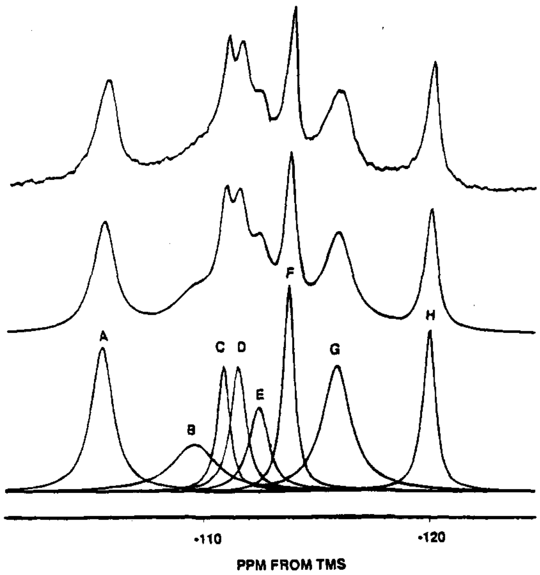

Figure 2. ^{29}Si MAS NMR spectra of highly siliceous MCM-22. (top) experimental; (middle) simulated; (bottom) components used in simulation.

Shown in Figure 2 from top to bottom are the experimental spectrum, simulated spectrum, and individual peaks used in the simulated spectrum for the siliceous MCM-22. The best fit to the experimental data was obtained by deconvoluting in terms of eight overlapping peaks as shown in the figure. A broad peak centered at −110 ppm from TMS was included in this simulation in order to fit the experimental data. This peak (labeled B in the figure) is probably associated with amorphous silica that could be inherent to the starting material and/or formed during the hydrothermal treatment. The other seven peaks correspond to crystallographically distinct T sites within the unit cell of MCM-22. However, the widths of some of the resonances suggest that they may be comprised of other narrower, overlapping resonances.

The spectra in Figures 1 and 2 indicate that the chemical shift range for MCM-22 is unusually large for a zeolite. For example, the 24 sites in the monoclinic form of ZSM-5 resonate over a chemical shift range of less than 8 ppm (from ca. −109.5 to ca. −117 ppm)[10] and the 7 sites in highly siliceous ZSM-12

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Table 1. Crystallographic Data for Framework Atoms in MCM-22

site	occupancy	av T−O−T angle, deg	site	occupancy	av T−O−T angle, deg
		A. Hexagonal Form			
T_1	1	153.8	T_5	1	154.5
T_2	3	143.0	T_6	3	161.5
T_3	3	150.5	T_7	3	158.5
T_4	1	153.8	T_8	3	154.8
		B. Orthorhombic Form			
T_1	1	147.5	T_8	1	157.0
T_2	1	139.0	T_9	2	152.8
T_3	1	148.5	T_{10}	2	151.0
T_4	1	149.5	T_{11}	1	162.8
T_5	2	144.0	T_{12}	1	149.5
T_6	2	142.5	T_{13}	2	143.5
T_7	1	150.0			

occur in a chemical shift range of approximately 5 ppm (from ca. −107.9 to −112.9 ppm).[8] However, as shown in Figures 1 and 2, the Si nuclei of individual T sites in MCM-22 resonate in a chemical shift range in excess of 15 ppm. This large chemical shift range indicates that an uncharacteristically large distribution of crystallographic environments exists in the MCM-22 structure, further substantiating the novel structure proposed by X-ray diffraction.[13]

The spectrum of the highly siliceous sample is a sensitive probe of the unit cell contents at the atomic level and can be directly related to the data from X-ray structural determinations. Presently, there are two proposed space groups for the structure of MCM-22 determined from X-ray diffraction studies.[13] The orthorhombic *Cmmm* structure is energetically favored over the hexagonal *P6/mmm* structure. Listed in Table 1 are the individual framework T atoms, their relative occupancies, and average interatomic angles for each of the two models. Thus, in the hexagonal form of the proposed structure of MCM-22 there are 8 T sites in the ratio of 1:3:3:1:1:3:3:3 and in the orthorhombic form there are 13 T sites in the ratio of 1:1:1:1: 2:2:1:1:2:2:1:1:2. The relative intensities of the 7 resonances (excluding peak B assigned to nonframework silica) are approximately 3:2:2:2:3:4:2. In light of the probability of peak overlap or degeneracies, these observed NMR peak intensities are consistent with the orthorhombic form of the structure.

Additional information to help differentiate one space group over the other can be obtained by combining the NMR data with geometric data from the diffraction studies. The differences observed in the chemical shifts reflect differences in the local magnetic environments of the individual silicon atoms. It has been shown that qualitative correlations exist between ^{29}Si chemical shifts and geometric data, such as average T−O−T angles, for zeolites.[19−25] It is important to note that correlations of this type must be used with caution because they are derived from structural parameters that vary over a limited range. Thus they cannot be used with a high degree of confidence to assign individual ^{29}Si resonances to distinct T sites. However, these correlations can be used in a qualitative way to discriminate between two possible structures, as in the present case of MCM-22. For example, the predicted range of average T−O−T angles (23.3°) obtained from the correlation in ref 24 is in better agreement with the orthorhombic form (range of 23.8°) than with the hexagonal form (range of 18.5°).

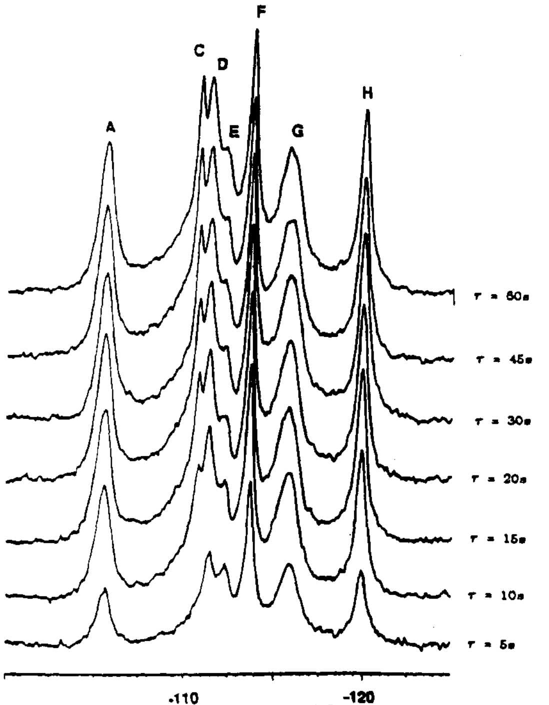

Figure 3. ^{29}Si spin−lattice relaxation time spectra of highly siliceous MCM-22. τ values are indicated on the figure.

Shown in Figure 3 are the ^{29}Si MAS NMR spectra of this sample obtained using a progressive saturation technique to probe the spin−lattice relaxation characteristics of the silicon nuclei. These spin−lattice relaxation time experiments provide additional insight and indicate that individual Si nuclei within the MCM-22 framework relax at differing rates. In particular, peak C at −110.8 ppm from TMS relaxes at a significantly slower rate than the other 6 peaks. The major contribution to the spin−lattice relaxation mechanism in highly siliceous zeolitic systems is interactions of the Si nuclei with molecular oxygen.[26,27] Thus, the longer relaxation time observed for peak C suggests that it is associated with Si nuclei occupying a T site that is not on the channel surface (i.e. not in contact with adsorbed oxygen) and is "buried" inside the three-dimensional framework of the MCM-22 structure. This spin−lattice relaxation phenomenon was also reported for highly siliceous ZSM-12[8] and used to assign the resonance associated with the buried T_5 site in ZSM-12. Thus, this observation in MCM-22 confirms that there is a buried T site in the framework[13] and indicates that peak C can be unambiguously assigned to T_3 in the orthorhombic structure or similarly to T_4 in the hexagonal form. Of course, intensity data show that at least one other T site with a very similar chemical shift contributes to peak C.

Interestingly, the predicted chemical shift for T_3 in the orthorhombic form is −110.6 ppm and for T_4 in the hexagonal form it is −113.9 ppm versus the observed experimental value of −110.8 ppm. Although, as noted above, it is accepted that these correlations should only be used in a qualitative sense and not to make definitive peak assignments, it is tempting to use this observation as another piece of evidence favoring the orthorhombic form over the hexagonal.

The tentative NMR peak assignments shown in Table 2 for the orthorhombic form of MCM-22 were made on the basis of the observed peak intensities, spin−lattice relaxation time behavior, and the qualitative relationship between average T−O−T angles and ^{29}Si chemical shifts. These assignments

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Table 2. Tentative Peak Assignments for the ^{29}Si MAS NMR Spectrum of Highly Siliceous MCM-22[a]

peak	chemical shift	rel area	assign
A	−105.5	3	$T_2 + T_6$
C	−110.8	2	$T_3 + T_1$
D	−111.5	2	T_{13}
E	−112.4	2	T_5
F	−113.7	3	$T_4 + T_7 + T_{12}$
G	−115.8	4	$T_9 + T_{10}$
H	−119.9	2	$T_8 + T_{11}$

[a] Peak assignments are tentative and are based on the observed peak intensities, spin−lattice relaxation time behavior, and a qualitative correlation between ^{29}Si chemical shifts and T−O−T angles in ref 24. Further work is in progress to establish definitive peak assignments.

are preliminary and are subject to revision. Two-dimensional NMR experiments to establish Si−O−Si connectivities would provide definitive peak assignments and unambiguous discrimination between the two proposed structures. Experiments of this nature were unsuccessful on this particular sample and a sample exhibiting a higher degree of spectral resolution would be required to make definitive peak assignments. Based on published work on other systems,[4−11] the NMR line widths in MCM-22 would have to be a factor of 3 or 4 narrower in order to obtain 2D NMR data. When such a sample becomes available, 2D connectivity experiments will be conducted.

Conclusions

NMR work done on a highly siliceous MCM-22 sample confirms that there is at least one "buried" T site in the framework structure that is not accessible to the channel surface. The relative peak intensities favor the proposed orthorhombic form of the structure. Qualitative correlations between geometric data obtained from X-ray diffraction studies (average T−O−T angles) and ^{29}Si chemical shifts provide further support for this conclusion. Further work involving 2D ^{29}Si MAS NMR is necessary to establish T−O−T connectivities and peak assignments.