*Chem. Mater.* **1997,** *9,* 1927−1932

# *Articles*

## $^{29}$Si$^{27}$Al and $^{1}$H Solid-State NMR Study of the Surface of Zeolite MAP

Stuart W Carr[*,†]

*Unilever Research, Quarry Road East, Bebington, Merseyside L63 3JW, UK*

Barbara Gore and Michael W Anderson

*Department of Chemistry, UMIST, PO Box 88, Manchester, M60 1QD, UK*

*Received October 24, 1995. Revised Manuscript Received September 27, 1996*[⊗]

Zeolite MAP (maximum aluminum P) is a zeolite of the gismondine family that has recently found utility as an ion exchanger for water softening in detergents applications. It is composed of spherical agglomerates of small crystallites which have appreciable external surface area. A combination of $^{27}$Al and $^{29}$Si single-pulse and cross-polarization MAS NMR experiments have been used to elucidate the nature of the surface of zeolite MAP. The $^{29}$Si experiments given an external surface area of approximately 8% of the total, which is consistent with that expected based the calculated particle size. The $T_{cp}$ is similar to amorphous aluminosilicates while the $T_{1\rho}$ values are significantly different, indicating protons with a different type of mobility. The $^{1}$H NMR is consistent with the silanols being located on the external surface of the crystallites.

### Introduction

In the late 1970s zeolite 4A was developed as a replacement water softener for detergent products where restrictions were placed on the use of phosphates. Zeolite 4A was chosen from a group of over 30 natural and more than 90 synthetic zeolites.[1,2] It was selected on the basis of its easy preparation, maximum ion-exchange capacity, and cost. Zeolite 4A, which is composed of sodalite cages connected by double 4-rings, typically consists of 3−5 μm cuboidal-shaped crystals. As a consequence its properties are dominated by the bulk properties with little contribution from the external surface of the zeolite. Recently zeolite MAP has been developed as an alternative zeolite 4A because of its improved ion-exchange behavior and water sorption properties and is being produced on a multithousand tone scale.[3,4,5] Zeolite MAP is a member of the GIS[6] family of zeolites, which includes natural analogues of the type gismondine,[7] amicite,[8] gobbinsite,[9] and garronite.[10] The structure of zeolite MAP[6,11] has been described as doubly connected crank-shaft chains composed of four-membered rings. The framework is very flexible and is known to undergo distortion. These distortions depend on a number of factors such as hydration and nature of exchanged cation. For MAP transmission electron microscopy has shown that the primary crystallites consist of 300 × 20−30 Å platelets.[4] These platelets agglomerate during synthesis to give 1 μm spheroidal and highly porous particles. Given the size of the primary crystallites, it is expected that the resultant external surface would contribute to the properties, but to date most of the work has concentrated on looking at the bulk properties of zeolite MAP.

There have been a few studies of external zeolite surface properties and characteristics. The zeolite catalysis literature suggests that the surface properties of zeolites become more important as the size of the crystallites get smaller. There have been several reports of the role of the external surface sites of zeolites mainly with respect to their catalytic activity.[12−16] It has been suggested that for zeolites with an internal-to-external surface area ratio of greater than 300 the contribution of the external surface is negligible. However, for crystals of less than 100 nm diameter the effect of the external surface can contribute to the catalytic activity. This is believed to be especially important for reactions that are rapid or are diffusion limited. The

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[†] Current address: ICI Explosives, P.O. Box 196, Kurri Kurri, 2327, Australia.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1997.

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S0897-4756(95)00510-2 CCC: $14.00

coking of ZSM5 was decreased significantly from smaller particle sizes. The superior ion-exchange kinetics of zeolite MAP has been partially attributed to its small primary crystallite size.[4]

There are a number of literature reports which describe the combined use of $^{29}$Si and $^{27}$Al single-pulse and cross-polarization (cp) MAS NMR experiments to distinguish framework atoms (Q4) from these associated with the presence of hydroxyl groups, typically silanol (Q3) and aluminum hydroxide species. A number of studies have demonstrated that by using a combination of $^{29}$Si cp and single-pulse MAS NMR experiments, it is possible to determine the nature of defect sites within zeolite structures typically as a result of thermal or hydrothermal treatment.[17−23] In the cross-polarization spectra the intensities of the resonances due to silicon atoms bearing OH groups are strongly enhanced. This enhancement factor is sensitive to the Si−H distance and chemically different silicon atom environments in the particular zeolite. In a recent publication a combination of $^{27}$Al single-pulse and cp MAS NMR techniques were used to characterize the non-framework aluminum of dealuminated zeolite Y.[25,27] As the framework aluminum cross polarizes very weakly, it was possible to selectively enhance the nonframework aluminum which contains quantities of Al OH groups.

All of the above studies were performed on zeolite samples (that is, larger crystals) which have a relatively small external surface area. The purpose of this paper is to use these techniques to characterize the external surface of zeolite MAP and to elucidate its structure with respect to the bulk.

## Experimental Section

NMR spectra were collected on a Bruker MSL 400 solid-state NMR spectrometer using double-bearing magic-angle spinning zirconia rotors. $^{29}$Si spectra were recorded with high-power proton decoupling at 79.494 MHz using a 4 $\mu$s $\pi/4$ pulse with a 20 s repetition time. $^{29}$Si−$^{1}$H cross-polarization experiments were performed with a 10.5 $\mu$s $^{1}$H $\pi/2$ pulse, and contact times varying between 1 and 30 ms − 3 s repetition times were used in these experiments. All $^{29}$Si spectra were recorded on samples spun at 3000 Hz in a 7 mm rotor and referenced to TMS. $^{27}$Al spectra were recorded with high-power proton decoupling at 104.262 MHz using a 0.6 $\mu$s $\pi/18$ pulse with a 0.5 s repetition time. $^{27}$Al−$^{1}$H cross-polarization experiments were performed with a 5 $\mu$s $^{1}$H $\pi/2$ pulse, and contact times varying between 1 and 5 ms − 1 s repetition times were used in these experiments. Selective $^{27}$Al pulses were given by keeping the power low in order not to excite satellite transitions. All $^{27}$Al spectra were recorded on samples spun at 10 000 Hz in a 4 mm rotor and referenced to $[Al(H_2O)_6]^-$. $^{1}$H spectra were recorded at 400.13 MHz using a single-pulse experiment with 6.5 $\mu$s $\pi/2$ pulse and 12 s repetition time. Samples were spun at 4000 Hz in a 7 mm zirconia rotor and referenced to TMS. To aid interpretation of the spectra, the number of scans is given in the figure captions.

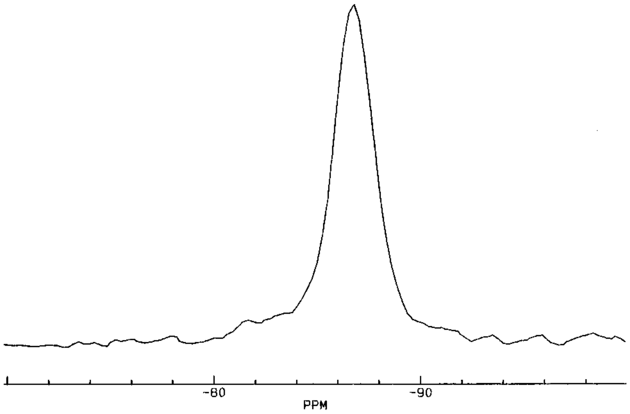

**Figure 1.** $^{29}$Si MAS NMR spectrum of hydrated MAP (500 scans).

Zeolite MAP (Batch RQ149) was obtained from the Crosfield group and was used as received. It was preequilibrated over saturated aqueous ammonium chloride solution. The anhydrous composition as determined by atomic adsoprtion was $Na_{1.1}(AlO_2)(SiO_2)_{1.04}$, and the water content was determined as 24% weight/weight by thermal gravimetric analysis. The X-ray powder diffraction pattern of the hydrated sample was typical of pseudocubic P type zeolite with $a = 10.13$ Å and $c = 9.98$ Å. The dehydrated sample was prepared by heating a thinly spread sample at 400 °C for 3 h and transferred under argon in a drybox to a rotor sealed with Teflon end caps to prevent rehydration.

## Results and Discussion

The $^{29}$Si MAS NMR spectrum of the hydrated MAP sample exhibited one main resonance at −86.6 ppm (Figure 1). This is characteristic of the Si(4Al) resonance of a synthetic zeolite P sample although the reported data is for a more silicous material.[28,29] To the higher frequency side of this resonance a small shoulder ($\approx$−83 ppm) of approximately 5% intensity is observed which is not readily assigned to a Q4 resonance of a P type zeolite but would be consistent with a Q3 [Si(3Al)-OH] environment.[29] Framework silicon atoms should show cross-polarization behavior very different from that of silanol groups. Figure 2 shows the $^{29}$Si cp MAS NMR spectrum of zeolite MAP with a significantly enhanced signal at −83 ppm, consistent with the proposal that this group can be assigned to a silanol group. To further characterize these two resonances a variable contact cross-polarization experiment was performed. The spectra for this experiment are shown in Figure 3. The two resonances exhibit significantly different $T_{1\rho}$ and $T_{cp}$ time constants as illustrated in Figure 4 and shown in Table 1. Although there are many reports[25,26,29] of the use of cross-polarization to

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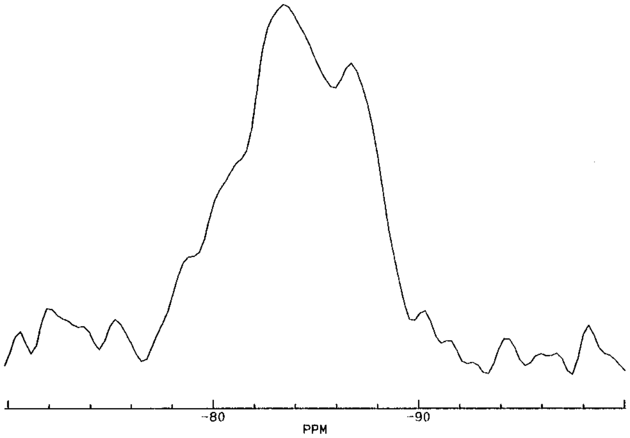

**Figure 2.** $^{29}Si-^{1}H$ CP MAS NMR spectrum of hydrated MAP-(2000scans).

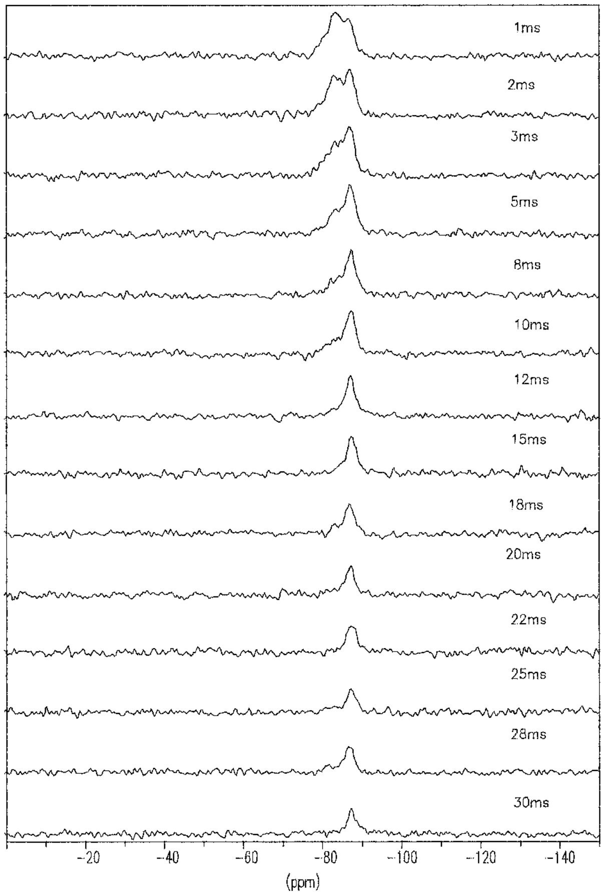

**Figure 3.** Variable contact time $^{29}Si-^{1}H$ CP MAS NMR spectra of hydrated MAP (2000 scans).

characterize zeolites, the only reports of $T_{1\rho}$ and $T_{cp}$[20,23,24] are for the siliceous zeolite ZSM5 (see Table 1). This is a relatively hydrophobic zeolite and would be expected to show a behavior different from that of zeolite MAP. A better comparison is with hydrated amorphous silicas. Typical $T_{1\rho}$ and $T_{cp}$ data are given in Table 1; these data are more similiar to those observed for zeolite MAP.[30,31,32,33] The $T_{cp}$ values compare favorably with MAP, but the different $T_{1\rho}$ indicate that the proton mobility in MAP is significantly different.

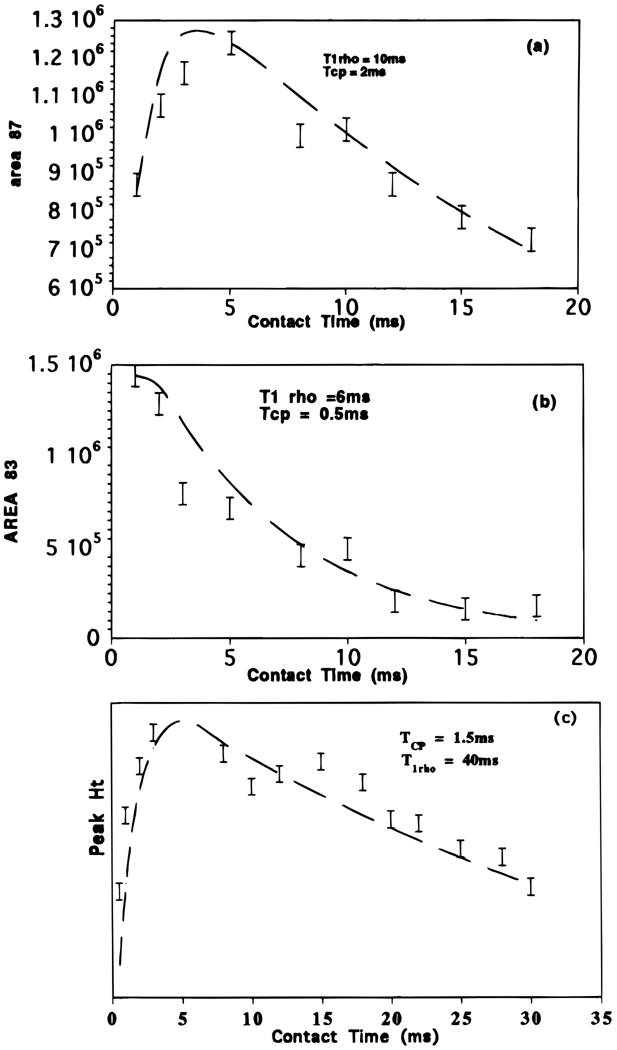

**Figure 4.** Graphical plots of contact time versus signal area for $^{29}Si-^{1}H$ CP MAS NMR for (a) hydrated MAP −86.3 ppm signal, (b) hydrated MAP −83 ppm signal, and (c) dehydrated MAP −80 ppm signal.

**Table 1. $T_{cp}$ and $T_{1\rho}$ (ms) Values for Zeolite MAP and Amorphous Silicas**

| sample (signal) | $T_{cp}$ | $T_{1\rho}$ |
|---|---|---|
| MAP hydrated (−86.6 ppm) | 2 | 10 |
| MAP hydrated (−83 ppm) | 0.5 | 6 |
| MAP dehydrated (−80 ppm) | 1.5 | 40 |
| amorphous silica gel Q3[b] | 1−3 | 15−25 |
| Amorphous silica gel Q4[b] | 2−15 | 15−30 |
| ZSM5 (−113 ppm)[a] | | 51 |
| ZSM5 (−102 ppm)[a] | | 11 |
| TPA ZSM5 (−113 ppm)[a] | | 35 |
| TPA ZSM5 | 4.6 | 80 |
| TPA ZSM5 (low coke) | 3.5 | |

[a] Reference 20. [b] References 30−32.

Several X-ray diffraction studies (powder and single crystal) have shown that P type zeolite framework is flexible and the degree of structural distortion depends on a number of factors including ion-exchangeable cation and the degree of dehydration.[11,34] In MAP, dehydration leads to a lattice contraction and it undergoes a change of symmetry.[4,5] A sample of MAP was

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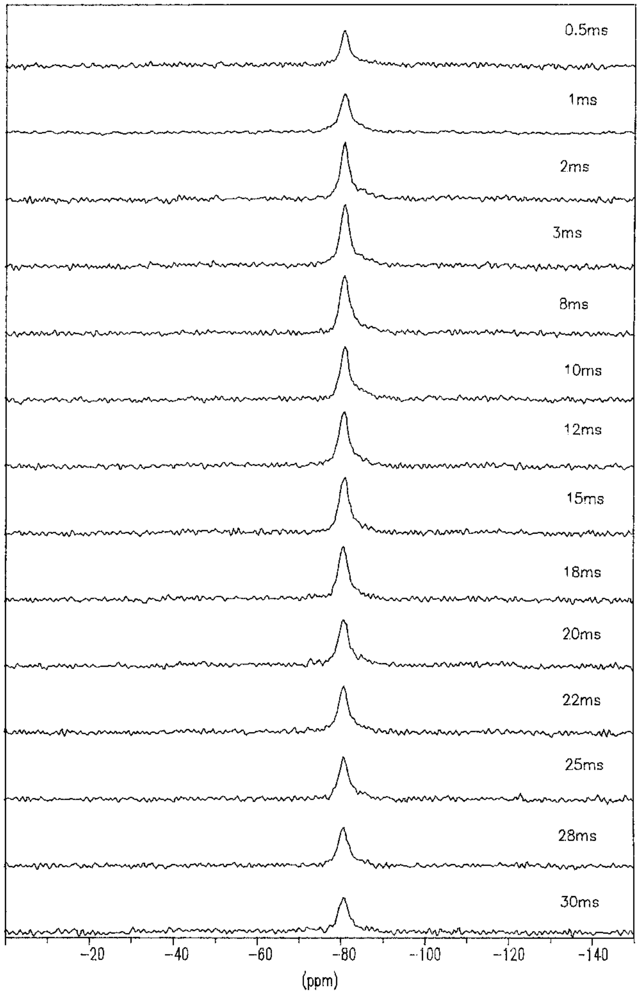

**Figure 5.** Variable contact time $^{29}Si-^{1}H$ CP MAS NMR spectra of dehydrated MAP(3000 scans).

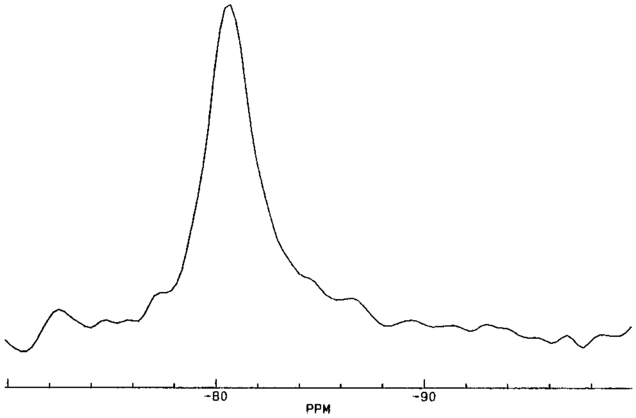

**Figure 6.** $^{29}Si$ MAS NMR spectrum of dehydrated MAP (1150 scans).

dehydrated at 400 °C, and the $^{29}Si$ single-pulse experiment gave a signal located at −80.3 ppm (Figure 6).

It is probably this lattice distortion which gives rise to the large shift in the $^{29}Si$ resonance upon dehydration. There are a number of reports of correlations of $^{29}Si$ chemical shift with the T−O−T angle measured from X-ray powder diffraction studies.[29] Most of these equations have been developed for siliceous zeolites and reasonable correlations are obtained. Ramdas and Klinowski reported a relationship for Si(4Al) containing zeolites.[35] A change of 7 ppm (from hydrated to dehydrated MAP) corresponds to an 8° reduction (hydrated 145°, dehydrated 137°) in the average Si−O−Al angle in the structure. In gismondine the average Si−O−Al angle is reduced from 146° to 132° upon dehydration.[34]

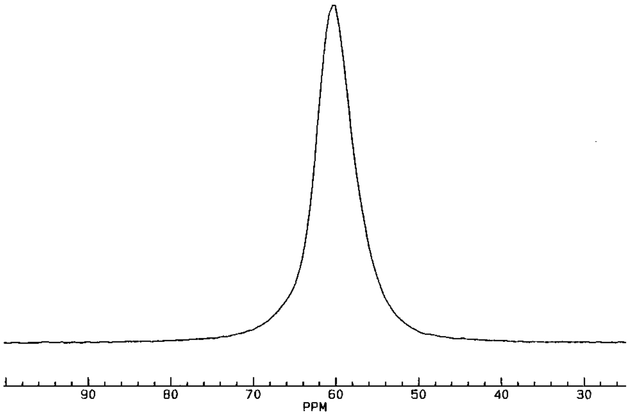

**Figure 7.** $^{27}Al$ MAS NMR spectrum of hydrated MAP (1000 scans).

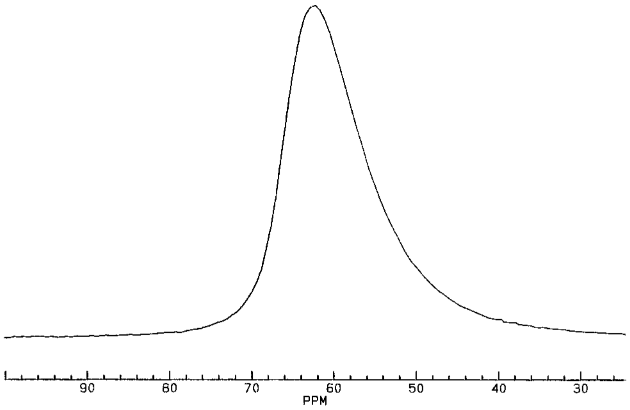

**Figure 8.** $^{27}Al$ MAS NMR spectrum of dehydrated MAP (2000 scans).

In the variable contact angle $^{29}Si$ cross-polarization experiment on dehydrated MAP only one signal at −80 ppm is observed, and this shows very strong cross-polarization behavior as evidenced by the spectra in Figure 5. It is possible to make a rough estimate of the relative intensities of the hydrated and dehydrated samples using the variable contact angle cp data. By extrapolation $T_{1\rho}$ to infinity and $T_{cp}$ to zero, a theoretical relative intensity of the hydrated and dehydrated samples was obtained and were approximately equal. The −80 ppm resonance has very different time constants to the hydrated sample (see Table 1). The $T_{1\rho}$ value for the main resonance is 40 ms, which is substantially longer than for the hydrated sample, indicating interaction with fairly immobile protons. These data are similiar to ZSM5 which is hydrophobic and possesses isolated protons (Table 1). This might seem consistent with the situation where every silicon is in an environment Si(3Al,1OH). However, this would require dealumination of the framework with the subsequent production of extraframework aluminum which is normally disordered octahedral, five cordinate, and tetrahedral aluminum.[25,29] This is not the case as evidenced by the $^{27}Al$ spectra which reveal that alumi-

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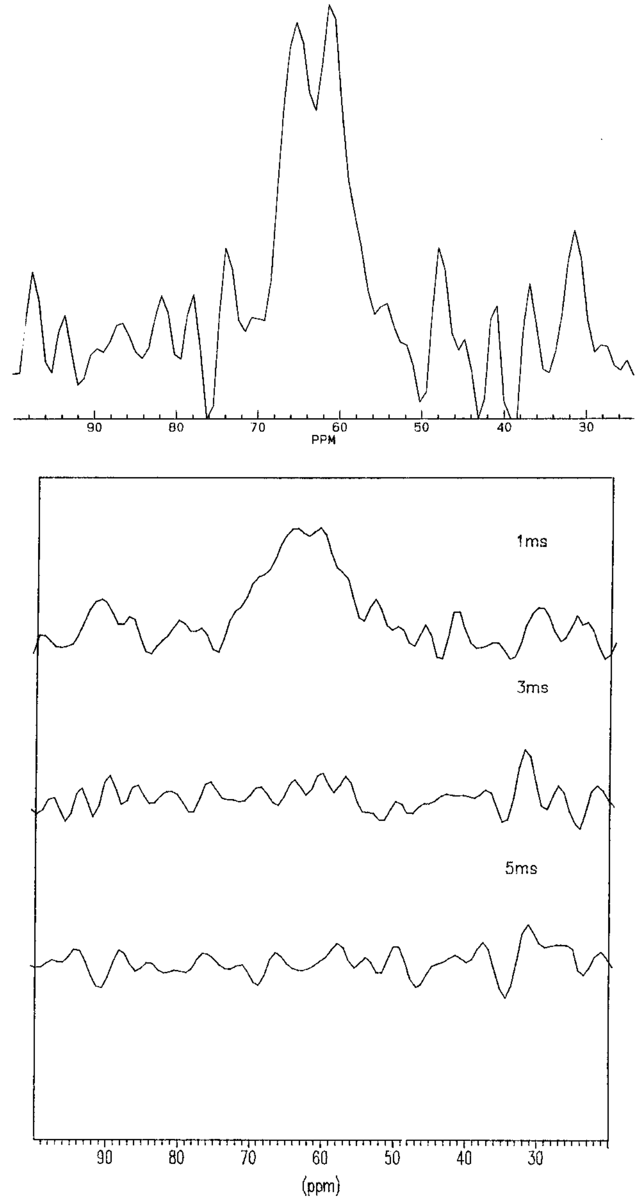

**Figure 9.** (a, top) $^{27}$Al−$^{1}$H CP MAS NMR spectrum of hydrated MAP (15 000 scans); (b, bottom) with variable contact time.

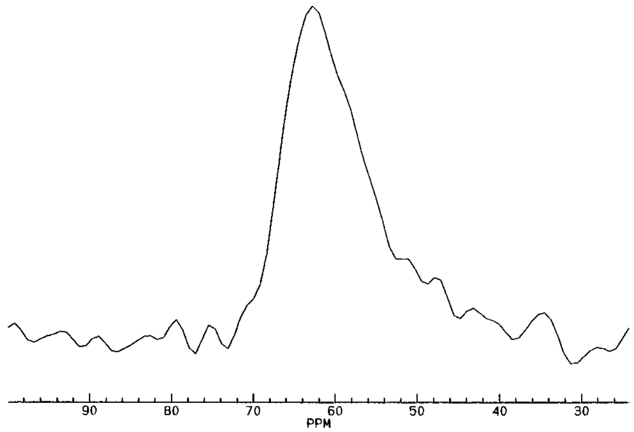

**Figure 10.** $^{27}$Al−$^{1}$H CP MAS NMR spectrum of dehydrated MAP (61 000 scans).

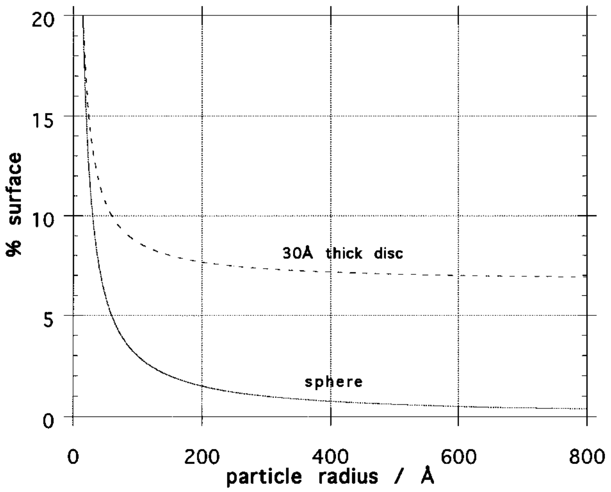

**Figure 11.** Percentage surface/volume ratio for a 30 Å thick disk-shaped crystal with varying radius

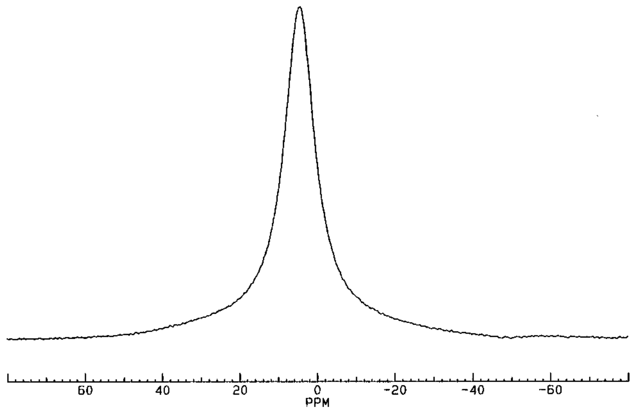

**Figure 12.** $^{1}$H MAS NMR spectrum of hydrated MAP.

num remains tetrahedral upon dehydration (see Figures 7 and 8, signal at 63 ppm). The $^{27}$Al signal does become somewhat broader upon dehydration which is indicative of lattice distortion. This is consistent with the observation of the changes in the X-ray diffraction pattern.[4,5] The $^{27}$Al cross-polarization experiment reveals that aluminum contacts much better with protons after dehydration. which is also consistent with hydrogen strongly bound, in some manner, to the framework after dehydration (see Figures 9 and 10). The data suggest that the $T_{1\rho}$ is very short. For the dehydrated material these data are consistent with water strongly bound to the zeolite framework or the presence of hydroxyl groups attached to the framework.

In the hydrated sample the small (ca. 5%) contribution from Si(3Al,1OH) is consistent with groups at the external surface. Figure 11 shows the surface-to-volume ratio for disk-shaped particles with 30 Å thickness as a function of diameter. At a diameter of 300 Å, as seen for MAP, about 8% of the material is at the surface. Conversely these data suggest that there is not a large number of internal silianol nest defect sites in either the hydrated or dehydrated sample and that the silanols are associated with the external surface.

High-resolution $^{1}$H MAS NMR has been applied successfully to the characterization of the proton environments in a range of zeolites. Observed chemical shifts are characteristic of particular types of proton environment.[29,36] $^{1}$H MAS NMR of hydrated MAP gives a relatively narrow signal fwhm = 6000 Hz (Figure 12)

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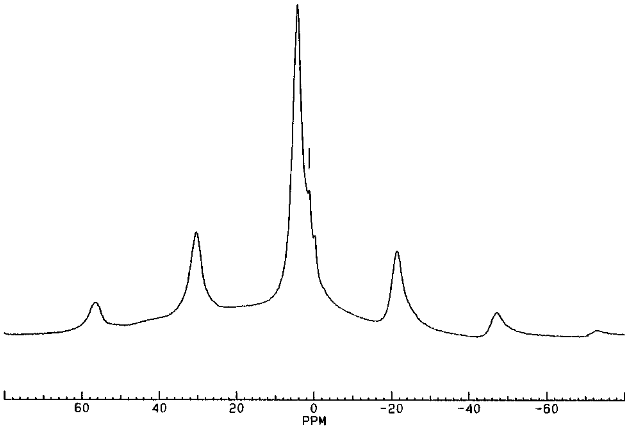

**Figure 13.** $^1$H MAS NMR spectrum of dehydrated MAP.

with a chemical shift of 4.5 ppm. This is indicative of relatively mobile intrazeolitic water.[29] After dehydration at both 200 and 400 °C (see Figure 13) a narrow resonance at 4.5 ppm with an associated spinning sideband pattern is observed with a smaller narrow shoulder at 1.3 ppm. The band at 4.5 ppm is consistent with the presence of residual water in the zeolitic structure or the presence bridging Si–O(H)–Al groups within the structure. It is hard to see how the bridging silanol groups would arise in zeolite MAP. The resonance at 1.3 ppm is readily assigned to terminal silanol groups which are most likely located on the exgernal surface of the zeolite MAP.

There is also a very broad resonance which accounts for 50% of the signal intensity. It is not possible to easily convolute this resonance but it is consistent with very immobile protons—these could be bridging silanols or strongly bound water.

## Conclusions

The use of NMR techniques has enabled the surface of MAP to be characterized and is consistent with a very small primary crystallite size with a large external surface area. The observed surface silanol concentration is consistent with that expected on theoretical grounds. It is believed that these are located almost exclusively on the surface of the crystallites. This is one of the first reported uses of NMR techniques to characterize the surface of a zeolite.

**Acknowledgment.** The authors would like to thank Drs. Minihan Adams and Graham of Unilever Research and the referees for helpful comments which improved the quality of the manuscript and Unilever Research for supporting this work.

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