

character in its conversion to an imine.

Tyrosine radicals have now been identified in several proteins or enzymes.<sup>40-43</sup> However, the results reported herein, together with additional recent results, effectively rule out this possibility for the radical observed in substrate-reduced amine oxidases. First, a significant <sup>14</sup>N/<sup>15</sup>N isotope effect on the X-band EPR spectrum of the *Arthrobacter* methylamine oxidase has been previously observed.<sup>7</sup> The results shown in Figure 2 establish that this arises from coupling between the nitrogen nucleus of the substrate amine and the unpaired electron. Second, this coupling is reasonably strong, as indicated by the hyperfine coupling constants obtained from the <sup>14</sup>N ESEEM simulations and the even-larger value inferred for <sup>15</sup>N (see above). It is, therefore, highly unlikely that the observed nitrogen modulations are due to nonbonded atoms. Since we are aware of no chemically plausible mechanism by which the nitrogen from the substrate amine can be incorporated into a tyrosine residue under physiological conditions, we conclude that

a tyrosine radical (or a radical derived from any other amino acid) is not the source of the EPR in substrate-reduced amine oxidases.

The presence of the substrate amine nitrogen in substrate-reduced amine oxidases is consistent with previous mechanistic suggestions<sup>1,2,4,44,45</sup> and with the reactivity expected of a quinone-like cofactor.<sup>3,46,47</sup> These results are also consistent with our previous proposal<sup>7,8</sup> that internal electron transfer from the reduced quinone to Cu(II) is the mechanism by which the semiquinone state of amine oxidases may be generated.

**Acknowledgment.** We thank Dr. William McIntire for several helpful discussions. This research was supported by National Institutes of Health Grants GM 27659 to D.M.D., RR02583 and GM 40168 to J.P., and GM 45795 to J.M.

**Registry No.** Diamine oxidase, 9001-53-0; methylamine oxidase, 80891-30-1.

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## Evaluation of Mn(II) Framework Substitution in MnAPO-11 and Mn-Impregnated AlPO<sub>4</sub>-11 Molecular Sieves by Electron Spin Resonance and Electron Spin-Echo Modulation Spectroscopy

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**Abstract:** MnAPO-11 and Mn-impregnated AlPO<sub>4</sub>-11 (Mn-AlPO<sub>4</sub>-11) samples were prepared with various manganese contents and studied by electron spin resonance (ESR) and electron spin-echo modulation (ESEM). At high manganese content (4.25 mol %), the spin-spin interaction broadens the ESR spectra of MnAPO-11 and Mn-AlPO<sub>4</sub>-11 so that they show only a broad line at  $g = 2.01$ . At low manganese content (0.1 mol %), the ESR spectra of MnAPO-11 and Mn-AlPO<sub>4</sub>-11 exhibit the same parameters ( $g = 2.01$  and  $A \approx 93.5$  G), but the spectra obtained from MnAPO-11 samples are better resolved. Two-pulse ESEM of MnAPO-11 and Mn-AlPO<sub>4</sub>-11 with adsorbed deuterium oxide shows that the local environments of manganese in the hydrated samples are different. This indicates that the manganese species environments in MnAPO-11 and Mn-AlPO<sub>4</sub>-11 are different, suggesting that Mn(II) is framework substituted in MnAPO-11 since it obviously occupies an extra-framework position in Mn-AlPO<sub>4</sub>-11. The framework incorporation in MnAPO-11 is confirmed by a three-pulse ESEM study of deuterium modulation resulting from interactions of deuterated adsorbates with manganese which indicate that the manganese occupies a negatively charged site in MnAPO-11.

### Introduction

A new class of microporous aluminophosphate molecular sieves (AlPO<sub>4</sub>) has been described.<sup>1</sup> Some of these materials are structurally similar to zeolites while others, like AlPO<sub>4</sub>-5 and AlPO<sub>4</sub>-11, have novel three-dimensional framework structures. The replacement of elements that constitute the framework of these molecular sieves has been studied for various AlPO<sub>4</sub> structures.<sup>2</sup> This is of particular interest since these materials do not show any Brønsted acidity due to their neutral framework resulting from an Al/P ratio of 1. Incorporation of silicon for

mostly phosphorus gives silicoaluminophosphates (SAPO) which are structurally analogous to the AlPO<sub>4</sub> series.<sup>3</sup> Some transition metal ions can also be incorporated which is of particular interest since various transition metal species are involved in catalytic processes.

The framework substitution of divalent manganese for some Al(III) in AlPO<sub>4</sub>-11, denoted MnAPO-11, has been reported.<sup>2,4</sup> Indirect evidence for framework incorporation of Mn(II) in MnAPO-11 includes chemical analysis and measurement of Brønsted acidity. Some chemical analyses of MnAPO-11 showed that it contained less aluminum than phosphorus, which is expected if manganese actually replaces aluminum within the framework

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since the Al/P ratio equals 1 in  $\text{AlPO}_4\text{-11}$ . Brønsted acidity measurements also showed that  $\text{MnAPO}_4\text{-11}$  is slightly more acidic than  $\text{AlPO}_4\text{-11}$  which is expected if Mn(II) replaces Al(III) to form a negatively charged site.<sup>2,5</sup>

Electron spin resonance (ESR) coupled with electron spin-echo modulation (ESEM) spectroscopy has been found to be powerful for studying the location of transition metal ions in molecular sieves.<sup>6</sup> We recently reported direct evidence for manganese incorporation into the  $\text{AlPO}_4\text{-11}$  framework in  $\text{MnAPO}_4\text{-11}$  by using ESEM to determine the coordination geometry of water near the Mn(II).<sup>7</sup> In the present work, we give full details and additional direct spectroscopic evidence for framework incorporation of Mn(II) based on ESEM studies with various adsorbates and strong indirect evidence for framework substitution based on comparison with Mn-impregnated samples and with  $\text{MnAPO}_4\text{-5}$  in which Mn(II) occupies an extra-framework position.<sup>8</sup>

### Experimental Section

$\text{AlPO}_4\text{-11}$  and  $\text{MnAPO}_4\text{-11}$  were both hydrothermally synthesized according to the following general procedure.<sup>4,9</sup> An aluminophosphate gel was prepared by combining 85% orthophosphoric acid (Mallinckrodt), aluminum oxide (Catapal alumina, Vista Chemical Co.), and deionized water (a Mn(II) solution prepared by dissolving  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was used instead of pure deionized water in the synthesis of  $\text{MnAPO}_4\text{-11}$ ). A templating agent (diisopropylamine from Aldrich Chemicals, 99%) was added, and the final reacting gel was stirred for 12 h. The mixture was then sealed in a stainless steel autoclave and heated at 200 °C for 24 h. The products were collected by filtration and characterized by X-ray diffraction (XRD) on a Philips PW1840 diffractometer. An XRD pattern characteristic of the  $\text{AlPO}_4\text{-11}$  structure was observed.<sup>10</sup> The high intensity of the peaks and the absence of baseline drift indicated high crystallinity. As-synthesized  $\text{AlPO}_4\text{-11}$  and  $\text{MnAPO}_4\text{-11}$  were then calcined for 48 h at 600 °C in air in order to remove the diisopropylamine template. The color of the calcined  $\text{MnAPO}_4\text{-11}$  sample turned from white to purple, and the XRD pattern was somewhat changed. This is consistent with literature reports that the  $\text{AlPO}_4\text{-11}$  structure changes upon calcination.<sup>11-14</sup> A  $\text{MnAPO}_4\text{-5}$  sample with 0.05 mol % (relative to phosphorus) was synthesized by a similar method using tripropylamine (Fluka) as a template, and was also calcined for 48 h at 600 °C in air.

The surface area was measured for both  $\text{AlPO}_4\text{-11}$  and  $\text{MnAPO}_4\text{-11}$  on a Quantachrome Monosorb surface analyzer by the single point Brunauer-Emmett-Teller (BET) method using  $\text{N}_2$ . This method is based on the measurement of the quantity of gas adsorbed on a solid surface by sensing the change in thermal conductivity of a flowing mixture of an adsorbate ( $\text{N}_2$ ) and an inert gas (He).<sup>15</sup> It was found to be 200  $\text{m}^2/\text{g}$  for the calcined samples and about 30  $\text{m}^2/\text{g}$  for the as-synthesized samples. This drastic increase in the surface area upon calcination is consistent with full occupation of the main 10-membered ring channel of the structure by the diisopropylamine template in the as-synthesized products.<sup>5</sup> Similar values can be found in the literature.<sup>16</sup> The high surface area obtained for the calcined samples confirms that the prepared materials have high crystallinity since the presence of amorphous material would be expected to lower significantly the surface area. Such material should obstruct the pores and the channels of the structure and contribute to the weight of the sample without being microporous itself. Both  $\text{AlPO}_4\text{-11}$  and  $\text{MnAPO}_4\text{-11}$  were also investigated by thermogravimetric analysis (TGA) on a Dupont 951 thermal analyzer at a rate of 10 °C/min in air.

Various  $\text{MnAPO}_4\text{-11}$  samples were prepared with 4.25, 0.85, 0.3, 0.1, and 0.05 mol % of manganese (100 Mn/(Mn + Al + P)). For each

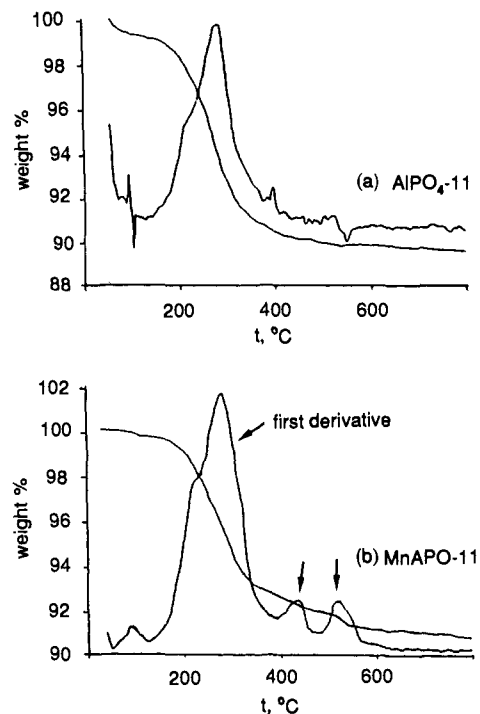


Figure 1. TGA curves of (a)  $\text{AlPO}_4\text{-11}$  and (b)  $\text{MnAPO}_4\text{-11}$  recorded under air with a heating rate of 10 °C/min.

synthesis, both the amount of manganese and aluminum incorporated were modified so that the ratio of (Mn + Al)/P was always kept equal to 1. One gram of calcined  $\text{MnAPO}_4\text{-11}$  was stirred in 100 mL of a 0.1 N  $\text{CaCl}_2$  solution at 70 °C for 5 h to attempt to exchange Ca(II) for extra-framework manganese. This was done for calcined  $\text{MnAPO}_4\text{-11}$  samples containing 4.25, 0.3, 0.1, and 0.05 mol % Mn. After this exchange, the crystals were filtered, and for the 0.1 mol % manganese sample, both the filtrate and the molecular sieve itself were sent for commercial chemical analysis (Galbraith Laboratories, Inc.). Some of these samples were evacuated up to 350 °C to less than  $10^{-5}$  Torr. In order to study the interaction of these samples with adsorbates, samples were prepared according to the following general procedure. About 10 mg of calcined sample was evacuated at 350 °C for 12 h to remove adsorbed water, and then it was exposed to the adsorbate at its room temperature vapor pressure for liquids or at a pressure of about 100 Torr for gases. The following adsorbates were used:  $\text{D}_2\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{OD}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$  (Aldrich Chemicals, 99.5 atom % D), *o*-xylene (Aldrich Chemicals), and  $\text{C}_2\text{D}_4$  (Cambridge Isotope Laboratories, 99 atom % D).

Mn(II) was impregnated into  $\text{AlPO}_4\text{-11}$  with various amounts of manganese according to the following general procedure.<sup>17</sup> One gram of calcined  $\text{AlPO}_4\text{-11}$  was added to 100 mL of a manganese acetate solution and stirred at 90 °C until the water was completely evaporated. Then, this sample was washed for about 1 h with deionized water at room temperature in order to remove the manganese accumulated at the surface. The impregnated samples will be denoted by Mn- $\text{AlPO}_4\text{-11}$  in distinction from the synthesized samples which are denoted by Mn- $\text{APO}_4\text{-11}$ .

Mn- $\text{AlPO}_4\text{-11}$  was prepared with 0.5, 0.2, 0.15, 0.1, and 0.05 nominal mol % manganese. These nominal mole percents refer to the amount of manganese introduced during impregnation, but, since the samples are subsequently washed with deionized water at room temperature, the manganese content of these samples is actually lower. A comparison of the intensities of the ESR spectra obtained from samples impregnated with nominally 0.05 to 0.3 mol % manganese before and after washing shows that the actual Mn(II) content of this sample is about 60% of the nominal impregnated content. The actual impregnated concentrations are used in the data reported.

X-band ESR spectra were recorded at 77 K with a Varian E-4 spectrometer. Q-band ESR spectra were recorded at 120 K with a Bruker ESP-300 ESR spectrometer. The ESEM signals were recorded at 4 K on a home-built spectrometer that has been described.<sup>18</sup> Two-pulse echoes were recorded with a  $\pi/2-\tau-\pi$  pulse sequence as a function of  $\tau$ .

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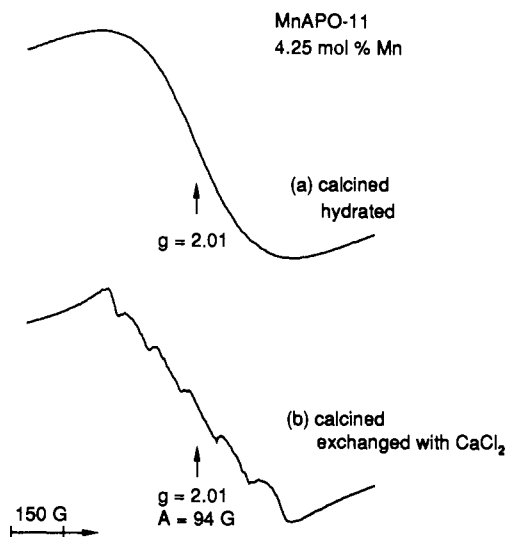
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**Figure 2.** X-band ESR spectra recorded at 77 K of (a) calcined MnAPO-11 with 4.25 mol % manganese and (b) calcined MnAPO-11 with 4.25 mol % manganese exchanged with  $\text{CaCl}_2$ .

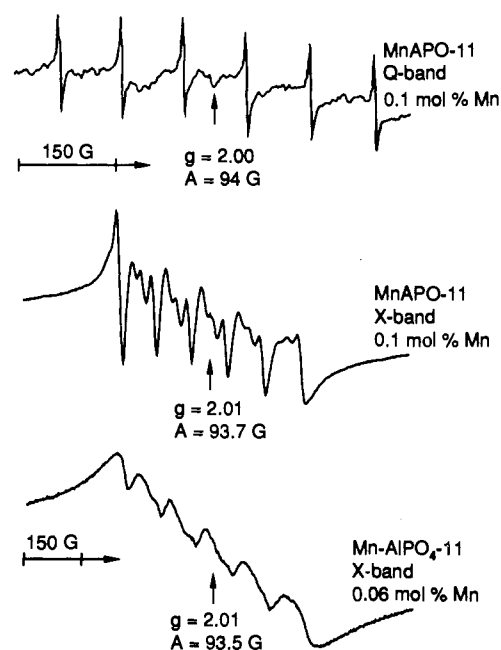
Three-pulse echoes were recorded with a  $\pi/2-\tau-\pi/2-T-\pi/2$  pulse sequence as a function of  $T$ . The value of  $\tau$  in the three-pulse experiment was selected to be  $0.27 \mu\text{s}$  to minimize the  $^{27}\text{Al}$  modulation.<sup>19</sup> Two-pulse glitches were eliminated by phase cycling.<sup>20</sup> The deuterium modulation was analyzed by a spherical approximation for powder samples in terms of  $N$  nuclei at distance  $R$  with an isotropic hyperfine coupling  $A$ .<sup>19</sup>

## Results

**TGA.** TGA of as-synthesized  $\text{AlPO}_4\text{-11}$  and  $\text{MnAPO}_4\text{-11}$  with 0.1 mol % manganese shows that the templating agent can be removed under air between 150 °C and 350 °C (Figure 1). Comparison of curves a and b in Figure 1 shows that the combustion of the template in  $\text{MnAPO}_4\text{-11}$  involves some extra steps at higher temperature as indicated by the two vertical arrows. After calcination,  $\text{MnAPO}_4\text{-11}$  shows a purple color while  $\text{AlPO}_4\text{-11}$  remains white. The strength of the purple color appears to depend upon the manganese concentration in  $\text{MnAPO}_4\text{-11}$ , but the  $\text{Mn-AlPO}_4\text{-11}$  sample remains white at any manganese content. The presence and absence of the purple color indicates that the chemical environment of manganese is different in the two samples.

**ESR.** At high manganese content (4.25 mol %), the ESR spectrum of  $\text{MnAPO}_4\text{-11}$  shows only a single intense broad line at  $g = 2.01$  (Figure 2). No hyperfine structure is observed, presumably because the spin-spin interaction is too strong at this concentration.<sup>21</sup> However, after exchange with  $\text{CaCl}_2$ , the intensity of the signal measured by double integration decreases by about 30% and some hyperfine is resolved (Figure 2). This decrease in intensity, as well as the improved resolution, indicates that some manganese was removed during the exchange.

The X-band ESR spectrum of a 0.1 mol % Mn sample shows well-resolved hyperfine lines (Figure 3) and is consistent with that obtained from axially symmetric divalent manganese species in molecular sieves<sup>22</sup> and other solids.<sup>23</sup> When the electric field around Mn(II) is not spherical, the energy levels corresponding to  $S > 1/2$  or  $S < -1/2$  vary rapidly with the angle  $\theta$  of the principal symmetry axis to the external magnetic field  $H$ .<sup>22,24</sup> Therefore, the resonant field for the transitions other than those between  $S = -1/2$  and  $S = +1/2$  also varies rapidly with respect to  $\theta$ . In a powder, since the direction of the axial symmetry axis is distributed at random relative to the external magnetic field, these outer



**Figure 3.** Q-band ESR spectrum recorded at 77 K of calcined  $\text{MnAPO}_4\text{-11}$  with 0.1 mol % manganese and X-band ESR spectra recorded at 77 K of  $\text{MnAPO}_4\text{-11}$  and  $\text{Mn-AlPO}_4\text{-11}$  with 0.06 actual mol % Mn in each.

**Table I.** ESR Parameters of Mn(II) in  $\text{MnAPO}_4\text{-11}$  and  $\text{Mn-AlPO}_4\text{-11}$

sample	$g$	hyperfine splitting, G
$\text{MnAPO}_4\text{-11}$ as-synthesized	2.01	87.7
$\text{MnAPO}_4\text{-11}$ calcined <sup>a</sup>	2.01	93.7
$\text{MnAPO}_4\text{-11}$ calcined <sup>a</sup> and evacuated at 360 °C	2.01	87.6
$\text{MnAPO}_4\text{-11}$ with adsorbed <i>o</i> -xylene	2.01	86.9
$\text{MnAPO}_4\text{-11}$ with adsorbed methanol	2.01	93.6
$\text{Mn-AlPO}_4\text{-11}$	2.01	93.5

<sup>a</sup> At 600 °C for 48 h.

transitions are typically not observed. Mn(II) basically behaves then like a spin  $1/2$  system in  $\text{MnAPO}_4\text{-11}$  with  $g = 2.01$  and  $A = 93.7$  G. Several additional lines can be observed inbetween the six main hyperfine lines; these additional lines are assigned to  $\Delta m_l = \pm 1$  forbidden transitions according to previous Mn(II) ESR studies.<sup>25</sup> The appearance of these transitions has been ascribed to off-diagonal terms of the Hamiltonian.<sup>26</sup> These terms produce a mixing of nuclear states  $|m\rangle$  with states  $|m \pm 1\rangle$  by amounts of order  $A/g\beta H$ . The transitions of type  $\Delta m = \pm 1$  become partially allowed with intensities proportional to  $A^2/g^2\beta^2 H^2$ . At 34.2 GHz microwave frequency (Q-band), the resonant external magnetic field increases 4-fold from that of the X-band (9.3 GHz), while the hyperfine splitting remains the same and the forbidden transitions are then weaker by a factor of  $\sim 16$  relative to the allowed transitions. The assignment of those additional lines is thus confirmed by Q-band ESR, as the Q-band ESR spectrum of calcined  $\text{MnAPO}_4\text{-11}$  shows only six sharp lines (Figure 3). This indicates that at low manganese content,  $\text{MnAPO}_4\text{-11}$  contains only one Mn(II) species within the resolution of the spectrum. The ESR spectrum of a  $\text{Mn-AlPO}_4\text{-11}$  sample containing 0.06 mol % manganese is also shown at the bottom of this figure. The parameters of this spectrum are basically identical with those of  $\text{MnAPO}_4\text{-11}$  and the forbidden transitions are also observed. This signal suggests that  $\text{Mn-AlPO}_4\text{-11}$  contains only one Mn(II) species.

X-band ESR spectra of  $\text{MnAPO}_4\text{-11}$  samples with 0.1 mol % manganese subject to various treatments are shown in Figure 4.

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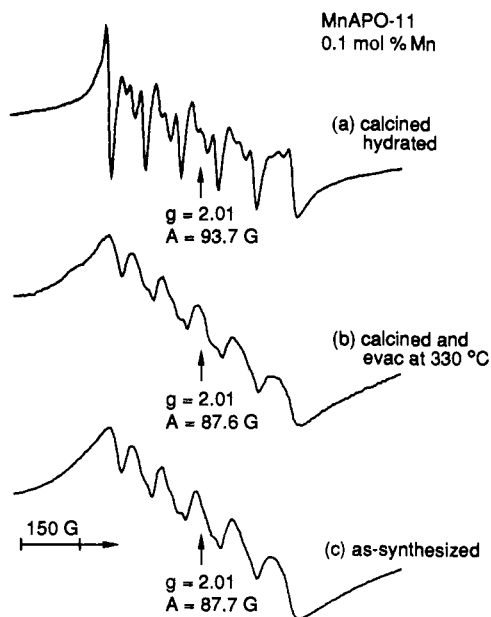


Figure 4. X-band ESR spectra recorded at 77 K of MnAPO-11 with 0.1 mol % manganese (a) calcined and hydrated, (b) calcined and evacuated at 330 °C, and (c) as-synthesized.

This figure shows that the ESR signal of calcined and hydrated MnAPO-11 is better resolved than that of as-synthesized MnAPO-11. In addition to this resolution enhancement, an increase of the hyperfine splitting of from 87.7 to 93.7 G is measured upon calcination (Table I). When the calcined and hydrated sample is evacuated up to 330 °C to remove water, the signal becomes broader and the hyperfine splitting decreases from 93.7 to 87.6 G (Table I). The line shape and the hyperfine splitting of this signal then becomes comparable to those of the signal obtained from as-synthesized MnAPO-11 which contains the diisopropylamine template which probably blocks the channels. More generally, when a small molecule which can penetrate the channels, like methanol or ethanol, is adsorbed, the ESR spectrum shows the same parameters as the hydrated sample, while samples with a molecule larger than the channel entrance, like *o*-xylene, yield a spectrum similar to that of an evacuated sample (Table I). The cross section of *o*-xylene calculated from a molecular model is  $0.68 \times 0.34$  nm,<sup>27</sup> while the main 10-ring channel has a free opening of  $0.67 \times 0.44$  nm.

When a calcined MnAPO-11 sample with low manganese content (0.1 mol %) is exchanged with CaCl<sub>2</sub>, the X-band ESR spectrum line shape and parameters are not affected, but the signal intensity decreases by 10–15% from double integration. This indicates that some manganese is removed by ion exchange, but a smaller fraction than in more concentrated samples. This is confirmed by chemical analysis of the filtrate obtained from exchange of the sample with nominal 0.1 mol % Mn. The filtrate contains about 10% of the manganese initially present in the molecular sieve. This is consistent with the chemical analysis of the molecular sieve itself after the exchange which shows that it still contains 0.09 mol % manganese. These results indicate that only about 10% of the manganese can be removed from MnAPO-11 with 0.1 mol % Mn.

X-band ESR spectra of MnAlPO<sub>4</sub>-11 and MnAPO-11 with 0.3 actual mol % manganese are shown in Figure 5. The signal corresponding to MnAPO-11 with 0.3 mol % Mn before ion exchange looks like a combination of the two signals obtained at high (4.25 mol %, Figure 2a) and low (0.1 mol %, Figure 4a) Mn(II) content. This indicates the existence of at least two species, one giving rise to a single broad line and the other showing hyperfine structure and forbidden transitions. The latter species has parameters similar to those of the signal obtained from MnAPO-11

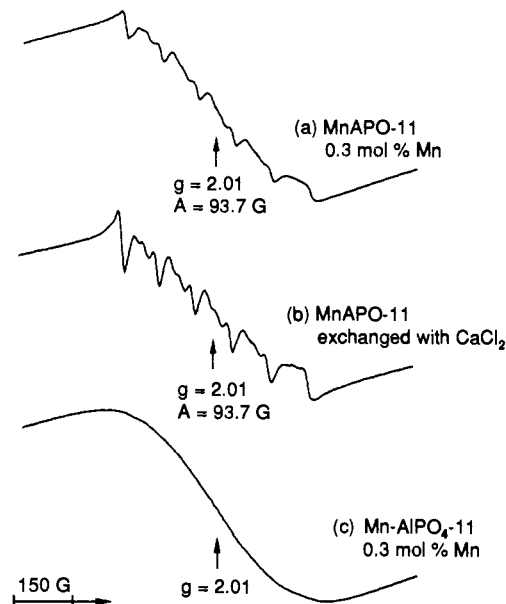


Figure 5. X-band ESR spectra recorded at 77 K of (a) MnAPO-11 with 0.3 mol % manganese after calcination, (b) MnAPO-11 with 0.3 mol % manganese after calcination and exchange with CaCl<sub>2</sub>, and (c) Mn-AlPO<sub>4</sub>-11 with 0.3 actual mol % manganese.

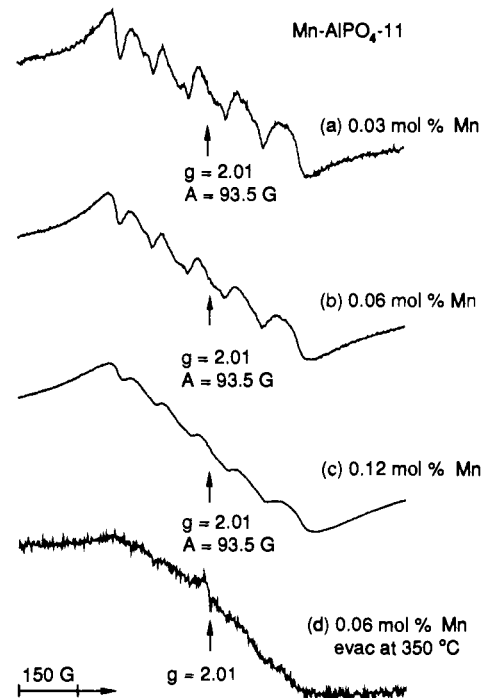
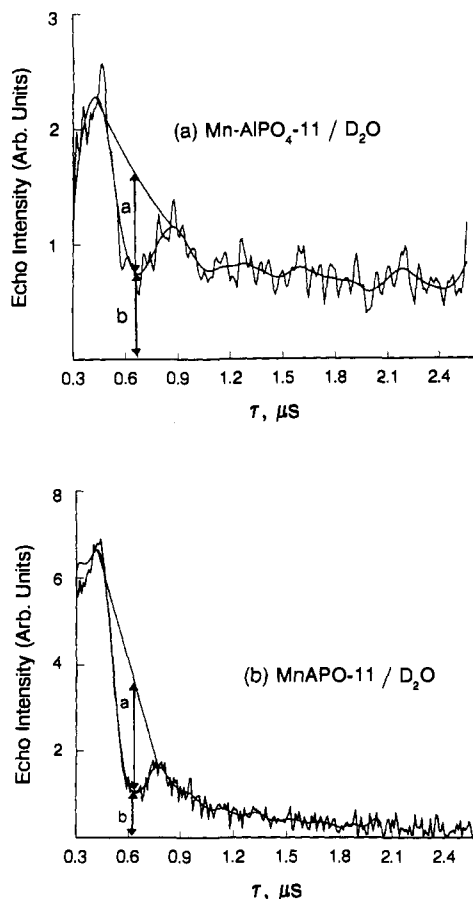


Figure 6. X-band ESR spectra recorded at 77 K of Mn-AlPO<sub>4</sub>-11 with (a) 0.03, (b) 0.06, and (c) 0.12 actual mol % manganese and (d) Mn-AlPO<sub>4</sub>-11 with 0.06 actual mol % manganese evacuated at 350 °C.

with 0.1 mol % manganese. When this MnAPO-11 sample is exchanged with CaCl<sub>2</sub>, the overall intensity of the spectrum decreases about 30% from double integration, and the resolved signal can be seen more clearly (Figure 5c). This suggests that the relative proportion of the species which gives rise to the resolved signal increases upon exchange with CaCl<sub>2</sub>. The signal obtained from Mn-AlPO<sub>4</sub>-11 with the same manganese content shows only a single broad line with unresolved hyperfine. This indicates that the species which corresponds to the resolved part of the spectrum is not present in this impregnated sample.

X-band ESR spectra of Mn-AlPO<sub>4</sub>-11 samples with various manganese contents are shown in Figure 6. All these spectra exhibit parameters comparable to those of MnAPO-11 (Table I). In these samples, the signal resolution also depends upon the

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**Figure 7.** Two-pulse ESEM recorded at 4 K of (a) Mn-AlPO<sub>4</sub>-11 with 0.03 mol % manganese and with adsorbed D<sub>2</sub>O and (b) MnAPO-11 with 0.05 mol % manganese and with adsorbed D<sub>2</sub>O. The solid line, which gives an estimate of a noise-free signal from the experimental data, was empirically generated using cubic spline fitting methods.

manganese concentration. When Mn-AlPO<sub>4</sub>-11 is evacuated at 350 °C for 12 h, the X-band ESR signal almost disappears and the hyperfine lines are not resolved anymore (Figure 6d).

Even though the ESR spectra obtained from Mn-AlPO<sub>4</sub>-11 and MnAPO-11 samples with the same manganese concentration have almost the same parameters, they show significant differences in terms of resolution. The spectra of the impregnated samples are less well resolved in comparison with those of MnAPO-11. No Mn-AlPO<sub>4</sub>-11 sample gives a spectrum as well resolved as that of MnAPO-11 with 0.1 mol % manganese (Figure 4a). In order to get relatively sharp hyperfine lines, it is necessary to impregnate AlPO<sub>4</sub>-11 with less than 0.03 mol % manganese (Figure 6). When the actual manganese content is greater than 0.3 mol %, no hyperfine is seen for Mn-AlPO<sub>4</sub>-11 in contrast to the resolution in MnAPO-11 samples with 0.3 mol % Mn. This indicates that the spin-spin interaction is much stronger in impregnated samples and suggests some aggregation of the Mn(II) ions on impregnated samples. No background Mn<sup>2+</sup> ESR signal was observed from AlPO<sub>4</sub>-11 prior to the Mn<sup>2+</sup> impregnation under the same ESR measurement conditions.

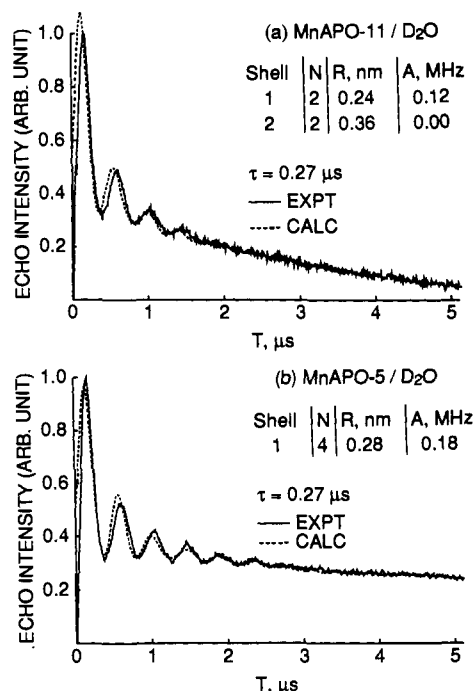
**ESEM.** ESEM also shows differences between the Mn-AlPO<sub>4</sub>-11 and MnAPO-11 samples. The ESR results indicate that the spin-spin interaction is stronger in impregnated samples. This shortens the phase memory time and makes it more difficult to see a spin-echo. In fact, no spin-echoes are observed in impregnated samples unless the concentration is less than 0.03 actual mol % manganese. After adsorption of deuterium oxide, this sample gave a very weak echo, and only a two-pulse echo signal could be observed (Figure 7a). On the other hand, the two-pulse ESEM signal of MnAPO-11 with 0.05 mol % Mn(II) and with adsorbed D<sub>2</sub>O was easier to observe (Figure 7b). Deuterium modulation can be identified on both signals, and the normalized modulation depths<sup>28</sup> (defined as  $a/(a+b)$ ; see Figure 7) are

**Table II.** Deuterium Modulation Depth from MnAPO-11 and Mn-AlPO<sub>4</sub>-11 with Adsorbed D<sub>2</sub>O

sample	normalized modulation depth
MnAPO-11	0.83
Mn-AlPO <sub>4</sub> -11	0.53
MnAPO-5	0.63

**Table III.** Simulation Parameters of Three-Pulse ESEM of Mn(II) in MnAPO-11 and MnAPO-5 Treated with Various Adsorbates

sample	shell	<i>N</i>	<i>R</i> , nm	<i>A</i> , MHz
MnAPO-11 + D <sub>2</sub> O	1	2	0.24	0.12
	2	2	0.36	0.00
MnAPO-11 + CH <sub>3</sub> OD	1	1	0.24	0.25
MnAPO-11 + CD <sub>3</sub> OH	1	3	0.30	0.15
MnAPO-11 + CH <sub>3</sub> CH <sub>2</sub> OD	1	1	0.24	0.11
	2	1	0.35	0.00
MnAPO-5 + D <sub>2</sub> O	1	4	0.28	0.18



**Figure 8.** Three-pulse ESEM recorded at 4 K of (a) MnAPO-11 with 0.05 mol % manganese and with adsorbed D<sub>2</sub>O and (b) MnAPO-5 with 0.05 mol % manganese and with adsorbed D<sub>2</sub>O.

significantly different as shown in Table II.

A three-pulse ESEM signal was readily obtained from MnAPO-11 with 0.05 mol % manganese and with adsorbed D<sub>2</sub>O (Figure 8). Simulations assuming all interacting deuteriums to be equidistant from Mn(II) did not yield a reasonable fit to the signal. The best fit requires a two-shell model with deuteriums located at two different distances. The best fit parameters are two deuteriums at a distance of 0.24 nm from the manganese and two other deuteriums at 0.36 nm (Table III). These parameters suggest the presence of two water molecules interacting with the manganese. The ESEM signal of MnAPO-5 with adsorbed D<sub>2</sub>O was recorded for comparison, as manganese has been reported to occupy an extra-framework position in MnAPO-5.<sup>8</sup> A one-shell model was satisfactory for the simulation of the signal (Figure 8), and the parameters (Table III) show that the local D<sub>2</sub>O structure around Mn(II) is clearly different in Mn-AlPO<sub>4</sub>-11 compared to MnAPO-11.

Simulation of the signals obtained from samples with adsorbed methanol fits a one-shell model (Figure 9). The best fit to the ESEM signals of MnAPO-11 with adsorbed CH<sub>3</sub>OD and CD<sub>3</sub>OH

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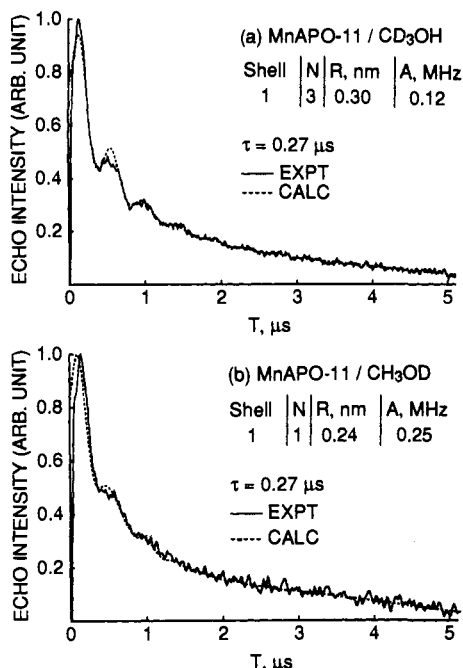


Figure 9. Three-pulse ESEM recorded at 4 K of MnAPO-11 with 0.05 mol % manganese and with adsorbed (a)  $\text{CD}_3\text{OH}$  and (b)  $\text{CH}_3\text{OD}$ .

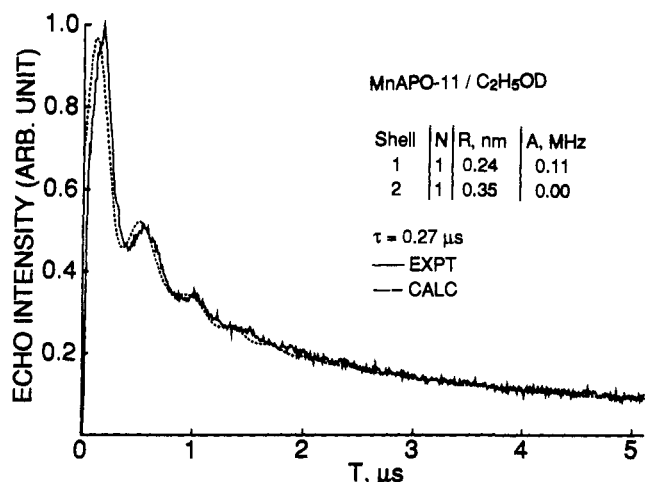


Figure 10. ESEM recorded at 4 K of MnAPO-11 with 0.05 mol % manganese and adsorbed  $\text{CH}_3\text{CH}_2\text{OD}$ .

was obtained using the parameters shown in Table III. These parameters show that there is only one methanol molecule next to the site occupied by Mn(II). For the sample with adsorbed  $\text{CH}_3\text{CH}_2\text{OD}$  (Figure 10), a two-shell simulation assuming two deuteriums at two different distances from the manganese is needed (Table III). The parameters obtained from this simulation suggest a similar coordination for ethanol and methanol to manganese since the short distance found for the deuterium of the first shell in the sample with  $\text{CH}_3\text{CH}_2\text{OD}$  adsorbed is identical with that found for the deuterium of  $\text{CH}_3\text{OD}$  in the corresponding sample.

### Discussion

The TGA of  $\text{AlPO}_4\text{-11}$  and  $\text{MnAPO-11}$  appear to be significantly different (Figure 1, a and b). The extra steps at high temperature involved in the combustion of the templating agent in  $\text{MnAPO-11}$  suggest that part of the diisopropylamine is protonated in this sample.<sup>29</sup> If part of the manganese is framework substituted, some negatively charged sites will be created which

can be balanced by a protonated amine.<sup>5</sup> This supports that at least part of the manganese is incorporated into the framework.

Extra-framework manganese exists in all synthesized  $\text{MnAPO-11}$  samples regardless of the manganese content. Ion exchange using a  $\text{CaCl}_2$  solution effectively removes some manganese, showing that it is located outside the framework. ESR spectra show a significant resolution enhancement by ion exchange of  $\text{MnAPO-11}$  samples with high manganese content, such as 4.25 mol % (Figure 2). Although resolution enhancement is not observed for  $\text{MnAPO-11}$  samples with manganese contents of 0.1 mol % or lower, the manganese present in the filtrate from the exchange indicates the existence of some extra-framework manganese.

Apart from the exchangeable extra-framework manganese, it is of more interest to note that most of the manganese in  $\text{MnAPO-11}$  with low manganese content cannot be exchanged. The ESR spectra of the nonexchangeable manganese show a great dependence upon the adsorption of small molecules, e.g., water molecules. The three-dimensional framework of  $\text{MnAPO-11}$  is presumably distorted by these small molecules entering the main channel, by analogy with the fact that the framework of  $\text{AlPO}_4\text{-11}$  is distorted by water adsorption.<sup>13,14</sup> It is expected that large molecules like *o*-xylene cannot enter the 10-ring channel and that small molecules like water can enter the main channel only when the templating agent is removed. This is consistent with the same Mn(II) hyperfine for  $\text{MnAPO-11}$  with adsorbed *o*-xylene and for as-synthesized  $\text{MnAPO-11}$  which has been calcined and evacuated, since neither of those samples has small molecules present in the channels. The significant variation of the hyperfine splitting of manganese in  $\text{MnAPO-11}$  upon framework distortion by water also suggests that the manganese is substituted into the framework.

At moderate manganese content (0.3 mol %), the ESR spectrum of  $\text{MnAPO-11}$  apparently indicates the superposition of two species. One of these species gives rise to a single broad line similar to the ESR spectrum of  $\text{Mn-AlPO}_4\text{-11}$  with 0.3 mol % manganese and can thus be identified as extra-framework manganese. The resolved signal also observed on this spectrum is comparable to that of  $\text{MnAPO-11}$  with 0.1 mol % manganese and can be attributed to framework-substituted manganese since manganese is incorporated into the framework in  $\text{MnAPO-11}$  with 0.1 mol % Mn and since its relative proportion increases when the sample is exchanged with  $\text{CaCl}_2$ .

The ESR and ESEM results show some significant differences between  $\text{MnAPO-11}$  and  $\text{Mn-AlPO}_4\text{-11}$ . X-band ESR indicates that the spin-spin interaction is stronger in the impregnated sample which suggests that the Mn(II) ions are closer to each other. Upon dehydration, the X-band ESR spectrum of  $\text{MnAPO-11}$  is still well resolved, while that of  $\text{Mn-AlPO}_4\text{-11}$  shows a weak broad line. This also shows that Mn(II) in  $\text{MnAPO-11}$  is trapped in a site where the ions cannot move into closer proximity when water is removed from the structure which is expected if Mn(II) is framework-substituted. Finally, the calculated normalized modulation depths of two-pulse ESEM signals obtained from  $\text{MnAPO-11}$  and  $\text{Mn-AlPO}_4\text{-11}$  with adsorbed  $\text{D}_2\text{O}$  are quite different, which confirms that these samples contain manganese in different environments. The manganese in  $\text{MnAPO-11}$  that is not incorporated into the framework is expected to be in the channels as in impregnated samples.

The three-pulse ESEM results from the manganese species present in  $\text{MnAPO-11}$  at low concentration provide good evidence for framework substitution. The simulation of the three-pulse ESEM signal obtained from  $\text{MnAPO-11}$  with adsorbed  $\text{D}_2\text{O}$  is inconsistent with a normal geometry of  $\text{D}_2\text{O}$  bonded to a transition metal cation in which the metal ion coordinates to the oxygen. The short interaction distance to D is rather similar to that found for water interacting with small negative ions.<sup>30,31</sup> This suggests a D-O bond orientation for water toward the manganese corre-

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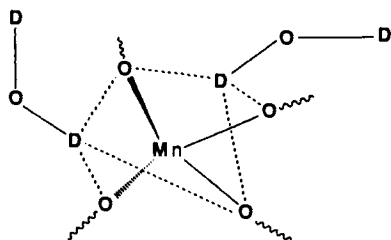


Figure 11. Proposed model of Mn coordination in MnAPO-11 hydrated with  $D_2O$ .

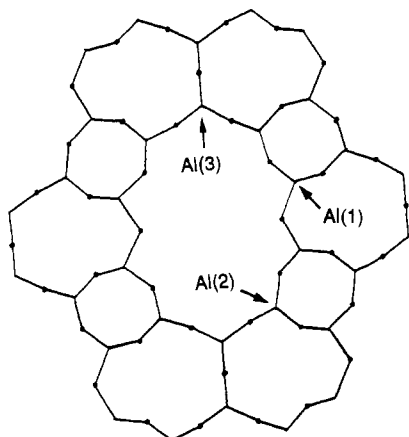


Figure 12. Projection of the framework topology of  $AlPO_4$ -11 along the  $c$ -axis. The intersections represent Al or P and the large dots represent oxygen. Three different framework aluminum sites are shown.

sponding to manganese occupying a negatively charged site.<sup>7</sup> The formation of such a site is possible if Mn(II) substitutes for Al(III) within the framework and is tetrahedrally bonded to four framework oxygen atoms (Figure 11). In this case, the manganese site is electrically equivalent to a negative charge. The simulation also shows that only two water molecules coordinate to the manganese. This is consistent with the fact that water can penetrate into the six-ring channels of the structure. Thus one molecule of water can approach the framework-substituted manganese from the main 10-ring while another water molecule can approach from the 6-ring. This suggests that manganese probably substitutes for aluminum in site Al(1) or Al(2) rather than Al(3) (see Figure 12) since Al(3) is next to two 6-ring channels and a 10-ring channel, so for Mn(II) occupying this site, one would expect to have three coordinated water molecules.

A comparison of three-pulse ESEM signals obtained from MnAPO-11 and MnAPO-5 with adsorbed  $D_2O$  shows that the water coordination is different in these two structures. If Mn(II) occupies an extra-framework position in MnAPO-5, it is expected

to be coordinated to the water through its oxygen as for ion-exchanged transition metals in zeolites.<sup>32</sup> A distance of about 0.28 nm between the deuteriums of  $D_2O$  and the paramagnetic center is then expected. The distance obtained from the ESEM simulation of MnAPO-5<sup>8</sup> is consistent with such a model, while this is not the case for MnAPO-11.

The simulation of the ESEM signal recorded from MnAPO-11 with adsorbed ethanol ( $CH_3CH_2OD$ ) shows that one ethanol interacts with the manganese at a rather short distance, 0.24 nm, from the deuterium to the Mn(II), and another ethanol at a longer distance. The short distance is consistent with that of MnAPO-11 with adsorbed  $D_2O$ , and the longer distance suggests the presence of another ethanol in an adjacent 10-ring channel.

A short interaction distance, 0.24 nm, is also obtained from the ESEM simulation for MnAPO-11 with adsorbed methanol ( $CH_3OD$ ). Since the echo decays more rapidly with adsorbed methanol than with adsorbed ethanol (Figures 9 and 10), any contribution to the echo modulation from methanol in an adjacent 10-ring channel becomes rather small. Therefore, a successful simulation has been achieved by considering only the one methanol at a short distance. The quality of the fit of the simulation is virtually the same if another methanol in an adjacent 10-ring channel at a longer distance is included.

### Conclusions

This study shows that manganese can be incorporated in the  $AlPO_4$ -11 framework at low manganese content ( $\sim 0.1$  mol %). At such a low manganese content, most of the manganese most probably substitutes for aluminum in the framework. As the manganese content increases, the relative amount of manganese substituted into the framework decreases, and the extra-framework manganese becomes more predominant. This study also indicates that manganese is not incorporated into the framework in MnAPO-5, and these opposite results for  $AlPO_4$ -11 and  $AlPO_4$ -5 indicate that manganese incorporation into the framework of  $AlPO_4$  molecular sieves is dependent on the structure type. These results also show that MnAPO-11 contains some extra-framework manganese in addition to framework-substituted manganese regardless of the Mn content. This conclusion is similar to that obtained in a recent study of cobalt in  $AlPO_4$ -5.<sup>29,33</sup>

**Acknowledgment.** This research was supported by the National Science Foundation, the Robert A. Welch Foundation, and the Texas Advanced Research Program. We thank Dr. D. Goldfarb for helpful discussions.

**Registry No.**  $H_3PO_4$ , 7664-38-2;  $Al_2O_3$ , 1344-28-1;  $Mn(CH_3COO)_2$ , 638-38-0;  $NH(Pr-i)_2$ , 108-18-9;  $AlPO_4$ , 7784-30-7.

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