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Characterization of Mg and Mn Substitution in $AlPO_4$-5

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We have examined the framework substitution of Mg and Mn into the $AlPO_4$-5 structure by studying the adsorption of reactive probe molecules, including ethylamine, isopropylamine, 2-propanol, and propene. Lattice parameters from X-ray diffraction suggests that there is a maximum framework substitution of 5 mol% for both metals. However, samples with 5 mol% Mg or Mn appear to contain large concentrations of defects in the structure, based on the observation of slow adsorption of branched alkanes. In simultaneous temperature-programmed-desorption (TPD)/thermogravimetric-analysis (TGA) measurements, both amines reacted to an olefin and ammonia in a well-defined decomposition feature between 575 and 650 K for isopropylamine and between 625 and 675 K for ethylamine. By comparison wth similar results on high-silica zeolites, the sites which decompose the amines are known to be Brønsted acid sites and decomposition occurs through an alkylammonium ion intermediate. For low concentrations of Mn and Mg (<1 mol%), the moles of isopropylamine and ethylamine which decompose in TPD–TGA are the same and equal to the moles of substituted metal atoms, indicating that the metals substitute for the Al in the framework to form Brønsted-acid sites. These same sites also catalyze the dehydration of 2-propanol above 400 K and the oligomerization of propene at 300 K.

INTRODUCTION

Isomorphous substitution of various metals for Al in the $AlPO_4$-5 structure has been the subject of a number of investigations since the introduction of aluminophosphate molecular sieves by Wilson *et al.* (*1*). However, determination of the catalytic properties of these materials is complicated by the fact that the metal cations may not be in the framework. The aluminophosphates are relatively sensitive materials which require careful calcination in order to maintain framework substitution (*2, 3*). Furthermore, there have been reports that some metals, such as Co and Mn, can exist in either the +2 or +3 oxidation states while remaining in the framework (*4–9*). This could give these materials unique catalytic properties.

The goal of this study was to examine framework substitution of Mn and Mg in an $AlPO_4$-5 structure by determining the acidic properties of the resulting materials and to look for changes in the oxidation state of Mn by looking for redox chemistry. When Mn^{+2} or Mg^{+2} are substituted for Al^{+3} in the framework, there should be one Brønsted-acid site for each substituted metal ion when the materials are in the proton-exchanged form (*10, 11*). If Mn^{+3} substitutes for Al^{+3}, one should not expect to generate acid sites; however, one should be able to detect the oxidation products formed during the reduction of Mn^{+3} to Mn^{+2}, particularly, if this occurs spontaneously upon adsorption, as has been suggested for CoAPO-5 (*6*).

Our group has previously developed a method for counting the number of strong, Brønsted-acid sites on a solid using temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of reactive amines and alcohols (*12–15*). On high-silica zeolites, well-defined complexes, corresponding to one molecule/framework Al, could be identified by the fact that the protonated amines and alcohols decomposed to

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olefins and either ammonia or water. In a study of SAPO-5 samples, it was shown that the TPD–TGA technique could also be applied to aluminophosphates to determine the number of Brønsted sites which are generated by Si in the structure (*2*). Besides looking for acid sites, the products in our system can also be trapped for analysis by gas chromatography in order to look for oxidation products (*16*). Since the sample weight is monitored throughout the experiment, the possibility of products remaining on the sample is excluded.

In this paper we will demonstrate that framework Mn^{+2} and Mg^{+2} substitute for Al^{+3} to form Brønsted-acid sites in a concentration equal to that of Mn and Mg for concentrations less than ~1 mol%. For higher Mg and Mn concentrations, the $AlPO_4$-5 structure appears to be highly defected, as indicated by a decreased concentration of acid sites and poor uptakes of branched hydrocarbons. While a color change was observed in the MnAPO-5 samples upon calcination, we found no evidence for changes in the oxidation state of framework Mn from adsorption and we suggest that more evidence is needed before the presence of Mn^{+3} in framework positions can be confirmed.

EXPERIMENTAL

To synthesize our samples, a stoichiometric quantity of phosphoric acid (85%) was first added to hydrated aluminum oxide (Catapal B, Vista Chemical Co.), followed by the addition of distilled water, the appropriate metal acetate at the desired framework concentration, and tetraethylammonium hydroxide (TEOH, 40%, Morton Thiokol, Inc.). Using the MnAPO-5(1.0) as an example, the precursor gel contained 41.29 mmol of P, 40.50 mmol of Al, and 1500 mmol of H_2O. This mixture was maintained at 350 K for 1 hr with vigorous stirring, after which a solution containing 470 mmol of H_2O and 20.07 mmol of TEOH was added to it. Finally, 0.84 mmol of Mn was added to the mixture with 15 min of stirring at 350 K. This solution was then placed in teflon-lined, stainless-steel autoclaves, which were in turn placed in an oven at 450 K for 24 h. Finally, the crystals from the autoclaves were filtered and washed with distilled water. X-ray diffraction showed that all of the samples had the $AlPO_4$-5 structure, with no amorphous halos or other crystalline phases.

TABLE 1

Physical Properties of Samples Used in This Study

Sample	%Me[a]		Unit cell volume (Å^3)	Pore volume (cm^3/g)
	Gel	Analysis		
$AlPO_4$-5	0.0	—	1354	0.153
MAPO-5(0.5)	0.5	—	1368	0.140
MAPO-5(1.0)	1.0	1.18	1370	0.124
MAPO-5(5.0)	5.0	5.02	1398	0.120
MAPO-5(9.0)	9.0	—	1395	0.108
MnAPO-5(1.0)	1.0	1.11	1366	0.142
MnAPO-5(5.0)	5.0	5.50	1383	0.092

[a] % Me = 100 × Me/(Me + Al + P).

Elemental analysis was carried out by Gailbraith Labs using ICP, and a list of the samples which were prepared is given in Table 1. The table shows that the Mg and Mn concentrations determined from ICP were in reasonable agreement with the gel concentrations. Pore volumes, determined from gravimetric uptakes of O_2 at 78 K and a pressure of 64 Torr ($P/P_0 = 0.4$), are also given in the table. These measurements assumed that O_2 in the molecular sieve has a density comparable to its liquid density and that the experimental conditions lead to complete pore filling (2). Since determination of the pressure necessary to obtain complete pore filling is arbitrary and one sample exhibited a pore volume greater than the theoretical value of 0.146 cm^3/g (*17*), the values reported in this paper and elsewhere should probably be used for comparison purposes only. Most of the calcined samples exhibited reasonable pore volumes compared to the theoretical value, indicating that the quality of the samples was good. The samples containing higher Mg or Mn concentrations exhibited somewhat lower pore volumes, perhaps due to occluded materials; however, attempts to ion exchange material out of the sample did not noticeably affect the pore volumes.

The first evidence that the metals were incorporated into the framework came from the size of the unit cell of the as-synthesized samples, as determined by X-ray diffraction. Lattice parameters were determined by measuring the positions of peaks between 50° and 60° 2θ, using the (222) line of NaCl, which had been physically mixed with the samples, as an internal reference. The size of the unit cell was found to increase in a regular manner with the metal content up to a metal concentration of roughly 5 mol%, as shown in Table 1. Above this, no changes in lattice parameters were observed, suggesting that the amount of metal which can be incorporated into the $AlPO_4$-5 structure is limited. The value of 5 mol% metal substitution is close to that which would be expected based on the limited space available for the template molecules. Assuming that there must be one tetraethylammonium cation for each metal ion incorporated into the framework, the volume of TEAOH (density = 1.2 g/cm^3) corresponding to 5 mol% is 0.123 cm^3/g, which is a reasonable fraction of theoretical pore volume.

The equipment and procedures used in the TPD–TGA measurements have been described elsewhere (*12*, *16*). TPD and TGA were carried out simultaneously using a microbalance mounted within a vacuum chamber. The system could be evacuated with a turbomolecular pump to a pressure of $\sim 10^{-7}$ Torr, and desorbing gases could be monitored using a quadropole mass spectrometer interfaced to a microcomputer. Alternatively desorbing gases could be evacuated with a liquid-nitrogen trap and transferred to a gas chromatograph for additional sensitivity and chemical discrimination (*16*). Approximately 15 mg of sample was spread in a thin layer over the sample pan of the microbalance in order to minimize bed effects during desorption (*18*, *19*). The heating rate was maintained at 10 K/min by a feedback controller, and adsorption was carried out by exposing the sample to between 2 and 10 Torr of adsorbate at 295 K until no further weight change was observed.

Calcination of the samples was carried out by heating in dry, flowing O_2 at 870 K for 2 hr. It should be noted that these samples were very sensitive to the conditions used for calcination. If the sample bed was too large or any water was present, the quality of the samples measured by the pore volumes was greatly decreased. Also, the number of acid sites measured in the TPD–TGA experiments decreased significantly, suggesting that Mg and Mn were removed from the framework. After calcination, the Mn-containing samples were found to turn from white to violet in color. Following adsorption and desorption of amines or olefins, the samples were found to change back to white. Unless otherwise stated, all of the results reported in this paper were carried out on samples which were white. UV–visible absorption spectroscopy was used on selected samples to characterize them in more detail. The spectra were obtained with a Perkin–Elmer Lambda 9 spectrometer. The samples were placed in a quartz cell with a 2-mm path length and examined under ambient conditions.

RESULTS

TPD–TGA results for isopropylamine on the calcined MAPO-5(0.5) and MnAPO-5(1.0) are shown in Figs. 1 and 2; the corresponding results on a pure $AlPO_4$-5 have been published elsewhere (*2*). Below 575 K, only unreacted amine (*m*/*e* = 44, 41, and 17) is observed leaving the sample. On the pure $AlPO_4$-5, all of the amine desorbs from the sample, unreacted, in this temperature region. On MAPO-5 and MnAPO-5, a substantial fraction of the amine desorbs as propene (*m*/e = 41) and ammonia (*m*/*e* = 17) from a well-defined feature between 575 and 650 K. It is important to note that, when the TGA results are converted from grams amine/gram of sample to moles/mole of sub-

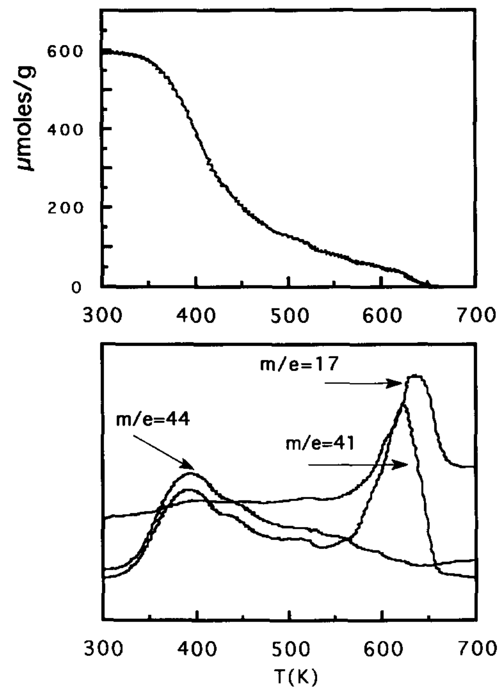

FIG. 1. TPD–TGA curves for isopropylamine on MAPO-5(0.5). The features correspond to isopropylamine (*m/e* = 44, 41, and 17), propene (*m/e* = 41), and ammonia (*m/e* = 17).

stituted Mg or Mn, the quantity of amine which decomposed on MAPO-5(0.5) and MnAPO-5(1.0) corresponded to one molecule per Mg or Mn, within experimental error, as shown in Table 2. Since the decomposition to propene and ammonia is not observed on the pure $AlPO_4$-5, the high-temperature feature must be associated with the Mg and Mn.

The TPD–TGA curves shown in Figs. 1 and 2 are virtually identical to previous curves for isopropylamine in H-ZSM-5 and other high-silica zeolites (*12, 13*). In the zeolite studies, a decomposition feature between 575 and 650 K was also observed, and the amount of amine corresponding to this feature was one molecule per framework Al. The amine decomposition reaction appears to occur through an alkylammonium ion, via a reaction similar to the Hoffman elimination reaction, as shown below:

$$(CH_3)_2CHNH_2 + ZOH \rightarrow (CH_3)_2CHNH_3^+ZO^-$$

$$(CH_3)_2CHNH_3^+ZO^- \rightarrow CH_3CH{=}CH_2 + NH_3 + ZOH.$$

It has been suggested that the decomposition of the isopropylammonium ion is not affected by the strength of the acid site so long as the ammonium ion is maintained up to the temperature at which the reaction occurs (*20, 21*). The implication of this mechanism is that the MAPO-5(0.5) and MnAPO-5(1.0) samples have strong, Brønsted-acid sites in a concentration equal to the Mg and Mn concentrations. Since substitution of Mg^{+2} and Mn^{+2} for Al^{+3} in lattice positions in the aluminophosphate should result in a lattice charge imbalance which would be balanced by a proton, the TPD–TGA curves indicate that both metals are divalent and in the lattice.

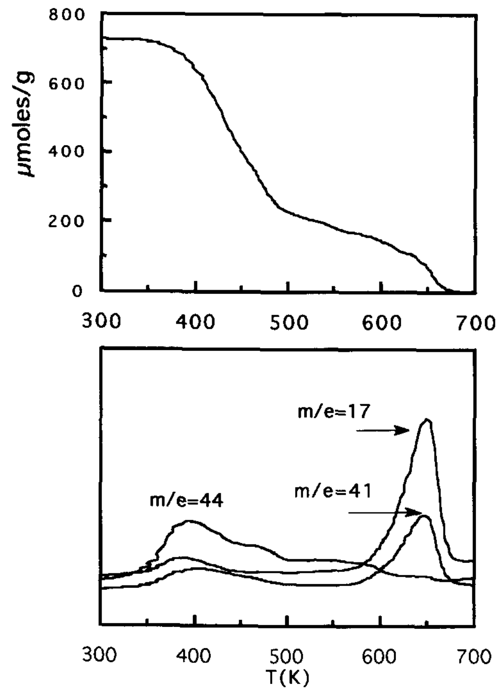

FIG. 2. TPD–TGA curves for isopropylamine on MnAPO-5(1.0).

The TPD–TGA curves for ethylamine on

TABLE 2

Acid-Site Concentrations Determined from the Amount of Isopropylamine and Ethylamine which Decompose in TPD

Sample	[Site] (μmol/g)		Moles/Me	
	Isopropylamine	Ethylamine	Isopropylamine	Ethylamine
AlPO$_4$-5	<10.0		—	
MAPO-5(0.5)	90.0	70.0	1.10	0.90
MAPO-5(1.0)	130.0		0.80	
MAPO-5(5.0)	70.0	230.0	0.09	0.27
MAPO-5(9.0)	70.0	150.0	0.05	0.10
MnAPO-5(1.0)	170.0	160.0	1.00	0.93
MnAPO-5(5.0)	130.0	150.0	0.16	0.18

each of the samples are very similar to those for isopropylamine, with the results for the MnAPO-5(5.0) shown in Fig. 3. Again, only unreacted ethylamine ($m/e = 30$) desorbs from the pure AlPO$_4$-5 below 550 K, while ethene and ammonia desorb simultaneously between 625 and 700 K on the metal-substituted samples. Again, the decomposition temperature for ethylamine on the MAPO-5 and MnAPO-5 samples is identical to that found on H-ZSM-5, suggesting that reaction occurs at simple, Brønsted-acid sites (*20*).

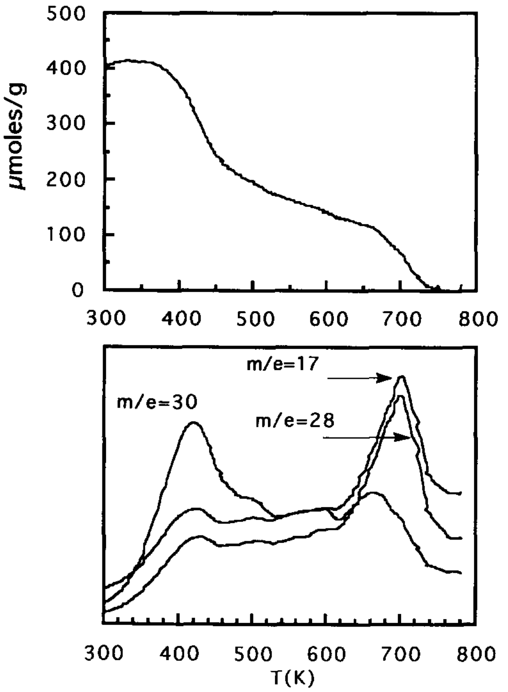

FIG. 3. TPD–TGA curves for ethylamine on MnAPO-5(5.0). The features correspond to ethylamine ($m/e = 30$), ethene ($m/e = 28$), and ammonia ($m/e = 17$).

The amounts of isopropylamine and ethylamine which decomposed on each of the samples are given in Table 2. For Mg and Mn concentrations of 1 mol% and less, the moles of ethylamine and isopropylamine which reacted during the TPD measurements on a given sample were essentially the same. Also, the concentration of sites which catalyzed the decomposition of amines is the same as the Mg or Mn concentration. However, these observations did not hold true for higher amounts of substitution. The 5 mol% samples did not show appreciably higher acid-site concentrations than the 1 mol% samples and the TPD results for the MAPO-5(9.0) actually showed a lower concentration of sites on this sample. Adsorption of isopropylamine on these samples was also difficult. The uptake rates on the 5 and 9 mol% samples were slow, requiring relatively long (~10 min) exposures to saturate the samples. The saturation uptakes were also low. The final coverages on the MAPO-5(5.0) and MnAPO-5(5.0) samples were 4.1 and 7.0 mg/g, respectively, compared to a final coverage of 70.7 mg/g on

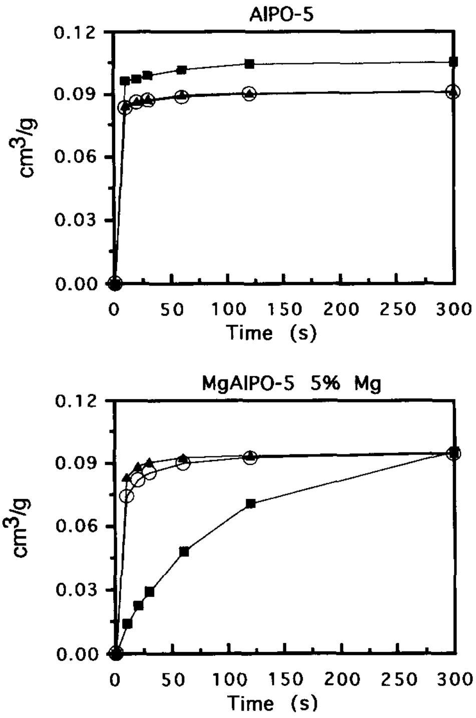

FIG. 4. Adsorption uptakes curves for *n*-pentane (▼), cyclopentane (○), and 2,2,4-trimethylpentane (■) on AlPO-5 and MAPO-5(5.0).

the pure AlPO$_4$-5. Finally, concentrations of acid sites were substantially higher on these samples when determined by ethylamine than by isopropylamine.

Since the porosities of all of the samples were reasonably high, the observations on the 5 and 9 mol% samples suggested either that some sites are partially blocked or that amine molecules adsorbed near the mouth of the pores could prevent other molecules from entering the pores and accessing interior sites. To determine whether strongly adsorbed molecules could limit adsorption, we measured uptake rates for *n*-pentane, cyclopentane, and 2,2,4-trimethylpentane on AlPO$_4$-5 and MAPO-5(5.0), with the results shown in Fig. 4. All three alkanes rapidly reached an equilibrium coverage in AlPO$_4$-5. While the rates of uptake for *n* = pentane and cyclopentane were also rapid on MAPO-5(5.0), the uptake of 2,2,4-trimethylpentane was very slow, even though the final coverage approached the same value found for AlPO$_4$-5. Therefore, the pores must be partially blocked on the MAPO-5 sample.

To determine whether the blockage was due to occluded material which could be removed by ion exchange, we washed the MAPO-5(5.0) sample with 1.0 *M* NH_4Cl at 360 K for 1 hr. However, this had no effect on either the pore volumes, the TPD–TGA results for isopropylamine, or the uptake rates for 2,2,4-trimethylpentane. While it is possible that occluded material cannot be removed by ion exchange, we suggest that high Mg and Mn concentrations may result in defects which distort the one-dimensional channels of the AlPO$_4$-5 structure. This could limit adsorption in a similar manner to that observed on AlPO$_4$-8, a material which has large channels but limited adsorption capabilities. At the present time, we have no method for determining which of these possibilities is responsible for the limited access to the pore volume.

The oligomerization of propene provides further evidence that strong Brønsted-acid sites are formed by the incorporation of Mn and Mg into the AlPO$_5$-5 structure. When the MAPO-5(1.0) and MnAPO-5(1.0) were exposed to 15 Torr of propene at room temperature, the pore volume rapidly filled with oligomers which could not be evacuated. Upon heating, multiple desorption products were observed in TPD–TGA, probably due to cracking of the oligomers in a manner similar to that observed in a previous study of H-ZSM-5 (*16*). In contrast to this, no oligomerization occurred in a pure AlPO-5 and all physisorbed propene could be evacuated at room temperature.

The Brønsted-acidic properties of the MAPO-5 and MnAPO-5 samples give strong evidence that Mg^{+2} and Mn^{+2} ions are present as framework, tetrahedral species in the AlPO$_4$-5 structure. However, there have been reports that Mn can also exist as Mn^{+3} in the AlPO$_4$-5 structure (*4*, *9*). The Mn-containing samples were found to change from white to violet upon calcination. This

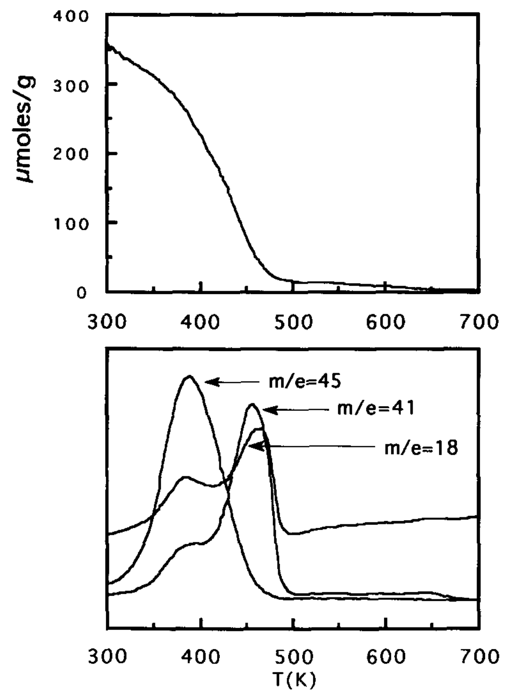

FIG. 5. TPD–TGA curves for 2-propanol on MnAPO-5(1.0). The features correspond to 2-propanol (*m/e* = 45, 41, and 18), propene (*m/e* = 41), and water (*m/e* = 18).

color change was reversible and the samples were found to change back to white following adsorption of either isopropylamine, propene, or 2-propanol. Unlike previous reports for color changes with CoAPO-5 samples (*6*), the conversion back to white did not occur at room temperature but was observed only after the adsorbate had been removed by heating. Others have suggested that the violet color is due to oxidation of Mn^{+2} to Mn^{+3} (*9*).

To investigate this possibility further, we looked for oxidation products corresponding to the apparent reduction of Mn^{+3}. First, TPD–TGA curves for 2-propanol were obtained from a violet sample, as shown in Fig. 5. Only 2-propanol (*m/e* = 45, 41, and 18), propene, (*m/e* = 41), and water (*m/e* = 18) were observed leaving the sample, with no observable formation of oxidation products like acetone. In order to make sure that no oxidation products were formed, a violet sample was next exposed to 10 Torr of 2-propanol and the excess 2-propanol which did not adsorb was collected in the liquid-nitrogen trap for GC analysis. Then a TPD–TGA measurement was carried out while collecting the products with the liquid-nitrogen trap for analysis. Again, the main products found in the GC analysis were 2-propanol and propene; essentially no oxidation products were found in any of the products collected. The amount of acetone collected in the trap corresponded to less than that which would be formed by a change in oxidation state of 2% of the Mn in the MnAPO-5(1.0). Also, the weight of the sample following an adsorption–desorption sequence was identical to the initial weight, excluding the possibility that some oxidation products remained in the sample.

We also attempted to quantify the possibility of an oxidation state change using UV–visible absorption spectroscopy, with spectra of the MnAPO-5(1.0), after calcination and after an adsorption–desorption sequence with isopropylamine, shown in Fig. 6. However, it is again difficult to conclude that framework Mn has variable oxidation states based these results. The calcined sample shows a broad band centered at 550 nm, while the spectrum of the sample after it had been exposed to the amine is feature-

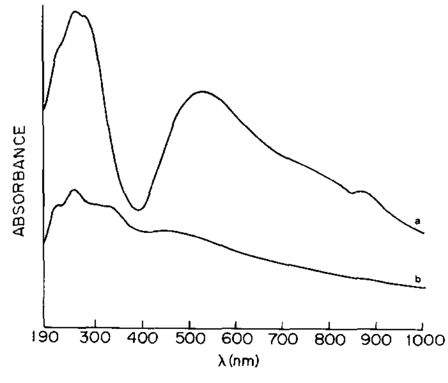

FIG. 6. UV–visible absorption spectra for MnAPO-5(1.0) after calcination (a) and after an adsorption–desorption cycle with isopropylamine (b).

less. In comparison, tetrahedral complexes of Mn^{+2} in solution are yellow-green in color and exhibit several sharp features in the visible region. Reference complexes with tetrahedral Mn^{+3} are difficult to find.

One difference which was observed between the white and violet samples of MnAPO-5(1.0) was in the rate of uptake for isopropylamine. Adsorption in the violet sample was much slower than in the white samples, and much longer exposures were needed to obtain the same coverage on the violet samples. This might indicate that significant defects exist in the MnAPO-5 samples following calcination and that these defects can be removed by exposure to a reactive molecule. The color changes may be associated with changes in the electronic environment (e.g., ligand field effects) rather than oxidation state. If there are oxidation state changes, the titration experiments indicate that only a very small fraction of the Mn can be involved.

DISCUSSION

This work clearly demonstrates that Brønsted-acid sites can be observed in MAPO-5 and MnAPO-5. For low Mg and Mn concentrations, the concentrations of these sites are equal to the concentrations of substituted metal ions, indicating that samples can be prepared in which most of the Mg and Mn are present in the framework as +2 ions. The Brønsted acidity is almost certainly due to the protons which balance the framework charge associated with the +2 ions. TPD–TGA measurements of reactive amines provide a simple method for measuring acid-site densities and, therefore, for determining the presence of framework Mg and Mn.

The Brønsted-acid sites formed by framework Mg and Mn appear to be comparable in strength to that of high-silica zeolites. The fact that MAPO-5 and MnAPO-5 oligomerize propene at room temperature demonstrates that these materials are able to donate a proton to very weak bases. It should be noticed that previous work has shown that H-[Fe]ZSM-5 is not able to oligomerize propene at this temperature, indicating that the ferrosilicate has weaker sites than either MAPO-5 or MnAPO-5 (*22*).

MAPO-5 and MnAPO-5 are relatively unstable materials. The addition of high concentrations of either Mg or Mn result in materials which appear to have many defects. Large molecules are not able to enter these materials and they exhibit low concentrations of acid sites. These observations suggest that tetrahedral Me^{+2} species are unstable. Further evidence for this is shown by the fact that the MAPO-5 and MnAPO-5 samples are very sensitive to calcination conditions. The increased acid-site densities and higher pore volumes for samples calcined in dry, flowing oxygen compared to calcination in laboratory air indicate that the lattice structure degrades easily.

In our titration measurements, we did not find evidence for a change in the oxidation state of Mn^{+3} to Mn^{+2} from framework species in $AlPO_4$-5. While there have been reports for such changes from spectroscopic measurements, it should be noted that Mn^{+3} is not very stable and does not normally exist in a tetrahedral environment (*23*). Caution must be used in the interpretation of spectroscopic data to avoid contribution from nonframework species, and spectroscopic data are acknowledged to be difficult to interpret (*23*). Therefore, we believe that definitive evidence for changes in the oxidation state of framework Mn have yet to be presented. Due to the potential importance of this question, there is clearly a need for additional work to clarify the issue.

SUMMARY

We have demonstrated that Mg^{+2} and Mn^{+2} can substitute for Al^{+3} in the framework of $AlPO_4$-5. Furthermore, TPD-TGA measurements with reactive amines demonstrate that that well-defined, Brønsted-acid sites are formed in a concentration equal to the concentration of the substituted metal ions for low (≤ 1 mol%) concentrations.

While color changes are observed upon calcination of Mn-containing materials, no evidence was found for changes in the oxidation state of framework Mn.

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