An Examination of the Acid Sites in SAPO-5

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We have examined a series of SAPO-5 materials using temperature-programmed desorption and thermogravimetric analysis (TPD–TGA) of isopropylamine, *n*-propylamine, ammonia, propene, and 2-propanol and compared the results to those for AlPO-5. For isopropylamine and *n*-propylamine, desorption of propene and ammonia was observed from well-defined features in the TPD–TGA curves, features which were not observed on AlPO-5. These desorption features appear to be due to simple Brønsted-acid sites, and the concentration of sites determined by both amines was the same. For low Si concentrations, there appears to be one acid site per framework Si. The differences between AlPO-5 and SAPO-5 materials could also be observed with propene, which oligomerized at 300 K in SAPO-5 but not in AlPO-5. While differences were observed between AlPO-5 and the SAPO-5s for TPD–TGA of ammonia and 2-propanol, desorption from sites present in AlPO-5 were difficult to distinguish from the stronger sites present in the SAPO-5s. The results suggest that adsorption of simple amines may be very useful for characterization of acid sites in silica aluminophosphate molecular sieves. © 1991 Academic Press, Inc.

INTRODUCTION

The acidity of crystalline silica aluminophosphate (SAPO) molecular sieves is commonly viewed as being a complex function of framework composition, framework charge, and structure type and is not well understood (*1*). For example, it is not clear how the site concentration will change with Si concentration, or even that one should view the acidity in terms of discrete sites. In this paper, we have tried to address questions concerning the nature of the acid sites by examining the adsorption of simple bases on a series of SAPO-5 materials with varying Si content. The approach we have used is similar to that used in previous studies in our laboratory of H-ZSM-5 and other high-silica zeolites (*2–5*). In that work, simultaneous temperature-programmed desorption/thermogravimetric analysis (TPD–TGA) measurements were made for a wide variety of bases, including simple alcohols and amines. With most simple bases, it was shown that well-defined adsorption complexes, corresponding to one molecule/framework Al, could be observed in the de-

sorption curves. Furthermore, these adsorption complexes appeared to be protonated, suggesting that the acidic properties of high-silica zeolites can be explained in terms of Brønsted sites associated with framework Al atoms. These complexes do not appear to be affected by Al concentration in H-ZSM-5 zeolites or by changing the structure in high-silica zeolites. The complexes formed in the 12-membered ring zeolite H-ZSM-12 were identical to those formed in H-ZSM-5.

A simple picture of SAPOs would imply that an acid site would be generated by the substitution of Si^{4+} for a framework P^{5+}, which would lead to an ion-exchange site capable of holding a proton. However, this picture is complicated by the fact that a Si–Si pair can substitute for an Al–P pair, leaving a neutral framework. Furthermore, it has been suggested that there is islanding of silica in the framework which leads to highly siliceous regions in the SAPO (*6*). It is possible, therefore, that strong acid sites are only generated by framework Al in the highly siliceous regions. In this case, the sites would be expected to be similar to those found in zeolites.

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To test these concepts, we have examined the adsorption of 2-propanol, isopropylamine, n-propylamine, propene, and ammonia on a series of SAPO-5 materials with varying Si content. The AlPO-5 structure has one-dimensional pores with 12-membered rings and has been described elsewhere (*18*). We found that distinct desorption features are observed for isopropylamine and n-propylamine on the SAPO-5 samples but not on AlPO-5. The amine molecules corresponding to these features react to form propene and ammonia and appear to be due to amine molecules associated with strong Brønsted sites. Differences between AlPO-5 and SAPO-5 were also observed for propene adsorption. On SAPO-5 samples, oligomerization occurred at 300 K, while no reaction occurred in AlPO-5, even at 420 K, again suggesting the presence of strong Brønsted sites in the SAPO-5's but not in AlPO-5. However, we observed similar TPD–TGA features for 2-propanol and ammonia on all samples, which implies that these may not be good probe molecules for studying acidity in SAPOs.

EXPERIMENTAL

Sample Preparation and Characterization

The synthesis procedures used were based on those originally developed by Wilson *et al.* (*18*). AlPO-5 was prepared by mixing 10.6 g of phosphoric acid (85%, Fisher), 4.6 g of hydrated aluminum oxide (Catapal B, Vista Chemical), and 59.8 g of distilled water. A solution of 17.0 g of tetraethylammonium hydroxide (40%, Morton Thiokol, Inc.) in 18.86 g of distilled water was then added. The resulting mixture was stirred at 350 K for 1 h and placed in a teflon-lined, stainless-steel autoclave. The mixtures were heated to 450 K for 6 to 8 days, after which the samples were filtered and washed with distilled water. The procedure for preparing the SAPO-5 samples was identical except for the addition of tetraethylorthosilicate (Alpha Chemical) to the tetraethylammonium hydroxide solution. The concentrations of the various materials prepared are

TABLE 1

Composition of Materials Used in the TPD–TGA Studies

Sample	Si[a]	Al[a]	P[a]
AlPO-5	0.00 (1.0)[b]	49 (50)	51 (49)
SAPO-5(0.5)	0.48 —	49 —	50 —
SAPO-5(16)	16. (12.)	42 (45)	43 (42)
SAPO-5(17)	17. (12.)	41 (45)	42 (43)

[a] All concentrations are reported as $100X/\text{Si} + \text{Al} + \text{P}$, where $X = \text{Si}$, Al, or P.
[b] Values in parenthesis were determined by ICP at Galbraith Labs.

listed in Table 1. Concentrations were determined by ICP for three of the materials; but, due to a variation in the results obtained on the same materials in separate analyses, we used Si gel concentrations for all the calculations in this paper. The gel concentrations and the ICP results are summarized in Table 1.

The samples were characterized with X-ray diffraction and gave sharp peaks with no amorphous halo. No additional crystalline phases were found in any of the samples. Lattice parameters for the as-synthesized materials were determined using the peaks between 50 and 60° 2θ, with the (222) line of NaCl, which had been physically mixed with the samples, used as an internal reference. The unit cell volumes, shown in Table 2, increased only slightly with increasing Si content, apparently due to the fact that the average of the Al–O and P–O bond lengths is approximately the same as the Si–O bond length. The morphology of the particles, determined by SEM, showed that the samples consisted of spherical aggregates of crystals between 10 and 35 μm in diameter. The individual crystals in these aggregates were hexagonal in shape and less than 0.1 μm in width.

Calcination conditions were found to be very important. The results following calcination in laboratory air were considerably different from those obtained on the same samples after calcining in flowing, dry O_2. The pore volumes and acid-site concen-

TABLE 2

Physical Characteristics of the Materials Used in the TPD–TGA Studies

Sample	Unit cell volume ($Å^3$)	Porosity[a]	
		Dry O_2 (cm^3/g)	Lab air (cm^3/g)
AlPO-5	1354	0.153	0.137
SAPO-5(0.5)	1356	0.171	0.133
SAPO-5(16)	1368	0.169	0.127
SAPO-5(17)	1368	0.150	0.146

[a] Determined with O_2 at 64 Torr and 78 K.

trations obtained following calcination in dry O_2 were always significantly higher. This difference appears to be due to the water vapor present in laboratory air. Calcination at higher or lower temperatures in laboratory air could not reproduce the higher pore volumes and site concentrations found with O_2 calcination. Unless otherwise stated, all of the SAPO-5 results reported in this paper were obtained following calcination in dry O_2 at 870 K for 2 h. Since calcination of the AlPO-5 sample in laboratory air appeared to introduce additional desorption features, most of the TPD–TGA results shown in this paper for the AlPO-5 sample were taken following calcination in laboratory air in order to demonstrate that desorption features observed on SAPO-5 samples were not introduced on AlPO-5, even for this more severe pretreatment. Following calcination, all samples were ion exchanged with 1.0 N NH$_4$Cl for 1 h at 373 K.

The differences between the samples calcined in lab air or dry oxygen were investigated mainly by measuring porosities and by comparing TPD–TGA results for various adsorbed bases. Porosities were determined from gravimetric uptakes of O_2, assuming O_2 packed with its liquid density in the cavities of the molecular sieve, and are reported in Table 2. The O_2 uptakes were measured at 64 Torr and 78 K ($P/P_0 = 0.4$) for comparison with literature values (7). It is obvious that the samples calcined in oxygen showed

a larger pore volume; however, some of the values given in Table 2 are higher than the theoretical value of 0.146 cm^3/g (8). An examination of the isotherms for O_2 in AlPO-5 shows that the choice of O_2 pressure at which the pores are considered to be filled is somewhat arbitrary (8) and that the measurements should be used mainly for comparison purposes. While the effects of water vapor on zeolites have been well documented, little is known about similar effects occurring in AlPO-5-based materials. The porosity measurements seem to suggest that Si, Al, or P may be removed from the framework when water is present, resulting in either partially blocked pores or the presence of amorphous material in the sample. X-ray diffraction measurements of the materials calcined in lab air showed decreased peak intensities (peak half-widths remained the same), but we did not attempt to quantify the changes.

The equipment and procedures used in the TPD–TGA measurements have been described in detail elsewhere (2, 3). The apparatus consists of a microbalance which is mounted inside a vacuum chamber equipped with a quadrupole mass spectrometer. Approximately 15 mg of sample was spread in a thin layer over a flat sample pan in order to minimize bed effects in desorption (9, 10). Each sample was first cleaned by heating to 800 K in vacuum and then exposed at 300 K to ~10 Torr of the adsorbate of interest until no further weight changes were observed in the sample. After the sample had been dosed, it was evacuated for ~2 h in order to remove some of the weakly adsorbed species. The desorption experiments were performed with a heating rate of 10 K/min, and all of the adsorbates in this study were found to be completely removed in the TPD–TGA experiment. All of the TPD curves reported in this paper are arbitrarily scaled. In order to quantify the amounts of each species desorbing from a given sample, we used the TPD curve to determine the temperature range at which a given product left the sample and the mass

changes from TGA to determine the quantity of that product.

RESULTS AND DISCUSSION

The TPD–TGA results for each of the adsorbates are discussed separately. It was found that, for some bases, adsorption on pure AlPO-5 made it difficult to distinguish the strong acid sites formed by the presence of framework Si from the much weaker sites present on the aluminophosphate parts of the sample. The clearest distinction between AlPO-5 and the SAPO-5 samples was observed with isopropylamine and n-propylamine. The number of new sites due to the presence of Si, counted by these two bases, was the same, suggesting that discrete acid sites are formed by Si in these materials. The adsorption of propene was also distinctive in that oligomerization occurred in the SAPO-5 samples at 300 K, a result which is also found on H-ZSM-5 (11), while no oligomerization occurred on the AlPO-5, even at 400 K. However, the TPD–TGA results for 2-propanol and ammonia were very similar on both the AlPO-5 and SAPO-5 samples. The results for these two adsorbates did follow certain trends with Si content, but desorption features could not be assigned to particular types of sites. All of the results shown in the following sections, unless otherwise stated, were obtained on the AlPO-5 sample after calcination in laboratory air and SAPO-5(16) after calcination in dry oxygen.

Isopropylamine

Representative TPD–TGA curves for isopropylamine are shown in Fig. 1. On all samples investigated, unreacted isopropylamine (m/e = 44, 41, and 17) desorbed as a broad peak centered at ~400 K, with a shoulder tailing to approximately 600 K. Since this feature was observed on pure AlPO-5, it must be associated with the aluminophosphate parts of the samples. It is possible that the amine molecules desorbing in this feature, particularly those desorbing in the high-temperature tail, are associated with
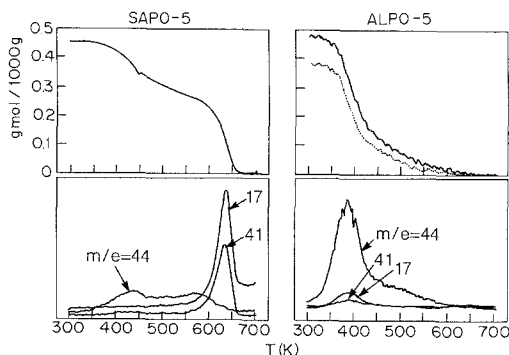

FIG. 1. TPD–TGA results for isopropylamine on the SAPO-5(16) and AlPO-5 samples. The intensities of the mass spectrometer signals are arbitrary and correspond to isopropylamine (m/e = 44), propene (m/e = 41), and ammonia (m/e = 17). The dashed line represents the AlPO-5 sample which was calcined under dry flowing O_2.

defects in the structure. When the AlPO-5 sample was calcined in dry oxygen, the high-temperature tail was much less pronounced. This is shown by the dashed line in the TGA curve for AlPO-5 in Fig. 1.

The main difference observed in the TPD–TGA results on the SAPO-5 samples was the desorption of propene (m/e = 41) and ammonia (m/e = 17) between 575 and 650 K. A similar desorption feature occurs at the same temperature in H-ZSM-5 and other zeolites (2, 3). For H-ZSM-5, the amount of isopropylamine desorbing as propene and ammonia corresponded to one molecule per framework Al (2, 3), and it has been suggested that the decomposition of isopropylamine at this temperature is due to reaction of the amine molecules which are protonated by Brønsted-acid sites (5). This decomposition temperature is the same for SAPO-5 and H-ZSM-5 and does not appear to be sensitive to the strength of the acid sites. The fact that this decomposition feature is observed only for SAPO-5 samples, and not on AlPO-5, implies that the amine molecules corresponding to this decomposition feature are associated with Brønsted-acid sites formed by Si substitution.

Table 3 is a quantitative summary of the

TABLE 3

Summary of Results for TPD–TGA
of Isopropylamine

Sample	Propene (gmole/1000 g)		Propenes/Si
	Dry O_2	Lab air	
AlPO-5	<0.00	<0.01	—
SAPO-5(0.5)	0.075	0.043	0.95
SAPO-5(16)	0.25	0.19	0.087
SAPO-5(17)	0.26	0.13	0.085

number of isopropylamine molecules which reacted in TPD–TGA for the different samples. Several features of interest are apparent from these results. First the amount of isopropylamine that reacts on the various samples increased with Si content, and this amount also increased for each sample when it was calcined in dry O_2. Second, the TPD–TGA results for the SAPO-5(16) and SAPO-5(17) samples, which had similar Si contents, were essentially identical after calcination in dry O_2, implying that synthesis of samples at a given Si content were reproducible. Third, for the sample with a low Si concentration, SAPO-5(0.5), the number of amine molecules that reacted to propene and ammonia was very close to one/Si, suggesting that well-defined acid sites are formed in this material, one for every Si which replaces a framework P. This result also suggests that the Si atoms must be isolated in this sample since no acid site should be generated if a pair of Si atoms were to replace an Al–P pair. Finally, for SAPO-5(16) and SAPO-5(17), the concentration of sites that catalyze the decomposition of isopropylamine is considerably less than the Si concentration. For these materials, the presence of Si–Si pairs is probably important.

One other difference observed in the TPD–TGA results for SAPO-5 samples compared to AlPO-5 is the presence of additional unreacted isopropylamine between 500 and 650 K. While this could be due to

weaker Brønsted acid sites or to Lewis acid sites which may not be able to catalyze decomposition of the amine, it is also possible that this additional adsorption is due to attractive interactions between molecules adsorbed at strong Brønsted sites and other amine molecules (4). It is not possible to assign this desorption feature at the present time.

n-Propylamine

TPD–TGA curves for n-propylamine on AlPO-5 and O_2-calcined SAPO-5(16) are shown in Fig. 2 and are qualitatively similar to those obtained with isopropylamine. Again, most of the unreacted n-propylamine ($m/e = 30$) desorbs from a broad feature centered at ~400 K, which is observed on both AlPO-5 and SAPO-5(16) samples. The major difference between the TPD–TGA curves on the two samples is that SAPO-5 again shows desorption of propene and ammonia. The decomposition reaction now occurs between 625 and 700 K, but this is the same temperature range observed for decomposition of n-propylamine on H-ZSM-5 (5). This suggests that, just as with isopropylamine, the reaction is limited by decomposition of the n-propylammonium ion formed by adsorption of the amine at Brønsted-acid sites. The amount of n-propylamine which decomposed to propene and ammonia for SAPO-5(16) was also the same as that for isopropylamine. This im-
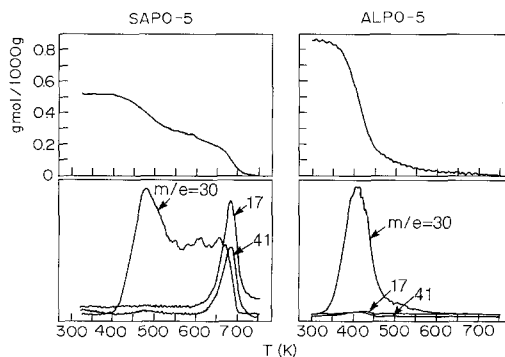

FIG. 2. TPD–TGA results for n-propylamine on the SAPO-5(16) and AlPO-5 samples.

plies that SAPO-5 contains a discrete number of sites and that the same sites are probed by both isopropylamine and *n*-propylamine. Finally, as with isopropylamine, an additional amount of unreacted *n*-propylamine is observed desorbing from the SAPO-5 samples between 500 and 650 K which may be due to weaker sites or association between molecules.

Propene

The differences between AlPO-5 and SAPO-5 were most dramatic for propene adsorption. When the SAPO-5(16) was exposed to propene at 300 K, oligomers formed in the channels that could not be removed by evacuation, a result which is also found on H-ZSM-5 (*11*). When the AlPO-5 sample was exposed to 15 Torr of propene at temperatures between 300 and 400 K, no reaction occurred. Only weakly adsorbed propene adsorbed in the AlPO-5, and this could be removed easily by evacuation. Since oligomerization probably requires protonation of propene, this is again evidence that the SAPO-5 samples contain strong, Brønsted-acid sites, associated with Si, which are not present in AlPO-5.

For the air-calcined SAPO-5(16), the weight change after exposure to 15 Torr of propene for 10 min at 300 K was 3.6 g/100 g. Assuming the density of the oligomers is ~0.9 g/cm³, a number typical of polypropylene, this coverage corresponds to ~30% of the pore volume of the sample. Since this is a substantial fraction of the available volume, oligomerization probably continues until propene can no longer reach the acid sites. The TPD–TGA results in Fig. 3 show that the oligomers crack and desorb as a wide range of products between 500 and 600 K. Peaks at m/e = 41, 43, and 55, all of which are common to a large number of hydrocarbons, are shown in the figure in order to demonstrate that propene is not the only species leaving the sample.

It is interesting to compare these results to those reported by Gricus Kofke *et al.*, for H-ZSM-5 (*11*). Propene oligomerization
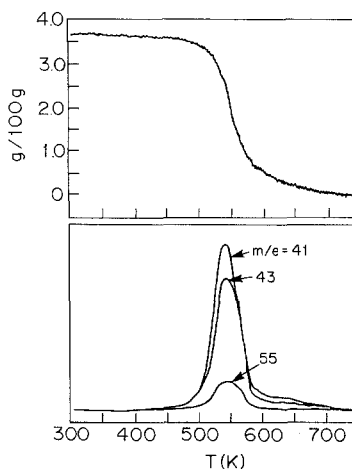

FIG. 3. TPD–TGA results following propene adsorption on SAPO-5(16).

also occurred at the Al sites in H-[Al]-ZSM-5 at 300 K; and the main difference between the TPD–TGA results on the two samples is that the oligomers crack at a lower temperature on H-[Al]-ZSM-5, with most products leaving the sample between 400 and 500 K. This lower reaction temperature for H-[Al]-ZSM-5 may be due to the zeolite having stronger acid sites than those present on SAPO-5. It is also interesting to note that propene did not oligomerize at 300 K on H-[Fe]-ZSM-5, which suggests that the acid sites in this material are weaker than those on SAPO-5 (*12, 13*). Adsorption of propene, then, implies that the strength of the sites in SAPO-5 lie between that of H-[Fe]-ZSM-5 and H-[Al]-ZSM-5.

2-Propanol

With 2-propanol, it was difficult to observe the strong Brønsted-acid sites which are present due to Si, as demonstrated by the TPD–TGA curves for AlPO-5 and O_2-calcined SAPO-5(16) shown in Fig. 4. The TPD–TGA curves on all samples were qualitatively the same. On all samples, unreacted 2-propanol desorbed as a broad peak centered at ~400 K, and substantial amounts of propene and water desorbed at higher temperatures. While more propene
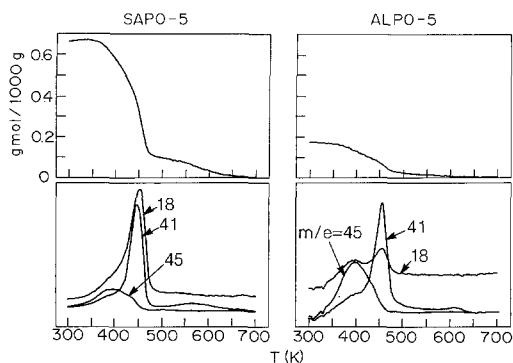
FIG. 4. TPD–TGA results for 2-propanol on the SAPO-5(16) and AlPO-5 samples. The peaks monitored in TPD correspond to 2-propanol (m/e = 45, 41, and 18), propene (m/e = 41), and water (m/e = 18). The relative intensities are arbitrary.

and water desorbed from the SAPO-5 samples and reaction appeared to occur at slightly lower temperature on SAPO-5, the fact that reaction occurred on AlPO-5 in the absence of Si makes it difficult to distinguish between molecules reacting on the aluminophosphate parts of the sample from those reacting at strong sites associated with Si. Whether the 2-propanol which reacts on AlPO-5 is associated with defects in the structure (14–16) or is inherent to AlPO-5 is not possible to determine from our results. In previous work on zeolites, there was no reaction of 2-propanol on highly siliceous materials; and only one molecule/Al desorbed as propene and water (2, 3). With silica aluminophosphates, 2-propanol does not appear to be as useful as a probe molecule for examining strong acid sites on aluminophosphate molecular sieves.

Ammonia

Ammonia is probably the most commonly used probe molecule for examining acid sites in molecular sieves; however, our results suggest that, like 2-propanol, it is difficult to distinguish between ammonia desorbing from strong sites associated with Si and other sites present in the samples. Figure 5 shows the TPD–TGA results for AlPO-5 and the O_2-calcined, SAPO-5(16)

samples. The results are very similar to those reported elsewhere (17) and show broad peaks which may indicate multiple desorption states. More of the ammonia desorbs at higher temperatures from the SAPO-5 and it may be possible to deconvolute the curves in order to assign different features to various types of sites; however, this deconvolution is not trivial and was not attempted in this study. No attempt was made to calculate desorption activation energies from these TPD results because calculations have shown that the desorption process is much too complicated for the calculated values to be meaningful (9, 10).

DISCUSSION

The most interesting result in this work is that well-defined desorption features are observed with simple amines in SAPO-5 materials that are not observed in AlPO-5. The sites responsible for these desorption features appear to be Brønsted-acid sites, and TPD–TGA allows the concentration of these sites to be quantified. While the strength of the Brønsted-acid sites in SAPO-5 cannot be determined directly, it can be inferred that these sites are stronger than those present in H-[Fe]-ZSM-5 based on the ability of the materials to protonate propene.

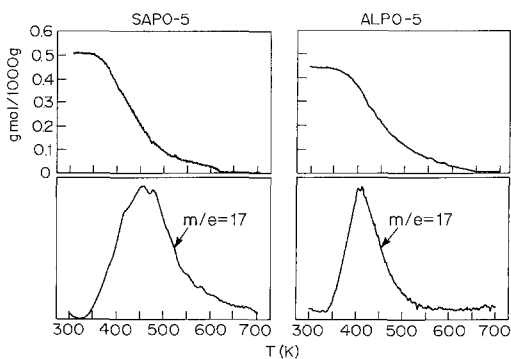The ability to quantify the number of acid sites allows certain features of SAPO-5 acid-

FIG. 5. TPD–TGA results for ammonia (m/e = 17) adsorbed on the SAPO-5(16) and AlPO-5 samples.

ity to be demonstrated. First, quantification of acid site concentrations demonstrates how sensitive these materials are to calcination conditions. While the materials which were calcined in laboratory air had properties which appeared acceptable, it was clear from the differences observed in the TPD–TGA of amines following dry O_2 calcination that significant damage had occurred when laboratory air was used. Calcination of aluminophosphate molecular sieves should always be carried out in very dry conditions. Second, it can be seen that reasonably strong acid sites can be formed by isolated Si in the aluminophosphate matrix. Since Si tends to form islands in aluminophosphate molecular sieves (6), it was conceivable that the only strong acid sites in SAPO-5 are due to tetrahedral Al in a siliceous part of the crystal. However, since there appears to be approximately one site/Si for low Si concentrations, strong sites must be generated by isolated Si. While we did not study the effect of Si concentration systematically, it is clear that there is extensive pairing at higher Si concentrations. TPD–TGA may be a complimentary technique to NMR for studying this phenomenon.

SUMMARY

Our results for isopropylamine, n-propylamine, and propene clearly demonstrate that TPD–TGA techniques can identify strong acid sites in SAPO-5. These strong sites appear to be discrete Brønsted-acid sites which are generated by the substitution of Si for P in the AlPO-5 framework. While it is not simple to determine the strength of these sites from TPD–TGA, desorption of isopropylamine or n-propylamine does appear to allow quantification of site concentrations. The concentration determined for a particular sample by both amines was the same, and, for dilute Si concentrations, the site concentration was virtually identical to the Si concentration. The sensitivity of the samples to calcination in laboratory air

points out the importance of maintaining dry conditions during pretreatment of SAPOs. Both pore volumes and acid site concentrations were increased significantly when dry calcination conditions were used.

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