Chem. Mater. **2006,** *18,* 1705−1710

Synthesis and Characterization of a New Microporous Material. 2. AlPO and SAPO Forms of EMM-3

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Received September 28, 2005. Revised Manuscript Received December 21, 2005

A *new* aluminophosphate (AlPO) material, EMM-3, was recently synthesized at ExxonMobil. EMM-3, ExxonMobil material no. 3, was synthesized in both the AlPO- and SAPO-forms. The structure of the AlPO-form of EMM-3 has been solved using FOCUS Fourier recycling method with the help of a series of characterization techniques. Multinuclear, multifield solid-state NMR, SEM, and powder XRD measurements were performed in order to help understand the molecular arrangement and structure of the material. Carbon-13 CPMAS NMR of the as-synthesized material shows that the structure-directing agent remains intact with no strong chemical shift anisotropy indicating considerable mobility of the structure-directing agent in the internal voids of EMM-3. The multitechnique characterization of EMM-3 shows that only one type of crystal morphology is present, indicating the high purity of the sample. The XRD pattern of calcined-dry EMM-3 is consistent with orthorhombic symmetry. Distinct changes in local symmetry of the P and Al atoms occur upon calcination and subsequent hydration, and these changes are observed by solid-state NMR. Whereas the ^{31}P MAS NMR of calcined-dry EMM-3 shows three peaks in a ratio of 1:2:3, upon rehydration, the ^{31}P MAS NMR of EMM-3 shows that there are at least five distinct environments for the P atoms in a ratio of 1:2:1:1:1. The calcined-rehydrated sample shows a strong octahedral ^{27}Al signal, due to framework hydration. SAPO-forms of EMM-3 were successfully synthesized and show acid activities. The Brønsted acidity was measured quantitatively by ^{1}H MAS NMR.

Introduction

Aluminophosphates[1] (AlPOs) and silicoaluminophosphates[2] (SAPOs) are crystalline microporous materials consisting of 3-dimensional frameworks with uniform pore openings, channels, and internal cages of dimensions ($<$20 Å) similar to most hydrocarbons. The compositions of the SAPO frameworks are such that they are anionic, which require the presence of nonframework cations to balance the negative charge. These nonframework cations are typically organic structure-directing agents (SDAs) such as tetraalkylammonium ions that are incorporated inside the pores during crystallization. After calcination in air to remove the organic SDA, the material is converted to the proton form, producing Brønsted acid sites having catalytic activity. The combination of acidity and restricted pore openings gives these materials unique catalytic properties due to their ability to exclude or restrict some of the products, reactants, and/or transition states in many reactions. Nonreactive materials, such as pure silica and aluminophosphate frameworks, are also useful in absorption and separation processes of liquids, gases, and reactive molecules such as alkenes.

We have recently discovered a new aluminophosphate material, designated EMM-3, that can be prepared with *N*,*N*,*N*,*N*′,*N*′,*N*′-hexamethyl-1,6-hexanediammonium (hereafter referred to as hexamethonium) cation. After characterization of EMM-3 with various techniques to determine its physical properties, the framework structure of the calcined-dry form of EMM-3 was determined[3] using FOCUS, a direct methods program that uses intensity data extracted from powder diffraction data.[4] The structure consists of 1-dimensional 12-ring channel pores intersected by 8-ring pores. The framework of calcined EMM-3 was found to reversibly hydrate in ambient air to form a structure having lower symmetry than the dehydrated form.

In this paper, part 2, we further investigate the reversible hydration/dehydration of EMM-3 as characterized by NMR techniques. We also discuss the preparation of the silicoaluminophosphate composition of EMM-3 and the characterization of its catalytic activity.

Experimental Section

Synthesis of EMM-3. EMM-3 was prepared from reaction mixtures having the stoichiometry $0.5R(OH)_2$:Al_2O_3:P_2O_5:$xSiO_2$:$45H_2O$ where R is hexamethonium, $(CH_3)_3N(CH_2)_6N(CH_3)_3^{2+}$. The AlPO-EMM-3 synthesis was described earlier.[3] The SAPO-forms of EMM-3 were synthesized by mixing together the appropriate

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molar quantities of 85% H_3PO_4, water, Catapal A alumina (Condea Vista, 74% Al_2O_3), and hexamethonium dihydroxide (SACHEM, 22% aq) with a silicon source (0−0.17 mol SiO_2) such as colloidal silica (duPont Ludox HS-40 colloidal silica, 40% SiO_2), tetraethyl orthosilicate (Aldrich, TEOS), or fumed silica (Nippon Silica, NipSil VN3). The mixtures were allowed to age at room temperature for 5 min and then were mixed again for about 1 min with a spatula. (The aging step gives time for the alumina to react with the phosphoric acid to reduce the viscosity of the mixture and allow for better homogenization.) The mixtures were vigorously mixed for an additional 5 min in a blender and then heated in Teflon-lined autoclaves for 1−2 days at 130−200 °C. Products were recovered by centrifugation, slurried with water, and recentrifuged four times to wash, and then they were dried at 115 °C in an air oven.

Characterization. Elemental analyses were performed by ICP-AES after Claise fusion digestion with lithium tetraborate/lithium carbonate flux. Scanning electron micrographs were taken on a Phillips XL-40 SEM instrument after coating the samples with gold. Gas absorption was performed on an automated gas absorption apparatus consisting of a Cahn vacuum microbalance with an MKS pressure manometer and controller. Calcined samples were heated overnight at 400 °C to a pressure $<10^{-4}$ Torr before uptake measurements at room temperature.

Solid-State NMR. ^{27}Al MAS NMR spectra were recorded at 8.4 T (Bruker AMX-360), 11.7 T (Varian InfinityPlus 500), and 18.8 T (Varian Inova 800) corresponding to ^{27}Al Larmor frequencies of 93.8, 130.1, and 208.4 MHz, respectively. The ^{27}Al MAS NMR spectra were obtained with a $\pi/12$ rad pulse length and a recycle delay of about 0.2 s. The ^{29}Si, ^{13}C, ^{31}P NMR spectra were obtained at 11.7 T, corresponding to ^{29}Si, ^{13}C, ^{31}P Larmor frequencies of 99.2, 125.5 and 202.1 MHz, respectively. The samples were loaded in MAS rotors and spun at the magic angle at rates of 5, 4.5, and 13 kHz, respectively, and all measurements were done at room temperature. The ^{13}C CPMAS NMR spectrum was recorded using a 1 s recycle delay, 3 ms contact time, and about 62 kHz rf fields for both cross-polarization and decoupling. The ^{27}Al and ^{31}P chemical shifts are referenced with respect to external solutions of $Al(H_2O)_6^{3+}$ ($\delta_{Al} = 0.0$ ppm) and 85% H_3PO_4 ($\delta_P = 0.0$ ppm), respectively. The ^{31}P and ^{27}Al spectra were recorded on the as-synthesized, calcined-dry (650 °C/3 h), and calcined-rehydrated samples. Rehydration of the calcined materials was done by exposing samples to a 100% relative humidity environment over a period of time, usually overnight. The ^1H MAS NMR spectra were recorded at 360 MHz, and quantification was performed by comparing the integrated signal intensity against an external standard.[5]

Powder X-ray Diffraction. XRD data were recorded on a Siemens D5000 equipped with secondary graphite monochromator, scintillation detector, and Cu Kα radiation and on a Scintag XDS 2000 equipped with a liquid N_2 cooled, solid-state germanium detector, Cu Kα radiation, and an Edmund Bühler 2.3 HDK high-temperature chamber.

Catalytic Testing. The α test was run at a constant temperature of 538 °C and a variable flow rate.[6] The α value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst, and it gives the relative rate constant of normal hexane conversion per volume of catalyst per unit time. It is based on the activity of silica−alumina cracking catalyst taken as an α of 1 (rate constant $= 0.016$ s^{-1}).

Table 1. Conditions and Recovered Products of EMM-3 Syntheses Having a Starting Composition of 0.5Hexamethonium$(OH)_2$:Al_2O_3:P_2O_5:$x$$SiO_2$:45$H_2O$

expt no.	SiO_2	Si source	temp, °C	time	product(s)
1	0		130	40 h	EMM-3 weak
2	0		150	16 h	EMM-3
3	0		200	16 h	EMM-3
4	0		160	20 h	EMM-3
5	0.2	colloidal	160	2 days	EMM-3
6	0.4	colloidal	130	40 h	EMM-3-sharp peaks
7	0.4	colloidal	160	28 h	EMM-3
8	0.4	colloidal	160	40 h	EMM-3-broader peaks
9	0.4	colloidal	200	16 h	SAPO-17
10	0.05	fumed silica	160	3 days	EMM-3 + SAPO-31
11	0.1	fumed silica	160	3 days	SAPO-31 > EMM-3
12	0.2	fumed silica	160	3 days	SAPO-31 > EMM-3 + SAPO-17
13	0.4	fumed silica	160	44 h	weak unknown phase
14	0.1	TEOS	160	2 days	EMM-3 + SAPO-31
15	0.2	TEOS	130	1 days	amorphous
16	0.2	TEOS	175	2 days	SAPO-17
17	0.4	predigested	160	2 days	AlPO-C > unknown
18[a]	0.4	predigested	160	2 days	EMM-3
19[a]	0.6	predigested	160	2 days	EMM-3
20[a]	0.8	predigested	160	2 days	EMM-3
21[a]	0.2	TEOS	160	2 days	EMM-3
22[a]	0.4	TEOS	160	2 days	EMM-3

[a] Seeded synthesis.

Results and Discussion

Materials Synthesis. EMM-3 is synthesized in conventional AlPO and SAPO syntheses with the use of hexamethonium as a structure-directing agent (SDA). In the AlPO form, EMM-3 can be synthesized at temperatures from 150 to 200 °C in 20 h with and without stirring. AlPO EMM-3 crystallizes in platelet morphology with dimensions of 0.5−2 μm by <0.05 μm thick.

Once the AlPO form of EMM-3 was prepared, experiments were performed in an attempt to introduce silicon into the lattice to give it catalytic activity, since it is well-known that tetravalent silicon can substitute for pentavalent phosphorus in many AlPO synthesis to give an anionic framework that can be charge balanced by a Brønsted proton. Silicon was introduced as colloidal silica, organic silicon (TEOS), or fumed silica. The conditions used in the synthesis and products recovered are summarized in Table 1. In the case of colloidal silica, SAPO EMM-3 could be prepared in 1−2 days at temperatures of 130−160 °C. Going to higher temperatures (200 °C) brings in SAPO-17, the AlPO analogue of which was not formed in the aluminophosphate preparations. The formation of SAPO-17 with the hexamethonium SDA has been observed previously.[7] Experiments using fumed silica or organic silicon brought in SAPO-31 or SAPO-17 as a major impurity.

To prevent the formation of impurities, the synthesis of SAPO EMM-3 was performed using seeds with TEOS and fumed silica as the silica source. The AlPO form of EMM-3 was used for the seeds and 50−100 mg was typically added per 75 g of reactant gel. The EMM-3 seeds were added as a solid and consisted of platelet shaped crystals of dimension 0.5−2 μm and <0.05 μm thick. In the case of fumed silica, it was predigested by first dissolving it in a Teflon bottle with hexamethonium dihydroxide in an air oven for several hours at 100 °C. The addition of seeds allowed pure SAPO-

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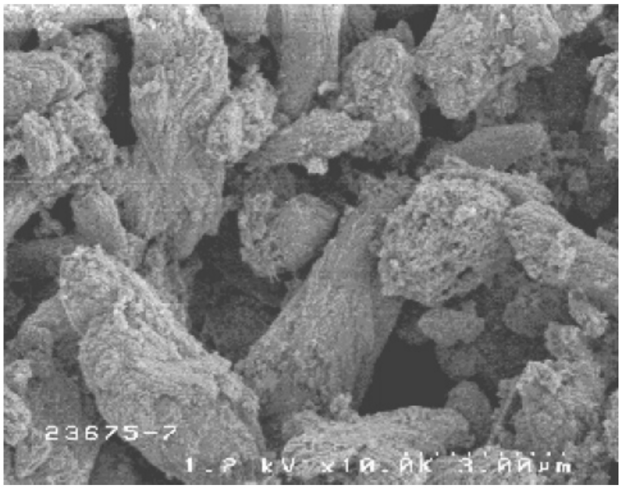

Figure 1. SEM micrographs of SAPO forms of EMM-3.

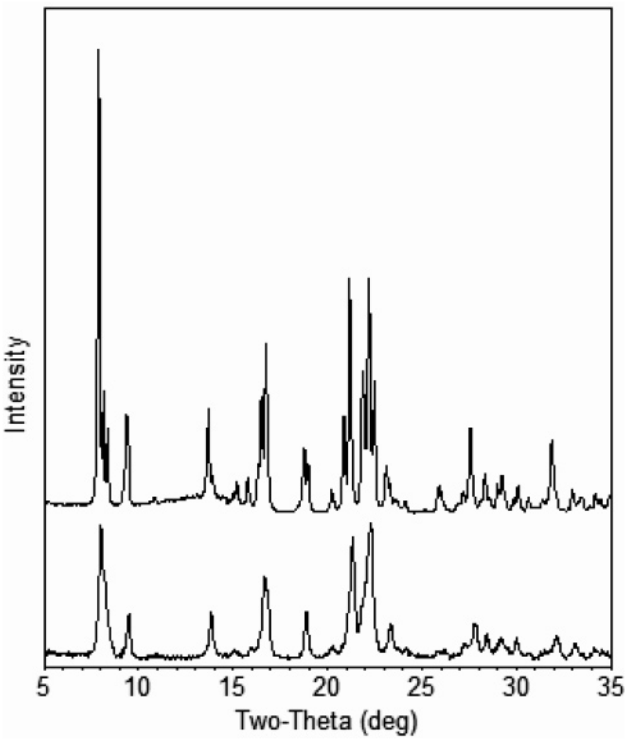

Figure 2. X-ray powder diffraction patterns of as-synthesized AlPO EMM-3 (top) and as-synthesized SAPO EMM-3 (bottom) measured with Cu Kα radiation.

EMM-3 to be prepared reproducibly at SiO_2:Al_2O_3 levels up to 0.80. The SEM micrograph of SAPO EMM-3 (Figure 1) shows agglomerates of small crystals. As shown in Figure 2, the SAPO form of EMM-3 has a similar diffraction pattern to the AlPO form, but there is significant peak broadening, indicating a smaller crystal size. MeAPO forms (Me = Zn, Fe, Co, Mg, Ge, and so forth) of EMM-3 were also successfully synthesized,[8] but the details are beyond the scope of this paper. It was found previously that the AlPO form of EMM-3 is stable to calcination in air but reversibly hydrates in ambient air to form a structure apparently having lower symmetry than the dehydrated form. The SAPO form behaves similarly.

Table 2. Conditions and Recovered Products of HF Containing EMM-3 Syntheses Having a Starting Composition of HF:0.5Hexamethonium(OH)$_2$:Al_2O_3:P_2O_5:$x$$SiO_2$:45$H_2O$

expt no.	HF	SiO_2	Si source	temp, °C	time	product(s)
23	1	0.0		130	2 days	phase A
24	1	0.2	colloidal	160	2 days	phase A
25	1	0.2	TEOS	160	2 days	SAPO-31
26	1	0.6	TEOS	160	2 days	phase A > SAPO-31
27	1	0.4	TEOS	160	2 days	SAPO-31 > phase A
28	1	0.6	TEOS	160	1 days	phase A ≫ SAPO-31
29	1	0.6	TEOS	130	2 days	phase A
30	1	0.6	TEOS	180	2 days	SAPO-31 ≫ phase A
31	1	0.8	TEOS	160	2 days	phase A
32	1	1	TEOS	160	2 days	phase A
33	1	0.2	TEOS	130	2 days	phase A
34	1	0.4	TEOS	130	2 days	phase A fair
35	1	0.4	TEOS	180	2 days	SAPO-31 ≫ phase A
36	1	0.4	TEOS	200	2 days	SAPO-31
37	1	0.6	TEOS	200	2 days	SAPO-31
38	1	0.6	predigested	200	2 days	SAPO-31

It is known that the addition of hydrofluoric acid to zeolite, aluminophosphate, and silicoaluminophosphate syntheses can greatly alter the products formed. In many cases, new structures can be made, which are not seen without the presence of fluorine. In aluminosilicate synthesis, the fluoride ion can act as a mineralizing agent, much like the hydroxide ion. Fluoride may also play an additional role as a co-structure-directing agent by interacting with the framework in small cages, such as double four-rings (D4Rs).[9] In this case, the fluoride may become part of the framework by bridging together two atoms, much the same way as a bridging oxygen atom. When this occurs, the framework atom typically changes from tetrahedral coordination to pentahedral or octahedral coordination.

As shown in Table 2, when hydrofluoric acid is added to hexamethonium-containing AlPO and SAPO type preparations, EMM-3 is replaced by SAPO-31 and/or a new crystalline phase (phase A) as the primary product. At higher temperatures, >180 °C, SAPO-31 is the main phase when HF is present. Scanning electron micrographs show needle morphology with crystal dimensions of 0.1−0.2 μm by 0.5−2 μm. SAPO-31 has a 12-ring single channel framework with puckered rings such that the pore size is 5.4 Å, similar to that of 10-ring materials. SAPO-31 has been shown to have *n*-octane isomerization activity and selectivity intermediate between that of SAPO-11 and SAPO-41.[10] At lower temperatures, 130−160 °C, phase A having needle morphology is the primary phase found in both AlPO and SAPO preparations. This material was found to be unstable to calcination in air at 650 °C, and no further work was done on its characterization.

It is fairly well established that quaternary ammonium ions usually survive hydrothermal zeolite synthesis and are incorporated into molecular sieves intact. Figure 3 shows the ^{13}C CPMAS NMR spectrum of the as-synthesized EMM-3. Comparison of this spectrum to that of aqueous hexamethonium hydroxide shows that the hexamethonium SDA remains intact. The ^{13}C spectrum of the as-synthesized EMM-3 also shows that there is no large chemical shift

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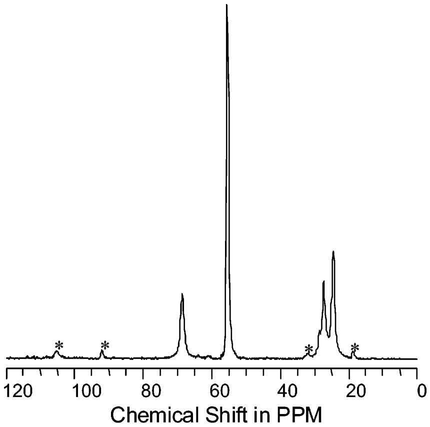

Figure 3. 125.5 MHz ^{13}C CPMAS NMR spectrum of the as-synthesized EMM-3 showing that the hexamethonium structure-directing agent, $(CH_3)_3N^+(CH_2)_6N^+(CH_3)_3$, remains intact. Asterisks indicate spinning sidebands.

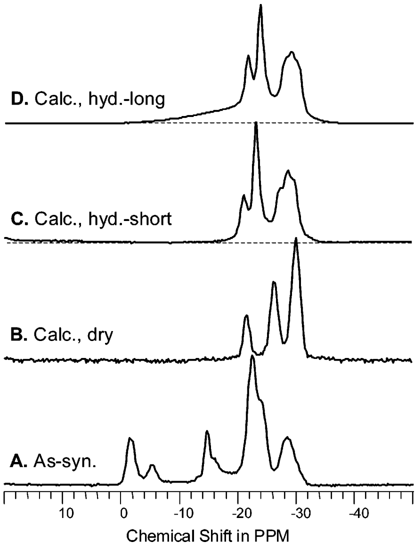

Figure 4. 202.1 MHz ^{31}P MAS NMR of as-synthesized (A), calcined-dry (B), and calcined-rehydrated forms of AlPO EMM-3. The rehydration was performed by exposing the sample to 100% RH for overnight (C) and for an extended period of time (33 days, D). The spectra were acquired at an MAS rate of 10 kHz, with a typical recycle delay of 300 s.

anisotropy (CSA), evidenced by sharp peaks and relatively small spinning sidebands. This indicates considerable mobility of the structure-directing agent and the presence of intracrystalline void geometries in EMM-3 that can accommodate the hexamethonium without restricting it severely. It was found by ^{13}C CPMAS NMR that phase A and SAPO-31, which were synthesized in the presence of HF, also retained the SDA intact (data not shown).

Figure 4 shows the ^{31}P MAS NMR spectra of AlPO EMM-3 recorded at 11.7 T. The spectra show that removal of the organic structure-directing agent by calcination greatly increases the local order. Three peaks are observed for the calcined dry material in a ratio of 1:2:3. This indicates that the space group symmetry for the unit cell of calcined EMM-3 must contain a minimum of three, or multiple of three, crystallographic T sites in the ratio of 1:2:3. The ^{31}P MAS spectrum of the calcined-rehydrated material shows that the presence of water reduces the space group symmetry. There appears to be a minimum of 5 T sites in the ratio of approximately 1:2:1:1:1, also consistent with six sites of equal population, in the unit cell of the calcined hydrated EMM-3. On extended hydration periods a broad component centered at $\delta_P \sim -17$ ppm appears.

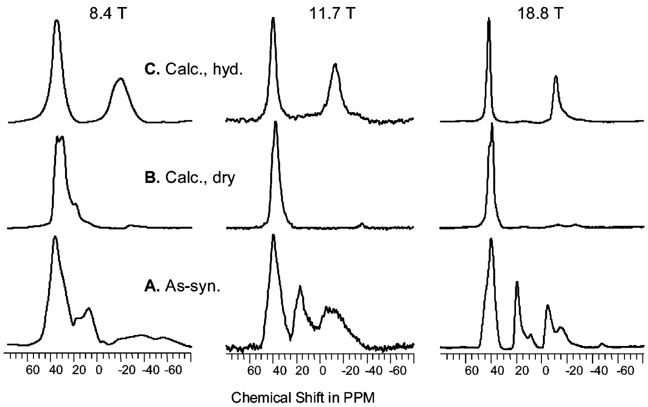

Figure 5. Multifield (93.8, 130.1, and 208.4 MHz) ^{27}Al MAS NMR of as-synthesized (bottom, A), calcined-dry (middle, B), and calcined-rehydrated (top, C) forms of AlPO EMM-3.

Figure 5 shows multifield ^{27}Al MAS NMR of AlPO-EMM-3 in all three forms, as-synthesized (bottom), calcined-dry (middle), and calcined-rehydrated (top). The 8.4 and 11.7 T spectra of the as-synthesized and calcined-dry samples are complicated by unaveraged quadrupolar broadening effects. The 18.8 T ^{27}Al MAS NMR spectrum of the as-synthesized sample clearly shows the presence of tetrahedral ($\delta \sim 40$ ppm), pentacoordinate ($\delta \sim 20$ ppm), and octahedral ($\delta \sim 0-15$ ppm) Al species. Calcination results in the entire Al being converted to T_d coordination. The multiplicity at 8.4 T and broadening at 11.7 T are due to unaveraged second order quadrupolar interactions. These interactions are inversely proportional to magnetic field strength, and as a result, what appear to be multiplicities at lower fields are substantially narrowed at higher fields. In the 18.8 T spectrum, the peaks are resolved indicating that they are actually due to crystallographically distinct sites. This was clearly shown in the 3QMAS NMR spectrum of the calcined-dry sample.[3]

The multifield ^{27}Al MAS NMR spectra of the calcined-rehydrated material are all similar, with both T_d and O_h species present, and may help explain the changes observed in the corresponding ^{31}P spectrum. The lowering of the local symmetry upon hydration of EMM-3 observed in the ^{31}P MAS spectra and the appearance of O_h Al in the ^{27}Al MAS spectra are consistent with the changes in the longer range ordering detected in the corresponding XRD patterns. As the calcined form of EMM-3 absorbs water, some of the framework aluminum T-atoms coordinate to water molecules to become 5- or 6-coordinate to lower the overall cell symmetry. This reversible hydration−dehydration of framework Al atoms is observed in many aluminophosphate materials such as $AlPO_4$-17[11] and SSZ-51.[12]

The SAPO forms of EMM-3 were also characterized with ^{1}H, ^{27}Al, ^{29}Si, and ^{31}P MAS NMR. Shown in Figures 6 and 7 are the ^{31}P and ^{27}Al MAS NMR spectra of as-synthesized and calcined SAPO EMM-3 samples, respectively. Com-

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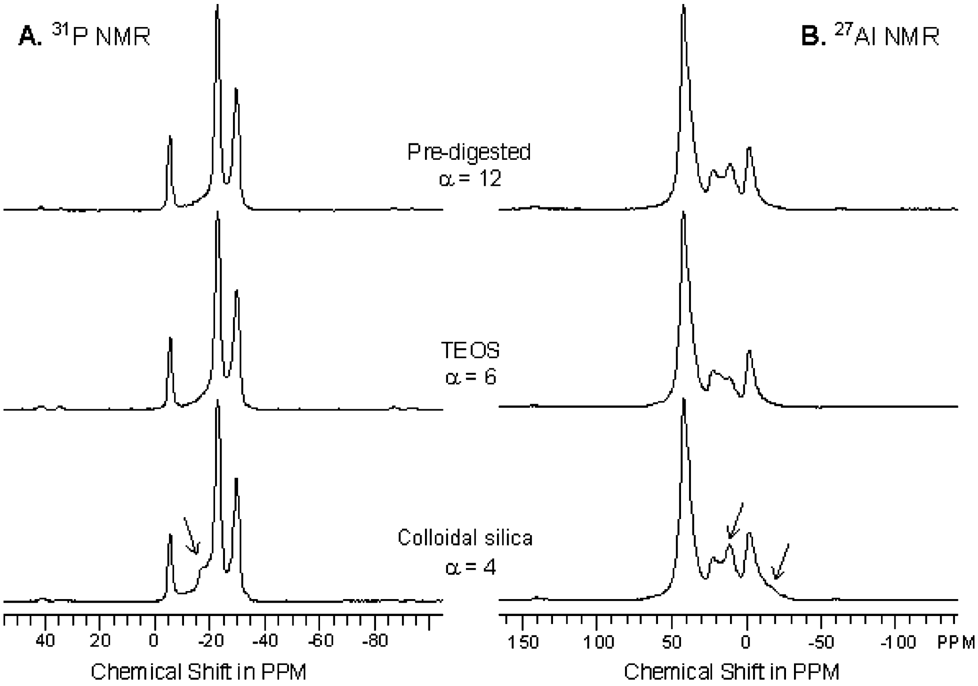

Figure 6. 202.1 MHz ^{31}P MAS NMR (left, A) and 130.1 MHz ^{27}Al MAS NMR (right, B) of as-synthesized SAPO EMM-3. The main changes are indicated by arrows.

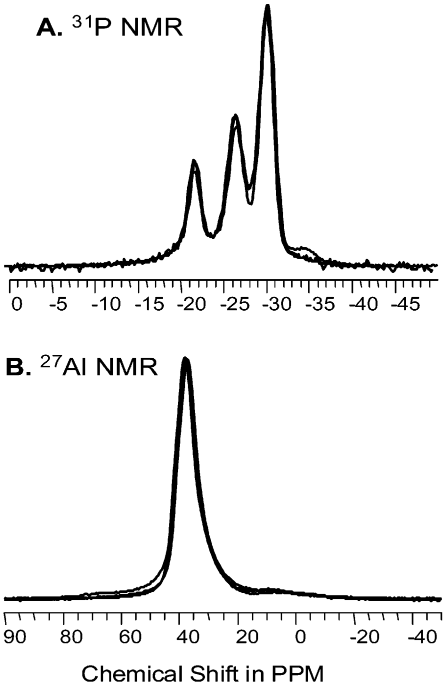

Figure 7. 202.1 MHz ^{31}P MAS NMR (top, A) and 130.1 MHz ^{27}Al MAS NMR (bottom, B) of calcined-dry forms of SAPO EMM-3 superimposed on to one another.

parison of the ^{31}P MAS NMR spectra of the as-synthesized SAPO-EMM-3 samples with those of AlPO EMM-3 suggests that the incorporation of Si into the framework results in higher local symmetry. Moreover, the extent of predigestion of the SiO_2 appears to impact the spectral appearance, and, presumably, the local order. The ^{31}P NMR of the as-synthesized SAPO EMM-3 shows at least four distinct resonances between 0 and −30 ppm, compared to the seven observed for AlPO EMM-3. However, like that of the AlPO EMM-3, ^{31}P NMR of calcined SAPO EMM-3 (Figure 7) shows only three resonances with an intensity ratio of 1:2:3, respectively, thus indicating a uniform Si substitution for all five phosphorus T-sites. As in the AlPO case, the ^{27}Al MAS NMR spectra of the as-synthesized SAPO EMM-3 all show the presence of tetrahedral ($\delta_{Al} \sim 40$ ppm), pentacoordinate ($\delta_{Al} \sim 20$ ppm), and octahedral ($\delta_{Al} \sim 0-15$ ppm) Al species, respectively. The pentacoordinated and octahedral Al peaks are due to hydration of the framework atoms. Calcination results in the entire Al being converted to T_d coordination with a resonance at about 37 ppm and a shoulder at 40 ppm. As is the case with the AlPO form, this indicates that the SAPO framework has a fully connected, 3-dimensional structure when dehydrated and that the octahedral aluminum seen in the hydrated samples is not due to extraframework aluminum species.

The ^{29}Si MAS NMR spectra of the calcined SAPO-EMM-3 samples and the corresponding ^{1}H MAS NMR spectra are shown in Figure 8. The broad peaks centered at $\delta \sim -90$ ppm are indicative of a broad distribution of Si-$(OAl)_4$ environments and/or silanols in the EMM-3 framework. The spectral intensity at $\delta = -110$ ppm (particularly in the colloidal silica case) is consistent with silicon islanding or the presence of amorphous silica that has not been incorporated into the EMM-3 framework (i.e., $Si(OSi)_4$). Si incorporation into neutral AlPO frameworks results in the introduction of framework charge that must be balanced by a counterion. The peak centered at $\delta_H = 4$ ppm in the ^{1}H MAS NMR spectra is associated with the Brønsted acid hydrogens, and the peaks in the 0−3 ppm region are due to hydroxyls (P−OH, Si−OH, and Al−OH).[5] The ^{1}H MAS NMR spectra were recorded quantitatively using a technique described elsewhere.[5] The amounts of H^+ determined from these NMR data are, from bottom to top in the figure, 0.38, 0.41, and 0.54 mmol/g, respectively. These values track qualitatively with the acid activities measured by hexane cracking (α test).

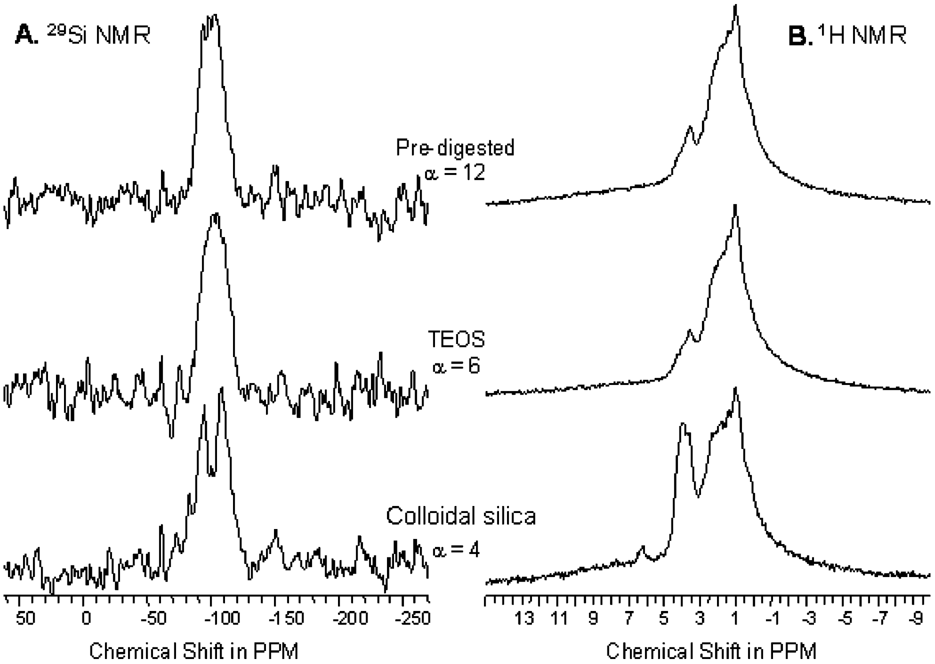

Figure 8. 99.2 MHz ^{29}Si MAS NMR (left, A) and 360 MHz ^{1}H MAS NMR spectra of the calcined-dry forms of SAPO EMM-3. The ^{29}Si and ^{1}H NMR spectra were acquired at 5 and 10-kHz MAS rate and a recycle delay of 360 and 30 s, respectively.

Table 3. α Values and Elemental Analysis for Selected SAPO EMM-3 Samples

expt no.	SiO_2:Al_2O_3	Si source	elemental analysis	α
7	0.4	colloidal	$Si_{.068}Al_{.516}P_{.417}$	4
18	0.4	predigested	$Si_{.072}Al_{.498}P_{.429}$	12
21	0.2	TEOS	$Si_{.032}Al_{.492}P_{.475}$	6
22	0.4	TEOS	$Si_{.068}Al_{.486}P_{.446}$	6

Catalytic Activity. Selected samples of EMM-3 were evaluated for acid cracking using the α test.[6] The SAPO-EMM-3 products were calcined in air at 650 °C for 3 h to remove the organic template. The calcined samples were then pressed into a pellet, crushed, and then sieved to 14−24 mesh sizes. These sieved samples were subjected to the α test. The results along with elemental analyses are given in Table 3 and demonstrate the ability of EMM-3 to crack hydrocarbons. The highest α value is for the sample prepared with predigested silica indicating this is the preferred method of incorporating the silica to give maximum catalytic activity. The lowest α value is for a sample prepared with colloidal silica. This sample contains a large amount of silicon islanding and/or amorphous silica, and in either case, a significant amount of silicon is not in catalytically active form. While very large silicon islands give a considerable amount of inactive silica at the center of the islands (i.e., $Si(OSi)_4$ environments), small silicon islands give stronger acid sites at the corners and edges compared to isolated silicon.[13] Therefore, one would expect the highest acid activity with samples containing the highest number of small silicon islands, but not too large to form a significant amount of inactive silicon at the island centers. The higher activity samples prepared with TEOS and predigested silica appear to show more dispersed silica with isolated and/or small siliceous islands in agreement with the ^{29}Si NMR.

Conclusions

EMM-3 is a new microporous material prepared in both aluminophosphate and silicoaluminophosphate compositions using hexamethonium as a template from 130 to 200 °C in 24−48 h. At higher temperatures, SAPO-17 is the preferred phase in the presence of silica. In the presence of HF and at higher temperatures (200 °C), SAPO-31 forms from similar reaction mixtures. The ^{31}P and ^{27}Al NMR spectra of the calcined-dry form are in agreement with a fully connected tetrahedral structure containing 5 unique phosphorus and aluminum atoms. Both the calcined AlPO- and SAPO-forms of EMM-3 reversibly absorb water to lower the unit cell symmetry due to hydration of some the framework T-atoms to form pentacoordinated and octahedral aluminum. The incorporation of silicon into the EMM-3 framework has been found to be better for samples prepared with TEOS and predigested sources of silicon. As shown by ^{29}Si NMR and the α activity test, these materials have better silicon dispersion and incorporation compared to samples prepared with colloidal silica.

Acknowledgment. B. Liang and C.E. Chase recorded the NMR spectra at 11.7 and 8.4 T, respectively. The 18.8 T ^{27}Al NMR spectra were recorded by Dr. X. Wu in Professor Kurt Zilm's laboratory at Yale University.

CM052175J

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(13) Barthomeuf, D. *Zeolites* **1994**, *14*, 394.