Aluminated Derivatives of Porous Clay Heterostructures (PCH) Assembled from Synthetic Saponite Clay: Properties as Supermicroporous to Small Mesoporous Acid Catalysts

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Mesostructured aluminosilicate intercalates belonging to the new class of solid acids known as porous clay heterostructures (PCH) have been prepared by the postsynthesis grafting of aluminum into the mesostructured intragallery silica framework of a PCH precursor derived from a synthetic saponite clay. Elemental analyses, powder X-ray diffraction, N_2 adsorption, and ^{27}Al MAS NMR spectroscopy were used to characterize the reaction products, which we designate Al−SAP/PCH. Depending on the choice of aluminum reagent ($AlCl_3$ or $NaAlO_2$), the Al−SAP/PCH derivatives exhibited basal spacings of 32−34.8 Å, BET surface areas of 623−906 m²/g, pore volumes of 0.32−0.45 cm³/g, and pore sizes in the large micropore to small mesopore range (14−25 Å). The aluminum content was strongly correlated with the Si/Al stoichiometry of the postsynthesis reaction mixture. Nearly all of the grafted aluminum was incorporated into tetrahedral sites in the intragallery silica framework. In comparison to the initial silica-intercalated SAP/PCH precursor, little or no change in textural porosity was observed when the alumination reaction was carried out under acidic conditions using aqueous $AlCl_3$ as the aluminum source. Also, only small decreases in surface area and pore volume were noted when $NaAlO_2$ was used as the alumination reagent under basic conditions. Both alumination reagents afforded protonated Al−SAP/PCH derivatives with increased acidity in comparison to the initial silica-intercalated SAP/PCH precursor, as verified by temperature-programmed desorption of cyclohexylamine and catalytic reactivity for cumene cracking.

Introduction

Over the past decade, several mesoporous silica molecular sieves[1−5] have been synthesized using surfactant micelles as the structure directing agents. Aluminum-doped derivatives such as Al−MCM-41 are of particular interest as solid acid catalysts. Previous studies[6−11] have shown that aluminum can be effectively incorporated into the walls of a MCM-41 framework via grafting reactions using different aluminum sources. Postsynthesis alumination reactions have been reported to increase the chemical stability, as well as the acidity, of MCM-41 materials.[12,13]

Recently, the discovery of a new class of solid acids known as porous clay heterostructures (PCH) has been reported.[14] These intercalation compounds are formed through the surfactant micelle ordering of silicate species in the restricted two-dimensional intragallery region of a host smectite clay. Thus, PCH materials combine the structural elements of a mesostructure with the intrinsic acidity of a lamellar smectite clay. Moreover, PCH materials exhibit pore sizes in the rarely observed supermicropore to small mesopore region, making them potential catalysts for size selective transformations of molecules with kinetic diameters too large to be processed over conventional zeolite catalysts. Modifying the chemical composition of the layered host of a PCH allows one to mediate the intragallery acidity.[15−18] However, it also should be possible to improve the acidic character of PCH materials through postsynthesis alumination reactions analogous to those developed for MCM-41.

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Here we report the incorporation of aluminum into the mesostructured silica gallery of a PCH intercalate derived from synthetic saponite via two different postsynthesis alumination procedures under acidic and basic conditions using aluminum chloride and sodium aluminate as the alumination reagents, repectively. We show that the structural integrity of the initial PCH is preserved in the alumination processes. In addition, the acidity of the aluminated heterostructure, denoted Al−SAP/PCH, is significantly enhanced, as indicated through temperature-programmed desorption and acid catalysis studies. Moreover, by using synthetic saponite as the layered host, we were able to specifically tailor the charge density on the silicate layers to facilitate the assembly of intragallery silica, while at the same time avoiding the complications that can arise from iron and other transition metal impurities associated with naturally occurring saponite minerals. The exceptional acidity of the resulting PCH intercalates, together with a pore structure in the supermicropore to small mesopore range, suggests that these aluminated PCH derivatives may be promising shape selective cracking catalysts.

Experimental Section

Al−SAP/PCH Synthesis. A silica-intercalated saponite PCH, denoted SAP/PCH, was prepared according to the previously described procedure.[15] Synthetic saponite with the anhydrous unit cell formula $Na_{1.2}[Mg_6](Si_{6.8}Al_{1.2})O_{20}(OH)_4$ was hydrothermally synthesized at 175 °C and then converted to a quaternary ammonium exchange form by ion exchange reacting with cetyltrimethylammonium chloride. Mixtures of the hydrated organoclay, neutral decylamine as a cosurfactant, and tetraethyl orthosilicate (TEOS) at molar ratios 1:20:150 were allowed to react for 4 h at room temperature. The product was recovered by centrifugation, dried under controlled humidity, and subsequently calcined at 650 °C using a temperature ramp rate of 1 deg/min. The obtained silica-intercalated SAP/PCH, with an anhydrous unit cell formula of $\{(SiO_2)_{13.7} \cdot H_{1.2}\}[Mg_6](Si_{6.8}Al_{1.2})O_{20}(OH)_4$, then was used to produce aluminated derivatives, denoted Al−SAP/PCH, via two synthetic routes.

In the first alumination route, SAP−PCH (0.5 g) was combined with 50 mL of aqueous $AlCl_3$ solution to give gallery Si/Al ratios of 10 and 20. After a reaction time of 12 h at 55 °C, the solid products were filtered, washed with water, dried at room temperature, and calcined at 600 °C for 4 h to obtain the protonated form of Al−SAP/PCH.

In the second route, 0.5 g of SAP/PCH in 50 mL of water was allowed to react with $NaAlO_2$ at room temperature for 3 h at gallery Si/Al ratios of 5 and 10. The solid powders were recovered by filtration and washed thoroughly with water. To form the protonated forms of the Al−SAP/PCH, the sodium ions in the as-made aluminated products were exchanged for ammonium ions by equilibrating in 1.0 M NH_4NO_3 and then calcining the ammonium exchanged derivatives at 600 °C for 4 h.

To distinguish between products prepared at different gallery silica-to-aluminum ratios we labeled the products Al−SAP/PCH-*X*, where the value of *X* is the ratio of gallery silica to aluminum used in the alumination reaction mixtures.

Cumene Cracking Reaction. Cumene cracking reactions were performed in a 6 mm i.d. fixed bed quartz reactor containing 200 mg of catalysts. The cumene flow rate was 4.1 μmol min^{-1} in a 20 mL min^{-1} carrier gas of N_2. Cumene conversions were reported under steady-state conditions after 30 min on steam at 300 °C.

Physical Measurements. Powder X-ray diffraction patterns were obtained on a Rigaku Rotaflex diffractometer equipped with a rotating anode (Cu Kα radiation) operated at 45 kV and 100 mA. The scattering and receiving slits were $^1/_6$ and 0.3°, respectively.

N_2 adsorption−desorption isotherms were obtained at −196 °C on a Micromeritics ASAP 2010 Sorptometer using static adsorption procedures. Samples were outgassed at 175 °C and 10^{-6} Torr for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot according to IUPAC recommendations.[19] The pore size distributions were calculated by the BJH method using the adsorption branch of the nitrogen isotherm.

^{27}Al MAS (magic angle spinning) NMR spectra were obtained on a Varian VXR 400 MHz spectrometer at 104.26 MHz using a 7 mm zirconia rotor and a sample spinning frequency of 4 kHz. A pulse duration of 9 μs and a delay time of 1 s allowed for a full relaxation of the Al nucleus. External Al-$(H_2O)_6^{3+}$ was used as a reference to determine the chemical shift values.

Temperature-programmed cyclohexylamine desorption (CHA−TPD) profiles were recorded on a Cahn TG system 121 analyzer. Calcined samples (∼30 mg) were transferred directly out of the cyclohexylamine vapor to the thermobalance and were kept at 150 °C for 2 h to remove physisorbed CHA. Desorption thermograms were recorded at a heating rate of 10 °C/min under a nitrogen flow. The mass loss between 200 °C and 450 °C was used to determine the acid content of the samples (in mmol of CHA/g of adsorbent).

Elemental analyses were provided by inductively coupled plasma emission spectroscopy at the University of Illinois Elemental Analysis Laboratory.

Results and Discussion

In accord with our previously reported procedure,[15] we assembled mesostructured silica in the galleries of synthetic saponite by first replacing the gallery sodium ions in the clay host with cetyltrimethylammonium ions as a cationic surfactant, subsequently swelling the hydrated clay galleries with decylamine as a cosurfactant, and then adding neat tetraethyl orthosilicate (TEOS) to provide a reaction mixture with an organoclay:amine:TEOS molar ratio of 1:20:150. After a reaction time of 4 h at ambient temperature, the resulting intercalate was collected by centrifugation, dried in air under a controlled humidity (60%) to complete the hydrolysis of intercalated TEOS, and subsequently calcined at 650 °C to remove the surfactant and cosurfactant.

The overall procedure for forming the silica-intercalated porous clay heterostructure (PCH) is shown in Figure 1. The use of a large excess of amine cosurfactant was needed to swell the galleries and to facilitate intragallery hydrolysis reaction upon the subsequent addition of TEOS. Owing to the structure-directing properties of the gallery surfactant and cosurfactant TEOS hydrolysis and silica mesostructure formation was confined almost exclusively to the gallery regions of the clay. Although a very large excess of TEOS is needed to partially displace some of the amine cosurfactant from adsorption sites in the gallery, TEOS hydrolysis occurs almost exclusively in the gallery region and not in extragallery regions. Selective intragallery hydrolysis of TEOS is favored in part by the sequestering of water in the gallery region of the clay. The presence of little or no extragallery silica in PCH

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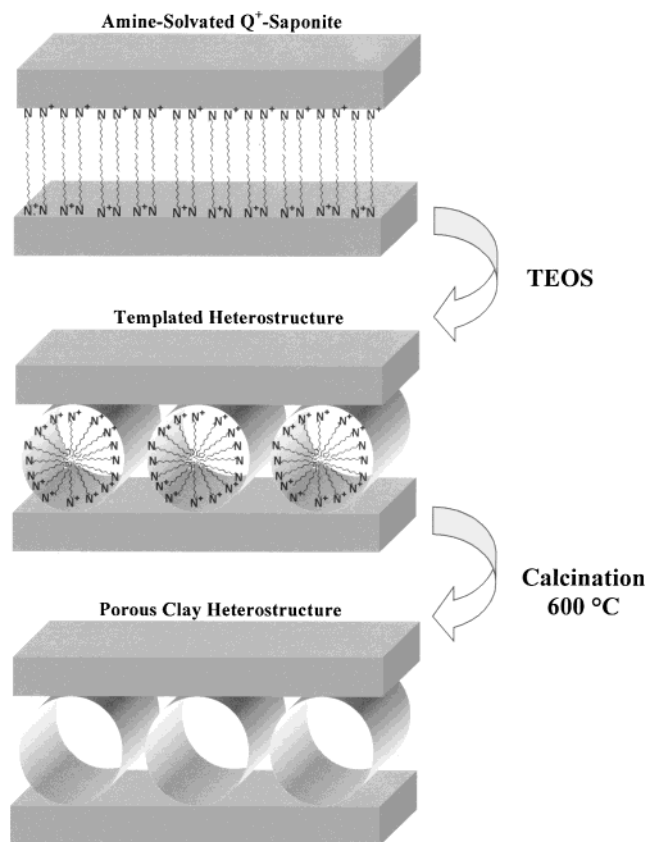
Figure 1. Schematic representation of porous clay heterostructure (PCH) formation through surfactant-directed assembly of mesostructured silica in the galleries of a quaternary ammonium ion-exchanged layered silicate (Q^+-saponite) co-intercalated by an electrically neutral amine cosurfactant. The intercalated mesostructured silica framework is represented as a tubular structure.

materials has been confirmed in our earlier studies[14,15,17] and independently verified by other workers.[18]

Elemental analyses indicated the calcined SAP/PCH reaction product contained 2.0 mol of mesostructured gallery silica per mole of silica in the mesostructured host layers, corresponding to an anhydrous unit cell formula of $\{(SiO_2)_{13.7}\cdot H_{1.2}\}[Mg_6](Si_{6.8}Al_{1.2})O_{20}(OH)_4$, where the silica in curly brackets represents the gallery silica. The intercalated silca represents approximately 52 wt % of the PCH on a dry basis. The X-ray powder diffraction pattern of the calcined PCH intercalate indicated a basal spacing of 31.3 Å, indicating that the gallery height (21.7 Å) is 2.26 times as large as the thickness of the saponite layer (9.6 Å). That is, the gallery represents ∼70% of the volume of the PCH intercalate. Yet, the ratio of space filling oxygen atoms in the gallery to those in the saponite layer is 27.4–24.0, as indicated by the unit cell composition. Although there are only 14% more space filling oxygen atoms in the gallery than in the saponite layer, the gallery volume is twice the volume of the layer. This clearly signifies that the gallery silica imparts substantial free volume to the intercalate. Thus, it is clear on the basis of chemical analysis and X-ray basal spacings alone that the observed surface areas and pore volumes (see below) are a consequence of a heterostructure that combines the structural elements of a layered host and an open framework gallery structure characteristic of mesostructured silica.
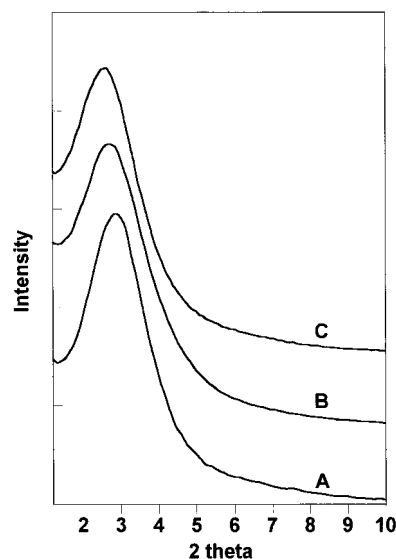
Figure 2. XRD patterns for (A) calcined SAP/PCH and the calcined Al–SAP/PCH derivatives formed by grafting reaction with (B) $AlCl_3$ and (C) $NaAlO_2$ at gallery Si/Al ratios of 10 and 5, respectively.

All of the aluminated Al–SAP–PCH derivatives obtained through grafting reactions with $AlCl_3$ and $NaAlO_2$ gave XRD patterns equivalent to the parent SAP/PCH, as shown in Figure 2. There were no significant changes in the XRD peak intensities and line widths, and no additional peaks appeared beyond the 2Θ region shown in Figure 2, indicating the absence of a segregated crystalline alumina phase. The basal spacings of the Al–SAP/PCH materials (Table 1) were larger that the spacing observed for the starting SAP/PCH and generally increased with the amount of incorporated aluminum. This is consistent with the incorporation of increasing amounts of alumina into the gallery mesostructure. That is, the gallery mesostructure expands upon alumination, which is consistent with the insertion of aluminum into the mesostructured silica. The expansion of the basal spacing may be more a consequence of increased hydration of the gallery under ambient conditions, rather than an increase the size of the gallery mesostructure. The polarity of the gallery silica surface is expected to increase with increasing alumination, and this should enhance the water adsorption capacity of the gallery region.

Figure 3 provides representative N_2 isotherm and BJH pore size distributions for Al–SAP/PCH materials obtained by $AlCl_3$ and $NaAlO_2$ grafting routes. The shapes of these isotherms are very similar to those previously reported for PCH intercalates.[14–18,24] All of the Al–SAP/PCH derivatives prepared in the present study exhibited a linear uptake of nitrogen in the partial pressure range 0.05–0.25, indicating the presence of framework pores that span the supermicropore to small mesopore range 14–25 Å.[20] A virtually identical isotherm shape was observed for the parent SAP/PCH. Table 1 provides the textural parameters for the parent

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Table 1. Properties of SAP/PCH and Al−SAP/PCH Derivatives

sample	alumination agent	Si/Al[a]	basal spacing[b] (Å)	BET surface area[b] (m²/g)	pore vol[b] (cm³/g)	acidity (mmol of CHA/g)
Al−SAP/PCH-20	AlCl₃	24.1	32.0	906	0.45	1.23
Al−SAP/PCH-10	AlCl₃	15.4	33.7	834	0.43	1.45
Al−SAP/PCH-10	NaAlO₂	12.7	34.5	786	0.40	1.51
Al−SAP/PCH-5	NaAlO₂	8.5	34.8	623	0.32	1.82
SAP/PCH	none		31.3	860	0.45	0.63

[a] The gallery Si/Al ratios found by elemental analysis. [b] The basal spacings, surface areas and pore volumes are for the calcined forms of the Al−PCH derivatives.
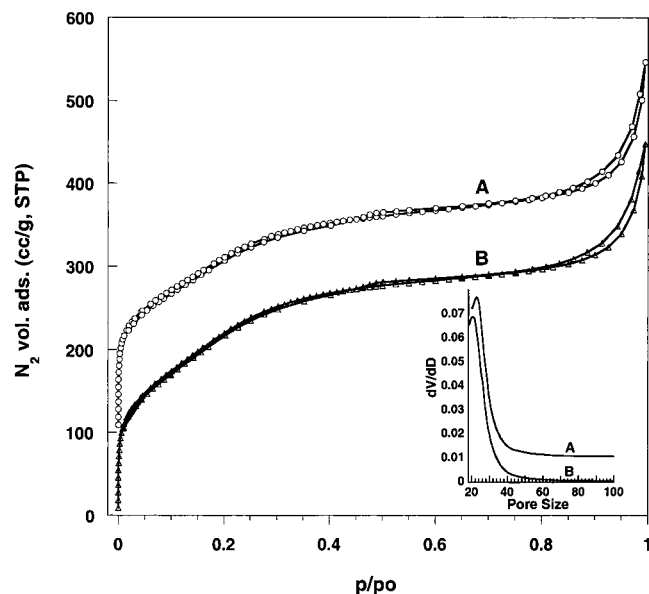

Figure 3. N₂ adsorption/desorption isotherms for Al−SAP/PCH-10 intercalates formed using (A) AlCl₃ and (B) NaAlO₂ as aluminating agents. The isotherms are offset by 100 cm³/g for clarity. Inset shows the BJH pore size distribution.

SAP/PCH and Al-grafted derivatives prepared in the present work.

The textural information derived from the nitrogen isotherms is in good agreement with the XRD patterns and confirms the retention of the structural integrity of the SAP/PCH after aluminum grafting. Alumination by grafting with AlCl₃ under acidic conditions does not affect the original pore structure of the parent SAP/PCH. When sodium aluminate is used as the aluminum source under basic conditions, a decrease in the surface area and pore volume is observed as the aluminum loading increases from a Si/Al ratio of 10 to 5. The basic NaAlO₂ solution may promote the cleavage of some Si−O bonds, perhaps resulting in a partial rearrangement of the interlayer mesostructure. Indeed, some of the observed decrease in surface area and pore volume may be simply related to an increase in the density of the intragallery framework upon aluminum incorporation.[11] In any case, the BET surface area (623 m²/g) and pore volume (0.32 cm³/g) obtained for the sample with the highest aluminum loading (Al−SAP/PCH-5) are still within the range usually obtained for PCH materials intercalated by mesostructured silica.[14]

To elucidate the nature of the incorporated aluminum in the protonated Al−SAP/PCH products, ²⁷Al MAS NMR spectra were obtained for the calcined derivatives. As shown in Figures 4 and 5, each aluminum derivative exhibited two resolved lines at 65 and 53 ppm. The 65 ppm resonance was assigned to tetrahedral aluminum in the 2:1 layer of the synthetic saponite, where the
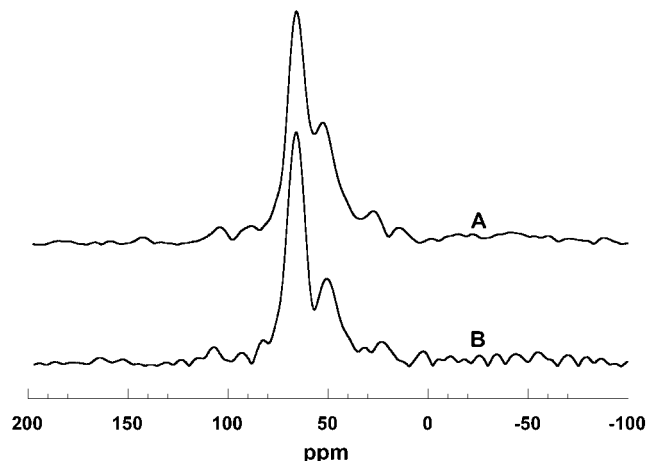
Figure 4. ²⁷Al MAS NMR spectra for calcined forms of (A) Al−SAP/PCH-10 and (B) Al−SAP/PCH-20 samples prepared by postsynthesis grafting with AlCl₃.
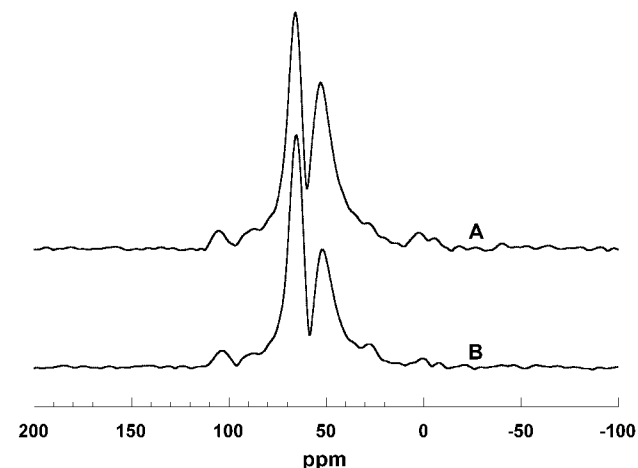
Figure 5. ²⁷Al MAS NMR spectra for calcined forms of (A) Al−SAP/PCH-5 and (B) Al−SAP/PCH-10 samples prepared by postsynthesis grafting with NaAlO₂.

metal is covalently bonded to three Si atoms and one Mg atom via oxygen bridges.[21] The line at 53 ppm can be assigned to tetrahedral aluminum grafted onto the gallery silica.[22] The absence of a signal near 0 ppm for octahedral aluminum indicates that nearly all the aluminum has been incorporated into the siliceous intragallery framework. The ²⁷Al MAS NMR spectra in Figure 4 for Al−SAP/PCH-10 and Al−SAP/PCH-20 prepared from AlCl₃ at gallery silica-to-aluminum ratios of 10 and 20, respectively, show that the aluminum content in the intercalate increases with the aluminum content of the reactant mixture. This result indicates that the aluminum incorporation in the interlayer can be controlled in part by the reaction stoichiometry. However, a further increase in AlCl₃ concentration at Si/Al ratios below 10 resulted in the appearance of an

undesired octahedral resonance at 0 ppm. Only in this latter case is the aluminum *deposited on* the meso-structured framework in the form of an octahedral species and not exclusively *grafted into* the framework as tetrahedral aluminum.

As shown by the ^{27}Al NMR spectrum for in Figure 5 for the product denoted Al−SAP/PCH-5, an alumination reaction could be carried out using NaAlO$_2$ at gallery silicon-to-aluminum ratios as low as 5.0 without forming octahedral aluminum. Essentially all the aluminum incorporated into the Al−SAP/PCH-5 product was in tetrahedral coordination. The strongly basic NaAlO$_2$ solution facilitates the insertion of aluminum into the gallery silica matrix. In comparison with the spectrum for the Al−SAP/PCH samples obtained using AlCl$_3$ as the alumination agent, the line at 53 ppm is much more intense. This indicates that a higher percentage of aluminum is incorporated into the framework of a Al−SAP/PCH derivative prepared through sodium alumi-nate alumination. However, grafting reactions carried out at gallery silica-to-aluminum ratios lower than 5.0 resulted in a loss of more than 50% of the surface area, suggesting that substantial degradation of the gallery mesostructures occurs at higher levels of alumination.

For both alumination procedures, we observed a good correlation between the NMR peak intensities and the amount of the incorporated aluminum found by elemen-tal analysis (see Table 1). Taken together, these obser-vations indicate that both AlCl$_3$ and NaAlO$_2$ are effec-tive, though not equivalent, reagents for aluminum grafting into tetrahedral sites on the clay gallery mesostructure. These aluminum sites generate acid centers that are accessible for chemical catalysis.

It is known that the alumination of silica mesostruc-tures through NaAlO$_2$ grafting reactions does not result directly in Bronsted acidity due to the presence of the Na$^+$ counterions.[24] However, the replacement of the sodium ions after alumination, first with ammonium ions and then ultimately with protons upon calcination, as was done in the present study, imparts useful catalytic acidity. Table 1 reports the concentration of acid sites in the Al−SAP/PCH and parent SAP/PCH intercalates, as determined by the temperature-pro-grammed desorption (TPD) of chemisorbed cyclohexy-lamine (CHA).[23] The samples were exposed to CHA vapors and then heated at 150 °C for 2 h to remove the physically adsorbed amine. The weight loss between 200 and 450 °C was used to quantify the acidity, assuming that each base molecule interacts with one acid site. As shown in Figure 6, the TPD profiles for the Al−SAP/PCH and parent SAP/PCH intercalates exhibit two types of acidic sites. The intensity of the first desorption peak at 230 °C is correlated with the clay layer acidity.[15] The stronger acid site, which is represented by the peak at 380 °C, is related directly to the number of aluminum centers incorporated onto the mesostructured silica. The relative peak intensities are in agreement with the amounts of tetrahedral aluminum grafted into the PCH as judged by NMR and further verify that NaAlO$_2$ is superior to AlCl$_3$ in providing higher concentrations of tetrahedral aluminum for PCH alumination.

Table 1 provides the total acidity values for the Al−SAP/PCH intercalates, as determined by CHA chemi-sorption. The observed acidity values (1.23−1.82 mmol/
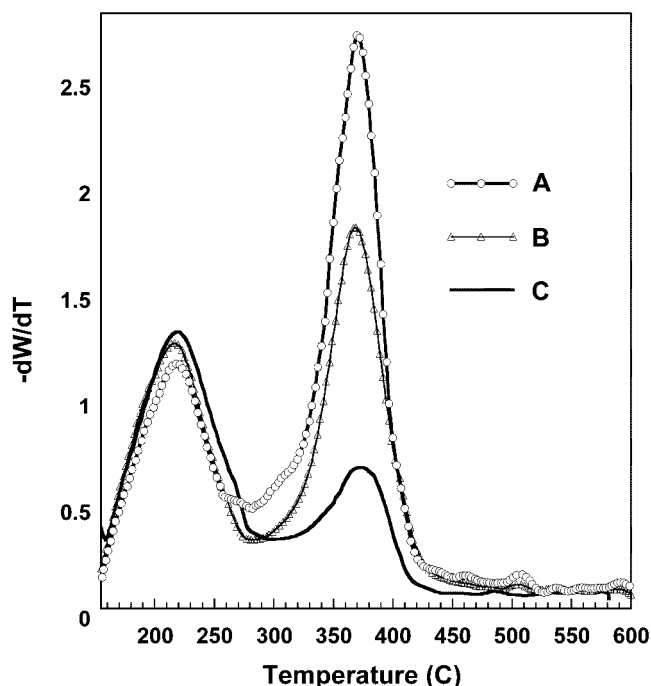
Figure 6. TPD profiles for the desorption of cyclohexylamine from the Al−SAP/PCH derivatives formed by grafting reaction with (A) NaAlO$_2$ and (B) AlCl$_3$ and from (C) the parent SAP/PCH.

g) are substantially higher than the value of 0.63 mmol/g for the pristine SAP/PCH prior to alumination. The number of observed acid sites are also substantially larger than the values recently reported for Al−SAP/PCH intercalates prepared by reaction with aluminum acetylacetonate as the alumination reagent (0.7−0.8 mmol/g) and for a PCH intercalate derived from the H$^+$-exchanged form of montmorillonite (0.25−27 mmol/g).

To provide further verification for the exceptional acidity of Al−SAP/PCH intercalates prepared in the present work, we compared the cumene cracking activ-ity of representative derivatives with those for SAP/PCH and for acidic derivatives of hexagonal Al−MCM-41 and wormhole Al−HMS molecular sieves containing 5% aluminum (Si/Al = 19). At this aluminum loading, all of the aluminum centers in the mesoporous molecular sieves are in tetrahedral sites. For each catalyst system, benzene and propene were the main reaction products, with only trace amounts of other products being formed, in accord with the presence of medium to strong Brönsted acid sites.[26] The cumene conversions reported in Table 2 show that the Al−SAP/PCH intercalates substantially outperform the protonated form of sapo-nite and the parent SAP/PCH as acid catalysts. As expected on the basis of the heterostructured nature of the PCH intercalates, the acid catalytic reactivities are comparable to aluminated forms of bulk Al−MCM-41 and Al−HMS mesostructures with hexagonal and worm-hole framework structures, respectively.

Conclusions

Porous clay heterostructure derived from synthetic saponite have been acid-functionalized through postsyn-

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Table 2. Cumene Cracking Conversions[a]

catalyst	alumination agent	conversion (%)
H$^+$−saponite		20.2
SAP−PCH		36.2
Al−PCH-10	AlCl$_3$	55.2
Al−PCH-10	NaAlO$_2$	58.8
Al−PCH-5	NaAlO$_2$	66.7
5% Al−HMS	NaAlO$_2$	48.9
5% Al−MCM-41	NaAlO$_2$	34.5

[a] Reaction temperature 300 °C; 200 mg of catalyst; 4.1 μmol/min cumene flow rate.

thesis grafting reactions using AlCl$_3$ and NaAlO$_2$ as alumination agents. The resulting Al−SAP/PCH intercalates retain the supermicroporous to small mesoporous integrity of the parent SAP/PCH and possess significantly enhanced acidity. The amount of tetrahedral aluminum incorporated into the saponite gallery structure is correlated with the concentration of aluminum in the grafting solution, but sodium aluminate is preferred over aluminum chloride for achieving higher loading of tetrahedra aluminum without forming extraframework octahedral aluminum or collapsing the intercalated galleries. Some loss of gallery mesostruc-

ture occurs at higher aluminum loadings (e.g., Si/Al = 5) with sodium aluminate, however, as indicated by the ∼ 30% reduction in surface area. ^{27}Al MAS NMR confirms that aluminum is inserted into tetrahedral positions within the gallery silica framework. Both aluminum grafting reagents generate Brönsted acid sites that increase in number as the Si/Al ratio decreases. All of the Al−SAP/PCH intercalates reported here exhibit high catalytic activity for cumene cracking reaction in comparison to the parent SAP/PCH intercalate, proton-exchanged saponite and all previously reported PCH intercalates. The enhanced acidity of Al−SAP/PCH intercalates, together with their stable, well-ordered supermicropore to small mesopore structures, opens up new opportunities for applications in acid catalysis.