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Ga_{13}, Al_{13}, $GaAl_{12}$, and Chromium–Pillared Montmorillonites: Acidity and Reactivity for Cumene Conversion

SUSAN M. BRADLEY AND RONALD A. KYDD[1]

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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A comparison has been made of the acidic characters of a series of metal polyoxocation pillar interlayered clay minerals (M–PILCs) by studying the infrared spectra of adsorbed pyridine. These comparisons were made for Ga_{13}–, Al_{13}–, and $GaAl_{12}$–PILCs, and for Na^+-exchanged montmorillonite (Na-STx-1). The Ga_{13}–PILC was found to exhibit the strongest Lewis acid sites, followed by the Al_{13}–, and $GaAl_{12}$–PILCs, and then the Na–STx-1. The relative number of Lewis acid sites, however, was found to be much greater for the $GaAl_{12}$–PILCs, particularly after calcination at higher temperatures, indicating that the Ga_{13} Lewis acid sites did not have as high a thermal stability. The Brønsted acidic characters for the pillared clays also depend on the pillar, and follow the general order of abundance of $GaAl_{12}$– > Al_{13}– > Ga_{13}–PILC, when expressed as absorbance per unit mass. When the acidities per unit surface area were estimated, however, the Ga_{13}–PILCs were found to have the greatest number. This indicates that while the pillars contribute to the PILC acidities primarily through increasing the exposed phyllosilicate sheet surface areas, there is also a significant effect arising from the acidic characters of the pillars themselves. The dehydrogenation activities of Ga_{13}–, $GaAl_{12}$–, Al_{13}–, and Na–STx-1, in addition to a chromium polyoxocation–PILC, were compared by observing the products formed upon reaction with the model compound cumene. The Ga_{13}– and chromium–PILCs and the Na–STx-1 exhibited almost exclusively dehydrogenation activities, whereas the Al_{13}– and $GaAl_{12}$–PILCs exhibited both cracking and dehydrogenation behaviors. These results prove that the pillars themselves can very strongly affect the catalytic activities of the PILCs.

INTRODUCTION

The types of catalytic reactions that are of primary interest in petroleum processing are hydrocarbon cracking, isomerizations, and oligomerizations. This is primarily due to the large demand for aromatic petrochemicals in the size ranges of C_6–C_{10} (gasoline) and paraffinic molecules of sizes C_{14}–C_{18} (diesel fuel). As bulk crude oil is generally not rich in these molecular types, chemical reactions must be initiated which will result in their formation (*1*). The reactions which are required to produce the desired hydrocarbon fractions are brought about through the use of acidic solids which activate the hydrocarbons through the formation of carbocations (*2*).

A new class of porous catalysts, the pillar interlayered clay minerals (PILCs), has recently received a great deal of attention for these types of reactions. These catalysts are created through the intercalation of metal polyoxocations by phyllosilicate sheets, followed by calcination, thereby forming two-dimensional porous acidic solids. The species which has primarily been used as the intercalant in these types of reactions is the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ polyoxocation (abbreviated Al_{13}) which is formed by the base hydrolysis of Al^{3+} aqueous solutions. Quite recently, in our laboratory, $GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (abbreviated Ga_{13}) and $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (abbreviated $GaAl_{12}$) polyoxocation species have also been isolated and characterized (*3–8*), and the thermal stabilities of their respective PILCs compared (*9*). The latter species,

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[1] To whom correspondence should be addressed.

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$GaAl_{12}$, is thought to be the only tridecameric species present if base hydrolysis and appropriate heating of solutions containing Ga and Al in molar ratios of 1 : 12 is carried out (*5*). Recently, two other groups have also reported the synthesis and characterization of gallium, aluminum, and mixed gallium–aluminum pillared clays (*10, 11*). In both cases, for the mixed solutions a range of ratios of aluminum to gallium (3 : 1, 1 : 1, and 1 : 3) was used, but in neither case was the identity of the pillaring polyoxocation established. Because of the Ga : Al ratios used, the mixed solutions would be expected to contain (depending on the specific ratio) mixtures of some or all of the Al_{13}, Ga_{13}, $GaAl_{12}$ cations, and possibly even analogous species such as Ga_2Al_{11}, Ga_3Al_{10}, etc. It was believed that Ga^{3+} itself was also present as an exchange cation, at least in one of the above cited works (*11*).

One of the purposes of the work reported here was to compare the acidity and catalytic activity of montmorillonite pillared specifically with the $GaAl_{12}$ cation to samples pillared (separately) with the Al_{13} and Ga_{13} cations. The $GaAl_{12}$ ion has been shown to have significantly enhanced thermal stability compared to the other two cations (*9*), and this might be expected to have catalytic repercussions. The acidities of the various pillared clay samples have been assessed using the well-known techniques of pyridine vapor adsorption combined with infrared spectroscopy. The peaks which are most suited for the study of the nature of surface acid sites are the 1530–1550 cm^{-1} band (pyridine adsorbed on Brønsted acid sites), and the 1445–1460 cm^{-1} band (pyridine on Lewis acid sites). In addition, the relative position of the Lewis acid band can be used as an indication of the strengths of these acid sites, as stronger acid sites produce bands at higher wavenumbers (*12*). Studies of this type have been previously undertaken for Al_{13}–PILCs (*13–17*), and the results obtained here also can be compared with those reported for the Ga_{13}– and mixed $GaAl_{12}$–pillared clays discussed above (*10, 11*).

Most catalytic studies involving the Al_{13}–PILCs have looked at hydrocarbon cracking reactions, although other types of proton catalyzed reactions, including isomerizations, disproportionations, and alkylations have been studied. In the work reported in this paper, the conversion of cumene over the Al_{13}–, Ga_{13}–, and $GaAl_{12}$–pillared clays has been investigated. In addition to this, it was noted that base hydrolysis of Cr^{3+} aqueous solutions produces a species which is intercalated by montmorillonite to produce clay layer spacings comparable to those produced by Ga_{13}. It has been speculated that this species is a $Cr_{12}(OH)_{28}(H_2O)_{12}^{8+}$ ion, which is proposed to have a structure analogous to the Al_{13} ion, but with the central tetrahedral position empty (*8, 18*). Since this identity has not been confirmed, the term Cr_x–PILC will be used in this paper to refer to PILCs prepared using hydrolysed Cr solutions as intercalants. This Cr_x–PILC was also included in the cumene conversion studies, to see if the chromium-containing pillar had different catalytic properties. Cumene is a convenient model compound for catalytic studies, because it undergoes different reactions over different types of active sites. Over Brønsted acid sites, cumene is cracked to benzene (plus propene), via a carbocation mechanism (*19*). Over dehydrogenation sites, however, cumene is converted into α-methylstyrene. The production of other products (e.g., ethylbenzene, toluene) is minimal. A comparison of the relative amounts of these two products over the Al_{13}–, Ga_{13}–, $GaAl_{12}$–, and Cr_x–pillared clays should provide some information about the relative effectiveness of the cracking and dehydrogenation sites on the different catalysts.

EXPERIMENTAL

STx-1 montmorillonite was the clay mineral used for these investigations. The chemical analysis of this material is given in the "Data Handbook for Clay Materials and Other Non-Metallic Minerals" (*20*), and shows it to contain 70.1% SiO_2 and 16.0% Al_2O_3. Analyses we had carried out agreed exactly with these published values, even for minor constituents. Samples of the Ga_{13}–, Al_{13}–, and $GaAl_{12}$–PILCs were prepared by pillaring the STx-1 montmorillonite as previously described (9). The pillared clays are quite stable. Even after prolongued heating at successively higher temperatures, including 12 h at 500°C, all samples retained more than 85% of their initial surface areas, which for the particular samples used in this study were 245, 210, and 195 m^2/g, respectively, for the $GaAl_{12}$–, Al_{13}–, and Ga_{13}–PILCs. After heating at even higher temperatures (600 and 700°C), the $GaAl_{12}$ pillar proved to be somewhat more stable than the others; more details of the thermal stabilities are provided elsewhere (9). The differences in the initial surface areas (Ga_{13}–PILC consistently has a slightly lower surface area than the others) may reflect the stabilities of the different polyoxocations in solution. Ga_{13} is the least stable of these three cations, and small amounts of other species (monomers, dimers, etc.) may be present in the pillaring solution, thereby affecting the surface areas of the materials produced. Samples of the Cr_x–PILCs were prepared by hydrolyzing Cr^{3+} aqueous solutions to OH/Cr ratios of ca. 2.25, under the same conditions as were employed for the Al^{3+} solutions (5, 9). The Cr_x–PILCs were then prepared in the same way as were the others. The variability in the surface area of the chromium-pillared clays was high. The particular sample used for this study had a surface area of about 200 m^2/g. Na^+-exchanged STx-1 montmorillonite (surface area 83 m^2/g) was studied as a comparison to the PILCs.

The acidic characters of the M–PILCs were studied through infrared spectroscopic investigations of the sorption of the probe molecule pyridine. PILC samples were calcined in oxygen for ten hours at specific temperatures (475, 550, 625, or 700°C) and then evacuated for 2 h at 475°C. They were then exposed to pyridine vapor for 1 min, following which the vapor was allowed to permeate into the wafers and adsorb to the surfaces by heating the pellets for one hour at 100°C. Infrared spectra of the samples following subsequent evacuations at successively higher temperatures were obtained on a Nicolet 8000 FT-IR spectrometer. Evacuation temperatures of 200°C or greater were used to eliminate overlap of the band due to physisorbed pyridine with the Lewis-pyridine band.

Cumene cracking reactions were carried out in a stainless-steel, continuous flow, fixed-bed bench-top reactor described in more detail elsewhere (*21*). Samples of the catalyst which had been previously ground to 80–100 mesh were accurately weighed (150mg) and packed in the sample holder between layers of quartz wool. Samples were activated by heating at 500°C for ninety minutes under a flow of helium, at a gas flow rate of 30 cm^3 per min.

The cumene was held in a presaturator which was kept at a constant temperature of approximately 21°C by a cooling water bath. Before the catalytic reactions were carried out, gas chromatographs were run of the cumene vapor itself to determine what, if any, aromatic impurities might be present.

The cumene reactions were carried out at a temperature of 400°C, with a carrier gas (helium) flow rate of 30 ml per minute. Gas chromatographs were obtained automatically using a Hewlett–Packard 5890 GC on samples which were collected every 20 min. Reactions were generally allowed to continue for 4 h. The GC results were used to calculate the percentage yields of each product, as well as the overall cumene conversion (*21*).

RESULTS

Relative Acidities of the Al_{13}, Ga_{13}, and $GaAl_{12}$-PILCs

A comparative study was made of the infrared spectra of pyridine which had been adsorbed onto the $GaAl_{12}$–, Al_{13}–, and Ga_{13}–pillared clay mineral samples. For comparison, the original STx-1 montmoril-

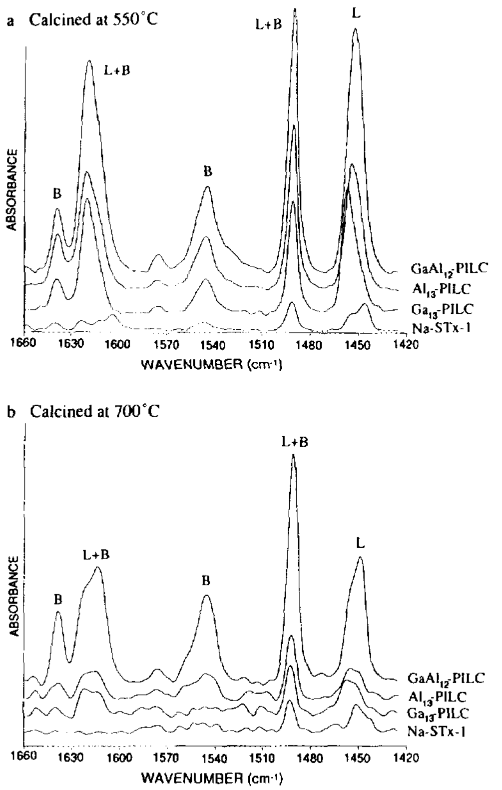

FIG. 1. Infrared spectra of pyridine adsorbed onto the $GaAl_{12}$–, Al_{13}–,and Ga_{13}–PILCs, and Na–STx-1, after calcining at 550 and 700°C.

lonite was also included, although it would not be expected to be as acidic as the pillared clays because of the presence of the Na^+ exchange cations. The samples were in the form of self supporting wafers (13-mm diameter) which had masses of between 25 and 30 mg. The pellets were calcined under oxygen in an infrared cell (which held all four pellets at once) at different temperatures, pyridine sorption/desorption studies were undertaken and infrared spectra were then obtained (Fig. 1).

Total number of Lewis acid sites. As expected on the basis of the PILC surface areas, the general order for the number of Lewis acid sites, where absorbance was corrected for sample mass, was found to be $GaAl_{12}$–STx-1 > Al_{13}–STx-1 > Ga_{13}–STx-1, with Na–STx-1 having a much lower acidity (Fig. 2). Although this was true regardless of calcination temperature, it was particularly remarkable that after calcination at 700°C the number of Lewis acid sites on the $GaAl_{12}$–STx-1 surpassed those of the other PILCs by an exceptionally large margin. This trend in acidities is in agreement with the high thermal stability of the $GaAl_{12}$–STx-1 (*9*). After calcining at this high temperature, the acidities of the Al_{13}– and Ga_{13}–PILCs were found to be almost the same as that of the Na–STx-1, even though their surface areas should have been somewhat larger. This could indicate that the pillars had collapsed in such a way that pyridine could no longer enter the pores and reach the acid sites, the bulk of which would be on the phyllosilicate sheet surfaces, but that the nitrogen gas which was used for surface area measurements (*9*) still could. This argument is consistent with the observation that the $GaAl_{12}$–PILC exhibited a fairly sharp d_{001} peak in the X-ray powder diffraction pattern after calcining at this temperature, whereas the Al_{13} and Ga_{13} species did not (*9*). The results found for the Brønsted acidities, however (*vide infra*), disagreed with this interpretation.

Number of Lewis acid sites per unit surface area. Calculations made for the relative absorbances per unit surface area still revealed the number of Lewis acid sites for the PILCs to follow the sequence $GaAl_{12}$–STx-1 > Al_{13}–STx-1 > Ga_{13}–STx-1, after calcining at 475°C. However this order gradually changed, and became $GaAl_{12}$–STx-1 > Ga_{13}–STx-1 > Al_{13}–STx-1 after calcining at higher temperatures (Fig. 3). For these calculations it was assumed that the specific surface areas would decrease with calcining temperature to the same degree as was seen in the thermal stability studies (*9*).

Relative strengths of Lewis acid sites. The relative strengths of acid sites are often determined by looking at the ease with which the pyridine is desorbed after evacuating at increasing temperatures. The stronger an acid site, the more tightly the

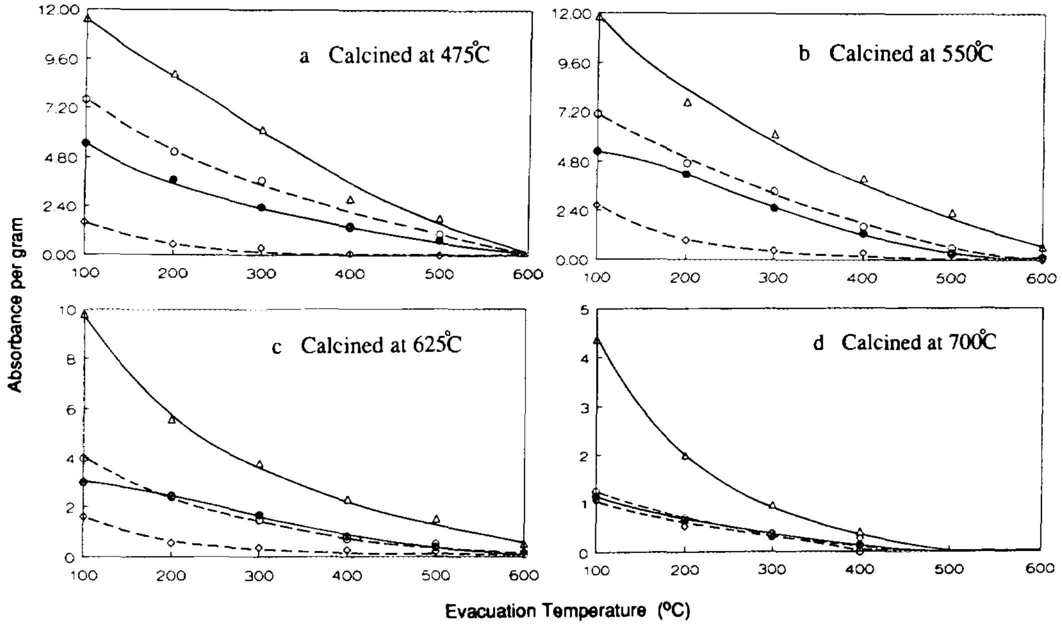

FIG. 2. Lewis acid sites: Pyridine infrared absorbance per gram of sample for the GaAl$_{12}$–, Al$_{13}$–, and Ga$_{13}$–PILCs and the Na–STx-1 montmorillonite. △ = GaAl$_{12}$, – PILC, ○ = Al$_{13}$ – PILC, ● = Ga$_{13}$ – PILC, and ◇ = Na – ST$_{x-1}$.

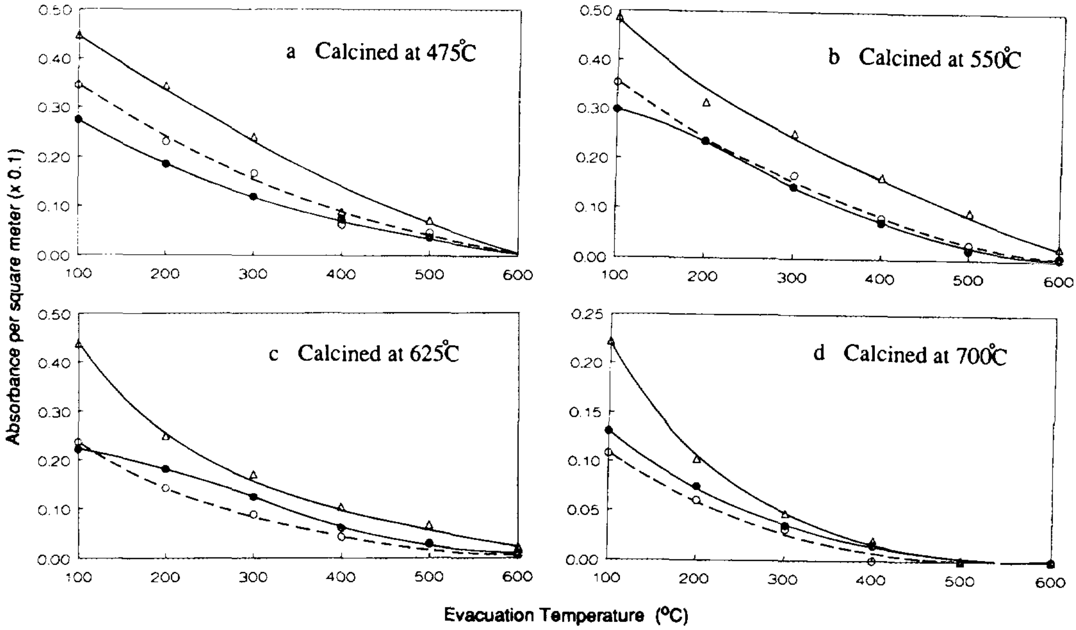

FIG. 3. Lewis acid sites: Pyridine infrared absorbance per unit surface area for the GaAl$_{12}$, Al$_{13}$–, and Ga$_{13}$–PILCs. For symbol meanings, see legend to Fig. 2.

TABLE 1

Positions of Lewis Acid Bands for $GaAl_{12}$–, Al_{13}–, Ga_{13}–, and Na–STx-1 after Calcining at Various Temperatures and Outgassing at 200°C

Sample	Band position (cm^{-1}) as a function of calcination temperature (°C)			
	475°C	550°C	625°C	700°C
$GaAl_{12}$–STx-1	1454.4	1454.7	$\underline{1455.6}$ + 1450	$\underline{1456.1}$ + 1450
Al_{13}–STx-1	1455.0	1455.1	$\underline{1455.7}$ + 1450	$\underline{1456.3}$ + 1450
Ga_{13}–STx-1	1457.9	1457.9	$\underline{1458.0}$ + 1450	$\underline{1457.3}$ + 1450
Na–STx-1	1455.7 + 1446.9[a]	1455 + $\underline{1446}$	~1454 + $\underline{1447}$	weak[b]

[a] In many cases, the band observed split at higher calcination temperatures. When one band was much stronger than the other, it has been underlined.

[b] For this sample, the Lewis acid band observed was too weak to determine an accurate band position.

pyridine would be bound, and therefore the greater the infrared absorbance would be expected to be after outgassing at higher temperatures. From this, it appears that the $GaAl_{12}$–STx-1 has the strongest acid sites. This method of interpretation, however, does not take into account the thermal stabilities of the PILCs themselves. For example, a site can be quite strongly acidic, but could also readily decompose at fairly low temperatures. As we have already shown that the thermal stabilities of the PILCs followed the order $GaAl_{12}$–STx-1 > Al_{13}–STx-1 > Ga_{13}–STx-1, this method of monitoring the infrared band intensities as a function of desorption temperature does not appear to be satisfactory. The strength of the Lewis acid sites can also be approximated by looking at the frequency of the infrared band used, which falls at ca. 1445–1460cm^{-1}. When this factor is taken into account (Table 1), it appears that the Ga_{13}–PILC contains the strongest Lewis acid sites, followed by the $GaAl_{12}$– and Al_{13}–PILCs, and then Na–STx-1.

Brønsted acid sites. The relative trends for the Brønsted acidities were somewhat different from those seen for the Lewis acidities. When expressed on the basis of absorbance per gram of sample, the order $GaAl_{12}$–STx-1 > Al_{13}–STx-1 > Ga_{13}–STx-1 > Na–STx-1 was followed after calcination at 400°C (Fig. 4). After calcining at higher temperatures, however, this trend slowly changed until after calcining at 700°C the order became $GaAl_{12}$– > Ga_{13}– ≈ Al_{13}– > Na–STx-1. When the absorbances were calculated per unit surface area, however, the Ga_{13} ion was found to produce the largest number of Brönsted acid sites (Fig. 5). This suggests that the gallium pillars contribute to the Brønsted acidity (at least as measured by pyridine adsorption) to a larger degree than is true for the $GaAl_{12}$ or Al_{13} pillars. It must be recognized, however, that after precalcination at 625 and 700°C these pyridine/Brønsted acid infrared bands were weak. Also, the specific high-temperature surface areas which were used in the calculations of absorbance per unit surface area (at elevated temperatures) were estimated from previous observations of the changes in surface area with temperature (*9*) rather than being directly measured; both of these factors introduce some uncertainty in the results obtained.

For all samples, the Brønsted acid site pyridine bands were found to disappear after outgassing at temperatures above 300 or 400°C, depending on the calcination temperature. This is in agreement with studies previously reported for the Al_{13} ion (*13, 17*), and for the Ga_{13} and mixed gallium–aluminum tridecamers (*10, 11*). In some of these other studies, the reasonable interpretation was made that this loss was due to the con-

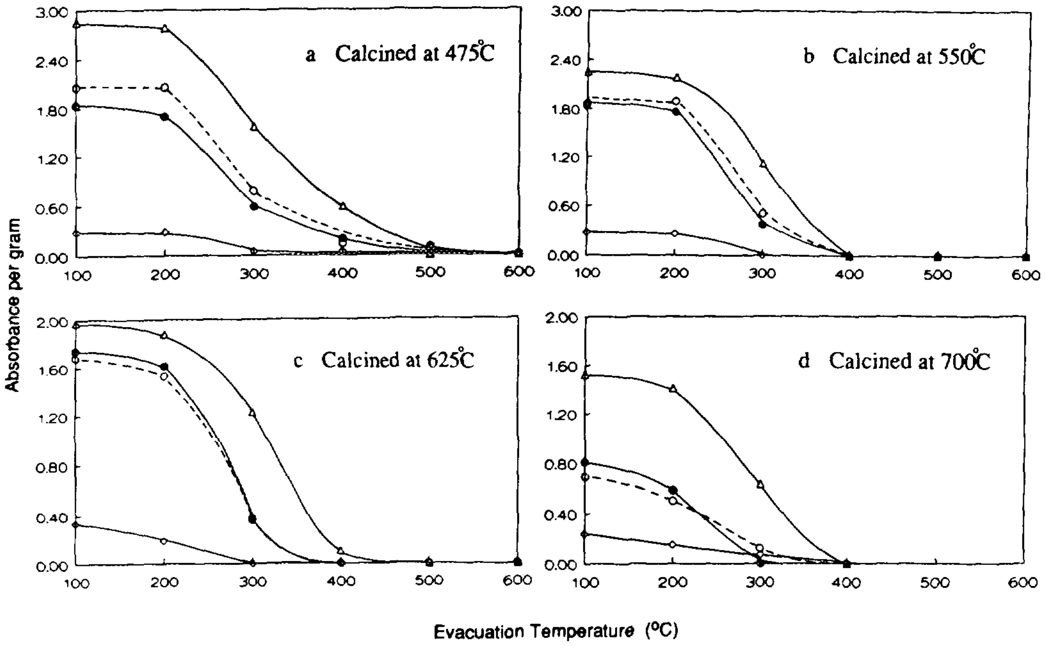

FIG. 4. Brønsted acid sites: Pyridine infrared absorbance per gram of sample for the $GaAl_{12}$–, Al_{13}–, and Ga_{13}–PILCs and the Na–STx-1 montmorillonite. For symbol meanings, see legend to Fig. 2.

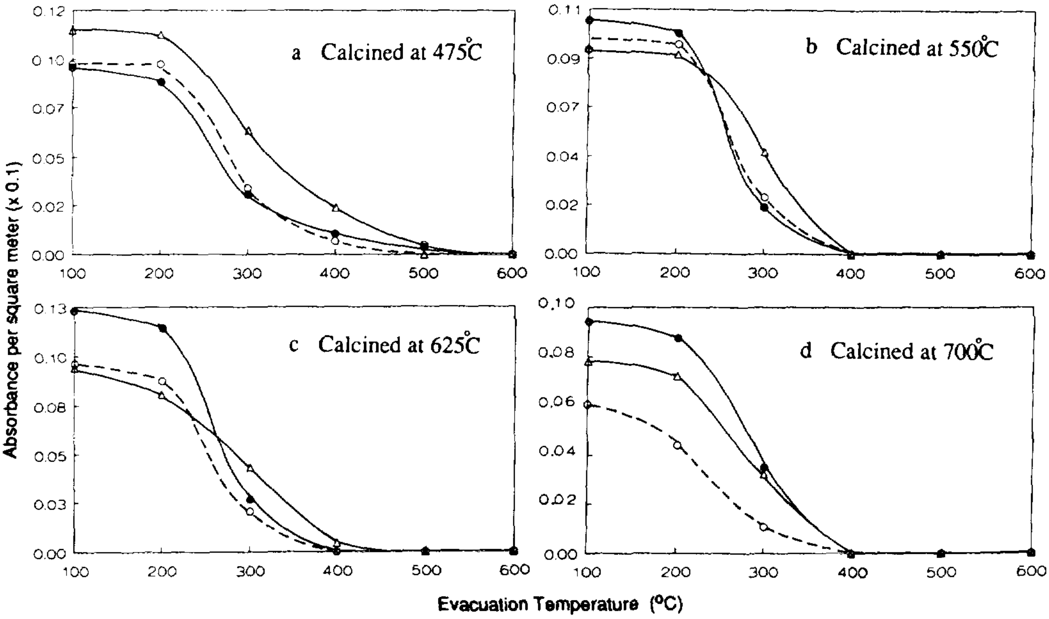

FIG. 5. Bronsted acid sites: Pyridine infrared absorbance per unit surface area for the $GaAl_{12}$–, Al_{13}–, and Ga_{13}–PILCs. For symbol meanings, see legend to Fig. 2.

version of the Brønsted sites into Lewis acid sites.

These results indicate that the surface area which is accessible to pyridine is the most important characteristic for increased acidities. This in turn means that the majority of the acidic sites are located on the exposed surfaces of the phyllosilicate sheets, as would be expected. However the presence of the pillars themselves also contributes to the measured acidity. In particular, the presence of the gallium pillars is seen to contribute to a strong Lewis acidity, and also to a larger number of Brønsted acid sites per square metre of surface. In addition, the results suggest that clay minerals and pillared clays are readily suited as supports for promoters, in much the same way as γ-Al_2O_3 is commonly used.

CUMENE CRACKING STUDIES

Cumene cracking studies were carried out for the Ga_{13}–, $GaAl_{12}$–, Al_{13}–, and Cr_x–STx-1 PILCs as well as for the starting clay mineral, Na–STx-1. The results are shown in Fig. 6, and summarized in Table 2. The Na–STx-1 itself exhibited mainly dehydrogenation activity, with very little benzene being formed. The Ga_{13}–pillared clay and the chromium–pillared clay also exhibited dehydrogenation activity almost exclusively; for both of these materials, the increase in overall conversion which was observed resulted from an increased yield of α-methylstyrene, with no appreciable increase in benzene production. Because of this, it is difficult to be sure whether the enhanced conversion for the gallium and chromium pillared clays arises from activity generated by the pillars, or simply from the additional exposure of the interior surfaces of the phyllosilicate sheets. It is rather surprising that the Brønsted acidities noted in the pyridine-IR studies for the Ga_{13}–PILC did not cause an increase in benzene production. If the pillars are involved in the catalytic process (see below), then the dehydrogenation capability which gallium oxides are known to possess clearly is more important than the acidity identified by the infrared results. It is also interesting that the Cr_x–pillared clay was active essentially completely for dehydrogenation rather than for cracking. Car-

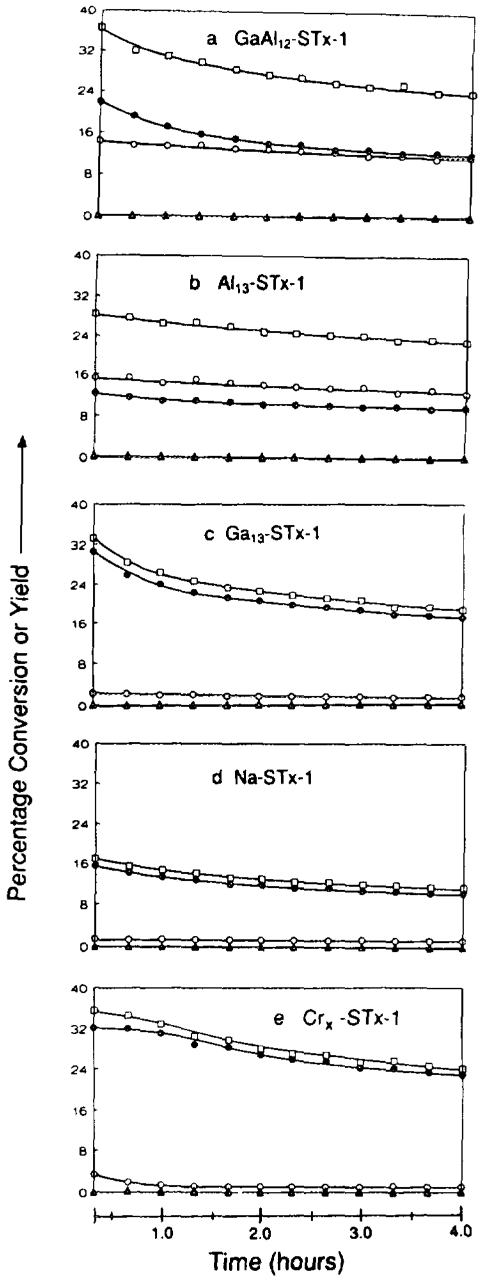

FIG. 6. Cumene cracking results as a function of time for $GaAl_{12}$–, Al_{13}–, Ga_{13}–, and Cr_x–PILCs and Na–STx-1. □ = cumene conversion, ● = α-methylstyrene, ○ = benzene, and ▲ = ethylbenzene.

TABLE 2

Cumene Hydrocracking Results over Pillared Montmorillonite

Pillaring cation	% Conversion		% Yield[a]		Cracking/dehydrog. ratio[c]	Surface area (m^2/g)
	Initial	After 4 h	Benz	αMeSty		
$GaAl_{12}$	36.7	24.6	12.1	12.4	0.98	245
Al_{13}	28.2	23.5	13.1	10.5	1.25	210
Ga_{13}	33.4	18.8	1.6	17.2	0.09	195
Cr_x	35.9	24.4	1.2	23.0	0.05	200
None[b]	17.9	12.3	1.6	10.7	0.15	83

[a] After 4 h.

[b] Results for unpillared Na-STx-1 montmorillonite.

[c] Ratio of benzene yield to α-methylstyrene yield.

rado *et al.* noted earlier that adding chromium to a bentonite clay, whether pillared or not, improved the overall behaviour of the catalyst for decane conversion (*21*). They used, among others, a Cr^{3+}-exchanged (not pillared) clay, and a clay pillared with a mixed Al–Cr pillar (structure not identified), but did not use a clay pillared with a chromium polyoxocation. Under the conditions of their experiments, it was found that both olefins and paraffins were produced, but as many of the lighter gases were not identified, it was not clear how chromium influenced the cracking/dehydrogenation ratio. The presence of chromium did appear to reduce the coke formed, however, which they suggested might be related to the acidity.

The most conclusive evidence of pillar involvement in the catalytic process is provided by the results for the $GaAl_{12}$- and Al_{13}-PILCs, which exhibit remarkably different results from those found for the others. For both the $GaAl_{12}$- and Al_{13}-PILCs there were almost equal yields of benzene and α-methyl styrene, i.e., the ratio of benzene to α-methyl styrene was larger by approximately an order of magnitude than for the Ga_{13}- and Cr_x-PILCs, and for the Na-STx-1 (see Table 2). This can not be attributed simply to differences in surface area (also given in Table 2). Clearly the pillars themselves must contribute to the catalytic activity.

The explanation for these results must involve the type of surface the cumene molecules encounter. The results for the unpillared clay mineral show that the exposed layer surfaces are not active for cracking to benzene. (Neglecting impurities, one montmorillonite layer consists of a sheet of aluminum octahedrally coordinated by oxygens and hydroxyls, sandwiched between two silicate sheets, so the exposed surface will be a silicate sheet.) The results for the Al_{13}-pillared clay suggest that the pillars (essentially aluminum oxide, after calcination) do possess cracking activity. The $GaAl_{12}$ pillars also would have an aluminum oxide exterior, unless during calcination some of the central, tetrahedrally coordinated gallium migrated to the surface. The observation of a slightly greater dehydrogenation activity for the $GaAl_{12}$-PILC as compared to the Al_{13}-PILC could suggest this, although it is also possible that a small number of gallium-containing species other than the tridecamers (monomers, dimers?) were present during the pillaring, and these could be deposited in the interlayer spaces, and contribute to the dehydrogenation.

It is interesting that the aluminum-containing pillars greatly increase the cracking ability of the materials. For γ-alumina itself, under identical conditions, cumene conversion (while low) was found to produce α-methylstyrene almost exclusively (*21*). The aluminum–pillared clay mineral behaves more like an acidic zeolite in this regard. It is tempting to speculate that the active sites for acidic reactions in the pillared materials might exist at the conjunction of the pillars and the clay sheets, where it would be possible to have hydroxyl groups bridging between Si and Al positions, creating sites which are similar to those which are responsible for the Brønsted acidity in zeolites. Whether or not this is true, however, it is clear that the nature of the pillars is important in determining the specific activity of the pillared clay minerals.

CONCLUSIONS

Investigations of the acidity of montmorillonite pillared with three different tridecameric cations showed that the pillars contribute to the acidic character primarily through increasing the interlayer spacing, thus increasing the surface areas, and further exposing the phyllosilicate sheet acid sites. However the pillars also contribute to the acidic characters, and most importantly, they contribute in different ways for the different pillars. For example, montmorillonite pillared with the Ga_{13} cation had the strongest Lewis acid sites and the greatest number of Brønsted acid sites. The different pillars also produce different catalytic results. Cumene cracking reactions revealed that the gallium and chromium PILCs and the Na–STx-1 montmorillonite exhibit almost exclusively dehydrogenation activity, whereas the $GaAl_{12}$– and Al_{13}–PILCs induced both dehydrogenation and cracking reactions. Apparently the strong dehydrogenation activity of gallium can compete successfully with the acidic sites which are known to be present, at least under the conditions of these cumene conversion studies.

The fact that the dehydrogenation and acid characteristics of the pillared clays can be "fine-tuned" by the choice of pillar make them suitable candidates for study as catalysts for reactions which require both types of site. To investigate this, studies of the dehydrocyclodimerization reactions of small alkanes (i.e., the Cyclar process) have been carried out (*8*, *23*).

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