

Characterization and Catalytic Activity of Aluminum- and Aluminum/Tetramethylammonium-exchanged Bentonites

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Three montmorillonites SWy-2 (Wyoming, USA), STx-1 (Texas, USA) and SAz-1 (Cheto, Arizona, USA) and a saponite Sap-Ca (California, USA) were activated with different amounts of Al^{3+} and tetramethylammonium (TMA^+) cations to obtain materials with a combined Al^{3+} and TMA^+ content equal to their CECs. The catalytic activity was evaluated by reacting α -pinene at 120 °C for 1 h to yield camphene, limonene, and other minor products and compared to clays prepared without TMA^+ . The total conversion over Sap-Ca, STx-1, SWy-2, and SAz-1 was 90%, 80%, 65%, and 25%, respectively, in samples treated with Al^{3+} alone. Similar yields were obtained over $\text{Al}^{3+}/\text{TMA}^+$ -exchanged forms when the TMA^+ content was less than 20% CEC, but in general the presence of TMA^+ significantly reduced the total conversion. The activity of the Al^{3+} -exchanged clays for this test reaction is attributed to their ability to remain expanded at the temperature of the activation process thus permitting easy access of the reagent. The comparatively low conversion over catalysts derived from SAz-1 was attributed to its high layer charge which restricted access to the active centers in the clay gallery.

Introduction

It is well established that the properties of bentonites can be systematically altered by replacing the naturally occurring exchange cations (e.g., Na^+ , K^+ , Ca^{2+}), which are strongly hydrated in the presence of water, with highly polarizing species such as aluminum, chromium, iron or polymeric metal oxyhydroxy cations.^{1–4} Indeed, the enhanced catalytic activity of Al^{3+} -exchanged montmorillonites, compared to Fe^{3+} - and Cr^{3+} -exchanged montmorillonites, has been attributed to the higher charge-to-radius ratio of the Al^{3+} cation resulting in greater polarization of the water molecules in its primary coordination sphere,^{2,5} which results in the generation of acidic protons in the interlayer gallery. In addition to the numerous examples of Brønsted acid catalyzed processes occurring over clays,^{1–5} the presence of these protons has been unequivocally demonstrated by the presence of the 1540 cm^{-1} band, which is diagnostic of the pyridinium ion, in the infrared spectrum of pyridine treated Al^{3+} -, Cr^{3+} -, and Fe^{3+} -exchanged montmorillonite.⁶ The polarizing power of the M^{3+} cations is diminished in the presence of substantial amounts of interlayer water, which means that hydration state of clay-based catalysts needs to be optimized prior to their use in a chosen process. Thus, prior to adsorption of the reagent the interlayer space of a clay catalyst is occupied by cations with no more than their primary coordination sphere of water. Treating clays with mineral acids also results in materials with useful properties^{7,8} (such as enhanced surface area, higher pore volumes, decolorising ability and/or catalytic activity), although care must be taken to select an appropriate combination of acid concentration, temperature and treatment time for the particular source clay utilized since the activation conditions must be matched to the elemental composition of the octahedral manifold.^{7–9} The extent of acid dissolution can

significantly influence the activity of a clay-based catalyst whether it is used as a support¹⁰ or as a catalyst in its own right.^{8,11}

Using the formation of tetrahydropyranyl ether from dihydropyran and methanol as a test reaction, Rhodes and Brown showed that the catalytic activity of acid-activated clay for reactions in polar media was optimized when the acidity and swelling ability of the clay was at a maximum.¹¹ This occurs at short acid treatment times. In contrast, the yield for the isomerization of α -pinene to camphene, which represents reaction in a nonpolar medium, is optimized when the leaching is extensive. The obvious conclusion was that reaction in polar media was optimized at short acid treatment times because the hydrophilic clay attracts the polar reagents to the surface where the catalytically active protons reside. This contrasts with the behavior in nonpolar media where the reaction yield was optimized when the clay was substantially leached, because the catalyst presented an essentially hydrophobic surface which served to attract the nonpolar reagents. This data is, however, limited to the study of one clay with a high octahedral aluminum content.

The surface properties of natural clays can be readily modified by replacing the resident inorganic exchange cations with larger alkylammonium ions.^{12–15} Globular tetralkylammonium cations can act as “pillars” which hold the aluminosilicate sheets permanently apart, increase the interlamellar spacing, and generate new sorption sites on the clay surfaces.^{16–18} More importantly, the organocations are weakly hydrated so that as the inorganic cations are progressively replaced by organic cations, the surface properties of the clay change from essentially hydrophilic to increasingly organophilic. These materials, referred to as organoclays, have received considerable attention because they exhibit high adsorption capacities toward hydrophobic pollutant molecules present as solutes in aqueous waste streams.^{19–21}

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This knowledge coupled with the recent interest in the properties and enhanced catalytic activity of pillared acid-activated clays^{22–24} led us to assess the catalytic activity of mildly acid-activated organoclays,^{25,26} which offer a balance between the hydrophilic and organophilic character on the clay surface and produce catalysts that promote reactions in nonpolar media. Four source clays of differing elemental composition, locus, and density of charge were chosen in order to evaluate the effect of these variables on the resulting activity. These studies demonstrated that both the nature of clay and the chosen organocation influence the activity of the resulting catalysts. For example, mildly acid activated (0.1 M HCl at 20 °C) long-chain alkyltrimethylammonium-exchanged clays were inactive when the galleries were congested with these large organocations, whereas this did not occur when symmetric, tetrahedral tetramethylammonium cations were utilized.²⁵ Indeed maximum yields (which were extremely competitive with the 60–80% yields obtained using zeolites,^{27,28} pillared interlayer clays²⁷ and layered phosphates²⁸) were achieved when about 30% of the exchange sites were occupied by TMA⁺ cations.²⁶ Comparable activity was also achieved using polycation-exchanged bentonites, but these required activation in hot 6M HCl.³⁰ Finally, it was evident that the layer charge played a significant role insofar as when using a high layer charge clay the combination of H⁺ and TMA⁺ cations acted to reduce the catalytic activity for the isomerization of α -pinene relative to its acid-activated counterpart.^{25,26} In contrast, the combination of TMA⁺ and H⁺ cations on the exchange sites in intermediate charge clays enhanced the activity compared to clays prepared using H⁺ alone.²⁶

Unfortunately, one of the selected source clays, in which the octahedral sheet is composed almost entirely of magnesium, was extensively leached even when using mild activation conditions. Therefore, it was not possible to compare its activity directly with that of the three other acid-activated organoclays nor to distinguish between the influence of substantial depletion of the octahedral sheet (which leads to a hydrophilic surface due to Al for Si substitution in the tetrahedral sheet) and the contribution of the TMA⁺ cations. Moreover, it is well known that even mildly acid-activated clays can undergo autotransformation in which the interlamellar protons enter the layer and replace Mg²⁺ and Al³⁺ cations from the octahedral sheet.^{9,31} Once released, these multivalent ions take up exchange positions within the gallery and may contribute to the observed catalytic activity. Autotransformation is known to be accelerated at elevated temperatures and could thus have occurred during thermal activation of the catalysts prepared using H⁺/TMA⁺. Thus, the aim of this study was use a combination of Al³⁺ and TMA⁺ cations on the exchange sites in order to compare all four clays directly without depleting the octahedral sheet and to evaluate whether the Al³⁺/TMA⁺ exchange mimics autotransformation in the H⁺/TMA⁺ clays and contributes to an enhanced activity. This was achieved by systematically varying the Al³⁺/TMA⁺ ratio within the gallery and evaluating its influence on the catalytic activity for the isomerization of α -pinene to camphene and limonene.

Experimental Section

Materials. Four source clays of differing elemental compositions, charge density, and locus of isomorphous substitution were selected: Na–Montmorillonite (SWy-2, dioctahedral, aluminum rich bentonite), Wyoming-USA; Ca–Montmorillonite (STx-1 dioctahedral, bentonite of low iron content), Texas-USA; Ca–Montmorillonite (SAz-1 dioctahedral, magnesium-rich bento-

nite), Arizona-USA; and Ca–Saponite (Sap-Ca trioctahedral, magnesium rich saponite), California-USA. All samples were obtained from The Clay Mineral Repository of the Clay Minerals Society and used without further purification. The cation exchange capacities (CEC) of SWy-2, STx-1, SAz-1, and Sap-Ca are 0.80, 0.84, 1.20, and 0.92 mequiv (g clay)^{–1}. Thus SAz-1 has a significantly higher charge density than the other two montmorillonites. Isomorphous substitution occurs only in the tetrahedral sheet of Sap-Ca, whereas it occurs predominantly in the octahedral sheet in the other three clays.

Equipment and Methods. Al³⁺-exchanged organoclays were prepared by adding 1 g of each clay to a solution containing selected volumes of 1 M tetramethylammonium chloride (TMACl, Aldrich, 97%) and 0.1 M Al³⁺ (AlCl₃·6H₂O, Aldrich, 99%) in different ratios to prepare samples in which the Al³⁺/TMA⁺ ratio was systematically varied without exceeding the CEC of the chosen clays. Al³⁺-exchanged clays were made in exactly the same way except that the TMACl was excluded. The mixtures were stirred vigorously overnight at room temperature and then centrifuged at 17 000 rpm for 20 min. The centrifugates were washed and centrifuged repeatedly with deionized water to remove excess exchanging salt. Clay samples were dried at 120 °C overnight, and ground <0.2 mm prior to storage. The Al³⁺ or Al³⁺/TMA⁺ treatment is identified in the sample name. Thus, SW-Al30 indicates that SWy-2 was treated with 30% of its CEC with Al³⁺ and SCA-Al40/TMA60 means that Sap-Ca was treated with 40% Al³⁺ and 60% TMA⁺.

Sample Characterization. A Spectro (Analytical Instrument) model P, direct emission spectrometer was used to determine the uptake of aluminum from the initial solutions and the amount of Ca²⁺, Mg²⁺, and Na⁺ displaced into solution during the various preparation procedures.

Thermogravimetric data were obtained on a Mettler TG50 thermobalance equipped with a TC10A processor. An amount, 8–12 mg, of the sample was weighed into a ceramic crucible and heated from 35 to 800 °C at 20 °C min^{–1} under a flow of 30 cm³ min^{–1} dry nitrogen carrier gas. The acidity was estimated using the thermal desorption of cyclohexylamine. Samples were exposed to reagent grade cyclohexylamine for periods in excess of 48 h. The weight loss observed between 240 and 350 °C was used to monitor the acidity.³² The TMA⁺ content was also monitored from the TG data, using the weight loss between 350 and 460 °C.

XRD and VT-XRD profiles were recorded using Cu–K α radiation (λ = 1.5418 Å) on a Phillips PW1140 diffractometer operating at 30 kv and 30 mA at a 2θ scan rate of 2°/min, utilizing a simple heating stage for VT-XRD.³³ Samples were presented to this heating stage as orientated films on glass slides and were heated at 100, 170, 220, and 300 °C. The samples were held at these temperatures for 25 min prior to recording the XRD trace.

Catalytic Activity. The ability of the aluminum-exchanged organoclays to act as acid catalysts was investigated using the isomerization of α -pinene to yield camphene, limonene, and other minor products as a test reaction. This reaction has been frequently used as a model for assessing activity^{11,25–27,30} and is of industrial significance because camphene is an important intermediate in the synthesis of camphor, which has high value due to its aroma and pharmaceutical properties.³⁴ Reaction conditions similar to those previously reported were chosen.²⁶ As an example, 100 mg of dried clays was added to 10 cm³ (0.06 mol) of preheated (120 °C) α -pinene at a constant temperature for 1 h. The reaction was subsequently stopped and

the product mixture was filtered and analyzed by gas chromatography with FID detection.

Results and Discussion

The amount of resident exchange cation (expressed as percentage of metal oxide released) as a function of the amount of Al^{3+} and/or TMA^+ in the initial exchange solution is shown in Figure 1 for samples derived from SAz-1. Samples derived from Sap-Ca, STx-1 and SWy-2 showed a similar trend (not illustrated). The complete displacement of the exchangeable Na^+ and Mg^{2+} by Al^{3+} or protons (from the acidic aluminum solution, $\text{pH} = 2.8$) was observed for all four clays, although resident Ca^{2+} ions were more difficult to displace (Figure 1a). In contrast, the removal of resident exchange cations during the preparation of $\text{Al}^{3+}/\text{TMA}^+$ clays did not depend on the $\text{Al}^{3+}/\text{TMA}^+$ ratio in solution because this always equalled 100% CEC (Figure 1b).

The amount of Al^{3+} occupying the exchange sites in all four clays correlated well with the amount offered in the 10–50% CEC region, but not so well in the >60% region, which suggests that some exchange sites were occupied by the protons available in the exchange solution. In general, the Al^{3+} content in Al^{3+} -exchanged clays followed the order: SWy-2 > Sap-Ca > SAz-1 > STx-1. The presence of TMA^+ cations did not significantly influence the uptake of Al^{3+} , but it did appear to reduce the number of protons on exchange sites, which agrees with earlier observations regarding the ability of TMA^+ cations to compete effectively with H^+ ions for exchange sites.²⁶

In the presence of acid, or in this instance acidic protons generated by the polarizing power of the substantially dehydrated Al^{3+} cations, α -pinene (**1**) isomerizes to form a mixture of products. Under nonaqueous conditions ring expansion, either by the shift of the methylene bridge to give α -fenchene (**2**) or by the shift of the *gem*-dimethyl bridge to yield camphene (**3**), is favored (Figure 2).³⁵ In highly polar protic solvents (e.g., H_2SO_4) monocyclic terpenes are formed via a ring-opening process to give a mixture of *p*-menthadienes including limonene (**4**), isoterpinolene (**5**), and α -terpinene (**7**). Figure 3 shows how the total conversion (based on α -pinene) varied with the aluminum content (expressed as % CEC) in Al^{3+} - and $\text{Al}^{3+}/\text{TMA}^+$ -exchanged samples. In the $\text{Al}^{3+}/\text{TMA}^+$ samples TMA^+ cations resided on the sites not occupied by Al^{3+} cations. The maximum yields obtained are very similar to those obtained using H^+ - and H^+/TMA^+ -exchanged clays²⁶ and are directly comparable with the conversion of α -pinene values of 80 and 90% reported for zeolite Y (USY), Al- and Al,Fe-pillared clays, and Pt- Al_2O_3 catalysts.^{27–29,36} Clearly, the type of clay used exerted a considerable effect on the total conversion obtained using this test reaction. In either the absence or presence of TMA^+ both Sap-Ca and STx-1 were more efficient catalysts for the process than SWy-2 and SAz-1. In all cases the presence of Al^{3+} resulted in improved catalytic activity. As little as 20% CEC of Al^{3+} resulted in a 3-fold increase in the activity compared to unmodified Sap-Ca and STx-1, the activity then increased steadily to 70% CEC. The increase in activity of SW-Al samples was less marked and SAz-1 achieved little more than 20% conversion at the highest Al^{3+} content. These observations concur with those of Purnell et al.³⁷ who observed a similar diminution in catalytic activity toward the esterification of ethanoic acid by hexene and the dehydration of pentanol as the loading of Al^{3+} increased above 70% CEC. Thus, it is clear that small amounts of interlayer Al^{3+} derived from autotransformation during thermal activation of the original H^+ clays and H^+/TMA^+ clays at 120 °C would make a significant contribution to the total conversion of α -pinene.^{25,26}

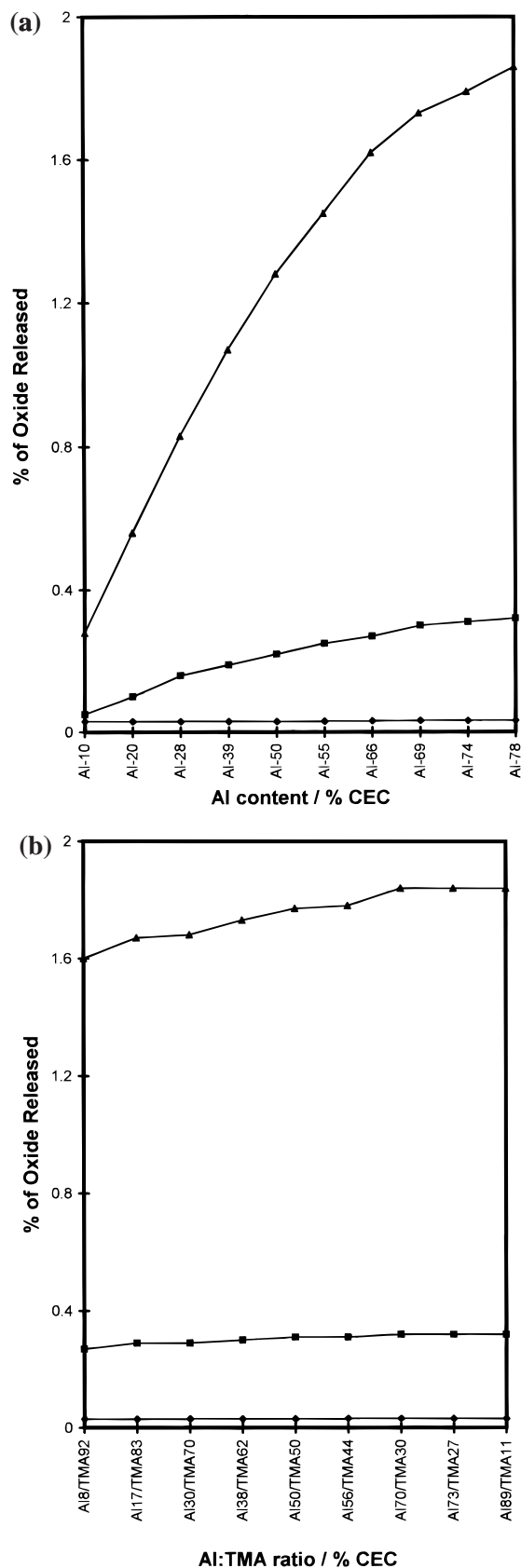


Figure 1. Percentage of metal oxide released during treatment of SAz-1 clay (a) Al^{3+} and (b) $\text{Al}^{3+}/\text{TMA}^+$. (\blacktriangle) CaO, (\blacksquare) MgO, and (\blacklozenge) Na_2O .

In general the distribution of products which make up the total conversion (Table 1) followed the order camphene (**3**) > limonene (**4**) > others, except for catalysts derived from STx-1 with high Al^{3+} contents (ST-Al60 to ST-Al100 and ST-Al170/

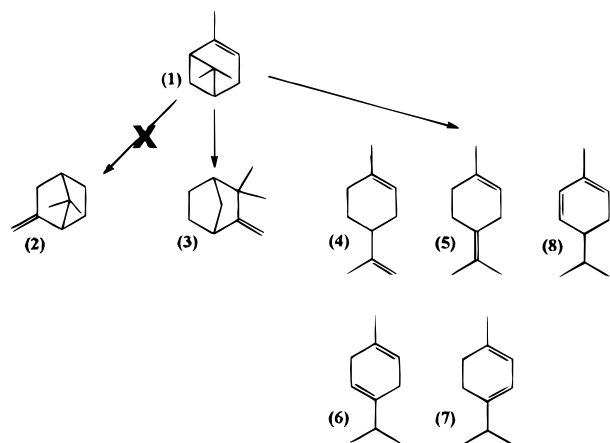


Figure 2. Major products for the acid-catalyzed isomerization of α -pinene.

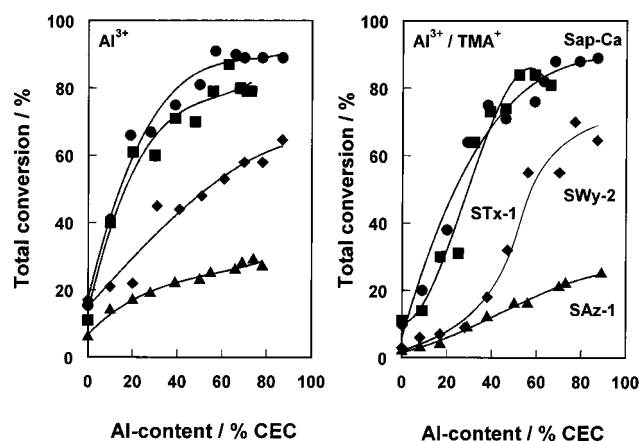


Figure 3. Total conversion versus percentage of aluminum incorporated in (a) Al³⁺-exchanged and (b) Al³⁺/TMA⁺-exchanged clays (●) Sap-Ca, (■) STx-1, (◆) SWy-2, and (▲) SAz-1.

TMA30 to ST-AI80/TMA20) where the yield of other products exceeded that of limonene. The selectivity toward camphene, limonene, and the minor products was very similar for all the clays and can be broadly represented as $57 \pm 7\%$, $26 \pm 5\%$, and $16 \pm 7\%$ to encompass all the catalysts, which is very similar to the values of $65 \pm 10\%$, $25 \pm 8\%$ and $12 \pm 8\%$ obtained over H⁺- and H⁺/TMA⁺ clays.²⁶ The ratio of camphene to limonene is near 2.2:1.0 which is identical to the value obtained at 80 °C for 2 h,²⁵ but marginally lower than the values of 2.6:1.0 obtained using H⁺/TMA⁺ clays²⁶ and 3.0:1.0 obtained over USY, Al-PILC, and Al,Fe-PILC.²⁷ Therefore, these clay catalysts are not as selective toward camphene as the permanently porous catalysts but the yields are extremely competitive and the catalysts are less expensive to prepare.

In contrast to the behavior of H⁺/TMA⁺ clays^{25,26} where the presence of TMA⁺ at intermediate loading enhanced the activity, even when conversions were low (e.g., H⁺-SAz-1), the Al³⁺/TMA⁺-exchanged clays gave lower conversions than their Al³⁺-exchanged counterparts at low Al³⁺ content (10–40% CEC). However, the values were similar at Al³⁺ contents >50% CEC when the amount of TMA⁺ present began to decrease significantly. Clearly, even SWy-2 and STx-1, which had shown an increase in activity when exchanged with a combination of H⁺ and TMA⁺ cations,²⁶ gave poor correlation with TMA⁺ loading in the Al³⁺/TMA⁺ forms. The reduced conversion of α -pinene to its isomers in the Al³⁺/TMA⁺ samples suggested a significant reduction in the number and/or accessibility of the acid centers available.

TABLE 1: Product Distributions for the Catalysts Derived from Sap-Ca, STx-1, SWy-2, and SAz-1

sample designation ^a		Sap-Ca	STx-1	SWy-2	SAz-1
Al10	C	22.9	20.2	10.7	7.1
	L	11.5	11.7	5.6	4.5
	O	6.7	7.6	4.3	1.9
Al20	C	41.5	31.2	10.7	9.2
	L	18.3	16.9	5.9	6.0
	O	6.0	12.5	4.9	2.0
Al30	C	46.2	31.2	21.9	10.2
	L	18.1	17.4	12.8	6.7
	O	6.4	11.6	10.4	2.0
Al40	C	50.6	36.9	21.7	11.3
	L	18.0	19.4	11.7	7.5
	O	5.9	14.8	9.9	2.7
Al50	C	50.8	35.9	25.1	12.5
	L	19.4	19.4	13.2	8.4
	O	10.9	14.6	10.3	2.4
Al60	C	55.4	41.0	29.5	13.2
	L	21.9	18.8	14.1	8.8
	O	13.8	19.4	9.4	2.6
Al70	C	55.7	44.3	31.0	14.0
	L	18.9	18.2	15.8	9.0
	O	15.6	23.8	10.6	2.9
Al80	C	57.8	41.5	36.0	15.5
	L	17.0	18.8	16.4	9.3
	O	14.5	19.4	5.4	2.7
Al90	C	58.5	42.8	42.5	16.2
	L	14.6	17.4	18.1	10.2
	O	15.8	18.6	2.2	2.8
Al100	C	56.5	41.6	44.6	15.8
	L	12.8	17.9	19.5	9.1
	O	20.1	19.0	18.4	2.4
Al10/TMA90	C	13.5	7.6	3.3	1.8
	L	4.5	3.4	1.2	0.6
	O	1.8	2.6	2.3	0.8
Al20/TMA80	C	26.3	16.6	3.2	2.6
	L	8.5	7.4	1.0	0.8
	O	2.9	6.1	1.5	1.0
Al30/TMA70	C	43.7	16.7	5.1	4.7
	L	14.7	7.8	1.6	2.2
	O	5.2	6.6	1.9	1.9
Al40/TMA60	C	48.8	35.7	11.3	5.6
	L	16.9	16.5	4.4	3.4
	O	9.7	11.9	2.2	2.5
Al50/TMA50	C	47.8	39.8	20.7	8.4
	L	16.5	19.3	7.4	4.4
	O	9.8	14.0	3.5	3.6
Al60/TMA40	C	49.5	40.0	38.2	8.6
	L	17.8	17.9	14.1	5.1
	O	8.0	15.9	2.6	2.7
Al70/TMA30	C	55.6	46.6	38.3	10.7
	L	18.1	18.3	14.9	6.1
	O	9.0	19.4	2.7	4.5
Al80/TMA20	C	59.8	45.4	49.9	10.8
	L	20.8	19.1	17.5	6.4
	O	7.5	19.0	2.5	4.8
Al90/TMA10	C	59.1	43.5	46.1	12.4
	L	21.0	19.9	20.4	7.6
	O	8.0	17.0	10.9	4.7

^a C = Camphene, L = Limonene, and O = Other Products.

It is well known that ion exchange with polyvalent cations increases the acidity of the interlayer water in montmorillonites due to the hydrolysis of the cation-solvating water molecules.³⁸ The release of these protons within the interlamellar region is generally accepted as the major source of the Brønsted acidity in these minerals.^{1–6} To understand how the acidity of Al³⁺- and Al³⁺/TMA⁺-exchanged clays correlated with the catalytic activity, catalyst samples were exposed to cyclohexylamine vapor at room temperature. Figure 4a presents the characteristic derivative thermogram for Ca²⁺/Na⁺-SWy-2 before treatment with cyclohexylamine vapor. The first maximum at 90 °C corresponds to the removal of physisorbed water and the second at 690 °C is associated with the dehydroxylation of the clay layer.^{32,39} The desorption of cyclohexylamine from samples with

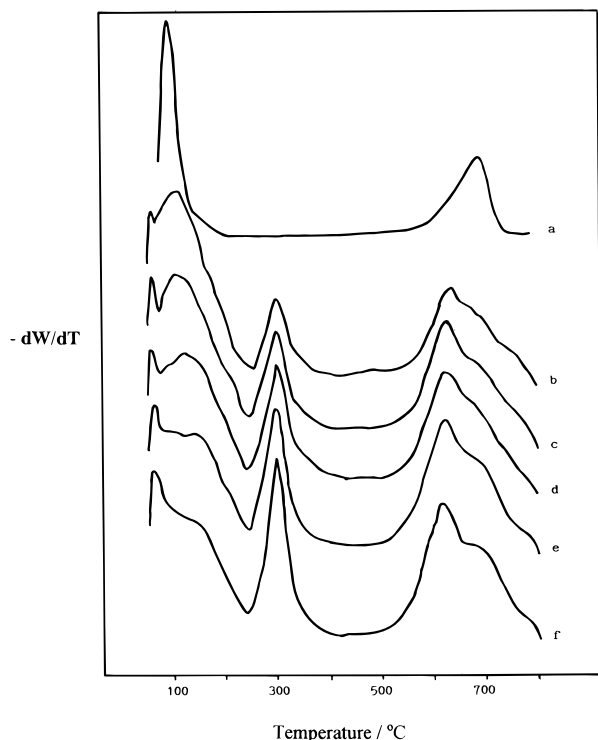


Figure 4. Derivative thermograms for (a) untreated SWy-2 and the desorption of cyclohexylamine from (b) SW-Al10, (c) SW-Al30, (d) SW-Al50, (e) SW-Al70, and (f) SW-Al90.

different aluminum contents (Figures 4b–4f) showed that, in addition to the peaks mentioned above, three maxima at 140, 310, and 620 °C were also clearly distinguished. These peaks have been attributed to (1) the desorption of physisorbed cyclohexylamine combined with water, (2) a sharp, intense maximum which corresponds to the desorption of cyclohexylamine from acid sites (chemisorbed cyclohexylamine), and (3) the desorption of water and CO₂ arising from a combination of layer dehydroxylation and oxidation of carbonaceous deposits derived from cyclohexylamine, respectively.^{32,39,40} Figures 4b–4f, show that the maximum at 310 °C increased with aluminum content, while that at 140 °C decreased slightly. These data confirmed that sites with sufficient acid strength to interact with cyclohexylamine were present in the Al³⁺-exchanged clays.

The derivative thermograms for the desorption of cyclohexylamine from SW-Al/TMA samples (Figures 5a–5e), contained the maxima described above together with that arising from the desorption of TMA⁺ at 410 °C,²⁶ which diminished as the Al:TMA ratio increased. ICP–AES results demonstrated that the amount of aluminum incorporated into both the Al³⁺- and Al³⁺/TMA⁺-exchanged samples was very similar. Nonetheless, a significant variation in the intensity of the maximum at 310 °C was clear when comparing these traces with those obtained in the absence of TMA⁺, and it was not visible in samples with an aluminum content <30% CEC. However, the 310 °C maximum increased significantly at aluminum contents above 70% CEC, but was still of lower intensity than the corresponding maxima in samples prepared without TMA⁺. The weight loss associated with the 310 °C maximum increased as the TMA⁺ loading decreased and the Al³⁺ loading increased. For all four clays, this weight loss was much less for the samples prepared using an Al:TMA ratio < 1 than for the corresponding Al³⁺-exchanged clays. Thereafter, as the Al:TMA ratio increased, this weight loss increased to a maximum. The weight loss decreased as SAz-1 > STx-1 > SWy-2 = Sap-Ca. For Al³⁺-

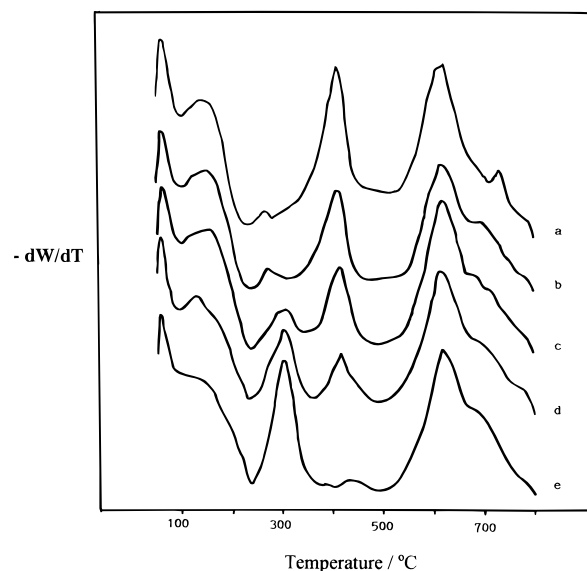


Figure 5. Derivative thermograms for the desorption of cyclohexylamine from (a) SW-Al10/TMA90, (b) SW-Al30/TMA70, (c) SW-Al50/TMA50, (d) SW-Al70/TMA30, and (e) SW-Al90/TMA10.

and Al³⁺/TMA⁺-exchanged Sap-Ca there was a reasonable correlation between this weight loss and the conversion of α -pinene. This was also true for STx-1 and SWy-2 and agrees with reports that the catalytic activity for the pentanol dehydration was proportional to the acidity (measured using the desorption of cyclohexylamine) of aluminum pillared clays⁴¹ and pillared acid-activated clays.²³ However, this correlation was not reflected in the percentage of the α -pinene converted, especially for the SAz-1 series. Undoubtedly, SAz-1 is a poor catalyst for the isomerization of α -pinene, whether in H⁺ or H⁺/TMA⁺²⁶ and Al³⁺ or Al³⁺/TMA⁺ forms.

A similar discrepancy between acidity values (determined using the desorption of cyclohexylamine) and the production of tetrahydropyranyl ether from dihydropyran and methanol was observed for acid-activated samples of SAz-1 and a Slovak montmorillonite.⁴² This was attributed to the strong basicity of cyclohexylamine ($pK_b = 3.3$) which enables it to interact with both weak and strong Lewis or Brønsted acid sites. Therefore, the high apparent acidity noted herein for Al³⁺-SAz-1 is attributed to the combined interaction of cyclohexylamine with the catalytically active Al³⁺ ions and the catalytically inactive Ca²⁺ ions which were progressively displaced by Al³⁺ ions.

In our previous publication,²⁶ the principal objective was to determine how the presence of TMA⁺ influenced the catalytic activity of a series of acid-activated organoclays. It was demonstrated that SWy-2 and STx-1 were more effective for α -pinene isomerization when they contained 25–30% TMA⁺ cations on the exchange sites than were those prepared without TMA⁺, whereas acid-treated samples derived from Sap-Ca and SAz-1 were more active than their TMA⁺-containing counterparts. This increased activity for Sap-Ca was attributed to the extensive depopulation of the magnesium-rich octahedral sheet of saponite using these relatively mild acid treatments. The poor yield over SAz-H⁺/TMA⁺ was attributed to reduced access to the active surface because of the inability of SAz-TMA⁺ to disperse in α -pinene. However, acid-activated organoclays (AAOCs) containing TMA⁺ cations were more effective than those containing alkyltrimethylammonium²⁵ or polycations.³⁰ This behavior was attributed to the congestion of the clay galleries at high loadings of large organo- or polycations so that the activity decreased.^{25,30}

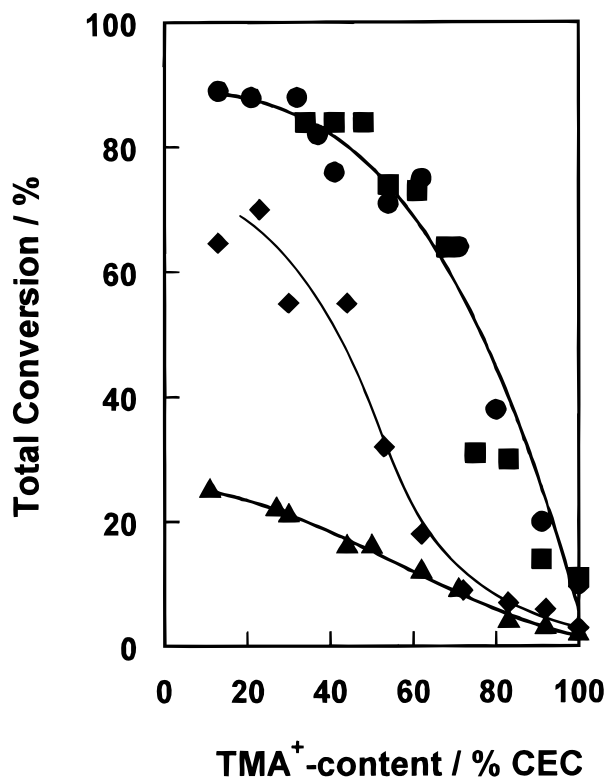


Figure 6. Total conversion versus TMA⁺ content on Al³⁺/TMA⁺-exchanged clays. (●) Sap-Ca, (■) STx-1, (◆) SWy-2, and (▲) SAz-1.

In the current investigation it has been demonstrated that the Al³⁺ forms were more active for α -pinene conversion than were the corresponding Al³⁺/TMA⁺-exchanged forms at low aluminum contents, although they were similar when Al³⁺ was the predominant exchange ion. Figure 6 shows that increasing the TMA⁺ content reduced the activity of all four clays for the isomerization process. The activity of Al³⁺/TMA⁺-SAz-1 decreased almost linearly with TMA⁺ content, whereas that for Sap-Ca and STx-1 fell off significantly as the TMA⁺-content exceeded 60% CEC. The activity of Al³⁺/TMA⁺-SWy-2 was relatively high at low TMA⁺ contents then decreased markedly as the TMA⁺ content increased from 30 to 60% CEC, after which the activity was very similar to that for Al³⁺/TMA⁺-SAz-1. SAz-1 has a high layer charge which, when fully exchanged with TMA⁺ cations, has a reduced capacity for the adsorption of organic species larger than benzene. This is attributed to the smaller distance between neighboring TMA⁺ cations than in intermediate charge clays such as SWy-2.^{20,21,26} In addition, it is anticipated that TMA⁺-rich SAz-1 is relatively well ordered and that the individual platelets do not readily disperse. The locus of charge in Sap-Ca resides in the tetrahedral sheet where Al³⁺ cations substitute for Si⁴⁺ cations and it is known to exhibit higher surface acidity than clays in which the isomorphous substitution occurs mainly in the octahedral sheet. Thus, the maintenance of isomerization activity to higher TMA⁺ contents probably reflects the greater acidity of the surface which remains accessible because the TMA⁺ cations hold the layers apart. The high activity of catalysts derived from STx-1 was unexpected, although an aqueous suspension of this mineral has a pH of 7.1 compared with 9.2 for SWy-2 which suggests that STx-1 is naturally more acidic although such measurements are not directly transferable to nonaqueous media. The similarity in yield to that exhibited by Sap-Ca suggests that STx-1 also contains significant tetrahedral substitution although this cannot be confirmed since no reports exist in the literature and the

presence of fine-grained silica impurities precludes a complete resolution of this issue using conventional chemical analysis approaches. Finally, Al³⁺/TMA⁺-SWy-2 exhibits a combination of these behaviors. At high Al³⁺ contents the activity is relatively high but it falls markedly at TMA⁺ contents between 30 and 60%, after which it closely follows that of the corresponding samples based on SAz-1. Al³⁺-SWy-2 has a lower activity than either Sap-Ca or STx-1, yet the combination of H⁺/TMA⁺ essentially doubled its activity (48% to 90%) for the isomerization process.²⁶ Hence the major difference in the activity of the four clays appears to result from the locus of isomorphous substitution and the magnitude of the layer charge. The former, if it is in the tetrahedral sheet, ensures continued activity at relatively high TMA⁺ contents, whereas the latter appears to restrict access to the gallery either by size-excluding the reactant or limiting effective dispersion of the catalysts in the liquor. Clays of intermediate charge and significant octahedral substitution exhibit high activity at high interlayer Al³⁺ contents which decreases substantially as the TMA⁺ content increases.

Thus, it is clear that the Al³⁺-exchanged clays were generally more active than Al³⁺/TMA⁺, H⁺/TMA⁺, or H⁺ clays. This contrasts with an earlier report which suggested that Al³⁺ exchange of an extensively leached clay did not increase the yield from this isomerization process; however, only one clay (which was similar to STx-1) was considered therein.¹¹ Our studies have shown that the nature of the selected clay can have a significant influence on the observed activity. In general, the activity of the four clays studied decreased as Sap-Ca > STx-1 > SWy-2 > SAz-1 whether they are in the H⁺ or Al³⁺ form. The effect of added TMA⁺ cations is mixed insofar as they always reduce the activity of samples derived from SAz-1 yet were able to increase the activity of the H⁺/TMA⁺ forms of SWy-2 and STx-1. However, there is little doubt that the presence of TMA⁺ cations significantly influenced the activity of the Al³⁺/TMA⁺ clays, particularly those derived from SWy-2 and SAz-1, for the reasons suggested above.

The initial results from the H⁺/TMA⁺ clays^{25,26} led us to believe that the activity for the isomerization process relied on factors including (i) the balance between acidity and organophilicity and (ii) access to that acidity either in the galleries or via the catalyst's ability to disperse in α -pinene. The dispersion/access issue is important since it enhances access to the acid sites and appears to be related to the charge density on the clay. SAz-1 has the highest layer charge and was the poorest catalyst overall. The incorporation of TMA⁺ cations, which are very resistant to displacement by protons in SAz-1, reduced the activity, implying that the acid sites were less accessible and that access to the galleries is an important step in the mechanism.²⁶ Preliminary studies suggest that reducing the layer charge using the well-established Hofmann-Klemen⁴² effect results in an enhanced activity for SAz-1. Thus, while the layer charge and locus of substitution are obviously important issues in determining the activity of the catalysts, it does not explain why fully exchanged Al³⁺-exchanged clays of intermediate charge, which should present a polar, hydrophilic surface, are so active in the presence of nonpolar, organophilic substrates. One possible explanation lies in the thermal stability of the basal spacing in the different cation-exchanged forms.

Kullaj has reported that when α -pinene is heated with bentonite treated with 10% HCl the products are camphene and tricyclene,⁴⁴ which led De Stefanis et al.²⁷ to suggest that the absence of tricyclene in the products derived from USY and PILCs indicated that the reactions were taking place within the pore network. Tricyclene was not identified in the mixture of

products derived from the Al^{3+} or $\text{Al}^{3+}/\text{TMA}^+$, which implies that the reaction takes place in the clay galleries. Indeed the catalytic activity is markedly reduced when the interlayer is made inaccessible due to the presence of large quantities of large organo- and polycations.^{25,30} The TMA^+ -expanded clays have a basal spacing of 13.6 Å that was stable to at least 250 °C which was much higher than the catalyst activation temperature of 120 °C. In contrast, the H^+ -exchanged clays are likely to be largely collapsed after activation at 120 °C. Thus, it appears that the 25–30% CEC of TMA^+ on the exchange sites in the most active H^+/TMA^+ catalysts serve to prop some of the galleries apart and facilitate ingress of α -pinene, thus contributing to the accessibility of the acid sites. Too many TMA^+ cations limit the number of acid sites, and fewer than 25–30% CEC result in too few expanded layers for α -pinene to gain access. Tennakoon et al.⁵ have shown that Al^{3+} -exchanged clays can remain expanded at 15.0 Å at temperatures near 120 °C, although this stability depends on the clay to some extent. Indeed, fully Al^{3+} -exchanged STx-1 maintained a spacing of 12.5 Å from 100 to 300 °C, whereas Ca^{2+} -exchanged STx-1 collapsed to 10.0 Å at 150 °C, which means that the clay gallery is no longer available. Partially Al^{3+} -exchanged STx-1 collapsed at temperatures between 150 and 300 °C, depending upon the level of Al^{3+} exchange. Therefore, a similar situation occurs with Al^{3+} -exchanged clays because the enhanced thermal stability of their gallery spacing also allows facile access of the α -pinene to the active sites. It is generally considered that clays containing a binary mixture of exchange ions result in segregation of the different ions in different galleries,⁴⁵ although careful control of the preparation conditions can result in mixed ion homostructures.⁴⁶ However, it is often difficult to prove that this segregation occurs using X-ray diffraction unless there are significant differences in the magnitude of the gallery expansion for the two different ionic forms. XRD studies on the mixed $\text{Al}^{3+}/\text{TMA}^+$ -exchanged clays used herein indicated that the observed d spacing was controlled by the TMA^+ cations at all but the highest Al^{3+} loadings and was constant at 13.4 ± 0.2 Å, although the 001 peak became broader and decreased in intensity as the Al^{3+} content increased. Unfortunately, recourse to variable temperature XRD did not distinguish between TMA^+ -expanded and Al^{3+} -expanded layers which may imply that if segregation has occurred that the layers are randomly interstratified.⁴⁵ Therefore, the access of α -pinene to the galleries in the Al^{3+} - and $\text{Al}^{3+}/\text{TMA}^+$ clays where the reaction took place was not adversely affected since the layers were sufficiently separated, although at low Al^{3+} loadings many fewer protons were produced, thus limiting the isomerization activity.

Conclusions

Mild activation using Al^{3+} - and $\text{Al}^{3+}/\text{TMA}^+$ treatment of STx-1, SAZ-1, SWy-2 and Sap-Ca produced materials in which the structure of the layer was unaffected. The acid centers produced were able to accelerate the isomerization of α -pinene to produce camphene, limonene, and other products in 60–90% yield. These conversions are comparable to those observed with zeolites or super active $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts. However, the incorporation of TMA^+ cations reduced the activity of the catalysts which contrasts with the behavior of some of their H^+/TMA^+ -exchanged counterparts. The low catalytic activity in samples derived from SAZ-1 has been attributed to its inability to accommodate the reagent because of its high layer charge. The Al^{3+} -exchanged clays were effective in this hydrophobic test reaction because of their ability to remain expanded at spacings of ≥ 12.5 Å at the activation temperature utilized. Thus,

the hydrated $(\text{Al}(\text{H}_2\text{O})_n)^{3+}$ “props” facilitated the access of α -pinene to the acid sites within the clay gallery.

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