

## ADSORPTION OF OLEFINS ON ALUMINUM- AND ALUMINUM/TETRAMETHYL-AMMONIUM-EXCHANGED BENTONITES

ALEXANDER MORONTA\*<sup>†</sup>, SCOTT TAYLOR AND CHRISTOPHER BREEN

Materials Research Institute, Sheffield Hallam University, Sheffield S1 1WB, UK

**Abstract**—One montmorillonite, STx-1 (Texas, USA), was activated with different amounts of Al and tetramethylammonium (TMA<sup>+</sup>) cations to obtain materials with a combined Al<sup>3+</sup> and TMA<sup>+</sup> content equal to its cation exchange capacity. The adsorption capacity of these samples was studied saturating them with hept-1-ene at room temperature. The samples were heated and the evolved gases analyzed by Fourier transform infrared spectroscopy and gas chromatography-mass spectrometry. Hept-1-ene reacted with the clays via proton transfer and resulted in the formation of a variety of reaction products (>60 hydrocarbons). In general, the presence of TMA<sup>+</sup> cations significantly reduced the population of protons to selectively produce isomerization and hydration products.

**Key Words**—Adsorption, Aluminum, Clays, Olefins, Organoclays.

### INTRODUCTION

M<sup>3+</sup>-exchanged montmorillonites can catalyze the addition of alkenes to give products of isomerization, oligomerization, condensation, etherification and hydration. These reactions work best if the acidity of the clay is increased by equilibrium at low relative humidity. M<sup>2+</sup>-exchanged montmorillonites show some reactivity while M<sup>+</sup>-exchanged clays, except for NH<sub>4</sub><sup>+</sup>-exchanged clays, are essentially unreactive (Adams *et al.*, 1979, 1984), therefore confirming that the Brønsted acidity of the clay is mainly due to dissociation of water molecules in the hydration sphere of exchangeable interlayer cations (Mortland and Raman, 1968).

Adams *et al.* (1979, 1984), found that when refluxing hex-1-ene, hept-1-ene or oct-1-ene in a range of cation-exchanged montmorillonites, the alkenes are converted to the corresponding bis-sec-alkylether in the temperature range 44 to 72°C. However, with an increase in temperature (100–120°C) the reaction gave a much more complex mixture, consisting of >40 products. Similar observations were also reported by Thomas (1982).

The nature of the adsorbed species derived from unsaturated hydrocarbons, adsorbed from the gas phase on clays or zeolites at room temperature is thus far unclear and remains a subject for discussion. It is natural to suggest that the reaction of a small olefin in the presence of an acidic catalyst should give rise to long-chain hydrocarbons. In this regard, Vogel *et al.* (1990), studied the adsorption/reaction of iso-butene on pure and metal-substituted synthetic mica-montmorillonite (SMM) using TG analysis. The adsorption reaction was

carried out isothermally at 30°C for 1 h and then the sample heated at 3°C min<sup>-1</sup> to 500°C. They noted that the conversion of the olefin over Ni-SMM was too low to analyze the gases evolved during the heating process. However, experiments in a micro-reactor showed that at 60–70°C the primary liquid product of iso-butene oligomerizations was a C<sub>12</sub> oligomer (66%) as well as ethane, propene, propane, isomers of butene and butane, hexene and hexane in the gas phase. They concluded that the incorporation of Ni<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> into the SMM increased the catalytic activity while the presence of water in the olefinic feed reduced it.

Choren *et al.* (1997a,b), reported the adsorption of propylene, but-1-ene and *cis*-but-2-ene over clays, alumina and a porous and non-porous silica at room temperature. They stated that the alumina and silica adsorb olefins and paraffins reversibly and are unable to condense olefins. Similar observations were found for paraffins adsorbed on clays, yet olefins were strongly bonded to the clay surface and were not desorbed under vacuum conditions. Infrared (IR) spectroscopy showed that the condensation products had a paraffinic oligomeric spectrum, because of the absence of the characteristic signal from the olefinic >C=C< moiety in IR spectra. However, the disappearance of the double bond could give rise to the formation of an alcohol. The lack of the signals from olefinic double bonds in adsorbed oligomers was explained in terms of the presence of carbonium ions being formed on the clay surface as a consequence of the polarized water. Nevertheless, they were not able to identify the products formed over the catalysts utilized.

Another interesting example of this problem appears during the adsorption of ethylene on zeolites at room temperature. Stepanov *et al.* (1998) showed that ethylene oligomers, in the form of carboxylic acids, strongly retained by the zeolite framework, give a mixture of at least 50 different oligomers with the length of the

\* E-mail address of corresponding author: amoronta@luz.ve

<sup>†</sup> Current address: Centro de Superficies y Catalisis, Facultad de Ingeniería, Universidad del Zulia, P.O. Box 15251, Maracaibo 4003A, Venezuela

hydrocarbons skeleton ranged from C<sub>5</sub> to C<sub>14</sub> and even higher (C<sub>14+</sub>) carbon atoms in a molecule.

In this paper, thermogravimetric (TG) analysis is combined with Fourier transform infrared spectroscopy (real time TG-FTIR) and with a gas trap module (OTM) connected to a gas chromatography-mass spectrometer (TG-OTM-GC-MS) to obtain additional information on the products desorbed during the adsorption/desorption of hept-1-ene over Al-activated clays (AIACs) and Al-activated organoclays (AIAOCs) at room temperature.

## MATERIALS AND METHODS

One source clay was selected: STx-1 (dioctahedral Ca-montmorillonite of low Fe content), from Texas, USA, obtained from The Clay Mineral Repository of The Clay Minerals Society and used without further purification.

The AIAOCs were prepared by adding 1 g of STx-1 to a solution containing 29 cm<sup>3</sup> of deionized water and selected volumes of 1 M tetramethylammonium chloride (TMACl, Aldrich, 97%) solution and 0.1 M Al<sup>3+</sup> (AlCl<sub>3</sub>·6H<sub>2</sub>O, Aldrich, 99%) in different ratios to prepare samples in which the Al<sup>3+</sup>/TMA<sup>+</sup> ratio was varied systematically without exceeding the cation exchange capacity (CEC) of the chosen clay (0.84 meq g<sup>-1</sup>). The exchange procedure was carried out once. The AIACs 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. The centrifugates were washed and centrifuged repeatedly with de-ionized water to remove excess exchanging salt. The clay samples were dried at 120°C overnight, and ground to <0.2 mm prior to storage. The Al<sup>3+</sup> or Al<sup>3+</sup>/TMA<sup>+</sup> treatment is identified in the sample name. Thus, ST-A1100 indicates that STx-1 was treated with 100% of its CEC with Al<sup>3+</sup>, and ST-A150/TMA50 means that STx-1 was treated with 50% Al<sup>3+</sup> and 50% TMA<sup>+</sup>.

X-ray diffraction (XRD) and variable temperature X-ray diffraction (VT-XRD) patterns were recorded using CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) on a Philips PW1130 diffractometer operating at 30 kV and 30 mA at a scan rate of 2°2 $\theta$  min<sup>-1</sup> utilizing a simple heating stage for VT-XRD (Brown *et al.*, 1972). All samples were run as oriented films on glass slides. Samples were heated at 100, 150, 200 and 300°C, holding them at those temperatures for 20 min prior to recording the VT-XRD trace.

Thermogravimetric analysis (TGA) was utilized to study the desorption of hept-1-ene. The TGA was carried out in a Mettler TG 50 thermobalance equipped with a TC10A processor. 8–15 mg of samples were weighed into a ceramic crucible and subjected to a heating program from 35–800°C at 20°C min<sup>-1</sup> under a 20 cm<sup>3</sup> min<sup>-1</sup> nitrogen carrier gas. In general, samples were conditioned in the nitrogen flow for 15 min until a stable weight was registered.

The AIACs and AIAOCs derived from STx-1 clay were exposed to hept-1-ene vapor (Aldrich, 99+%) at room temperature for periods in excess of 48 h using a gas jar saturator. The desorption profiles were monitored using TG and the identification of the products formed at room temperature was carried out using TG-OTM-GC-MS (Synergic Chemical Analysis).

The thermal desorption of the olefin from Al<sup>3+</sup> and Al<sup>3+</sup>/TMA<sup>+</sup> samples was carried out using a thermobalance (TG131, Cahn) connected through a heated transfer line to an infrared gas cell (10 cm path length) contained in a FTIR spectrometer (Infinity Series, Mattson). Usually, 20–40 mg of samples were placed in the TG sample crucible and then heated from 25°C to 900°C at 20°C min<sup>-1</sup> in a dry nitrogen purge gas at atmospheric pressure (60 cm<sup>3</sup> min<sup>-1</sup>).

The TG-FTIR system is connected through another transfer line to an adsorbent trap (VOCARB 4000, Supelco) contained in an organic trap module (OTM, Cahn). The outlet from the OTM is also coupled to a gas chromatograph-mass spectrometer (Automass System 2, Unicam). Upon completion of the TG run, the species contained in the trap were thermally desorbed (at 250°C for 4 min) onto the GC capillary column (DB-1, 30 m × 0.25 mm id) where the compound mixture was separated before identification by MS. The transfer lines were maintained at 250°C throughout the analysis. In an ordinary experiment the capillary column was held at 35°C for 4 min before increasing the temperature at 5°C min<sup>-1</sup> to 250°C. The final temperature was held for 5 min. To ensure cleanliness of the trap, it was baked for 3 h at 300°C before starting the subsequent analysis (Breen and Last, 1999).

## RESULTS AND DISCUSSION

The VT-XRD patterns of selected AIACs and AIAOCs exposed to hept-1-ene vapor are listed in Table 1. The traces for STx-1 exchanged with different

Table 1. Basal spacings ( $\text{\AA}$ ) for the adsorption of hept-1-ene on selected AIACs and AIAOCs.

	$d_{001}$ RT	$d_{001}$ 100°C	$d_{001}$ 150°C	$d_{001}$ 200°C	$d_{001}$ 300°C
ST-A120	14.3	13.8	13.5	11.6	10.2
ST-A1100	14.5	14.0	13.5	12.8	12.6
ST-A110/TMA90	14.2	14.1	14.0	14.0	13.8
ST-A190/TMA10	14.1	13.6	13.6	13.5	12.8

Al contents (20% and 100% CEC) show that heating at 200–300°C causes a sudden reduction of the expanded layers to 10.2 Å, especially for ST-Al20. Certainly, the high calcium content (80% CEC) has a considerable influence on this particular sample. In the ST-Al100 sample, a  $d$ -value of  $12.6 \pm 0.2$  Å dominated, indicating that the layers are still expanded even at 300°C in the presence of hept-1-ene. This result further supports the previous findings for AlACs (Breen and Moronta, 2000), in which the catalytic activity for the isomerization of  $\alpha$ -pinene was attributed to the expanded layers of AlACs that allowed the penetration of the reactant molecule to the interlamellar space, increasing the conversion.

The adsorption of hept-1-ene was carried out at room temperature on samples dried at 120°C overnight, where a  $d$ -value of 14.0 Å was observed for AlACs. In fact, the reactant molecules find favorable conditions to access the interlamellar space and reach the acid centers.

The effect of the heating process upon AlAOCs is different to that of AlACs. At high TMA<sup>+</sup> content, the  $d_{001}$  is governed completely by the presence of the organocation and no significant changes in basal spacing are noticed. The TMA<sup>+</sup> cations are resistant to thermal decomposition and hold the layers permanently apart even when the sample is dehydrated (Barrer and Macleod, 1955). At low TMA<sup>+</sup> loading (10% CEC), the basal spacing at room temperature is similar to that obtained at high loadings. Nevertheless, heat treatment causes a slight diminution in the  $d_{001}$  value that remains essentially unchanged at further temperature increments

(100–200°C). Again the high Al content controls the expansion process, still at 300°C. Comparing ST-Al90/TMA10 with the ST-Al100 counterpart, it is clearly observed that the  $d_{001}$  of the former are slightly higher than the latter in the temperature range 150–300°C. This observation indicates that even small TMA<sup>+</sup> loadings have a significant influence on maintaining the layers expanded.

Figure 1a shows the desorption profiles for AlACs. The derivative thermograms exhibit four desorption peaks with maxima at 90, 140, 235 and 620°C. The peaks at 90 and 620°C correspond to the desorption of physisorbed water combined with desorption of the physisorbed alkene and lattice dehydroxylation together with CO<sub>2</sub> evolution (Breen *et al.*, 1987; Breen and Moronta, 1999). The peak at 140°C is attributed to the desorption of hept-1-ene on Ca cations that were not displaced by Al<sup>3+</sup> ions. This peak is very intense in ST-Al20, which still contained ~80% CEC Ca<sup>2+</sup>. However, as the Al content increased, the peaks decreased in intensity and is very weak at Al<sup>3+</sup> >60%. Additionally, the region between 80–120°C is significantly changed as the exchangeable Ca is displaced by Al, the shape of the peak in this region is controlled by the desorption of the physisorbed water and hept-1-ene (90°C) that becomes sharper and was shifted to lower temperatures as the amount of Al<sup>3+</sup> increased. The maximum at 235°C corresponds to the desorption/decomposition of hept-1-ene and it is increased with Al content. These data indicate that sites with sufficient acid strength to interact

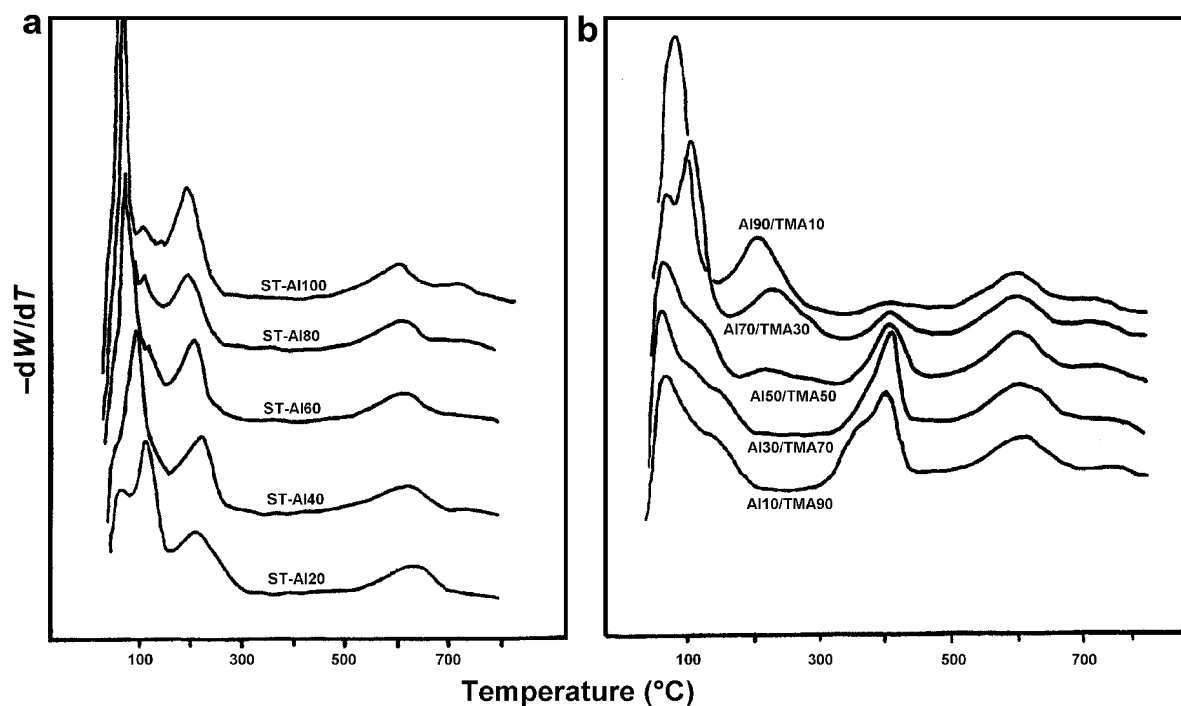


Figure 1. Desorption thermograms of hept-1-ene from (a) AlACs and (b) AlAOCs.

with hept-1-ene are present in the AIACs. Nonetheless, the assignments already given for the species being desorbed from the clay are, at this stage, only realistic assumptions that will be correlated against the TG-FTIR and TG-OTM-GC-MS data.

The derivative thermograms for the desorption of hept-1-ene from AIAOCs (Figure 1b) show the maxima described above together with that arising from the desorption/decomposition of TMA<sup>+</sup> at 410°C (Breen and Moronta, 2000). This peak is reduced in intensity as the Al:TMA ratio increased. The desorption peak attributed to the desorption of hept-1-ene from Brønsted acid sites at 235°C is not visible in samples prepared with high TMA<sup>+</sup> content. This peak starts to occur at Al<sup>3+</sup> >70%. It is worth noticing that a broad and prolonged peak, extending from 100–200°C, is observed in samples with low Al:TMA ratio, which changed as the ratio increased. The most plausible explanation is perhaps that, in samples with low Al:TMA ratio, hept-1-ene is desorbed unaltered from the interlamellar space where the reactant molecules do not find sufficient acid sites, due to displacement by TMA<sup>+</sup> cations, able to cause protonation and further transformation of hept-1-ene. However, as the Al:TMA ratio increased, a significant fraction of molecules effectively interact with protons arising from the polarization of water molecules in the interlamellar region. These protonic centers are sufficient acids to cause protonation of the double bond. Therefore, the maximum at 235°C increased significantly in intensity.

Figure 2 shows the 3D-IR spectra for the desorption of hept-1-ene from ST-Al100 as a function of time. During the first 10 min (isothermal at 22°C), only the bands associated with the olefin can be identified reliably in this spectrum. Intense bands at 2937 and 2879 cm<sup>-1</sup> belong to the asymmetric C–H and symmetric C–H stretch in the –CH<sub>2</sub>– groups. Another vibration band at 2953 cm<sup>-1</sup> is seen as a left shoulder to the band at 2937 cm<sup>-1</sup> arising from asymmetric C–H stretch of the CH<sub>3</sub> group of the olefin. Additionally the =CH stretching band, which occurs at 3090 cm<sup>-1</sup> is clearly noticed. Two bands at 1469 and 1649 cm<sup>-1</sup> belong to the deformation vibration

of the –CH<sub>2</sub>– and the olefin double bond vibrations. Two other bands at 999 cm<sup>-1</sup> and 912 cm<sup>-1</sup> are clear in the spectrum and correspond to the olefinic C–H out-of-plane deformation. As the temperature is increased, the spectra change considerably. At 20 min (93°C) the =CH stretching band at 3090 cm<sup>-1</sup> decreased in intensity as well as that at 1649 cm<sup>-1</sup>.

The two bands at 3090 and 1649 cm<sup>-1</sup> disappear completely with a further temperature increment (28 min, at 225°C where the maximum desorption/decomposition of hept-1-ene occurs) and the spectrum is dominated by the presence of bands at 2960, 2937 and 2879 cm<sup>-1</sup> from asymmetric and symmetric vibration of CH<sub>2</sub> and CH<sub>3</sub> groups. This evidence indicates the paraffinic nature of oligomeric species being desorbed or perhaps hydration products of 1-heptene.

The C–O stretching band in the IR spectrum occurs in the frequency range 1050–1300 cm<sup>-1</sup> while the O–H appears at 3590–3650 cm<sup>-1</sup>, but the assignment of these bands to an alcohol is uncertain because the intensity of these bands is, in general, very weak. Additionally, this behavior is further evidenced by the disappearance of the bands at 999 and 912 cm<sup>-1</sup> and the appearance of two bands at 1458 and 1383 cm<sup>-1</sup> that are assigned to the deformation vibration of the –CH<sub>2</sub>– and CH<sub>3</sub>– groups in oligomeric products. Carbon dioxide bands at 2362 and 2316 cm<sup>-1</sup> appear in the whole spectra of ST-Al100 at very low intensity.

Figure 3 shows the contribution of the gases evolved to the total IR chromatogram. Four peaks are clearly seen in the reconstructed chromatogram at 3, 22, 26 and 28 min (21, 93, 140 and 230°C). The evolution temperatures of all these peaks are exactly the same as those observed before (Figure 1a). At 21°C there is only the contribution of the hept-1-ene as described in the paragraph above. At 93°C there are contributions of unsaturated hydrocarbons along with water, alcohol, aliphatic hydrocarbons, and a small amount of CO<sub>2</sub>. The peaks at 140 and 230°C only represent the contribution of aliphatic and small amounts of unsaturated hydrocarbons.

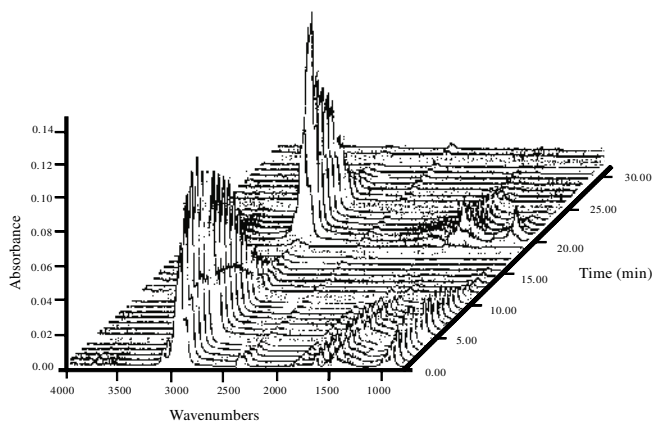


Figure 2. 3D-FTIR spectra for the desorption of hept-1-ene from ST-Al100.

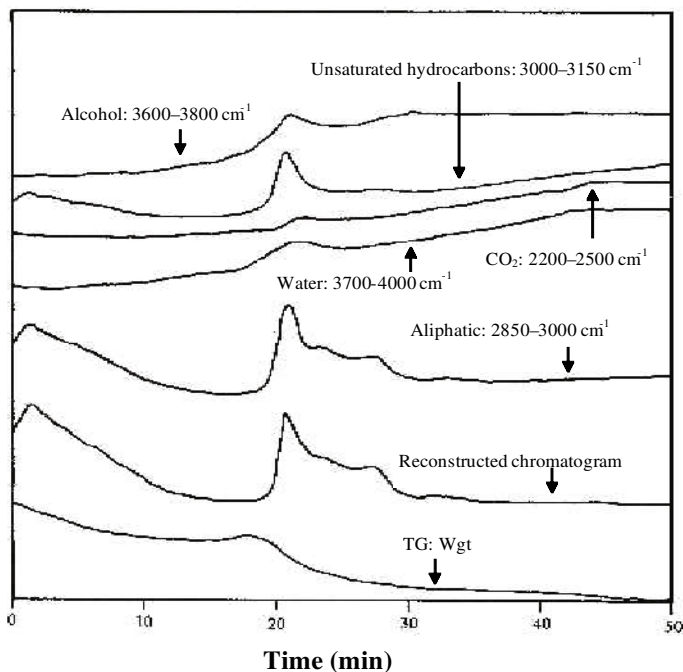


Figure 3. FTIR chromatogram for the desorption of hept-1-ene from ST-Al100.

The data presented demonstrate that the AIAOCs possess acid centers of sufficient strength to cause the protonation of the olefin. Certainly, Trombetta *et al.* (1997) found only reversible adsorption (at room temperature) of the *n*-butene on/from the surface hydroxyl of alumina, as on silica and or the HZSM5 zeolite. They stated that the isomerization of olefins at room temperature was favored by the formation of allyl species, whereas at high temperature H-bonded olefins were assumed to be the precursor for carbonium ions that produce the isomerization. Taking into consideration their conclusions, it is possible to predict both isomerization and oligomeric products during the reaction process.

Figure 4a illustrates the total ion chromatogram (TIC) vs. time curve obtained after ST-Al100 saturated with hept-1-ene was heated up to 500°C and a similar product distribution was observed for the other AIAOCs. As can be seen, the GC-MS chromatograms of the desorbed compounds consist of a complex mixture of >60 peaks. The data obtained are in line with the results reported by Stepanov *et al.* (1998) who extracted the products formed during the adsorption of ethylene on acidic zeolite HZSM5 at room temperature and found a similar product distribution.

The individual compounds resulting from the desorption of hept-1-ene were identified, using a computer-matching search, from their fragmentation patterns and parent ions. It was found that the product gases were a mixture of 1,1-dimethyl-1-butene, hept-2-ene, 2,3-dimethyl-1-pentanol, hept-3-ene, heptan-1-ol and hept-

tan-2-ol that appeared next to the hept-1-ene peak, all at short retention times, but not well separated. At retention times >7 min linear and branched *n*-alkanes, ranging from C<sub>8</sub> to C<sub>16</sub>, were found. Some aromatic compounds were also found in the reaction mixture and they might have resulted from a dehydrocyclization reaction.

The presence of TMA<sup>+</sup> in AIAOCs exerted a remarkable influence on the total ion chromatogram. Figure 4b shows the distribution products during the desorption of hept-1-ene from ST-Al170/TMA30. At short retention times (<7 min), the shape and position of the peaks for ST-Al170/TMA30 are similar to those for ST-Al100. In this region the peaks correspond mainly to the desorption of the isomerized alkenes and hydration products. However, the series of peaks attributed to the evolution of *n*-alkanes and the aromatic compounds, which appear at higher retention times (8–25 min), are not visible. A reasonable explanation for these experimental facts in accord with previous results (Breen and Moronta, 2000), may be that hept-1-ene finds insufficient acid sites to interact in the interlamellae due to the high population of the TMA<sup>+</sup> cation, which effectively displaces protons during the exchange treatment, or that TMA<sup>+</sup> cations break the intermolecular contact between the reactant molecules, preventing their isomerization. Whatever the reason, hept-1-ene may selectively take the protons available in AIAOCs (prepared with intermediate TMA<sup>+</sup> loadings) to produce only isomerization and hydration products and desorption of unaltered hept-1-ene.

We propose that the mechanisms involved in the formation of the reaction mixture could be:

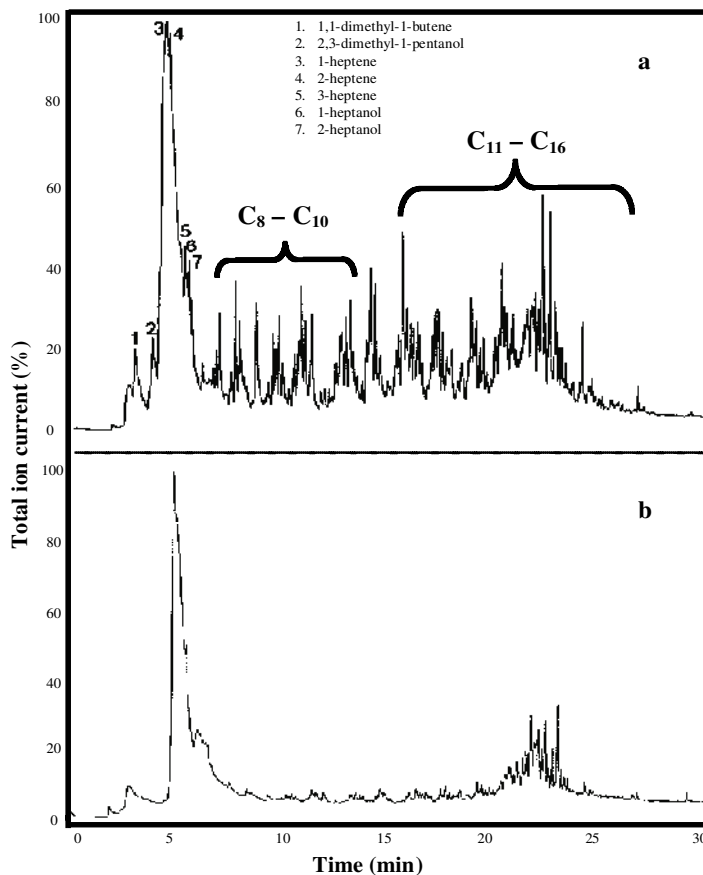


Figure 4. GC-MS chromatograms of the products evolved during the thermal desorption of hept-1-ene from (a) ST-A1100 and (b) ST-A170/TMA30.

(1) Isomerization of hept-1-ene arising from the formation of more stable species, in this case a secondary carbonium ion is produced upon protonation of the double bond. (2) Formation of alcohols catalyzed by protons and the participation of water molecules (Ballantine *et al.*, 1981). However, the formation of the dialkyl ether was not observed in the reaction products. (3) Interaction of acid sites in the galleries with hept-1-ene results in the formation of carbonium ions that can react in the interlayer region with hydrocarbons to give the corresponding formation of oligomeric species, strongly retained inside the clay framework.

The different adsorbed species that may exist in AIACs are in the form of three interconverting species: alkoxides, carbonium ion and olefin. Stephanov *et al.* (1998), stated that the alkoxy species were the main adsorption state in zeolites saturated with ethylene at room temperature. In this system, it is believed that the carbonium ion might be the major adsorption state due to the considerable number of acid sites arising from the high polarization power of Al ions (especially in those samples where the Al content was high).

## CONCLUSIONS

The results outlined in this paper have further corroborated and proved the conclusions reported elsewhere (Breen and Moronta, 2000), in which the remarkable activity shown by AIACs towards the isomerization of  $\alpha$ -pinene was attributed to the ability of Al to keep the layers permanently apart allowing ingress to the incoming molecules. Additionally, it has confirmed the supposition that TMA<sup>+</sup>, at high loadings, reduces the population of acid sites creating unfavorable conditions for the catalytic transformation of  $\alpha$ -pinene as well as hept-1-ene.

## ACKNOWLEDGMENTS

One of the authors (A.M.) gratefully acknowledges maintenance grants from Consejo Nacional de Investigaciones Científicas y Tecnológicas de Venezuela (CONICIT) and La Universidad del Zulia (Venezuela). Thanks to Victor Ferrer for improving the figures.

## REFERENCES

- Adams, J.M., Ballantine, J.A., Graham, S.H., Laub, R.J., Purnell, J.H., Reid, P.I., Shaman, W.Y.M. and Thomas, J.M.



- (1979) Selective chemical conversion using sheet silicate intercalates: low-temperature addition of water to 1-alkenes. *Journal of Catalysis*, **58**, 238–252.
- Adams, J.M., Clapp, T.V., Clement, D.E. and Reid, P.I. (1984) Reactions of alk-1-enes over ion-exchanged montmorillonites. *Journal of Molecular Catalysis*, **27**, 179–194.
- Ballantine, J.A., Davies, M., Purnell, H., Rayanakorn, M. and Thomas, J.M. (1981) Chemical conversions using sheet silicates: novel intermolecular dehydration of alcohols to ether and polymers. *Journal of Chemical Society, Chemical Communications*, 427–428.
- Barrer, R.M. and Macleod, D.M. (1955) Activation of montmorillonite by ion exchange and sorption complexes of tetra-alkylammonium montmorillonite. *Transactions of the Faraday Society*, **51**, 1290–1300.
- Breen, C. and Last, P.M. (1999) Catalytic transformation of the gases evolved during the thermal decomposition of HDPE using acid-activated and pillared clays. *Journal of Materials Chemistry*, **9**, 813–818.
- Breen, C. and Moronta, A. (1999) Influence of layer charge on the catalytic activity of mildly acid-activated tetramethylammonium-exchanged bentonites. *Journal of Physical Chemistry B*, **103**, 5675–5680.
- Breen, C. and Moronta, A. (2000) Characterization and catalytic activity of aluminum- and aluminum/tetramethylammonium-exchanged bentonites. *Journal of Physical Chemistry B*, **104**, 2702–2708.
- Breen, C., Deane, A.T. and Flynn, J.J. (1987) The acidity of trivalent cation-exchanged montmorillonite. Temperature-programmed desorption and infrared studies of pyridine and n-butylamine. *Clay Minerals*, **22**, 169–178.
- Brown, G., Edwards, B., Ormerod, E.C. and Weir, A.H. (1972) A simple diffractometer heating stage. *Clay Minerals*, **9**, 407–414.
- Choren, E., Moronta, A., Varela, G., Arteaga, A. and Sánchez, J. (1997a) Condensation of olefins on clays. Gas-solid systems. Part I. Gravimetric Methods. *Clays and Clay Minerals*, **45**, 213–220.
- Choren, E., Moronta, A., Arteaga, A. and Sánchez, J. (1997b) Condensation of olefins on clays. Gas-solid systems. Part II. Spectroscopic Methods. *Clays and Clay Minerals*, **45**, 221–225.
- Mortland, M.M. and Raman, K.V. (1968) Surface acidity of smectites in relation to hydration, exchangeable cation and structure. *Clays and Clay Minerals*, **16**, 393–398.
- Stepanov, A., Luzgin, M.V., Romannikov, V.N., Sidelnikov, V.N. and Paukshtis, E.A. (1998) The nature, structure, and composition of adsorbed hydrocarbon products of ambient temperature oligomerization of ethylene on acid zeolite H-ZSM-5. *Journal of Catalysis*, **178**, 466–477.
- Thomas, J.M. (1982) Sheet silicate intercalates. New agents for unusual chemical conversions. Pp. 56–99 in: *Intercalation Chemistry* (M.S Whittingham and A.J. Jacobson, editors). Academic Press, New York.
- Trombetta, M., Busca, G., Rossini, S.A., Piccoli, V. and Cornaro, U. (1997) FTIR studies on light olefin skeletal isomerisation catalysis I. The interaction of C<sub>4</sub> olefins and alcohols with pure  $\gamma$ -alumina. *Journal of Catalysis*, **168**, 334–348.
- Vogel, A.P., O'Connor, C.T. and Kojima, M. (1990) Thermogravimetric analysis of the iso-butene oligomerization activity of various forms of synthetic mica-montmorillonite. *Clay Minerals*, **25**, 355–362.

(Received 25 May 2001; revised 11 October 2001; Ms. 547)