# Influence of Preparation Variables on the Structural, Textural, and Catalytic Properties of Al-Pillared Smectites

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Al-pillared montmorillonites and saponites have been prepared with different pillaring solutions and their properties compared with those of similar materials obtained following a standard procedure. Characterization of the pillared clays includes X-ray diffractometry, determination of the residual cation exchange capacity, acidity measurements (ammonia), and textural properties from nitrogen adsorption−desorption isotherms. The catalytic properties of Pt-impregnated samples have been evaluated in the hydroconversion of heptane. It is shown that the textural, structural, and surface properties of the pillared clays may be influenced to some extent by the preparation method and also by the crystallinity (stacking order) of the starting clay. The catalytic performances, however, are principally dependent on the type of clay: pillared clays issued from smectites with structural tetrahedral lattice substitutions (saponites) are significantly more active than equivalent materials produced from clays with structural octahedral substitutions (montmorillonites). The preparation method and, in particular, the nature of the pillaring solution only have a secondary effect. The catalytic results are discussed in terms of nature, content, and strength of the acid sites.

## Introduction

In recent years, modified methods for the preparation of Al-pillared clays have been described in the literature. For instance, Michot and Pinnavaia[1] obtained well-pillared clays using Al-hydroxy solutions containing a nonionic surfactant. With respect to usual procedures involving partially titrated Al solutions[2] or Al-chlorhydrol,[3] several beneficial effects due to the presence of surfactant were noticed: improved pillar distribution and stacking of the layers in the *c* direction, increased hydrolytic stability of the pillars, and enhanced uniformity of the microporosity.

In another approach followed by Schoonheydt et al.,[4] pillaring was achieved with solutions containing $Al_{13}$ Keggin ions at the exclusion of other Al species, obtained through precipitation−redissolution steps.

Other pillaring procedures have also been described, such as contacting the clay with a solution of an alkali metal carboxylate before pillaring,[5] pillaring in the presence of poly(vinyl alcohol),[6,7] or treating the clay with a silanating agent.[8,9] Recently, Mokaya and Jones[10,11] reported that clays submitted to an acid activation prior to their pillaring exhibited enhanced acid properties and catalytic activities in comparison with unactivated pillared clays.

All these methods generally provided pillared materials with appropriate textural and structural characteristics such as heat resistant 18 Å spacings, high surface areas, and microporosities. However, the information on a possible influence of the starting pillaring solution on the acid and catalytic properties of Al-pillared clays is still fragmentary. Pinnavaia et al.[12] showed that montmorillonites pillared with base-hydrolyzed $AlCl_3$ or Al-chlorhydrol solutions had comparable initial activity in the cracking of *β*-isopropylnaphthalene, but deactivation with time was more pronounced over the former one. Thus, this type of information may be of some usefulness, for instance, in attempts to optimize the catalytic properties or when a choice of a preparation procedure has to be done for scaling-up purposes.

In this study, saponites and montmorillonites have been pillared with base-hydrolyzed Al solutions (with and without use of a nonionic surfactant), Al-chlorhydrol, and $Al_{13}$ solutions. The structural, textural, and acid properties of the pillared clays were investigated, and the catalytic properties of platinum-impregnated samples have been compared in the hydroisomerization−hydrocracking reaction of heptane.

## Experimental Section

**Materials.** Al-pillaring experiments have been performed using two types of swelling clays from different origins: two montmorillonites from Chile and Spain, respectively, Minclay (W-140P) supplied by Deltamat Paquet, Belgium, and Serrata Blanca (SB), and three saponites: Ballarat saponite (SAPCA) provided by Source Clay Minerals Repository, University of Missouri, Columbia; Vicalvaro saponite (SC-27) and Esmectita de Yunclillos (EY), both from Spanish deposits. Samples SB, SC-27, and EY were obtained from Tolsa S.A., Madrid. The different clays will be referred hereafter as M1 and M2 for, respectively, the Chilian and Spanish montmorillonites and S1, S2, and S3 for, respectively, the Ballarat, Vicalvaro, and Yunclillos saponites.

The two montmorillonites were exempt from detectable amounts of other X-ray crystalline phase(s), while the Spanish saponites contained sepiolite as major contaminant (about 10% in sample S3 and 10−20% in S2). The X-ray diffraction patterns of S2 and, to a lesser extent, S3 saponites showed poor stacking order as compared with the other clays. S2 saponite has been recently characterized by Casal et al.,[13] whereas Ballarat saponite (S1), a well-ordered swelling clay, has been described by Post.[14]

Generally, pillaring was achieved using the $<2\mu$ fractions collected by usual sedimentation methods; occasionally, pillaring was done with the raw clays.

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

**Pillaring Procedures.** The first pillaring method is similar to the one described by Lahav et al.[2] and used in previous work.[15] It consisted of adding to the clay suspension (usually 2 wt %) the required volume of pillaring solution to supply 20 mequiv of Al/g of clay. The pillaring solution was prepared by dropwise addition of 0.5 M NaOH solution to 0.2 M Al-$(NO_3)_3$ solution, using the volume of base necessary to achieve an OH/Al molar ratio of 1.6 (2.4 when specified). The final suspension (clay suspension and pillaring solution) was aged at room temperature for 24 h. Continuous stirring was maintained during the preparation steps. At the end of the aging period, the excess salt was eliminated, as in earlier work,[15-17] by dialysis, the washing water being regularly renewed until the conductivity was reduced to its initial value. The pillared material was freeze-dried. This method will be referred in the following as standard procedure, and the pillared samples are symbolized by the type of clay followed by (S).

The second method, reported by Michot and Pinnavaia,[1] consisted of adding the pillaring solution (prepared as in the first method, but with OH/Al = 2.4) to a solution of 600 mg of tergitol, $[C_{12-14}H_{25-29}O(CH_2CH_2O)_5H]$, dissolved in 500 mL of deionized water. It was controlled so that the pH of the final solution (4.47) was, indeed, unchanged by the presence of the surfactant. This solution was added dropwise and under vigorous stirring to 2 wt % clay suspensions, and the final suspensions were aged overnight. The amount of Al supplied per gram of clay was 20 mequiv (occasionally 35 mequiv). The products were washed by dialysis. As in the method described by the authors, the clay suspension (0.6 wt %) was added dropwise to the pillaring solution; a sample of M2 was pillared following this sequence of addition. One part of the pillared material was washed by dialysis (sample M2(T)/d), and a second one by filtration (sample M2(T)/f). In order to detect a possible dilution effect on the pillaring process, a sample was prepared with an identical total volume of pillaring solution but free of surfactant (sample M2(ST)).

In a third method, use was made of Al-chlorhydrol as the pillaring solution. Indeed, pillaring has been successfully achieved with this source of hydroxy−aluminium species (it has a high content of $Al_{13}^{7+}$) in the pioneering work of Lussier and Vaughan.[3] The pillaring solutions were prepared by diluting commercial chlorhydrol solution (from Reheis Chem. Co.) to 0.1 M and aging at 60 °C for 2 h. A sufficient volume of this solution (with OH/Al = 2.4) was slowly added to the clay suspensions (2 wt %) in order to provide 20 mequiv/g clay. The final suspensions were stirred for 2 h either at room temperature or at 60 °C in the case of M1 and at 80 °C for the other clays, and aged overnight at room temperature. The solids were washed by dialysis and oven-dried. This series of samples will be indicated by adding (ACH) to the clay.

The fourth method was essentially similar to the one described by Schoonheydt et al.[4] It consists of the selective precipitation of the Keggin ions ($Al_{13}^{7+}$) formed in base-hydrolyzed solutions (OH/Al = 2.4) with a sulfate. The precipitate is isolated from the solution, washed, and brought in contact with a barium chloride solution. The precipitate of barium sulfate is removed by centrifugation, leaving an $Al_{13}$ solution supposedly free of other Al species. Using this procedure, an adequate volume of the final solution (20 mequiv/g clay) was slowly added to the clay suspension (2 wt %). The exchange process was carried out at room temperature for 48 h. Excess salt was again removed by dialysis, and the solids were oven-dried. The series of pillared clays obtained by this method will be symbolized by ($Al_{13}$).

**Characterization.** X-ray diffraction spectra were recorded on samples dried at room temperature and after calcination of separate specimens for 2 h at different temperatures, with a D-5000 Siemens instrument and Cu anticathode (Kα radiation). The oriented film preparation method onto glass slides was adopted.

The initial and residual (after pillaring) CECs were determined by micro-Kjeldahl analyses. The pillared samples were previously calcined at 400 °C and subsequently exchanged with ammonium (2 M ammonium acetate solution, pH = 7.2). Excess salt was removed by repeated washings.

The textural characteristics (surface areas and micropore volumes) were obtained from nitrogen adsorption−desorption isotherms established at liquid nitrogen temperature with an ASAP 2000 sorptometer from Micromeritics. The samples were previously calcined for 2 h at 400 °C (the same temperature as for the activation step preceding the catalytic test) and outgassed for 4 h at 200 °C. The external surface areas and micropore volumes were determined according to a method recently proposed.[18]

The acid content of the pillared materials was established from ammonia adsorption measurements performed at 250 °C, followed by temperature-programmed desorption between 250 and 400 °C, with a plateau of 16 h at 400 °C. The experimental conditions have been detailed elsewhere.[19] Prior to adsorption, the samples were calcined at 400 °C for 2 h. At the adsorption temperature adopted (on the basis of catalytic poisoning experiments), ammonia is mostly adsorbed on the acid sites involved in the reaction investigated. In the determination of the acid content, it has been assumed that each mmol of ammonia adsorbed (or desorbed) corresponded to 1 mmol of protons.

**Catalytic Activity.** Bifunctional hydroisomerization−hydrocracking of heptane was used to evaluate the catalytic performances of the different pillared clays, in view of evidencing possible effects related to the pillaring procedure. The reaction was carried out in a fixed bed reactor operated at atmospheric pressure over samples previously impregnated with a solution of tetrammineplatinum(II) chloride ($5 \times 10^{-3}$ M), using the required volume of solution to load the solids with 1 wt % of metal. Activation of the catalyst (typically 200 mg) and reduction of the metal were done as follows: the reactor containing the catalyst sandwiched between pure small sized quartz layers was heated at 400 °C at a heating rate of 7 °C/min under a flow of dry air and maintained at the final temperature for 2 h. The reactor was purged with helium. Reduction of the metal was achieved by flowing pure hydrogen through the catalyst bed for 2 h at 400 °C. After this activation step, the reactor was cooled to 150 °C and stabilized at this temperature. A stream of hydrogen saturated with heptane vapor was generated by passing hydrogen through a thermostated glass saturator filled with heptane and kept at constant temperature (27 °C). The total flow (hydrogen−heptane) was 10 mL/min, with a weight hourly space velocity of 0.9 g of heptane/g of catalyst·h. The reaction was carried out in temperature-programmed mode between 150 and 400 °C, at a heating rate of 1.5 °C/min. On-line gas phase analysis was made in a HP-5880 gas chromatograph equipped with FID, on a CPSil-5 capillary column from Chrompack. The methodology adopted for the treatment of the catalytic results has been detailed elsewhere.[19]

## Results

**X-ray Diffraction Data.** The values of the *d* spacings (001 reflection, in Å) of samples prepared with the <2μ fractions

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**TABLE 1: Basal Spacings (in Å) after Calcination at Increasing Temperatures**

| clay | rt | 200 °C | 400 °C | 600 °C |
|---|---|---|---|---|
| M1(S) | 20.8 | 17.3 | 17.3 | 17.3 |
| M2(S) | 18.8 | 18.4 | 17.5 | 16.1 |
| M2(S)/2,4 | 20.3 | 18.4 | 18.0 | 16.1 |
| S2(S) | 18.4 | 17.7 | 17.0 | 16.1 |
| S3(S) | 18.2 | 17.3 | 17.0 | 16.7 |
| S3(S)/2,4 | 18.8 | 18.2 | 17.0 | 16.8 |
| M2(T) | 19.2 | 18.4 | 17.3 | 15.8 |
| M2(ST) | 18.8 | 18.4 | 17.7 | 17.0 |
| M2 (T)/f | 19.6 | 16.1 | 16.0 | 15.5 |
| M2 (T)/d | 19.0 | 17.7 | 16.7 | |
| S3(T)/20 | 18.8 | 17.7 | 16.7 | 16.6 |
| S3(T)/35 | 19.2 | 18.0 | 16.4 | 15.2 |
| M1(ACH)/60 | 21.5 | 18.8 | 18.4 | 18.0 |
| M1(ACH)/rt | 21.0 | 18.8 | 18.2 | 17.0 |
| S1(ACH) | 19.6 | 18.4 | 18.6 | 17.0 |
| S2(ACH) | 20.1 | 18.8 | 18.8 | 18.0 |
| S3(ACH) | 19.2 | 18.4 | 18.0 | 16.7 |
| M2($Al_{13}$) | 19.9 | 18.8 | 17.7 | 17.3 |
| S1($Al_{13}$) | 19.0 | 18.2 | 18.4 | 17.0 |
| S2($Al_{13}$) | 19.6 | 19.2 | 18.4 | 18.4 |
| S3($Al_{13}$) | 19.2 | 18.8 | 18.0 | 18.0 |

**TABLE 2: Values of Half-Height Peak Width (°2$\theta$)**

| clay | rt | 200 °C | 400 °C | 600 °C |
|---|---|---|---|---|
| M1(S) | 0.75 | 1.15 | 1.10 | 1.45 |
| M2(S) | 0.95 | 1.05 | 1.05 | 1.40 |
| M2(S)/2,4 | 1.15 | 1.25 | 1.25 | 1.50 |
| S2 (S) | 1.35 | 1.50 | 1.80 | 1.30 |
| S3(S) | 1.45 | 1.75 | 1.70 | 1.80 |
| S3(S)/2,4 | 1.50 | 1.90 | 2.15 | 2.30 |
| M2(T) | 0.95 | 1.05 | 1.15 | 1.45 |
| M2(ST) | 1.05 | 1.15 | 1.20 | 1.50 |
| M2(T)/f | 1.15 | 1.50 | 1.70 | 1.50 |
| M2(T)/d | 1.45 | 1.55 | 1.50 | |
| S3(T)/20 | 1.30 | 2.70 | 2.00 | 2.60 |
| S3(T)/35 | 1.55 | 1.60 | 2.20 | 2.80 |
| M1(ACH)/60 | 0.95 | 0.75 | 0.85 | 1.30 |
| M1(ACH)/rt | 0.90 | 0.80 | 0.85 | 1.20 |
| S1(ACH) | 0.85 | 0.73 | 0.65 | 0.90 |
| S2(ACH) | 1.40 | 1.45 | 1.55 | 1.60 |
| S3(ACH) | 1.50 | 1.40 | 1.95 | 2.15 |
| M2($Al_{13}$) | 1.05 | 1.05 | 1.20 | 1.40 |
| S1($Al_{13}$) | 0.95 | 0.95 | 0.85 | 1.15 |
| S2($Al_{13}$) | 1.40 | 1.45 | 1.50 | 2.30 |
| S3($Al_{13}$) | 1.40 | 1.35 | 1.55 | 2.30 |
| M1 i[a] | 1.25 | 2.15 | 0.65 | |
| M2 i | 1.30 | 2.10 | 1.35 | |
| S2 i | 2.25 | 1.90 | 2.80 | |
| S3 i | 2.10 | 2.50 | 2.40 | |
| S1 i | 1.55 | 1.80 | 0.70 | |
| S1 i/r[b] | 0.75 | 1.15 | 1.45 | |

[a] i: initial sample. [b] r: raw (unrefined) clay.

(unless otherwise specified) examined after drying at room temperature and treatment at different temperatures are compiled in Table 1. Globally considered, the spacings correspond to those generally found for Al-pillared materials. Stable pillars are formed, as inferred from the values obtained after calcination at high temperatures. A closer examination reveals, however, some differences according to the pillaring method. Indeed, pillaring with Al-chlorhydrol and $Al_{13}$ solutions provides materials with slightly but significantly higher spacings, especially in their calcined forms, compared with the series prepared with the standard method (series S) or with a surfactant (series T). This improvement is more appreciable for saponites S2 and S3, particularly those prepared with $Al_{13}$ solutions. The pillared clays obtained in the presence of surfactant, at the opposite, offer poorer resistance to thermal treatments at 400 and 600 °C with respect to those prepared with the other pillaring solutions. Sample M2(ST), prepared in diluted conditions and without surfactant, exhibits higher spacings after calcination at 400 and 600 °C than those obtained with tergitol, thus indicating that using more diluted pillaring solutions does not play a marked role. Note that a *d* value of 15.3 Å was quoted by Michot and Pinnavaia[1] for a surfactant-modified pillared clay calcined at 500 °C. For this series of samples, it is also observed that the sequence of addition, namely, pillaring solution (with tergitol) added to the clay suspension or vice versa, yields samples with only slightly different spacings (compare M2(T) and M2(T)/ d). It has been shown elsewhere[19] that the pillared materials obtained with the raw clays or the <2$\mu$ fractions (using the standard solutions) had similar *d* spacings. Differences ranging between 0.3 and 0.9 Å were noticed for the same series of clays after a calcination at 600 °C.

Schoonheydt et al.[4] reported that the quality of the pillars could be estimated from the half-height width of the d001 line. For a well (Al)-pillared sample of saponite (from Ballarat), these authors found a width at half-peak height of about 3 Å after freeze-drying (precursor form), which increased to 5 Å after calcination (pillared form). Michot and Pinnavaia[1] showed that pillaring in the presence of a surfactant noticeably improved, among others, the layer stacking in the *c* direction (smaller line width at half-height, higher peak intensity). It was thus appropriate to examine to what extent the half-height line widths (which provide an appreciation of the quality of the pillared materials), were influenced by the preparation mode.

The values determined from the X-ray recordings are compiled in Table 2. They are expressed in °2$\theta$. Several features may be underlined. First, whatever the pillaring solution, the calcined Al-pillared montmorillonites and Ballarat saponite (S1) exhibit smaller line widths than the two pillared Spanish saponites (S2 and S3). The unpillared forms of these two saponites also show larger half-height peak width (hhpw) values (poorer stacking order or crystallinity) compared with the other clays. It seems, therefore, that the stacking order of the pillared clays is also, and perhaps primarily, related with the stacking order of the starting clays (Na forms). As shown below, these less ordered clays also have lower initial cation exchange capacities. The poor "crystallinity" of Vicalvaro saponite (S2) was attributed to the high proportion of small particles.[13] A second observation is that the four pillared samples obtained with the standard solution (OH/Al = 1.6) and calcined at 600 °C exhibit smaller line widths than those prepared with the other pillaring solutions (with initial OH/Al = 2.4) and with the standard solution with OH/Al = 2.4. Adding a surfactant to the pillaring solution has no clear effect on the half-height peak width and, in any case, it does not improve the stacking order as was observed by Michot and Pinnavaia,[1] for a reason which presently remains unexplained. Indeed, in the case of M2, pillaring with a solution containing the surfactant has only a slight effect on the quality of the pillars (compare the line widths of M2(T) and M2(ST)). For sample S3(T), the line width is not different from the values found for the same clay prepared with the other pillaring solutions. In summary, these observations suggest that the stacking order (pillar quality) of a pillared clay is conditioned, at least to some extent, by the stacking order of its initial unpillared form, which as seen below may be related to the layer charge density (CEC). Beside, no relation could be found between *d* spacings and half-height peak widths. Poorly ordered clays, such as S2 and S3, may exhibit heat stable 18 Å spacings.

**Residual Cation Exchange Capacities.** The residual cation exchange capacities (CECs) of the pillared clays determined over ammonium exchanged samples are given in Table 3. The

**TABLE 3: Residual CECs**

| clay | CEC (mequiv/100 g) | fraction compensated |
|---|---|---|
| M1(S) | 35.3 | 56.4 |
| M2(S) | 41.2 | 62.5 |
| M2(S)/2,4 | 32.4 | 70.5 |
| S2(S) | 28.5 | 49.1 |
| S3(S) | 35.0 | 42.6 |
| S3(S)/2,4 | 30.5 | 50.0 |
| M2(T) | 27.5 | 75.0 |
| M2(ST) | 29.5 | 73.2 |
| M2(T)/f | 21.9 | 80.1 |
| M2(T)/d | 20.0 | 81.8 |
| S3(T)/20 | 31.0 | 49.2 |
| S3(T)/35 | 30.8 | 49.5 |
| M1(ACH)/60 | 26.6 | 67.2 |
| M1(ACH)/RT | 20.0 | 75.3 |
| S1(ACH) | 18.3 | 79.2 |
| S2(ACH) | 21.4 | 61.8 |
| S3(ACH) | 22.7 | 62.9 |
| M2($Al_{13}$) | 32.6 | 70.4 |
| S1($Al_{13}$) | 28.8 | 67.3 |
| S2($Al_{13}$) | 23.6 | 57.8 |
| S3($Al_{13}$) | 19.6 | 67.9 |

CEC values of the starting smectites ($<2\mu$ fractions) were as follows: M1, 81; M2, 110; S1, 88; S2, 56; S3, 61 mmol/100 g. The corresponding fractions of the CEC lost upon Al pillaring (assumed to reflect, in first approximation, the fraction of charges neutralized by Al species) are also indicated. The samples prepared by the standard method (pillaring solutions with OH/Al molar of 1.6) have higher residual CECs than those obtained with either chlorhydrol, $Al_{13}$ solutions, or the standard solution with OH/Al = 2.4. The effect of the molar ratio of the pillaring solution on the residual CEC of the clay has been observed in earlier work.[15] It is, therefore, not surprising to find those discrepancies. Within each series of preparations, the relative loss of CEC of pillared S2 and S3 is, with the exception of S3($Al_{13}$), lower than for the other pillared clays. This difference is particularly more pronounced for the series (S) and (T). Addition of surfactant to the pillaring solution seems to improve, in the case of M2 clay, the fraction of charge compensated by Al species with respect to the standard and $Al_{13}$ methods, while no effect is noticed in the case of S3 (compare S3(T)/20 and S3(S)/2.4). However, the improvement noticed for M2 may as well be attributed to the higher dilution conditions, since the sample of this series obtained without surfactant (same dilution, same OH/Al ratio) exhibits a comparable loss of CEC (compare M2(T) and M2(ST)). Still, for the series with surfactant, the sequence of addition (pillaring solution to clay suspension or the reverse) has some influence, as lower residual CECs are obtained when the clay suspension is added to the pillaring solution (compare M2(T) with M2-(T)/f and M2(T)/d). Finally, this table also shows that supplying 20 or 35 mequiv of Al/g of clay (series with surfactant) or washing by filtration or dialysis leads to materials with similar residual CECs. For pillared S2 and S3, the relative loss of CEC is more pronounced (higher degree of compensation by interlayered Al species) when either chlorhydrol or $Al_{13}$ solutions are used. The same samples also had improved *d* spacings.

**Textural Characteristics.** The textural characteristics derived from nitrogen sorption isotherms carried out on unpillared and pillared samples previously calcined at 400 °C for 2 h are presented in Table 4. The Na-exchanged forms of S2 and S3 exhibit unusually high surface areas, mainly contributed by the presence of a non-negligible microporosity. In normally collapsed smectites, microporosity should be absent or reduced to a very small value. The surface area determined by Casal et al.[13] for uncalcined S2 saponite was 202 m²/g (185 in this study).

**TABLE 4: Textural Characteristics of the Al-Pillared Clays at 400 °C**

| clay | $S_{BET}$ (m²/g) | $S_{BEText}$ (m²/g) | micropore vol. (cc/g) |
|---|---|---|---|
| M1(S) | 175 | 60 | 0.055 |
| M2(S) | 243 | 62 | 0.086 |
| M2(S)/2,4 | 249 | 71 | 0.082 |
| S2(S) | 257 | 133 | 0.060 |
| S3(S) | 240 | 95 | 0.070 |
| S3(S)/2,4 | 256 | 99 | 0.076 |
| M2(T) | 341 | 83 | 0.122 |
| M2(T)/f | 156 | 76 | 0.038 |
| M2(T)/d | 258 | 102 | 0.083 |
| S3(T)/20 | 268 | 121 | 0.070 |
| S3(T)/35 | 284 | 137 | 0.070 |
| M1(ACH)/60 | 212 | 62 | 0.071 |
| M1(ACH)/rt | 220 | 60 | 0.068 |
| S1(ACH) | 353 | 73 | 0.128 |
| S2(ACH) | 303 | 155 | 0.071 |
| S3(ACH) | 320 | 151 | 0.081 |
| M2($Al_{13}$) | 312 | 96 | 0.100 |
| S1($Al_{13}$) | 350 | 80 | 0.110 |
| S2($Al_{13}$) | 285 | 164 | 0.058 |
| S3($Al_{13}$) | 328 | 159 | 0.081 |
| iM1 | 86 | 78 | 0.004 |
| iM2 | 83 | 53 | 0.014 |
| iS2 | 158 | 117 | 0.020 |
| iS3 | 138 | 97 | 0.020 |
| iS1 | 30 | 23 | 0.003 |
| iS1/R[a] | 10 | 7 | 0.001 |

[a] R: raw clay.

Contamination sepiolite would contribute for at most 30−60 m²/g (10−20 wt % sepiolite with specific surface area of about 300 m²/g), which is insufficient to account for the high value obtained. Typical values for fully collapsed smectites are merely in the range 30−70 m²/g. Casal et al.[12] invoked the significant abundance of small particles in S2, which is consistent with the relatively poorer X-ray diffraction pattern (deficient stacking order) of this saponite. A similar explanation could be proposed for S3 saponite which, as well, has a high initial surface area, a significant micropore volume, a lower sepiolite content than in S2, and a slightly better X-ray crystallinity.

All the pillared clays exhibit surface areas and microporous volumes in the range of expected values with, however, significant differences among the clay samples and according to the pillaring method. The samples pillared following the standard method exhibit, in most cases, lower specific surface areas and smaller micropore volumes and, as mentioned earlier, higher residual CEC. Pillared M2 and S1 which have higher micropore volumes also have smaller half-height line widths (at 400 °C), which may reflect a more regular distribution of the pillars. No clear relationship could be found between microporous volume and half-height peak width, the experimental values being scattered along a line whose general tendency shows, however, a diminution of the micropore volume as the line width increases. Independent of the pillaring method, the highest micropore volumes are observed for the most crystalline (ordered) S1 and M2 clays.

**Acid Content.** The amounts of ammonia adsorbed at 250 °C (IA) and released between 250 and 400 °C (TPD) are given in Table 5. They are expressed in mmol/g of solid. Differences are noticed between the two sets of values. They are probably due to incomplete desorption of ammonia at 400 °C, in spite of the fact that this temperature was maintained for 16 h. The correspondence is nevertheless acceptable, the average relative difference between the two sets of values being lower than 9%. Obviously, Al-pillared saponites have higher acid contents (higher quantities of ammonia adsorbed) than Al-pillared

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**TABLE 5: Isothermal Adsorption (IA) and Temperature Programmed Desorption (TPD) of Ammonia**

| clay | IA (mequiv/100 g) | TPD (mequiv/100 g) |
|---|---|---|
| M1(S) | 13.0 | 11.1 |
| M2(S) | 16.5 | 14.8 |
| M2(S)/2,4 | 16.8 | 15.0 |
| S2(S) | 21.6 | 20.0 |
| S3(S) | 20.8 | 18.4 |
| S3(S)/2,4 | 23.2 | 21.0 |
| M2(T) | 14.5 | 14.0 |
| S3(T)/20 | 15.5 | 14.2 |
| S3(T)/35 | 15.9 | 14.4 |
| M1(ACH)/60 | 15.7 | 13.6 |
| M1(ACH)/rt | 16.0 | 14.8 |
| S1(ACH) | 29.8 | 27.5 |
| S2(ACH) | 23.0 | 22.0 |
| S3(ACH) | 24.4 | 23.8 |
| M2(Al$_{13}$) | 14.0 | 13.7 |
| S1(Al$_{13}$) | 31.3 | 28.6 |
| S2(Al$_{13}$) | 20.8 | 17.7 |
| S3(Al$_{13}$) | 25.0 | 22.7 |

montmorillonites. Ballarat saponite (S1) again distinguishes itself from the other saponites by its higher acid content (higher number of tetrahedral charges). Using Al-chlorhydrol as the pillaring solution slightly improves the acid content of the pillared materials compared with the standard method. The samples prepared in the presence of surfactant, on the contrary, have lower acid contents. For S3, the diminution amounts to about 25% with respect to the sample pillared with the standard solution. Besides, using pillaring solutions with an OH/Al molar ratio of 1.6 or 2.4 (standard method), or supplying 20 or 35 mequiv of Al/g clay at the preparation step (series with surfactant) has a limited effect, if at all, on the acid content.

**Catalytic Evaluation: Hydroconversion of Heptane.** The catalytic activity of Pt-loaded samples has been evaluated using hydroisomerization−hydrocracking of heptane as the model reaction. The catalytic results are presented separately for each type of clay in Figures 1−5. Each figure compares the catalytic performances (total conversion, hydroisomerization, and hydrocracking yields vs reaction temperature) achieved over the pillared clays prepared following the different methods.

The upper curves of Figures 1−5 (total conversion of heptane vs temperature) show that whatever the preparation method Al-pillared montmorillonites are less active than Al-pillared saponites.

Figure 1 shows that M1 montmorillonites pillared with Al-chlorhydrol (ACH) or with the standard solution exhibit similar variation of heptane conversion up to about 330 °C. Above this temperature, slightly lower conversions are achieved over the ACH clays with, however, a significant improvement of the isomerization conversion as a result of the lower cracking activity. At maximum isomerization conversion, the selectivities to C7 isomers are 64 and 91% for the materials pillared with the standard method and with chlorhydrol, respectively. Besides, aging the final clay−chlorhydrol suspension at room temperature or at 60 °C has no effect on the catalytic behavior.

The results obtained over Al-pillared M2 montmorillonites are given in Figure 2. The four samples exhibiting similar conversion curves were pillared in the absence of surfactant, whereas the three samples obtained with use of surfactant are less active. The addition of tergitol to the pillaring solution has thus a detrimental effect on the catalytic activity of the resulting materials, which is consistent with the lower acid contents found for these samples. However, interestingly enough, the cracking activities are noticeably reduced, and as a
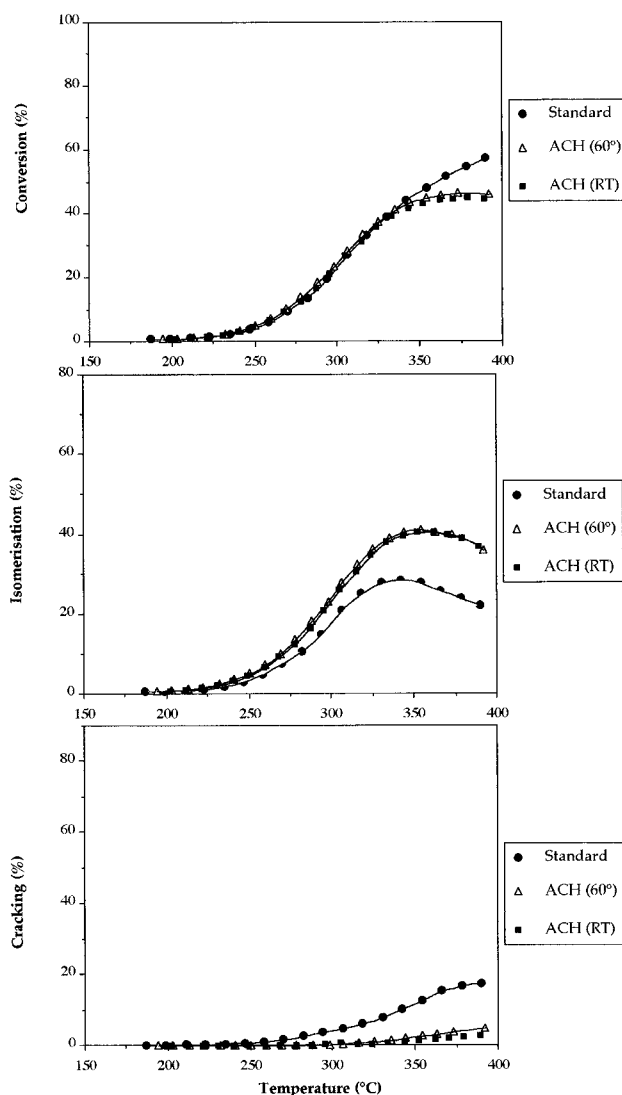


**Figure 1.** Al-pillared M1 montmorillonite: variation of conversion, isomerization, and cracking vs reaction temperature. Pillaring solutions: standard (OH/Al = 1.6) and Al-chlorhydrol (ACH).

result, the isomerization activity is significantly improved. With respect to the pillared M1 clays, the M2 samples reach higher conversions.

Figures 3−5 show the results obtained over the Al-pillared saponites. The reference saponite (S1) pillared with Al$_{13}$ solution (Figure 3) is slightly more active than the sample prepared with Al-chlorhydrol. Both catalysts show signs of deactivation at temperatures above 325 °C. The most remarkable results are the larger amounts of isomers produced. Indeed, at maximum isomerization conversion, nearly 72% of the reaction products are isomers of C7, which is about twice as much as over pillared montmorillonites.

The catalytic results obtained over pillared S2 saponites are compared in Figure 4. As for S3 saponite, the sample pillared with the standard solution is slightly more active than those prepared with either Al-chlorhydrol and or Al$_{13}$ solution. These two last samples also produce slightly lower amounts of isomers at maximum isomerization conversion and less cracking products with, as noticed earlier, a decreasing cracking activity beyond 350−360 °C.

The results obtained over Al-pillared S3 saponite are shown in Figure 5. The samples obtained with the standard procedure (OH/Al = 1.6 and 2.4) are slightly more active than those prepared with the other methods for which the curves of total
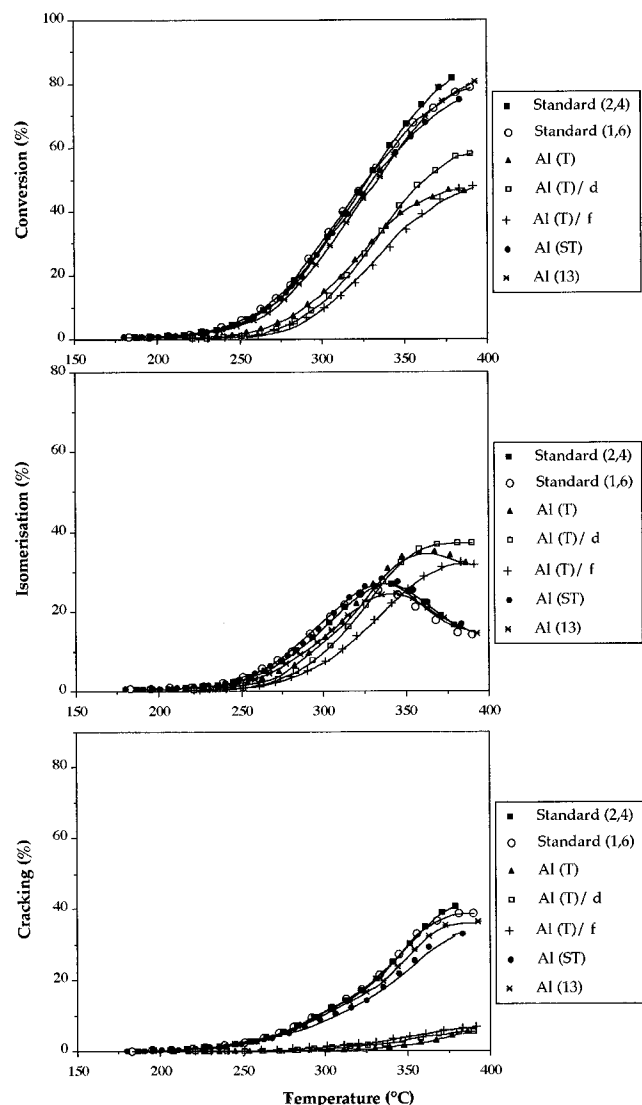
**Figure 2.** Al-pillared M2 montmorillonite: variation of conversion, isomerization, and cracking vs reaction temperature. Pillaring solutions: standard (OH/Al = 1.6 and 2.4), with surfactant (series T), and $A_{13}$.
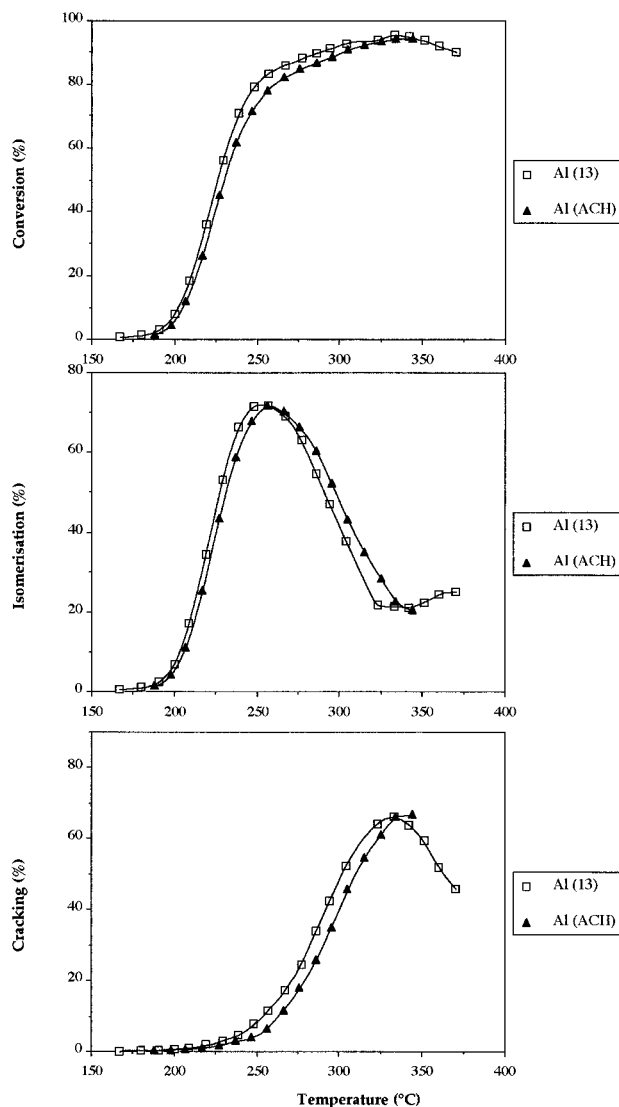
**Figure 3.** Al-pillared S1 (Ballarat) saponite: variation of conversion, isomerization, and cracking vs reaction temperature. Pillaring solutions: Al-chlorhydrol (ACH) and $Al_{13}$.

conversion are superimposed up to reaction temperatures of 260−270 °C. The yields of isomers at maximum isomerization are slightly higher for the samples pillared in the presence of surfactant than for those prepared with the standard method, in spite of a lower total acid content. As for M2(S) montmorillonite, the addition of surfactant to the pillaring solution seems, for this series also, to depress the cracking activity, although the effect is less marked. The catalytic results obtained for the clays pillared with Al-chlorhydrol and $Al_{13}$ solution are intermediate. The cracking curves show a diminution at temperatures above 350 °C, except for the sample pillared with the standard solution. A similar observation was also made for the S1 and S2 saponites, both prepared under similar conditions.

**Activation Energy.** The apparent activation energies for the isomerization reaction determined from the Arrhenius' plots (ln $K_{app}$ vs $1/T$) are given in Table 6 (with correlation coefficients between 0.992 and 1.0). The values obtained for the pillared montmorillonites are much lower than for the pillared saponites. In some cases, a factor exceeding 2 between the two types of pillared clays is observed. Values obtained over a series of Pt/ dealuminated H-Y zeolites tested under identical reaction conditions[20] were in the range of 125−140 kJ/mol, namely, close to those of the pillared saponites prepared with the standard

solution. It may be seen that for the least active clay (M1), the $E_a$ values are little affected by the type of pillaring solution used in their preparation. whereas for the most active clays (S1 and S3 saponites), greater variations are noticed according to the type of pillaring solution. The fluctuations are less important for pillared M2 (more active than the M1 clays) and S2 (less active than the two other saponites).

## Discussion

Paraffins with seven (and more) carbon atoms react over well-balanced bifunctional catalysts (with acid and metal functions) to give isomers as primary products, which, as temperatures increases, are hydrocracked into smaller fragments (mainly propane and isobutane in the case of heptane). At still higher temperatures, cyclization products may appear. Poor balance of the two functions (too low acidity) is noticed by hydrogenolysis products (butane from heptane). The reaction of normal paraffins has been thoroughly investigated over Pt/H-zeolites, and the isomerization mechanism via protonated cycloalkanes intermediates has been clearly established.[21−24]

Al-pillared montmorillonites impregnated with noble metals were shown to exhibit ideal bifunctional behavior in the hydroisomerization of C5, C6, and C7,[25] C8,[26] and C10.[16,17]

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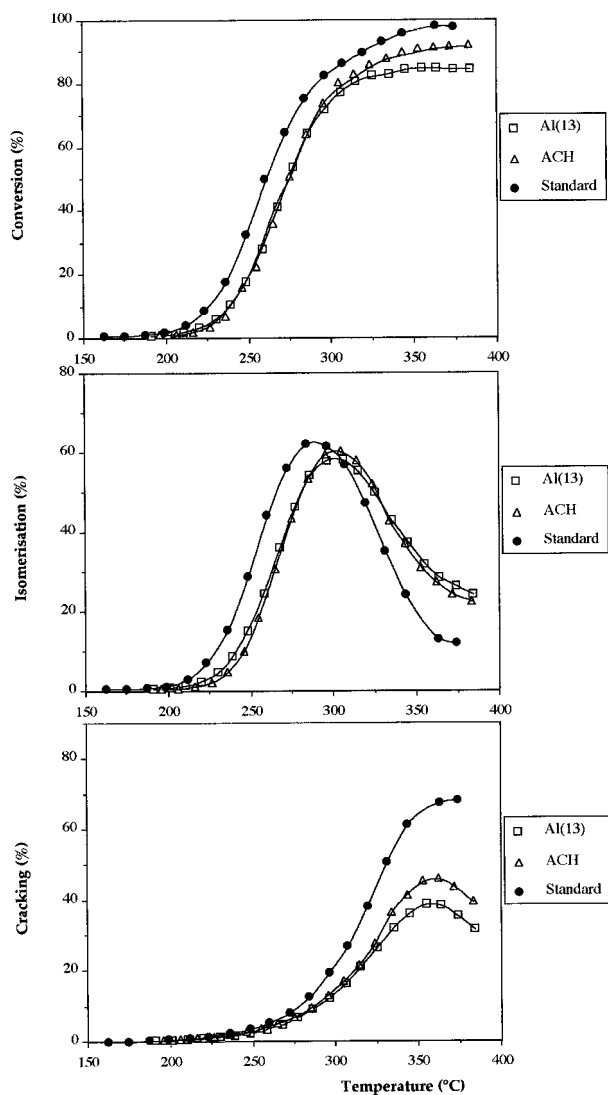*J. Phys. Chem. B, Vol. 101, No. 9, 1997* **1575**



**Figure 4.** Al-pillared S2 saponite:variation of conversion, isomerization, and cracking vs reaction temperature. Pillaring solutions: standard, Al-chlorhydrol (ACH), and Al$_{13}$.



**Figure 5.** Al-pillared S3 saponite: variation of conversion, isomerization, and cracking vs reaction temperature. Pillaring solutions: standard (OH/Al = 1.6 and 2.4), Al-chlorhydrol (ACH), Al$_{13}$, and with surfactant (T).

Two main aspects will be discussed in relation to the type of pillaring solution: its influence on the textural and structural characteristics of the pillared materials, on the one hand, and on the acid and catalytic properties, on the other hand.

As each one of the pillaring solutions considered in this study has been successfully employed by the different authors referred to in the Introduction section to obtain pillared clays exhibiting heat resistant interlayer distances of 17−18 Å, it is not surprising that the X-ray diffraction data collected in this study do not show major differences according to the type of clay and pillaring solution. However, as it has been underlined, the thermal resistance of the pillared clays obtained with both chlorhydrol and Al$_{13}$ solutions was significantly improved in comparison with samples prepared either with the standard solution (OH/Al = 1.6), or when adding a surfactant to the pillaring solution. A tempting explanation would be to attribute this improvement to the higher proportion of Al$_{13}$$^{7+}$ species with Keggin structure in solutions with OH/Al = 2.4 (and a fortiori in the Al$_{13}$ solutions) than in solutions with lower molar ratio (1.6 in the standard solution),[15,27,28] assuming, of course, that this polymeric species is the one constituting the pillars' precursors. However, this assumption cannot account for the lower thermal resistance observed for the clays pillared with surfactant-containing solutions which, as chlorhydrol solutions, have an OH/Al molar ratio of 2.4 and, therefore, should contain
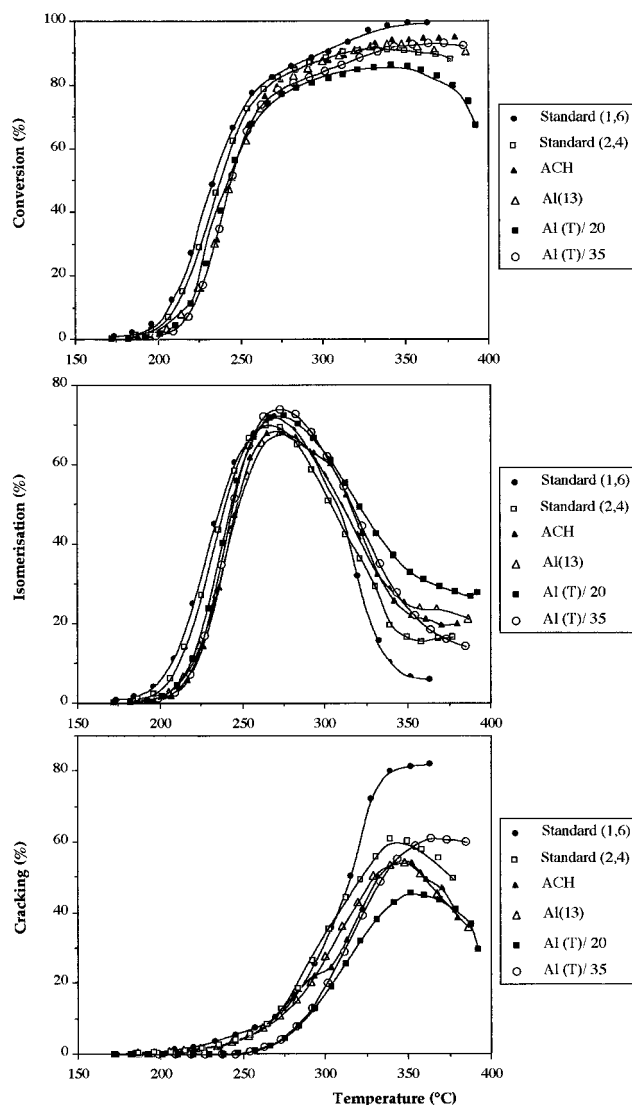
similar amounts of Al$_{13}$$^{7+}$ species. Besides, this assumption was found inadequate to account for observations reported in previous work[15] and questioned again more recently by Schoonheydt et al.[29] The main experimental difference between samples pillared with the standard solution and with chlorhydrol or Al$_{13}$ solutions concerns the amounts of Al fixed by the clays (established by chemical analysis, structural Mg being taken as an internal reference). Indeed, the values obtained for the different samples analyzed (in mmol/g) were 1.53 (M1(S) and 2.0 M1(ACH); 1.70 and 2.0 for, respectively, M2(S) and M2-(ACH); 1.60, 2.17, and 2.20 for, respectively, S2(S), S2(ACH), and S2(Al$_{13}$); 1.34, 2.38, and 2.40 for, respectively, S3(S), S3-(ACH), and S3(Al$_{13}$). Note that higher amounts of interlayered Al were also observed by Chevalier et al.[30] and Lambert et al.[31] when saponites were pillared with chlorhydrol instead of base-hydrolyzed Al solutions (OH/Al = 2.2). These authors advocated the participation to the pillaring of more highly condensed polycations than Al$_{13}$ present in chlorhydrol, which might result in higher Al densities.[32]

Considering the information provided by the half-height peak widths, it has been observed that clays exhibiting a well-ordered stacking in their initial state (<2 $\mu$m fractions, Na-exchanged), generate pillared forms which are also well ordered, independent of the type of pillaring solution employed. Besides, the stacking

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**TABLE 6: Activation Energies and Apparent Reaction Rates at 250 °C and Corresponding TOFs**

| clay | $E_a$ (kJ·mol$^{-1}$) | R × 10$^7$ (mol·g$^{-1}$·s$^{-1}$) | TOF × 10$^4$ (s$^{-1}$) |
|---|---|---|---|
| M1(S) | 84.9 | 0.9 | 7.0 |
| M2(S) | 88.6 | 1.5 | 9.0 |
| M2(S)/2,4 | 88.4 | 1.2 | 7.3 |
| S2(S) | 135.9 | 7.8 | 36.3 |
| S3(S) | 141.6 | 16.1 | 74.5 |
| S3(S)/2,4 | 150.9 | 14.4 | 69.4 |
| M2(T) | 94.3 | 0.4 | 3.1 |
| M2(ST) | 87.9 | 1.2 | |
| M2(T)/f | 101.3 | 0.2 | |
| M2(T)/d | 110.7 | 0.2 | |
| S3(T)/20 | 181.4 | 13.6 | 87.6 |
| S3(T)/35 | 188.9 | 12.4 | 78.1 |
| M1(ACH)/60 | 85.7 | 1.2 | 7.8 |
| M1(ACH)/rt | 86.6 | 1.1 | 6.9 |
| S1(ACH) | 184.7 | 17.4 | 58.3 |
| S2(ACH) | 154.1 | 3.1 | 13.9 |
| S3(ACH) | 192.2 | 12.3 | 50.4 |
| M2(Al$_{13}$) | 89.1 | 1.0 | 7.3 |
| S1(Al$_{13}$) | 172.1 | 19.2 | 61.2 |
| S2(Al$_{13}$) | 128.6 | 4.3 | 20.7 |
| S3(Al$_{13}$) | 155.0 | 15.1 | 60.3 |

**TABLE 7: Catalytic Activity:Hydroconversion of Heptane**

| catalyst | $T_{10iso}$ (°C) | $t_{max}$ (°C) | conv (%) | $Y_{iso}$ (%) | $Y_{cr}$ (%) | select (%) | mono- (%) | di- (%) |
|---|---|---|---|---|---|---|---|---|
| M1(S) | 280 | 342 | 44.3 | 28.5 | 10.2 | 64.3 | 92.2 | 7.8 |
| M2(S) | 282 | 333 | 53.7 | 25.4 | 21.5 | 47.3 | 91.7 | 8.3 |
| M2(S)/2,4 | 277 | 335 | 54.4 | 31.4 | 17.0 | 57.7 | 92.3 | 7.7 |
| S2(S) | 228 | 284 | 75.4 | 62.2 | 12.5 | 82.5 | 84.9 | 15.1 |
| S3(S) | 207 | 269 | 82.9 | 70.8 | 12.1 | 85.4 | 79.4 | 20.6 |
| S3(S)/2,4 | 210 | 264 | 78.8 | 70.1 | 8.5 | 88.9 | 80.5 | 19.5 |
| M2(T) | 292 | 358 | 42.8 | 35.1 | 2.3 | 82.0 | 92.1 | 7.9 |
| M2(ST) | 282 | 335 | 52.9 | 27.9 | 18.0 | 52.7 | 91.9 | 8.2 |
| M2(T)/f | 311 | 383 | 47.4 | 32.2 | 6.4 | 67.9 | 92.8 | 7.2 |
| M2(T)/d | 300 | 381 | 57.2 | 37.1 | 5.5 | 64.8 | 91.4 | 8.6 |
| S3(T)/20 | 218 | 275 | 77.4 | 72.3 | 4.6 | 93.4 | 82.8 | 17.2 |
| S3(T)/35 | 221 | 273 | 78.3 | 74.1 | 4.2 | 94.6 | 82.8 | 17.2 |
| M1(ACH)/60 | 269 | 354 | 44.9 | 41.0 | 2.6 | 91.3 | 91.2 | 8.8 |
| M1(ACH)/rt | 271 | 362 | 44.1 | 40.4 | 1.7 | 91.7 | 91.3 | 8.6 |
| S1(ACH) | 206 | 256 | 78.2 | 71.9 | 6.3 | 91.9 | 80.8 | 19.1 |
| S2(ACH) | 246 | 305 | 80.2 | 60.2 | 17.1 | 75.1 | 83.2 | 16.8 |
| S3(ACH) | 222 | 274 | 81.9 | 68.2 | 13.1 | 83.3 | 79.6 | 20.4 |
| M2(Al$_{13}$) | 288 | 344 | 57.8 | 24.5 | 23.7 | 42.3 | 90.6 | 9.4 |
| S1(Al$_{13}$) | 203 | 257 | 83.5 | 71.8 | 11.7 | 86.0 | 78.8 | 21.2 |
| S2(Al$_{13}$) | 241 | 306 | 77.4 | 58.2 | 16.3 | 75.2 | 83.2 | 16.8 |
| S3(Al$_{13}$) | 219 | 272 | 79.1 | 67.7 | 10.8 | 85.6 | 81.0 | 18.1 |

order seems to be related with the initial CECs: clays poorly ordered in the *c* direction (S2 and S3 saponites) have low CECs, poor stacking order of their pillared forms, and yet heat resistant pillars (or spacings). A similar effect was recently observed by Bergaoui et al.[32] for a series of synthetic saponites with different layer charges. From the values of the half-height peak widths, it is difficult to decide whether a particular pillaring solution exerts a beneficial "ordering" influence on the clay-pillar assemblies, even when tergitol was introduced at the pillaring step. However, as underlined earlier, the samples prepared with the standard solution (with OH/Al = 1.6) and calcined at 600 °C have somewhat smaller hhpw values compared with those obtained with the other pillaring solutions. Using a standard solution with OH/Al = 2.4 instead of 1.6 results (see Table 2) in an increase of the hhpw in the calcined samples.

With respect to the fraction of charges neutralized by Al species (inferred from the values of the residual CECs and chemical analysis data), pillaring with chlorhydrol, as said earlier, results for all the clays in enhanced amounts of Al taken up by the clay (2.2 ± 0.2 vs 1.54 ± 0.15 mmol/g for those prepared with the standard solution, average value) and in improved thermal resistance of the *d* spacings. A similar trend was also noticed for S2 and S3 saponites pillared with Al$_{13}$ solutions (2.3 ± 0.1 mmol/g). S3 saponites pillared in the presence of surfactant or with the standard solution (OH/Al = 2.4 in both solutions) have similar residual CECs, whereas for M2 montmorillonite (with higher layer charge), a lower residual CEC was found when the surfactant was added to the pillaring solution compared with samples pillared with the standard and Al$_{13}$ solutions. This is probably to be related with the higher amounts of interlayered Al, although this point was not verified by chemical analysis. The higher values of the residual CEC obtained for the series of clays pillared with the standard method are consistent with the lower amounts of Al fixed by the clay and also with the higher percentages of monomeric Al species present in base-hydrolyzed solutions with OH/Al = 1.6 compared with 2.4 (as in chlorhydrol), namely, 33% vs 4% as established by NMR in a previous work.[15] Upon ammonium exchange, these monomeric species with lower net positive charge (hence, more weakly held in the interlayers) could be displaced from the exchange positions. Another explanation could be that the pillars which, as evidenced by Bandosz et

al.[33,34] by potentiometric measurements, contain amphoteric surface groups that can be protonated and deprotonated according to the pH (in the occurrence, the exchange solution had a pH of 7.2), could themselves, by sorbing ammonium ions, participate in the CEC. In other words, the residual CECs established by ammonium exchange would be the resultant of two contributions: that of the clay layer and that of the pillars. If this hypothesis is valid, it would indicate that the interlayered Al species should have a different sensitivity to pH variation according to the type of pillaring solution. Another way to solve this question would be to estimate the fraction of layer charge neutralized by the Al species, starting from the chemical analysis data. This would require the knowledge of the positive charge per pillar, which untill now has not been established with sufficient certainty.

In order to discuss the catalytic results in relation to pillaring method and type of clay, values taken from the different figures have been collected in Table 7, where $T_{10iso}$ refers to the temperature at which the yield of C7 isomers reaches 10%. The other columns report the values taken at maximum isomerization conversion, namely, the temperature at maximum isomerization ($T_{max}$), total conversion (conv.), yields of isomers ($Y_{iso}$) and of cracked products ($Y_{cr}$), and selectivities to C7 isomers. The last two columns contain the relative percentages of the mono- and di-branched isomers of heptane, still at maximum isomerization conversion.

The activity of the catalyst, which is reflected by the values of $T_{10iso}$ or $T_{max}$, is globaly little affected by the pillaring method. It is primarily governed by the type of clay. Indeed, within each series of samples, pillared saponites have lower $T_{10iso}$ and $T_{max}$ values than pillared M1 and M2 montmorillonites. They also produce more isomers of C7. The origin of the higher catalytic performances of Al-pillared saponites has been related, as in the case of Al-pillared beidellites,[35−39] to structural features which differentiate the two types of swelling minerals. In saponites (as in beidellites), isomorphic Si for Al substitutions principally occur in the tetrahedral layers. Upon pillaring, proton attack of the Si−O−Al bonds generate Si−OH···Al acid sites exposed at the surface of the micropores. Equivalent sites are not formed in Al-pillared montmorillonites because most of the framework substitutions (Al for Mg) are located within the octahedral layers. In Al-pillared beidellites, these sites were evidenced by an IR OH stretching band showing up at 3440 cm$^{-1}$.[36] In Al-pillared Ballarat saponite (S1), a new OH

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stretching band located at 3595 cm$^{-1}$ was assigned by Chevalier et al.[30] to similar acid groups. The presence of this new band was recently confirmed in pillared S1 and S3 saponites, while it was not found in pillared M2 montmorillonite.[19] As for pillared beidellite, the acid nature of these silanol groups was established by IR spectroscopy of adsorbed pyridine: the new OH stretching band was completely suppressed, whereas the band at 1540 cm$^{-1}$ which identifies pyridine in interaction with protonic sites was found.

In a recent study, Fetter et al.[40] proposed that strong sites would be associated with the tetrahedral aluminium present in the pillars, whereas Bergaoui et al.[32] provided IR evidence that in pillared saponites, the Brønsted acidity was due to both pillars bridging OHs and lattice Si−OH−Al and to pillars bridging OH in the case of montmorillonite.[33] Although the acid sites originating from the pillars probably contribute as well as the protons liberated during dehydration−dehydroxylation of the pillars[3] to the reaction, they certainly do not constitute the main source of acidity (and activity) in pillared saponites for the following reasons: neither the acid contents and catalytic activities of pillared saponites and montmorillonites nor the apparent activation energies found for the two types of pillared materials could be explained. On the basis of such a hypothesis, one would expect pillared montmorillonites, which not only have higher initial CECs but also higher fractions of charge compensated by Al species (as inferred from the residual CEC), to be at least as active as the pillared saponites. No relation could be found between the fraction of charge lost upon pillaring and catalytic activity. The samples pillared with the standard solutions (with average interlayered Al 1.54 mmol/g) are as active as, or even more active than, those with higher Al contents (2.2 mmol/g). Also, no direct link between either quality (or stacking order) of the pillared solids or microporosity and catalytic results could be established. On the contrary, the important differences of the activation energies as well as the higher proportions of dibranched isomers of C7 stem from solids with different acid strengths (and amounts), as discussed by Corma et al.[41] in the case of H-zeolites. Another illustration of the difference of the acid strengths is provided by the apparent reaction rates and turnover frequencies established at 250 °C (Table 6). A factor of about 10 in the TOF values is found between the most and least active samples, with intermediate values for the S2 saponites. No such difference should be obtained if the catalytic sites had similar acid strengths.

Among the Al-pillared saponites, the S1 samples perform slightly better than the pillared S3 and both show significant differences with respect to S2 saponite. As mentioned earlier, the three saponites, in their unpillared and pillared forms, differ from each other by their relative "crystallinity" (stacking order), S1 clays exhibiting higher crystallinity than S3 and S2, which showed the poorest stacking order. The OH stretching band (near 3595 cm$^{-1}$) of tetrahedral Si−OH−Al bonds mentioned earlier was more intense in pillared S1 than in pillared S3,[19] which is consistent with the higher tetrahedral charge (or CEC) of the former one (88 for S1 vs 61 mequiv/100 g for S3) and with its greater acid content. A relation between amount of tetrahedral charges and catalytic activity has been observed in the hydroisomerization of decane[35] over Pt/Al-pillared clays and hexane over a series of Pd/synthetic Ni-substituted saponites.[42,43]

As shown in the different figures and in Table 7, pillared saponites are not only more active but also more selective than pillared montmorillonites. Compared with the results obtained over Pt-impregnated dealuminated H-Y zeolites and H-mordenites tested under similar conditions, pillared S1 and S3 saponites produce higher amounts of isomers of C7 (around
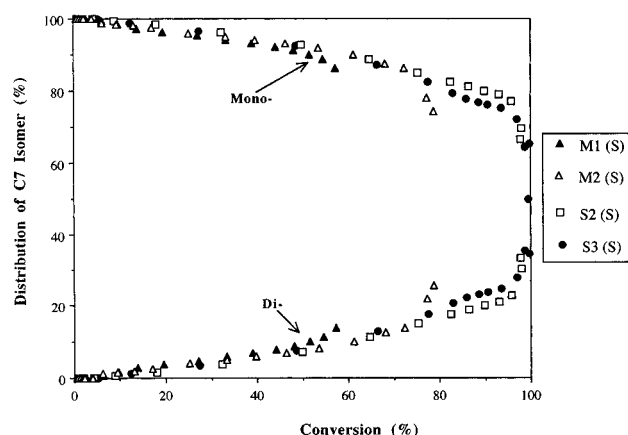
**Figure 6.** Variation of the percentages of mono- and di-branched isomers of C7 vs conversion of heptane. Series of clays pillared with the standard solution.

60% for the zeolites vs 70%).[19,41] With respect to the results obtained over samples pillared with the standard solution, the selectivity to isomers is substantially improved when the montmorillonites are pillared either with Al-chlorhydrol or in the presence of tergitol, as a result of the substantial diminution of the cracking activity, which may be accounted for by an improved balance between the metal and acid functions. Indeed, lower amounts of butane (less hydrogenolysis) were noticed. Total conversions of heptane, however, are barely modified.

A similar effect is noticed for S3 saponite obtained with use of surfactant. Pillaring S3 with either chlorhydrol or Al$_{13}$ solution does not change the catalytic properties much with respect to the sample pillared with the standard solution, whereas pillaring in the presence of surfactant, as for the montmorillonites, lowers the cracking activity (improved selectivities to C7 isomers).

Another observation from Table 7 concerns the relative percentages of the mono- and di-branched isomers of heptane obtained over the different clays. At maximum isomerization conversion, Al-pillared saponites produce about twice as much di-branched isomers as compared with Al-pillared montmorillonites, whatever the pillaring method. However, when plotting the evolution of the mono- and di-branched isomers against conversion of heptane, all the experimental values fall on the same curves, irrespective of the type of clay and its pillaring method. This is illustrated in Figure 6 for the series of clays pillared following the standard method. It is noteworthy that almost identical results were obtained over a series of dealuminated H-Y zeolites.[44] This observation stems from a similar reaction mechanism.

The relative activity of the different samples has been estimated from the $T_{10iso}$. At this temperature, the only reaction products are the C7 isomers. Plotting these values against the corresponding acid contents (IA values of Table 5) yields the relation shown in Figure 7. In spite of the scattering of the experimental values, the trend is obvious. All the experimental points located at the upper left part of the figure refer to pillared montmorillonites, irrespective of their preparation method. Of course, a similar variation is obtained with the $T_{max}$'s, but the slope is slightly different (5.79 vs 5.01). Using the TPD data of Table 5 yielded similar relationships.

## Conclusions

Pillaring of two montmorillonites and three saponites has been achieved using different Al solutions. The comparison of the main characteristics of the pillared materials with those of analogues obtained using base-hydrolyzed Al solutions showed
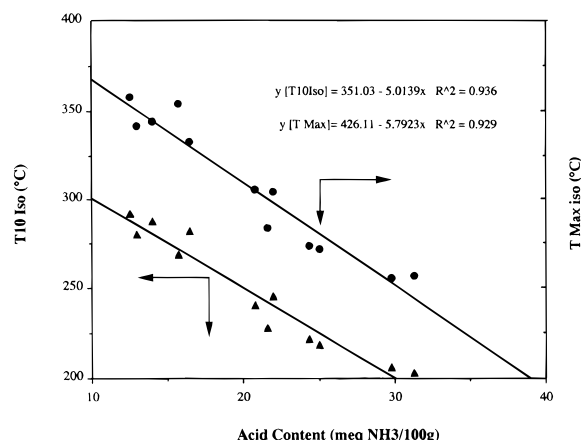
**Figure 7.** Relation between $T_{10iso}$ and $T_{max}$, and acid contents of different pillared clays.

that the interlayered pillars formed from either Al-chlorhydrol or Al$_{13}$ solutions have a better resistance to thermal treatments than those issued from base-hydrolyzed Al solution, which is consistent with the greater amounts of interlayered Al. Pillaring with solutions containing a surfactant did not result, contrary to expectations, in materials with improved properties.

The stacking order in the *c* direction of a pillared clay was found to be related to the stacking order of its Na form (as inferred from the half-height peak widths), which in turn was linked to the CEC. Higher micropore volumes characterized better ordered pillared materials, possibly due to a more regular distribution of the pillars.

In terms of acidity, Al-pillared saponites exhibited higher acid contents than pillared montmorillonites, and clays pillared with Al-chlorhydrol and Al$_{13}$ solutions had slightly improved acid contents in comparison with those prepared with the standard solution. Adding a surfactant to the pillaring solution depressed the acid contents.

The catalytic results clearly established the superior performances of pillared saponites over pillared montmorillonites. The preparation method had only a limited influence on the catalytic properties, insofar as it modified the acid amounts of the pillared smectite. The different catalytic behavior has been interpreted in terms of type, strength, and amount of acid sites.

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