Solid acid catalysts from clays
Evaluation of surface acidity of mono- and bi-pillared smectites by FT-IR spectroscopy measurements, NH₃-TPD and catalytic tests

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Abstract

Alumina-pillared and double-pillared montmorillonite and saponite samples have been prepared and characterised from the point of view of their thermal stability, porosity and structure. Surface acidity was studied by ammonia TPD, iso-propanol conversion and n-butene skeletal isomerisation catalysis, and by FT-IR spectroscopy of the surface hydroxy-groups, and of adsorbed acetonitrile and pivalonitrile.

The data show that the alumina pillars of pillared montmorillonite carry stronger Lewis sites than those of pillared saponite. Additionally, stronger Brønsted sites are carried by the montmorillonite layers with respect to those of saponite. Finally, pillared montmorillonite is more active in converting iso-propanol. However, it is also too active in converting n-butene, so giving rise to faster coking and more extensive cracking. So, pillared saponite has a more selective behavior in converting n-butene into iso-butene. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Smectite clays are sheet silicates in which the basic building blocks are Si(O, OH) tetrahedra and M(O, OH) octahedra (M = Al, Mg, Fe). Among smectite clays, montmorillonites and saponites are the most widely present in nature. In saponites Al for Si substitution occurs in the tetrahedral sheets, while in montmorillonites Mg substitutes Al in the octahedral layer [1]. Cation substitution results in a negative clay charge that, in the former case is very localized, whereas in the latter is delocalized on the layer. Exchanging the charge-compensating cations of a smectite clay with an oligomeric polyoxy-metal cation results in a two-dimensional zeolite-like mate-
rial known as pillared clay (PILCs). Upon heating, the cationic pillars form oxide clusters that permanently open the clay layers, creating an inter-layer space of molecular dimensions and a well-defined pore system. Clays pillared with aluminum polyoxycations like the [Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$]$^7^+$ Keggin-type ion, are the most documented and easy to prepare in a reproducible way [1–4]. The pillaring process is known to generate Brønsted and Lewis acid centres in the inter-layer region of the clay. The nature and strength of the acid sites depend upon the starting clay and the pillaring agent. If the pillaring process is repeated on a pillared clay, the cation exchange capacity (CEC) of which was previously restored, both thermal stability and the number of acid sites were found to increase [5]. The intercalation of the aluminum Keggin ion between the layers, and the following pillaring process, is quite different in the tetrahedrally substituted saponite and in the octahedrally substituted montmorillonite [6–8]. In montmorillonites the proton released during calcination can migrate into the octahedral sheets’ vacant sites but this does not occur in saponites, where they remain located in the inter-layer spacing. Moreover, pillars in pillared saponite are presumably strongly anchored to the layer by covalent Al–O–Al as proposed by various authors [9–11] while in pillared montmorillonites there is no evidence of this pillar/layer anchoring [6–8,11]. By analysing the pillaring process by molecular modelling, it was recently proposed [14] that a more homogeneous distribution of the pillars must be achieved in pillared tetrahedrally Al/Si-substituted smectites. The surface acidity of these materials has been the object of various studies, mainly making use of FT-IR measurements [9–13,15]; nevertheless several questions are still debated. Nitrile compounds can be successfully used as a probe to characterise both Brønsted and Lewis acid sites, but their adsorption was not studied previously on pillared clays.

Moreover, the extent of the shift of the OH stretching band caused by the H-bonding of the nitrile with surface OHs can be taken as a measure of the strength of this interaction, and consequently, of the strength of the OH group as a Brønsted site [12,15–18]. Pivalonitrile adsorption allows investigation of the cavity dimension because this bulky molecule does not enter into cavities with diameter smaller than 6 Å [19].

Another widely used way to study the surface acidity of a solid catalyst is through the product distribution analysis of some model catalysed reactions [20]. The n-butene isomerisation is one of the model reactions most used, because of its great simplicity.

On the other hand, the catalytic decomposition reaction of iso-propanol has long been regarded as one of the typical reactions for investigating the acid–base properties of the catalytic sites of metal oxides. The catalysts can be classified with regard to their propensity toward the dehydration or the dehydrogenation activity to propene or to acetone, respectively.

In this work we will correlate the catalytic activity of mono- and bi-pillared saponite (APS and AP2S) and montmorillonite (APM and AP2M) samples in the n-butene isomerisation and iso-propanol conversion with the FT-IR analysis of the acid sites of their surface, before and after adsorption of pivalonitrile and acetonitrile vapours.

2. Experimental

2.1. Materials

The clays used in this study were two different smectites:

1. Detercal P1$^{TM}$ is a natural calcium-rich bentonite (montmorillonite 97%) of North African origin (Nador, Morocco), used as received from Industria Chimica Carlo Laviosa S.p.A. (Livorno, Italy). (CEC = 84 meq/100 g). Unit cell formula: $\text{Ca}_{0.13}\text{Na}_{0.43}\text{K}_{0.15}\left(\text{Si}_{7.56}\text{Al}_{0.44}\right)\left(\text{Al}_{3.23}\text{Fe}_{0.22}\text{Mg}_{0.54}\right)\text{O}_{20}\left(\text{OH}\right)_{4}$.

2. Saponite C27 is a natural saponite used as received from Tolsa (Spain). (CEC = 80 meq/100 g). Unit cell formula: $\text{Ca}_{0.28}\text{Na}_{0.09}\text{K}_{0.04}\left(\text{Si}_{7.28}\text{Al}_{0.71}\right)\left(\text{Fe}_{0.08}\text{Mg}_{5.88}\right)\text{O}_{20}\left(\text{OH}\right)_{4}$. 


Chlorhydrol™ is a commercial 5/6 basic aluminum chloride salt (ACH) produced by Reheis and was kindly given by Eigenmann & Veronelli (Milano).

Acetone 99% is a technical grade reagent from Janssen Chimica.

2.2. Preparation of mono- and bi-pillared clays

2.2.1. Preparation of the aluminum pillared montmorillonite (APM)

20 g of natural calcium montmorillonite clay were swollen in acetone (50% w/w). The suspension was aged for 17 h at room temperature. An aqueous solution of Chlorhydrol (50 wt%) was added to the clay suspension (30 meq Al/g) under stirring at room temperature. The suspension was shaken in an high-speed orbital shaker for 24 h at room temperature, centrifuged and washed with a total of 20 ml/g of water. The washing–centrifuging procedure was repeated for four cycles. A thin film of the resulting pillared clay was air-dried at 333 K, finely ground (>40 mesh) and calcined for 18 h at 673 K in a ventilated oven.

2.2.2. Preparation of aluminum pillared saponite (APS)

The preparation was carried out similarly to that described for APM, except that a natural calcium-rich saponite was used as starting clay.

2.2.3. Preparation of aluminum bi-pillared clays (AP2M, AP2S)

APM and APS pillared clays, after the restoration of the cation exchange capacity (CEC) by treatment with NH₃ vapours, were re-intercalated with aluminum polyoxycations to give respectively the AP2M and AP2S re-pillared derivatives. The cross-linking process was carried out similarly to what described for the APM preparation. A thin film of the resulting cross-linked pillared clay was then air-dried at 333 K, finely ground (>40 mesh) and calcined for 18 h at 673 K in a ventilated oven.

2.3. Characterization methods

2.3.1. Elemental analyses

Elemental analyses were accomplished by Atomic Adsorption Spectroscopy with a Perkin-Elmer PE 3100 instrument.

2.3.2. Nitrogen adsorption/desorption

Adsorption–desorption experiments using N₂ were carried out at 77 K on a Sorptomatic 1900 Carlo Erba porosimeter. Before each measurement the samples were outgassed at 423 K and 1.33 × 10⁻³ Pa for 6 h. The N₂ isotherms were used to determine the specific surface areas (SA) using the BET equation. The α-plot method was used to calculate the micropore volume. The starting clay was used as reference material.

2.3.3. X-ray diffraction spectra

X-ray diffraction spectra were measured with a Philips diffractometer using Cu Kα radiation. The samples were disc-shaped pressed powders and were previously treated at 673 K in a ventilated oven.

2.3.4. FT-IR spectroscopy measurements

The IR spectra were recorded on a Nicolet Magna 750 Fourier Transformation Instrument, using pressed disks of pure catalyst powders, activated by outgassing at different temperatures into the IR cell.

2.3.5. NH₃-TPD (ammonia temperature-programmed desorption)

The total acidity of the pillared samples was determined by temperature-programmed desorption of ammonia (NH₃-TPD). Before the adsorption of ammonia the samples were treated under helium at 773 K (from 298 to 773 K in 20 m) for 1 h. The samples were then cooled at 373 K in He flow, then treated with a NH₃ flow for 5 m at 373 K. The physisorbed ammonia was eliminated by flowing He for 1 h at 573 K. The NH₃-TPD was run between 373 and 773 K at 10 K/min and followed by an on-line gas chromatograph provided with a thermal conductivity detector.

2.3.6. Catalytic 1-butene isomerisation test

Catalytic 1-butene isomerisation tests were performed in a tubular glass flow microreactor. The catalyst samples were pre-treated for 2 h in N₂ flow at 673 K. Experiments were performed at \( \tau = 2.4 \frac{\text{g(cat)}}{\text{g(1-butene)}} \cdot \frac{1}{\text{h}} \). The 1-butene was at 5% abundance in nitrogen and the time-on-stream was 120 min. The unconverted 1-butene and the reaction products were analyzed on-line in a gas chromatograph (HP 5890 series II) equipped with a wide-bore
Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_{001}) (nm)</th>
<th>SA (m(^2)/g)</th>
<th>(V\mu) (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APM</td>
<td>1.87</td>
<td>370.0</td>
<td>0.16</td>
</tr>
<tr>
<td>AP2M</td>
<td>1.87</td>
<td>252.1</td>
<td>0.10</td>
</tr>
<tr>
<td>APS</td>
<td>1.88</td>
<td>308.8</td>
<td>0.14</td>
</tr>
<tr>
<td>AP2S</td>
<td>1.87</td>
<td>283.5</td>
<td>0.13</td>
</tr>
</tbody>
</table>

KCl/AlCl\(_3\) column (\(\phi = 0.53\) mm, \(l = 50\) m) and a flame ionization detector (FID).

The amount of coke was deduced from the weight loss of the spent catalyst during burning in air in the range 363–1073 K, measured by thermogravimetry (TG).

2.3.7. Catalytic iso-propanol dehydration test

The catalytic activity of the samples in the decomposition reaction of iso-propanol was tested at 493 K in a fixed-bed tubular glass microreactor at atmospheric pressure using about 30 mg of catalyst without dilution. The iso-propanol was fed into the reactor by bubbling a flow of helium through a saturator–condenser at 303 K, which allowed a constant flow of 25 cm\(^3\)/min with 7.4% of iso-propanol and space velocity of 41 m\(^3\)/mol g\(^{-1}\) s\(^{-1}\). Before the catalytic test, the samples were pre-treated at 493 K in helium flow for 2 h and then kept for 1 h at 493 K under a static helium atmosphere. The gas carrier was passed through a molecular sieve trap before being saturated with iso-propanol. The reaction products were analysed by an on-line gas chromatograph provided with a FID and a fused silica capillary column SPB1.

3. Results and discussion

3.1. Pillared clays characterisation

3.1.1. Analytical data

In Table 1 some structural (\(d_{001}\) basal spacing) and textural data (BET surface area and micropores volume) of the pillared and re-pillared samples are summarised.

The pillared clays exhibit the typical \(d_{001}\) basal spacing of an Al-pillared clay in their X-ray diffraction patterns (Fig. 1) that is also kept after the re-pillaring of the samples. The pillared clays have a good BET surface area that decreases after re-pillaring. As is shown by porosity data, the re-pillared montmorillonite AP2M loses about the 40% of its microporous volume compared to the mono-pillared derivative, while only 7% is lost by the re-pillared saponite sample.

3.1.2. \(NH\textsubscript{3}\)-TPD measurements

The \(NH\textsubscript{3}\)-TPD method, widely employed to characterize the acidity of solid catalysts, lacks in selectivity, because ammonia can titrate acid sites of any strength and type. Moreover, the ammonia molecule can be adsorbed by a hydrogen bond or a dipolar interaction. In Table 2 the acidity data (\(\mu\)mol g\(^{-1}\)) determined by Temperature-Programmed Desorption of ammonia (\(NH\textsubscript{3}\)-TPD) of the pillared and re-pillared samples are reported.

The samples were pre-treated at 873 K and the desorption of ammonia was run between 373 and 873 K, to allow the total evacuation of \(NH\textsubscript{3}\) molecules. Among the clay samples the mono-pillared saponite, APS, shows the higher value of total acidity on mass basis. However, the total acidity of montmorillonite calculated per unit area increases strongly by double pillaring, while that of saponite strongly decreases by double pillaring. In other words, according to these data, considering also the relative amounts of ammonia desorbed at different temperatures (this being a measure of the strength of the adsorbing site) the pillars of montmorillonite carry stronger sites than the layer surface, while the reverse is observed for saponites. In fact, double pillaring increases the amount of ammonia desorbing at the highest temperatures from montmorillonite, while in the case of saponite the number of the strongest sites decreases strongly. In all the samples the majority of \(NH\textsubscript{3}\) (about 40%) desorbs between 473 and 573 K.

3.2. FT-IR spectroscopy studies

3.2.1. Pillared montmorillonites

3.2.1.1. Surface hydroxy groups. The IR spectrum in the OH stretching region of the starting montmorillonite sample, after outgassing at 673 K, is reported in Fig. 2a.
The spectrum shows two bands, with different intensities. The band near 3740 cm$^{-1}$ is attributable to the silanol groups (Si–OHs) of the edge or defect sites of the external layer surface, while the broader band centred near 3650 cm$^{-1}$ is due to Al$_2$OH groups of the octahedral layer [13]. The IR spectra in the OH stretching region of the two pillared montmorillonites, after outgassing at 673 K, are shown in Fig. 2b and c, respectively. The spectra are similar to those of the parent material, but an increase of the relative intensity of the band near 3740 cm$^{-1}$ (external silanols) was observed with respect to that of the Al octahedral OHs. A broadening of this band with the formation of a tail towards lower frequencies, together with a slight shift upwards of the main maximum was also observed. This can be interpreted as an effect of pillaring, that generates in the inter-layer region a new system of micropores where silanol groups similar to those of the ‘external’ surface are exposed. The formation of alumina pillars is probably responsible for the further broad absorption in the region 3700–3000 cm$^{-1}$.

These effects are more evident in the double-pillared than in the mono-pillared sample.

3.2.1.2. Interaction of pivalonitrile (PN) and acetoni-trile (AN) with the surface hydroxy-groups. The IR spectra, at room temperature, in the OH stretching region of the starting montmorillonite and of the two pillared montmorillonite derivatives, upon adsorption and desorption of PN, are reported in the Fig. 3 (top). It is evident that, in all cases, upon adsorption of PN, the band at 3740 cm$^{-1}$ decreases in intensity, while the band near 3650 cm$^{-1}$ is not affected. This confirms that the former band is due to external OHs (silanols), while the latter is due to ‘internal’ OHs of the octahedral layer, that are unavailable for H-bonding with PN. However, the band due to external OHs fully disappears in the case of unpillared montmorillonite while it decreases only in part in the mono-pillared, and

<table>
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<th>Sample</th>
<th>Total acidity (μmol/g)</th>
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<th>473–573 K</th>
<th>573–673 K</th>
<th>673–773 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>APM</td>
<td>755</td>
<td>30</td>
<td>293</td>
<td>250</td>
<td>182</td>
</tr>
<tr>
<td>AP2M</td>
<td>786</td>
<td>31</td>
<td>307</td>
<td>262</td>
<td>186</td>
</tr>
<tr>
<td>APS</td>
<td>938</td>
<td>45</td>
<td>375</td>
<td>283</td>
<td>235</td>
</tr>
<tr>
<td>AP2S</td>
<td>650</td>
<td>44</td>
<td>258</td>
<td>189</td>
<td>159</td>
</tr>
</tbody>
</table>
Fig. 2. FT-IR spectra of (a) the montmorillonite, (b) APM pillared montmorillonite and (c) AP2M bi-pillared montmorillonite in the OH stretching region (4000–2600 cm\(^{-1}\)) after outgassing at 673 K.

in particular in the bi-pillared montmorillonites. This indicates that double pillaring causes the formation of cavities some of which, although containing free silanols, are too small to be entered by PN. The formation of a new component centred at about 3200 cm\(^{-1}\), due to the silanols of the inter-layer space interacting with PN via H-bonding, is evident in the subtraction spectra of the pillared samples (Fig. 4, left, c–f). In the case of unpillared montmorillonite a band at 3460 cm\(^{-1}\) is found (Fig. 4, left, a). This suggests that pillaring with alumina causes an increase of the acid strength of the OHs of the inter-layer region, possibly because of the strong perturbation by the Al\(^{3+}\) of the pillars. In the case of the double-pillared sample, a small fraction of the OHs absorbing near 3650 cm\(^{-1}\) could also participate in H-bonding, according to the subtraction spectra (Fig. 4, left, e,f). In all cases, outgassing at room temperature gradually restores the spectra of the activated samples, in particular the band at 3740 cm\(^{-1}\).

The IR spectra in the OH stretching region of the montmorillonite sample and of the two-pillared montmorillonites after AN adsorption and desorption, at room temperature, are reported in the Fig. 3 (bottom).

Features similar, but not identical, to those reported for PN adsorption, are observed for the montmorillonite sample interacting with AN (Fig. 3 AN, a,b). After adsorption of AN, the band at 3742 cm\(^{-1}\) disappears, the band near 3650 cm\(^{-1}\) is only in part affected and the band at 3440 cm\(^{-1}\), due to the external silanols interacting with AN via H-bonding, is very broad (Fig. 4, right, a). The spectra arising from AN adsorption on pillared samples (Fig. 3 AN, c–f) show that, also on these samples, both the external OHs and those of the inter-layer space are involved in AN interaction. This behaviour, that is quite different from that observed for PN adsorption, indicates that the less bulky AN molecule is able to interact with the OHs of the micropores surface also.

AN adsorption leads to the formation of a broad band with two components near 3420 and 3200 cm\(^{-1}\) for both single- and double-pillared samples, as can be observed in the subtraction spectra of Fig. 4, right. The shifts of the OH stretching band, measured upon ad-
Fig. 3. FT-IR spectra in the OH stretching region (4000–2600 cm$^{-1}$) recorded after pivalonitrile adsorption (PN top) and from acetonitrile adsorption (AN bottom), on the montmorillonite (a,b), APM pillared montmorillonite (c, d) and AP2M bi-pillared montmorillonite (e,f) and after successive outgassing at room temperature (b,d,f).

sorption of both PN and AN on external OHs ($\Delta \nu = ca$ 300 and $ca$ 500 cm$^{-1}$) indicate that normal silanols are present on the external surface of unpillared montmorillonite. In fact, the shift observed in this sample is similar to that reported in the literature for the pure silica samples [21,22]. This band, can be reasonably assigned to the following H-bonded species [16].

However, stronger Bronsted acid sites are present at the surface of the pillared samples. Nevertheless, they are apparently weaker than those characterizing the most active sites of amorphous and mesoporous silica–aluminas [19,23].

3.2.1.3. Interaction of pivalonitrile (PN) and acetonitrile (AN) with surface sites. Analysis of the $\nu$C≡N modes. The spectra of PN adsorbed on the starting montmorillonite sample and on the two pillared mont-
morillonites derivatives in the CN stretching region are reported in Fig. 5 (left).

The spectrum of PN adsorbed on montmorillonite (Fig. 5 PN, a,b) shows bands at 2300, 2250 and 2235 cm\(^{-1}\). By comparison with previous data and looking at the stability of the species upon outgassing, we can assign the band at 2235 and at 2250 cm\(^{-1}\) to two different H-bonded species over non-acidic and weakly acidic OHs, while the weak band at 2300 cm\(^{-1}\) observed here behaves in parallel with the previous ones, and is due to a weak overtone band observable in the spectra of both liquid and weakly adsorbed PN.

Pillaring of montmorillonite heavily changes the nature of the surface, with the appearance of a strong concentration of Lewis sites. In fact, a strong band at 2290 cm\(^{-1}\), with a shoulder near 2275 cm\(^{-1}\) appears for the single-pillared sample (Fig. 5 PN, c,d), certainly due to PN bonded to strong alumina-like Lewis acid sites. In particular, the band at a higher frequency must be assigned to species interacting with very strong Lewis sites, likely Al\(^{3+}\) on partly unsaturated coordination, like those of transitional alumina [24]. In the case of the double-pillared sample (Fig. 5 PN, e,f), this band is further shifted to 2296 cm\(^{-1}\) while a second component, also very strong, appears at 2262 cm\(^{-1}\). These bands, that can be due to PN adsorbed on aluminum pillars, are similar to those found on pure transitional aluminas. It can be deduced, on the basis of their Lewis acidity, that the pillars have a structure similar to that of spinel-type aluminas, at least from the point of view of surface Lewis acidity.

Outgassing at room temperature causes the almost complete disappearance of the band at 2235 cm\(^{-1}\), while the bands at about 2290 and 2260 cm\(^{-1}\) become predominant in all cases. The last band, in the case of the mono-pillared sample, is more intense in comparison with that observed on the bi-pillared sample.

The spectra, in the CN stretching region, of AN adsorbed on unpillared montmorillonite and on its pillared derivatives are reported in Fig. 5 (right). For each sample the upper spectra are those recorded in contact with AN gas (the gas-phase spectrum is subtracted).
Fig. 5. Subtraction FT-IR spectra in the CN stretching region (2500–2000 cm\(^{-1}\)) of the adsorbed species arising from pivalonitrile adsorption (PN left) and from acetonitrile adsorption (AN right), on the montmorillonite (a,b), APM pillared montmorillonite (c,d) and AP2M bi-pillared montmorillonite (e,f) and after successive outgassing at room temperature (b,d,f).

while the lower one was recorded after outgassing. In this region liquid AN shows a strong doublet at 2294, 2254 cm\(^{-1}\), the latter band being definitely more intense than the former. The bands are originated by the Fermi resonance between the C≡N stretching and a \(\delta\)CH\(_3\) + νC–C combination \([25]\). The spectrum of the montmorillonite (Fig. 5 AN, a, b), in the presence of the gas, showed the bands due to AN molecularly adsorbed at 2297 and 2255 cm\(^{-1}\), the latter, with a shoulder at 2260 cm\(^{-1}\), being apparently split into two components. The slight upwards shift of both components, with respect to the liquid, agrees with a weak electron withdrawal from the nitrogen lone pair, caused by medium–weak hydrogen bonding. Outgassing at room temperature causes the disappearance of the band at 2255 cm\(^{-1}\), while the band at 2294 cm\(^{-1}\) persists and is shifted to lower frequency (2291 cm\(^{-1}\)). After outgassing it appears that the other doublet is actually a couple of doublets with components at 2330, 2295 and 2310, 2280 cm\(^{-1}\). According to the work of Krietenbrink et al. \([26]\) the higher frequency doublet is due to AN coordinated on tetrahedral Al\(^{3+}\) cations. This is confirmed by the analysis of the spectra observed on alumina samples \([23]\), which also presents such a doublet after outgassing. The doublet at 2310, 2280 cm\(^{-1}\) is associated to octahedral Al\(^{3+}\) ions. Similar features are also observed for the acetonitrile interaction with the bi-pillared sample (Fig. 5 AN, e, f).
The main difference with the mono-pillared sample is that the two bands at 2310 and 2280 cm\(^{-1}\) are relatively more pronounced showing again that a higher concentration of octahedral Al\(^{3+}\) exists on this sample.

3.2.2. Pillared saponite

3.2.2.1. Surface hydroxy groups. The IR spectra in the OH stretching region (4000–2600 cm\(^{-1}\)) of the commercial saponite and of the pillared saponite samples after activation at 673 K, are reported in Fig. 6. In agreement with Lambert et al. [9,11], the saponite shows two bands with different intensity ratios (Fig. 6a).

The band near 3740 cm\(^{-1}\), sharp and weak, is due again to silanol groups (Si–OHs) exposed in defect sites of the external layer surface, while the stronger peak at 3675 cm\(^{-1}\) is due to the octahedral Mg\(_3\)OH groups of the lattice. The higher frequency and sharpness of the ‘internal’ OHs of the saponite lattice with respect to those of the montmorillonite can be likely related to the lower H-bonding perturbation exerted on such groups by the neighbouring OHs or by the nearest oxygen atoms, probably associated to their lower acidity.

The spectra in the OH stretching region of the two pillared saponites (Fig. 6b, c) are similar to those of the parent material, but we clearly observe an increase of the absorption in the region 3750–3600 cm\(^{-1}\) with, in particular, the appearance of some absorption between the two main peaks and of a tail towards lower frequencies. These are likely due to OHs at the surface of the aluminum pillars.

3.2.2.2. Interaction of pivalonitrile (PN) and acetoni- trile (AN) with the surface hydroxy groups. The IR spectra, in the OH stretching region, of the commercial saponite sample and of the two pillared saponites upon adsorption and desorption of PN, are reported in the Fig. 7 (top).

It is evident in all cases, that, upon adsorption of PN, the band at 3740 cm\(^{-1}\) disappears, while the band near 3675 cm\(^{-1}\) is not affected. This confirms that the former band is due to external OHs (silanols) available for H-bonding with PN, while the latter is due to the unavailable structural ‘internal’ OHs. The formation of weak new components centred at 3480 cm\(^{-1}\) can only be observed looking at subtraction spectra. These components are due to the external
silanols interacting with PN via H-bonding. The shift is a little bit lower than that observed on pure silica (ca. 3400 cm$^{-1}$). The IR spectra in the OH stretching region of the commercial saponite sample and of the two pillared saponites upon adsorption and desorption of AN are reported in the Fig. 7 (bottom). AN adsorption on saponite causes the disappearance of the band at 3740 cm$^{-1}$, while the band at 3675 cm$^{-1}$ seems not to be involved in this interaction. A new broad band centered at about 3450 cm$^{-1}$ becomes visible in the subtraction spectra. Outgassing at increasing temperature restores progressively the original spectrum. Similar features are observable in the pillared samples. These results show that silanol groups (Si–OHs) exposed on the external layer surface in edges and/or defect sites interact with AN, while Mg$_3$OH groups in the lattice are not accessible and do not interact. The response of AN and PN adsorption is identical showing that, unlike what was observed on pillared montmorillonite, in the case of pillared saponites no OHs unavailable to PN, but available to AN, exist.
3.2.2.3. Interaction of pivalonitrile (PN) and acetonitrile (AN) with the surface sites. Analysis of the $\nu$C≡N modes. The spectra of PN adsorbed on the commercial saponite sample and on the two pillared saponites are reported, in the CN stretching region, in Fig. 8 (left). In the case of PN adsorbed on ‘pure’ saponite (Fig. 8 PN, a,b) we find three components, at 2235, 2260 and 2278 cm$^{-1}$. The stability of the corresponding species under outgassing is, as expected, stronger the higher the corresponding CN stretching frequency. By comparison with the previous data and looking at the stability of the species (Fig. 8 PN, a), we can assign the band at 2235 cm$^{-1}$ to H-bonded species over non-acidic external OHs, while the two components at higher frequencies can be assigned to species adsorbed on Lewis acid sites. The band at 2278 cm$^{-1}$ should be assigned to species interacting with quite strong Lewis sites, likely surface-pentacoordinated Al$^{3+}$, while the band at 2260 cm$^{-1}$ could be due to exposed Mg$^{2+}$ ions, in surface defects.

Pillaring of saponite causes the band near 2278 cm$^{-1}$ to grow very much, while that near 2260 cm$^{-1}$ apparently disappears. The relative intensity of the band at 2278 cm$^{-1}$ increases with respect to that at 2235 cm$^{-1}$, showing that the Lewis-to-Bronsted acid site ratio increases by pillaring, as was observed for the pillared montmorillonite samples and in previous studies [9,11]. However, the data show that apparently the pillars in pillared montmorillonite samples have predominantly Lewis acid sites stronger (band at 2290 cm$^{-1}$) than those of pillared saponite (band at 2278 cm$^{-1}$). Pillars in pillared montmorillonite apparently resemble the spinel-type alumina while pillars in pillared saponite are more similar to the octahedrally coordinated aluminum of the Keggin-type pillaring polycation. In Al-pillared saponites there is a contribution to Bronsted acidity due to the OH groups of the pillars and, possibly, to the accessible OHs of the layers.

The spectra of AN adsorbed on the commercial saponite sample and on the two-pillared saponites are reported, in the CN stretching region, in Fig. 8 (right). For each sample the upper spectra are those recorded in contact with AN gas (the gas-phase
Table 3
Catalytic activity data in the dehydration of iso-propanol for mono- and bi-pillared samples

<table>
<thead>
<tr>
<th>Activity (µmol g⁻¹ s⁻¹)</th>
<th>APM</th>
<th>APS</th>
<th>AP2M</th>
<th>AP2S</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.05</td>
<td></td>
<td></td>
<td>23.55</td>
<td>15.87</td>
</tr>
<tr>
<td>0.060</td>
<td>0.059</td>
<td>0.093</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>Conversion(%)</td>
<td>46.72</td>
<td>38.67</td>
<td>49.40</td>
<td>33.63</td>
</tr>
</tbody>
</table>

spectrum is subtracted) while the lower one was recorded after outgassing. On the saponite (Fig. 8 AN, a,b), in the presence of the gas, we found the bands due to AN molecularly adsorbed at 2290 and 2255 cm⁻¹, with the last band apparently split into two components, the more important of which is that at 2275 cm⁻¹. As found for montmorillonite samples the slight shift upwards of the higher component agrees with a weak electron withdrawal from the nitrogen lone pair, as it occurs upon a medium–weak hydrogen bonding, like that of the species I-AN. A new band also appears in the presence of the gas near 2310 cm⁻¹, assignable to AN coordinated on tetrahedral Al³⁺ cations [26] already present in saponite. In fact, in the pillared saponite samples in the presence of AN gas, we observed three main bands at 2315, 2290 and 2255 cm⁻¹, where the last two are due to AN weakly adsorbed, while the first is due to AN coordinated on Al³⁺ sites exposed on the pillars. In agreement with the increased number of pillars, the bi-pillared sample shows a more intense peak at 2315 cm⁻¹ with respect to the mono-pillared one. In all cases outgassing at room temperature causes the disappearance of the bands of H-bonded AN while the bands near 2315 and 2290 cm⁻¹ remain, confirming the observations reported above for PN adsorption.

3.3. Reactivity studies

3.3.1. Iso-propanol decomposition test

The conversion of iso-propanol is a widely used reaction to test the acid–base and redox properties of catalysts. The reaction, that does not need strong acid sites, can give disopropyl ether, propene and acetone as products. Propene is produced by Lewis and Brønsted acid-catalysed dehydration while ether formation must involve an inter-molecular coupling reaction. Finally, acetone is formed in the presence of basic or redox sites via oxidative dehydrogenation [27]. In Table 3 and Fig. 9 the catalytic activity data are reported for both mono- and bi-pillared samples (in all cases the selectivity to propene is 100%).

APM and AP2M show higher activity (on weight basis) than APS and AP2S. On surface area basis, pillared montmorillonite and saponite have the same activity, which is definitely increased (by a factor 1.5) by double pillaring only in the case of montmorillonite. This suggests that the activity of APM is mainly associated to the pillar surface that contains strong Lewis acid sites. The lack of increase in activity of APS by double-pillaring agrees with the weaker sites present at the pillar surfaces and possibly suggests that the saponite layers or the defects can also be involved in the reaction. In any case, the data of isopropanol conversion fully agree with those of ammonia TPD showing a definite increase of acidity by double-pillaring of montmorillonite and a decrease of acidity by double pillaring of saponite, on surface area basis.
Table 4
Product distribution (wt%) for the 1-butene conversion on the pillared clays

<table>
<thead>
<tr>
<th>Sample</th>
<th>Product gas composition (%)</th>
<th>Conv (%)</th>
<th>(S_{L}^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C3</td>
<td>Iso-butane</td>
<td>N-butane</td>
</tr>
<tr>
<td>APM</td>
<td>3.36</td>
<td>0.97</td>
<td>0.44</td>
</tr>
<tr>
<td>AP2M</td>
<td>1.65</td>
<td>0.58</td>
<td>0.35</td>
</tr>
<tr>
<td>APS</td>
<td>2.66</td>
<td>0.99</td>
<td>0.44</td>
</tr>
<tr>
<td>AP2S</td>
<td>3.10</td>
<td>1.91</td>
<td>0.57</td>
</tr>
</tbody>
</table>

\(a 100 \times (\text{wt\% iso-butene})_{\text{effluent}}/(\text{wt\% n-butenes})_{\text{feed}} - (\text{wt\% n-butenes})_{\text{effluent}}\).

3.4. Catalytic 1-butene isomerisation test

The distribution of some of the reaction products (iso-butene, n- and iso-butanes, and the products of coking) can give some information on the strength and type of the acid sites. In Table 4 the distribution of the products of the reaction, the percentage of conversion and selectivity to iso-butene are summarised.

In Table 5 we give the evaluation of the total amount of the skeletal isomerisation products (the amount of iso-butene is added to that of iso-butane, assuming that iso-butane originates from iso-butene) versus the total BET surface area of the samples.

As shown in Tables 4 and 5, after 120 min on stream APS converts less than APM. However, the selectivity to isobutene is definitely higher on APS than on APM. On the other hand, definitely more coke and also more cracking products (C3 and C5) are formed on APM than on APS. Double-pillaring causes a definite decrease in activity with respect to mono-pillared montmorillonite, with also a definite decrease in the formed coke, without important decrease in iso-butene selectivity. On the contrary, double-pillaring results in an increase in activity with respect to mono-pillared saponite, with a further small increase in selectivity also. The higher activity of pillared montmorillonites with respect to saponites, with the detrimental effect of more coking, more deactivation and more cracking, agrees with the detection, on such samples, of stronger Brønsted acid sites that are strongly perturbed by nitriles. In fact, it seems quite ascertained that the active sites for olefin skeletal isomerisation are Brønsted sites [23]. These sites are silanols, but their acidity can be enhanced by the presence of alumina-like pillars. These sites are possibly located in the intersection between the layers and the pillars. The activity of saponite, weaker but for this reason more selective towards iso-butene, can be associated to Brønsted sites on the alumina pillars, according to the increase of activity with double-pillaring. In fact it has been shown that alumina can carry Brønsted sites of sufficient acidity to catalyze very selectively n-butene skeletal isomerisation to iso-butene [23,24].

4. Conclusions

The IR spectroscopy of adsorbed basic probe molecules and the catalytic isomerisation of 1-butene provide an evaluation of both the strength and the relative amount of Lewis and Brønsted acid sites of Al-pillared clays.

The data show that pillaring and, above all, re-pillaring with aluminum polioxocations a montmorillonite or a saponite clay deeply modify the type and strength of the acid sites of the internal surface of these porous materials.

The IR spectroscopy of the adsorbed nitriles on the starting clays shows that the montmorillonite presents, after thermal treatment, only weakly acidic surface OHs, identified as silanols, and does not show any surface Lewis acidity. The saponite, besides weakly acidic surface OHs, identified as silanols, presents two
types of very weak Lewis acid sites, identified as coordinatively unsaturated Al\(^{3+}\) and Mg\(^{2+}\) cations of the octahedral layer.

Al-pillaring of the smectites under study also makes available for the interaction with nitriles the silanols of the inter-layer space, some of them being more acid by interaction with the aluminum cations of the pillars. On the bi-pillared montmorillonite, the formed pores are too small and in part inaccessible to pivalonitrile. This does not occur in the case of the bi-pillared saponites.

Al-pillaring of both clays originates at Lewis acid centres, very likely located on Al cations on the pillar surface. Pillars in pillared montmorillonite are apparently structurally similar to spinel-type alumina, with strongly acidic tetrahedral Al\(^{3+}\) cations, while pillars in pillared saponite are more similar to corundum-type alumina, with less acidic octahedral Al\(^{3+}\) cations. This gives rise to higher conversion of iso-propanol on APM and AP2M than APS and AP2S, on surface area basis.

Both the pillared saponite derivatives are more selective than pillared montmorillonite samples towards the skeletal isomerisation of \(n\)-butenes, possibly due to the weak Bronsted acidity of the surface OH groups of the alumina pillars.

Pillared montmorillonite, in particular the bi-pillared derivative, resulted in having inferior performances in butene skeletal isomerisation, due to higher Bronsted acidity, mainly attributable to the protonic acid sites of the layer’s internal surface. This too-high Bronsted acidity of the layer silanol groups results in excessive coking and cracking, which are detrimental for olefin skeletal isomerisation activity. These data are in line with the previous ones concerning the catalytic activity of different materials belonging to the silica–alumina system [19,23].

The results of this work show the very complex acid–base behavior of these materials, where different kinds of Lewis and Bronsted sites are active, and also show that the analysis of the surface acidity made by using different methods (in this case IR spectroscopy, NH\(_3\)-TPD, iso-propanol conversion and butene skeletal isomerisation) needs a complex analysis of the conditions of measurements to allow obtaining of a reliable picture. In fact, some of the data obtained here are in apparent contrast with each other, but allow, if carefully analyzed, a reasonable interpretation.

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References