Novel pillared structures were synthesized from the intercalation of iron-substituted cubic silsesquioxanes in a sodium and an acid-activated montmorillonite nanoclay and evaluated as acid catalysts. Octameric cubic oligosiloxanes were formed upon controlled hydrolytic polycondensation of the corresponding monomer (a diaminoalkoxysilane) and reacted with iron cations to form complexes that were intercalated within the layered nanoclay matrices. Upon calcination iron oxide nanoparticles are formed which are located on the silica cubes (pillars) and on the surfaces of the clay platelets. Acid activation of the nanoclay was performed in order to increase the number of acid active sites in the pristine clay and thus increase its catalytic activity. A plethora of analytical techniques including X-ray diffraction, thermal analyses, Fourier transform infrared, Raman, Mössbauer and X-ray photoelectron spectroscopies and porosimetry measurements were used in order to follow the synthesis steps and to fully characterize the final catalysts. The resulting pillared clays exhibit high specific area and show significant catalytic activity in the catalytic dehydration of isopropanol.

6.1. Introduction

The field of engineering nanomaterials has a continuing need of well-defined building blocks that imbue functionality and allow for nanoparticle-by-nanoparticle assembly of a wide variety of materials with precise control over the nanoarchitecture.\textsuperscript{[1]}\textsuperscript{[2]}

Silsesquioxanes possess a pronounced aptitude to form three-dimensional cage-like highly symmetric frameworks known as polyhedral oligosilsesquioxanes (POSS) with cubic, hexagonal, octagonal, decagonal, dodecagonal or even open cage-like morphology.\textsuperscript{[3]}\textsuperscript{[4]}\textsuperscript{[5]} Cubic silsesquioxanes (cubes), synthesized from the hydrolytic condensation of the corresponding trifunctional organo-silicon monomers, is the most common polyhedral structure and provide the opportunity to design and “construct” materials with extremely well-defined dimensions and behaviour.\textsuperscript{[3]}\textsuperscript{[6]}\textsuperscript{[7]}\textsuperscript{[5]}\textsuperscript{[4]}\textsuperscript{[8]}\textsuperscript{[9]}\textsuperscript{[10]}\textsuperscript{[11]}\textsuperscript{[12]}\textsuperscript{[13]} In this context, cubic silsesquioxanes of the type $X_8Si_8O_{12}$ where $X$ is $-(CH_3)_3NH_2$, $-(CH_3)_3NR_2$ and $-(CH_3)_3NH(CH_2)NH_2$ have been successfully employed as precursor reagents for pillaring inorganic layered solids such as clays,\textsuperscript{[14]}\textsuperscript{[15]}\textsuperscript{[16]}\textsuperscript{[17]}\textsuperscript{[18]}\textsuperscript{[19]} metal (IV) hydrogen phosphates,\textsuperscript{[20]}\textsuperscript{[21]}\textsuperscript{[22]} photonic titanoniobates,\textsuperscript{[23]} graphenes and graphene oxide,\textsuperscript{[3]}\textsuperscript{[24]}\textsuperscript{[25]}\textsuperscript{[26]} graphene oxide nanoribbons,\textsuperscript{[27]} halloysite nanotubes\textsuperscript{[28]} and perovskites.\textsuperscript{[29]} Protonation of the amino groups generates oligomeric cationic species with expendable and bulky organic groups that can easily be inserted into the interlayer space of a phyllomorphous clay in amounts exceeding the cation exchange capacity of the mineral and can successively be removed by thermal treatment, resulting in silica pillared structures.\textsuperscript{[15]}\textsuperscript{[14]} This excess being in the form of physically adsorbed ion pairs influences the free distance between the layers and the surface area as well as the porosity of the silica-pillared composites.

On the other hand, these various mono- or bi-functional amino-silanes possess the ability to bind metal ions, $M^{n+}$ (e.g. Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{3+}$, Al$^{3+}$), yielding metal complexes, $M_n^{n+}[X_8Si_8O_{12}]_n$, and thus enabling the design and synthesis of metal complexes in which the redox active metal centre is coordinated to the functionalized group of the siloxane octamer.\textsuperscript{[22]} The resulting cationic complexes are expected to be
excellent pillaring precursors and may be further calcined to remove the organic side arms and produce cross-linked metal-substituted silica-pillared clays of high porosity and thermal stability. Upon calcination the metal ions may retain isolated as metal oxides located on both the clay surface and the pillar or may be integrated into the silica pillar. The clays pillared with metal oxide silica are solid acids with moderate or high Brønsted and Lewis acidity originating from acid sites located on the pillars and the clay surface; they can be used as acid catalysts in the range 100-600 °C, in which most catalytic reactions take place. Isopropyl alcohol decomposition is one example of a specific reaction where this type of pillared clay can be used as efficient catalyst. Furthermore the use of acid-activated clays instead of sodium-intercalated ones as efficient substrates for the synthesis of pillared structures could enhance the acid properties and subsequently their catalytic activity.\textsuperscript{[30]} \textsuperscript{[31]} \textsuperscript{[32]} \textsuperscript{[33]} \textsuperscript{[34]} \textsuperscript{[35]}

The first attempt to intercalate metal POSS in pillared structures was performed by Khattou \textit{et al.}\textsuperscript{[36]} \textsuperscript{[37]} who intercalated a Cu$^{2+}$-octa(diaminoalkyl) siloxane complex into a-zirconium phosphate and examined the pillaring materials obtained after calcination by electron paramagnetic resonance (EPR) spectroscopy. In this case the metal ions act as probe for the determination of the evolution of local symmetry and structure during the pillaring process when using an element specific technique.

More recently Carniato \textit{et al.}\textsuperscript{[38]} demonstrated the intercalation of a bifunctional protonated titanium-containing aminopropyl isobutyl POSS, within the interlayer space of a synthetic sodium saponite and its use as filler in a polystyrene-based nanocomposite designed to enhance the thermooxidative properties. The same group\textsuperscript{[39]} also intercalated Ti-containing aminopropylisobutyl polyhedral oligomeric silsesquioxane in synthetic saponite and investigated the catalytic activity of this composite in cyclohexene oxidation. Other catalysts based on clay-POSS hybrids include synthetic laponite clay first modified by octaaminopropyl polyhedral oligomeric silsesquioxane and then used to support a nickel alpha-diimine late-transition-metal catalyst for ethylene polymerization;\textsuperscript{[40]} laponite and
montmorillonite functionalized with (3-aminopropyl)triethoxysilane and use both as supports for the vanadyl(IV) acetylacetonate catalysis\cite{41} and POSS intercalated bentonites\cite{42} for metal uptake of copper, cadmium and lead.

In this work we report the intercalation of Fe$^{3+}$-substituted cubic silsesquioxanes in a sodium and an acid-activated montmorillonite to form novel catalytic pillared structures. A plethora of analytical techniques including X-ray diffraction (XRD), thermal analyses (DTA/TGA), Fourier transform infrared (FTIR), Raman, Mössbauer and X-ray photoelectron (XPS) spectroscopies and porosimetry measurements were used in order to follow the synthesis steps and to fully characterize the final catalysts. The resulting pillared clays exhibit high specific area and a narrow pore size distribution and show significant catalytic activity in the catalytic dehydration of isopropanol.

### 6.2. Results and Discussion

For the development of the catalytic pillared clays, a sodium montmorillonite (Na-T) and its acid activated form (HT) were used. Acid activation was performed in order to increase the number of acid active sites in the pristine clays and thus increase its catalytic activity during the dehydration of the isopropanol, which is an acid catalyzed reaction. For the pillaring solution, octameric cubic oligosiloxanes were formed upon controlled hydrolytic polycondensation of the corresponding monomer (EDAPT莫斯) in an ethanol-water mixture and immediately reacted with ferrous cations to form complexes of the type $\text{Fe}^{2+\chi}[\text{X}_\text{8Si}_8\text{O}_{12}]_\gamma$. The colour of the solution changed from pale orange to dark green, indicative of the complexation of ferrous cations with the amino functional group of the corresponding siloxane molecules. When the pillaring solution was added to an aqueous dispersion of the clay an immediate flocculation of clay particles was observed due to the insertion of complex in the clay galleries by ion exchange. The colour of the slurry changed gradually within 1 h after the addition of iron-complex from green to orange, pointing to the oxidation of Fe(II) to Fe(III).
Finally, intercalated samples were calcined at 500 °C in air to obtain pillared clays. The calcination procedure contributes to the removal of the organic chains of the organo-silane cubes and to the creation of iron oxide nanoparticles, which are immobilized on the silica cubes and on the surfaces of the clay platelets. A schematic representation of the experimental procedure is depicted in Figure 6.1.

X-ray diffraction was employed to reveal the successful intercalation of iron-silsesquioxane complexes as well as the formation of the pillared structures. The XRD patterns of intercalated samples (for both Na-T and HT clays) before and after calcination at 500 °C are displayed in Figure 6.2. The insertion of iron-silsesquioxane complexes between the aluminosilicate layers increases the interlayer distance. More specifically, for TFeED obtained by intercalation in Na-T clay, the basal d_{001}-spacing, which is 12.6 Å in the initial montmorillonite clay, becomes 18.2 Å after the modification; this corresponds to an interlayer separation of 18.2–9.6 = 8.6 Å, where
9.6 Å represents the thickness of a clay layer.\footnote{43} \footnote{44} This value is reasonable if we consider that the edge of the siloxane cube (Si-O-Si distance) is 6.0 Å\footnote{14} and, due to complexation with the ferric cations, the flexible organic chains adopt a inclined orientation between the clay layers. Moreover, the interlayer distance of 8.6 Å is actually higher compared to the one observed (7.1 Å) upon clay intercalation with this particular aminosiloxane not complexed with ferric cations.\footnote{42} Similar results were obtained for the acid-activated montmorillonite. The XRD pattern of the HTFeED sample (Fig.6 2b) shows a $d_{001}$ spacing of 17.2 Å, which corresponds to an interlayer separation of 7.6 Å. The interlayer distance in this case is slightly lower than for TFeED. However, a similar geometrical arrangement must be adopted in this case too with the flexible side chains of the siloxane cubes in an inclined orientation with respect to the aluminosilicate platelets. Upon calcination at 500 °C, the $d_{001}$ spacing was decreased to 16.3 and 15.4 Å, for TFeED-500 and HTFeED-500 respectively, indicative of the removal of the side organic groups of the siloxane cubes and the subsequent reduction in the interlayer distance. Moreover, the absence of reflection peaks of the crystalline phase of iron oxides (see below) in the 2$\Theta$ region 2-80° indicates that iron oxide nanoparticles produced upon calcination are small enough and are not aggregated on the external clay surfaces but rather homogeneously dispersed in the clay matrix.

\textbf{Figure 6.2.} X-ray diffraction patterns of intercalated clay samples, TFeED and HTFeED, and the corresponding pillared structures produced upon calcination, TFeED-500 (left) and HTFeED-500 (right). Insets: pristine clays, Na-T and HT.
Figure 6.3 shows the infrared spectra of the pristine acid activated clay (HT) and of HTFeED and HTFeED-500; the spectrum of the Fe-EDAPTMOS complex which was obtained as solid (orange) after the centrifugation of the complex solution during the synthetic procedure, is also shown. The infrared spectrum of HT consists of three absorption bands at lower frequencies (below 1300 cm\(^{-1}\)); the first, at 1000-1200 cm\(^{-1}\) corresponds to stretching vibrations of Si-O-M bridges (where M= Si, Al, Mg, Fe), the second one at 800-1000 cm\(^{-1}\) to vibration modes of the OH groups of the octahedral layers and the third at 400-700 cm\(^{-1}\) to bending vibrations of the Si-O-Si and Si-O-Al bridges of the clay framework.\(^{[45]}\) These same bands are also present in the spectrum of HTFeED. The NH\(_2\) deformation of the aliphatic chains of the silicon cubes, expected at 1620 cm\(^{-1}\), is superimposed on the broad band at 1650 cm\(^{-1}\), which arises from the vibrations of interlayer water. Analogously the asymmetric stretching band of Si-O-Si linkages of the polysiloxane in the 1000-1200 cm\(^{-1}\) region (Fig. 3d) is not clearly distinguishable in the intercalated clay composites (Fig. 3b and c) due to the existence of the same type vibrations (Si-O-Si) of the clay framework in the same spectral region. The band at 690 cm\(^{-1}\) and the broad band at 1458 cm\(^{-1}\) observed in the spectrum of Fe-EDAPTMOS can be attributed to CH bending vibrations and NH wagging of the aliphatic chains of the EDAPTMOS cubes\(^{[14]}\)\(^{[15]}\) respectively. The appearance of these bands in the spectrum of HTFeED is indicative of the insertion of organosilicon cubes in the clay galleries. Both bands disappear upon calcination, as seen in the spectrum of HTFeED-500. Analogous results were obtained for the samples based on sodium-montmorillonite, Na-T, TFeED and TFeED-500 (see supporting appendix).
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Figure 6.3. FTIR spectra of pristine HT, HTFeED and HTFeED-500; the spectrum of the Fe-EDAPTMOS complex (FeED) is added for comparison.

Figure 6.4 shows typical Mössbauer spectra of the pillared hybrid materials after calcination at 500 °C. Both quadrupole and magnetically split components are observed in the spectra and their resonant lines possess some degree of broadening. In addition the absorption area of the magnetic components increases at 10K (-263.15 °C), relative to that observed at 300K (26.85 °C), at the expense of the area of the quadrupole split component. The IS, quadrupole splitting (QS), quadrupole shift \( (2\varepsilon) \) and hyperfine magnetic field \( (B_{hf}) \) values (listed in Table S.I, see Appendix), correspond to Fe\(^{3+}\) high spin \((S=5/2)\) ions in α-Fe\(_2\)O\(_3\) (hematite) nanoparticles\(^{[46][47][48]}\). These nanoparticles acquire a distribution of particle sizes and are subjected to superparamagnetic relaxation phenomena.\(^{[49][50]}\)
Figure 6.4. Mössbauer spectra of TFeED-500 (a) and HTFeED-500 (b) samples recorded at different temperatures.

XPS spectroscopy was also used to identify the constituents of TFeED and HTFeED and to verify the successful incorporation of the iron complexes in the montmorillonite matrices. In every survey spectrum (see Appendix) iron peaks were observed at the expected binding energies (Fe2p$_{3/2}$ at 710 eV and Fe2p$_{1/2}$ at 723 eV). To identify which iron and nitrogen species are present we fitted the core level spectra shown in Figure 6.5. In the case of iron we followed the approach of Grosvenor, et al.$^{[51]}$ For both TFeED and HTFeED five iron components are present, Fe(O)OH, FeCl$_2$ being the most dominant ones. Additionally, the nitrogen spectra reveal two nitrogen components, a first one peaked at around 401 eV binding energy, which accounts for 55% and 51% of the total N1s intensity for TFeED and HTFeED respectively, and which we attribute to protonated terminal amines of the silsesquioxane moieties and a second one at 399 eV, which makes up 45% and 51% of
Figure 6.5. X-ray photoemission spectra of the Fe2p3/2 (left) and N1s (right) core level regions of TFeED and HTFeED

the total N1s intensity for TFeED and HTFeED respectively) and which is due to secondary amine groups of the same moieties. Finally the intensity ratio silicon Si2p/aluminum Al2s increased from 2.6 for Na-T to 4.9 and 4.5 for TFeED and HTFeED respectively. This increase is due to the extra silicon stemming from the incorporation of silsesquioxanes and confirms, together with the FTIR spectra and the XRD data discussed above, the successful intercalation of the iron complexes in the clay matrices.

Figure 6.6 shows the DTA-TGA curves, of the intercalated hybrid HTFeED and of the pristine acid-activated montmorillonite, HT. HT shows a 10% weight loss up to 120 °C, related to the removal of the intercalated water. The amount of adsorbed water is considerably lower (6 wt%) in the case of HTFeED revealing the less hydrophilic
character of this hybrid structure. Moreover, HTFeED presents three exothermic peaks between 150 and 420 °C accompanied by an approximately 10% weight loss. Considering the mass percentage, these signals must correspond to the removal of the organic chains of the silsesquioxane cubes, which takes place in three exothermic steps. Consequently, considering an octahedral complex of the type Fe\(^{3+}\)\(_{8/3}\)[X\(_8\)Si\(_8\)O\(_{12}\)], where X is H\(_2\)N(CH\(_3\))\(_2\)NH(CH\(_2\))\(_3\)\(^-\), the amount of Fe-EDAPT莫斯 incorporated within the clay is estimated to account for 17 % of the total mass. Analogous results were obtained for TFeED. In this case, the organic part of intercalated moieties was found to correspond to about 15 wt% of the total mass (see Supporting Information) and thus the percentage of the organosilicon cubes to about 25 wt%.

Nitrogen adsorption-desorption measurements at 77K (-196.15 °C) were performed on both pillared clays in order to determine the porosity in each case. We not only obtained the specific-surface-areas (S\(_{\text{BET}}\)) obtained from the isotherms through BET analysis, but, in order to distinguish between the external plus mesoporous surface area and micropore volume, we also made use of the \(a_s\)-plot method.\(^{[53]}\)\(^{[54]}\) The \(a_s\) plots, defined as \(a_s = (n_s/n_{0.4})_{\text{ref}}\) where \(n_s\), \(n_{0.4}\) are the amounts of N\(_2\) adsorbed by a
reference solid at \( P/P_0 = s \) and \( P/P_0 = 0.4 \), have been proposed\(^{[53] \,[54]} \) as a very valuable tool to investigate the porosity of solids. According to Gregg and Sing\(^{[53]} \) it is convenient to set \( \alpha_s = 1 \) at \( P/P_0 = 0.4 \), since monolayer coverage and microporous filling occur at \( P/P_0 < 0.4 \), while capillary condensation takes place at \( P/P_0 > 0.4 \). In the present study two treatments with two different reference solids were carried out. As reference material Na-T, heated at 800 °C for 3 hs to eliminate the pores, with a specific surface area of 5 m² g⁻¹ was employed. The slope of the linear part of the \( V-\alpha_s \) plot gives the meso+external surface area, \( S_{m,e} = 2.87 \times V_{ads}/\alpha_s \) while the positive intercept gives the microporous volume, \( V_{\mu p} \), after conversion of the gas volume adsorbed at 77 K: \( V_{\mu p} = V_{ads}(STP) \times 0.001547 \).

The values of specific surface area (\( S_{BET} \)) and total pore volume (\( V_p \)) from the experimental measurements as well as the mesoporous plus external surface (\( S_{m,e} \)), the micropores volume (\( V_{\mu p} \)) and micropores surface area (\( S_{\mu p} \)) calculated as described above are reported in Table I.

**Table I.** Results from \( \alpha_s \) analysis, using as reference material Na-T, heated to 800 °C to eliminate the pores.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{BET} ) (m² g⁻¹)</th>
<th>( V_p ) (cm³ g⁻¹)</th>
<th>( S_{m,e} ) (m² g⁻¹)</th>
<th>( V_{\mu p} ) (cm³ g⁻¹)</th>
<th>100(( S_{m,e} )/( S_{BET} )) %</th>
<th>100(( V_{\mu p} )/( V )) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFeED-500</td>
<td>248.8</td>
<td>0.256</td>
<td>107.4</td>
<td>0.068</td>
<td>43.2</td>
<td>26.6</td>
</tr>
<tr>
<td>HTFeED-500</td>
<td>230.2</td>
<td>0.263</td>
<td>102.7</td>
<td>0.061</td>
<td>44.6</td>
<td>23.2</td>
</tr>
<tr>
<td>HT</td>
<td>107.8</td>
<td>0.151</td>
<td>67.3</td>
<td>0.022</td>
<td>62.4</td>
<td>14.6</td>
</tr>
<tr>
<td>Na-T</td>
<td>61</td>
<td>0.126</td>
<td>54.8</td>
<td>0.006</td>
<td>89.8</td>
<td>4.8</td>
</tr>
</tbody>
</table>
As obvious from the values of Table I, the BET specific surface area ($S_{BET}$) of the pristine clay increased after the acid activation. In addition TFeED-500 and HTFeED-500 hybrids show a significant increase in $S_{BET}$ as compared to the pristine clay materials. More specifically the $S_{BET}$ of TFeED-500, 248 m$^2$g$^{-1}$, amounts to 4 times the value of Na-T (61 m$^2$g$^{-1}$) while in the case of HTFeED-500 the $S_{BET}$ was almost double (230 m$^2$g$^{-1}$ as compared to 107 m$^2$g$^{-1}$ for HT). Moreover $S_{m,e}$ also increased for the intercalated hybrids (in the case of TFeED-500 $S_{m,e}$ doubled) while the values of $V_{μp}$ for both hybrids (0.068 cm$^3$g$^{-1}$ for TFeED-500 and 0.061 cm$^3$g$^{-1}$ for HTFeED-500) are indicative of pillared structures.

### 6.3. Isopropanol decomposition.

The total degrees of conversion of isopropanol (Fig. 6.7a) as well as the selectivity towards propene and diisopropylether (Fig. 6.7b) are depicted as a function of reaction temperature. The data in Fig. 9(a) clearly indicate that both samples show a high catalytic activity due to the presence of acid sites on the surface. Since the decomposition of isopropanol is an acid catalyzed reaction, which is favored by catalysts with large number of acid sites, it is not surprising that HTFeED-500, which has been prepared using as starting material acid-activated clay, shows a higher activity. Moreover, as evidenced from Fig. 9(b) the selectivity to diisopropylether of TFeEDW-500 slightly predominates the selectivity to propene up to 105 °C, while in the case of HTFeED-500, the selectivity to propene starts from the values around 75%, and remains constant up to 105 °C.
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Figure 6.7. (a) The total degrees of conversion of isopropanol and (b) the selectivity towards propene (dark symbols) and diisopropylether (open symbols) as a function of reaction temperature for TFeED-500 and HTFeED-500 pillared clays.

Generally, the product profiles show that both propene and diisopropylether are present from the onset of the reaction, indicating that both reaction products are formed by direct dehydration; i.e., they are primary reaction products coming from isopropanol through a parallel reaction network. According Campelo et al.\cite{55} the pathway of formation of both products from 2-propanol conversion on AlPO$_4$ catalysts is a combination pathway of parallel and consecutive reactions presented in Figure 6.8.
Therefore, propene is a primary plus secondary reaction product while diisopropylether is a primary unstable product. In our case, it is clear that for all samples, the production of propene predominates at high reaction temperature and reaches 100% above 130 °C, independently of how many intermediates may be involved in its formation. On the other hand the differentiation on the onset selectivity to diisopropylether for the examined samples might be connected to stereochemical parameters. Thus the selectivity for the larger product (diisopropylether) is favoured on the catalyst with higher d-spacing (TFeED-500).

6.4. Conclusions
Intercalation of Fe$^{3+}$-substituted cubic silsesquioxanes in layered aluminosilicate nanoclays resulted in the formation of novel catalytic pillared structures. Octameric cubic oligosiloxanes, formed upon controlled hydrolytic polycondensation of the corresponding bi-functional amino-silane monomer (EDAPTMOS), were reacted with iron cations to form iron-siloxane complexes. These cationic complexes were intercalated in a sodium and an acid activated nanoclay and the resulting intercalated
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structures were further calcined to remove the organic side arms and produce cross-linked metal-substituted silica-pillared clays of high porosity and thermal stability. XRD measurements revealed the successful intercalation of iron-silsesquioxane complexes within the clay interlayers as well as the formation of the pillared structures upon calcination. The absence of reflection peaks of the crystalline phase of iron oxides indicates that iron oxide nanoparticles produced upon calcination are small enough and are not aggregated on the external clay surfaces but rather homogeneously dispersed in the clay matrix. The incorporation of the organosilicon cubes in the clay galleries was confirmed by infrared and X-ray photoelectron spectroscopies. The amount of the iron-silicon cubane complexes incorporated within the clay was estimated by thermal analysis between 17% and 25% of the total mass. Mössbauer spectra of the pillared materials after calcination at 500 °C, showed the existence of α-Fe₂O₃ (hematite) nanoparticles in the final hybrid systems. Nitrogen adsorption-desorption measurements showed that the specific surface area (S\text{BET}) of the calcined intercalated clays was increased up to four times compared with that of pristine clays while the pore characteristics as estimated by the a₅-plot method are indicative of pillared structures. Finally, pillared clays showed high catalytic activity for isopropanol decomposition due to the presence of acid sites on the surface. In fact, pillared clay prepared using acid-activated clay as starting material showed a higher activity due to the large number of acid sites. The selectivity to diisopropylether of the pillared clay prepared from sodium-clay, slightly predominates the selectivity to propene up to 105 °C, while in the case of acid activated pillared clay, the selectivity to propene starts from the values around 75%, and remained constant up to 105 °C. This differentiation on the onset selectivity is a to stereochemical parameters. The resulting pillared clays exhibiting high specific areas and narrow pore size distribution could also be used as catalysts in many catalytic reactions in organic synthesis.
References


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45, 1894–1898.


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Appendix

**Figure S1.** Thermogravimetric analysis: weight loss in % for the intercalated hybrid TFeED.

**Figure S2.** X-ray photoemission survey spectra of the pristine clays HT and Na-T as well as of the intercalated hybrids TFeED and HTFeED.
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Figure S3. FT-IR spectra of the pristine Na-T clay, the intercalated hybrid TFeED and the pillared clay TFeED-500.

Table S.I. Mössbauer hyperfine parameters as resulting from the best fits of the Mössbauer spectra of the TFeED-500 and HTFeED-500 samples recorded at 26.85 °C and -263.15 °C. IS is the isomer shift (relative to α-Fe at 26.85 °C), Γ/2 is the half line-width, QS is the quadrupole splitting, $2\varepsilon$ is the quadrupole shift, $B_{hf}$ is the central value of the hyperfine magnetic field, $\Delta B_{hf}$ is the hyperfine magnetic field spreading (symmetric in single column, or asymmetric denoted by the < and > symbols in the relative columns) around $B_{hf}$ and A is the relative spectral absorption area of the components used to fit the spectra. Typical errors are ±0.02 mm/s for IS, Γ/2, $2\varepsilon$ and QS, ±0.3 T for $B_{hf}$ and ±5 % for A.
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<th>T(K)</th>
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<th>$\Gamma$/2</th>
<th>QS or Z$\varepsilon$</th>
<th>$B_{hf}$</th>
<th>$\Delta B_{hf}$</th>
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<td>mm/s</td>
<td>kOe</td>
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