FÉ(III)-PILLARED MONTMORILLONITES: PREPARATION AND CHARACTERIZATION

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ABSTRACT: Porous, high surface area solids have been prepared by intercalation of a trinuclear acetato hydroxy-iron(III) complex cation between the layers of montmorillonite and the resulting materials have been characterized in order to identify the nature of the iron intercalates formed during and after the cation exchange step. Spectroscopic studies demonstrated that at 623 K, the iron complex was partially decomposed and α-Fe₂O₃ was only detected in samples heated at high temperatures, > 923 K. Under these conditions, the dehydroxylation of the montmorillonite layers led to the collapse of the structure.

Pillared clays are materials prepared by intercalating metal oxide precursors between the silicate layers of smectite type clays. On heating, small pillars are formed, building a stable zeolite-like structure. The cavities, or pores, thus produced depend on the nature, size and shape of the intercalated species and are generally much larger than the typical zeolite cages. In addition, high surface areas and acidity are features that make the pillared clays useful as catalysts and adsorbents. In this context, iron oxide pillared clays are materials of increasing potential interest. They have been recently proposed as demetallization catalysts (Burch & Warburton, 1987a,b). Further applications may be envisaged after findings that the iron oxide pillars may be converted to sulphide pillars with no significant structural change (Burch & Warburton, 1987a; Warburton, 1988).

Iron oxide pillared clays have been prepared by different methods (Burch & Warburton, 1987a,b; Warburton, 1988; Hererra & Peech, 1970). However, the introduction of trinuclear acetato hydroxy-iron(III) cations in the interlayer space of montmorillonite has been proved to be a very useful way of obtaining stable iron intercalates that persist even after heating up to 773 K.

Notwithstanding, systematic surveys of the physical and chemical properties of iron oxide pillared clays are still lacking in the current literature and only a few papers may be found (Doff et al., 1988; Gangas et al., 1985; Yamanaka & Hattori, 1988; Dhar et al., 1986) devoted to the spectroscopic characterization and identification of the iron pillars.

This paper reports the preparation and characterization of iron intercalated montmorillonites. An attempt has been made to identify the actual iron species in the interlayer space and their transformation during and after the preparation stage. Several techniques have been used in characterizing the samples, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy.
EXPERIMENTAL

Materials

The Na-exchanged form of a Wyoming montmorillonite, supplied by Eccagum International, was used as the starting material. The cation exchange capacity (CEC) of the air-dry clay was 86 mEq/100 g.

Trinuclear acetato hydroxy-iron(III) nitrate, Fe$_3$(OCOCH$_3$)$_7$OH.2H$_2$ONO$_3$, was used as the cation source for exchanging with the Na-montmorillonite. It was prepared following the procedure described by Yamanaka et al. (1984). 80.8 g Fe(NO$_3$)$_3$.5H$_2$O dissolved in 50 cm$^3$ of ethyl alcohol, was reacted with 140 cm$^3$ of acetic anhydride, with the evolution of heat. The solution was then cooled in an ice bath and the resulting precipitate was separated and used without further purification in the pillaring procedure.

Cation-exchange

A 0.04 mole 1$^{-1}$ aqueous solution of the trinuclear acetato hydroxy-iron(III) nitrate was added to a stirred 1% Na-montmorillonite aqueous suspension. The concentration ratio of the mixture was 3.5 mEq of the iron complex per 1 g of Na-montmorillonite, the mixture being at pH = 3.2. After reacting for 3 h at 313 K, the resulting trinuclear iron complex-exchanged montmorillonite was separated by centrifugation and washed with water several times to remove excess iron ions up to constant conductivity and dried in air at 313 K.

Characterization

The characterization techniques have been used to control and determine the physical and chemical properties leading to the preparation of a stable solid of high porosity and surface area, and to identify the structure of the pillared structure obtained.

Chemical analysis of the sample was carried out by atomic absorption spectrometry. Thermogravimetric analysis (TGA) was performed with a Setaram G70 thermobalance, weight loss was recorded in the range 293–1273 K, at a heating rate of 10$^$°/min. Differential thermal analysis (DTA) was carried out under similar conditions using Fe-montmorillonite samples homogeneously dispersed in an inert media of α-Al$_2$O$_3$.

The basal spacings of oriented samples were determined by XRD, using Ni-filtered Cu-K$\alpha$ radiation. This technique was also used to identify the iron oxides and oxyhydroxides.

XPS spectra were obtained using a VG ESCA MkII electron spectrometer with an Mg anode as source.

Mössbauer spectra were obtained at 298 K, using a constant acceleration Mössbauer spectrometer with a $^{57}$Co/Rh source.

RESULTS AND DISCUSSION

Physical and chemical characterization

Chemical and thermal analyses. The chemical analysis data for the iron intercalated montmorillonite are given in Table 1. The sample was previously calcined for 2 h at 623 K. The CEC value evaluated by ammonium acetate exchange and determined for this sample is
**Fe(III)-pillared montmorillonites**

**TABLE 1. Chemical analysis (wt%) and CEC of the montmorillonite exchanged with the trinuclear iron complex cation, calcined at 623 K for 2 h.**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>57.49</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.86</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>24.65</td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>1.82</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.15</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.28</td>
</tr>
<tr>
<td>(H₂O⁻)</td>
<td>4.70</td>
</tr>
</tbody>
</table>

CEC(mEq/100 g) | 37.5

also included. As acetyl groups associated with the trinuclear acetato hydroxy-iron(III) cations might have escaped during the thermal pretreatment, the observed weight loss was recorded only as water loss (H₂O⁻).

This assumption was supported by TGA and DTA curves obtained for the air-dried sample, as shown in Fig. 1. A broad exothermic peak was recorded in the range 313–513 K, corresponding to 11.7% weight loss. This was interpreted as the decomposition and oxidation of acetyl and nitrate groups adsorbed on the surface of the washed sample. Desorption of physisorbed water also contributed to this weight loss. An intense exothermic peak in the range 533–623 K was associated with the decomposition of the trinuclear iron cationic complex interlayers and a weight loss of 5.8% was recorded over this temperature range. The dehydroxylation of the montmorillonite layers started at about 853 K, and the last exothermic peak was interpreted in terms of the crystallization of α-Fe₂O₃.

From the chemical analysis, the sample contained 24-65% Fe₂O₃. This suggested that nearly 1 mmol of the trinuclear acetato hydroxy-iron(III) nitrate per g of clay actually interacted with the montmorillonite during the cation-exchange step. However, the CEC of the sample was determined to be 37.5 mEq/100 g, compared to 86 mEq/100 g for the initial air-dry montmorillonite. Thus, the host interlayer space was not completely saturated with respect to the acetato iron(III) complex cations. Furthermore, part of the interlayer iron ions and protons as well as the unexchanged interlayer cations may be exchangeable and contribute to the residual CEC observed. It is possible that part of the total Fe₂O₃ content in the sample may be due to a surface-deposited complex.

Assuming that the total weight loss recorded up to 623 K (17.5%) was due only to the decomposition of the acetyl groups, then the molar ratio acetyl/Fe in the sample (2.97/1.07) is much smaller than the ratio determined after heating 1 g of the trinuclear acetato hydroxy-iron(III) nitrate for 2 h at 623 K (8.2/3). This would appear to confirm the previous assumption that the trinuclear acetate complex cations are taken up by the montmorillonite in some partially hydrolysed state. Similar conclusions have already been presented by Yamanaka et al. (1984).

**XRD and N₂ adsorption analyses.** Typical XRD patterns of the montmorillonite intercalated with the trinuclear iron complex are shown in Fig. 2. For the room-temperature
sample it may be seen that the peak corresponding to the (002) plane ($2\theta \cong 8^\circ$) has a higher intensity than that corresponding to the (001) plane. However, the peak practically disappears when the sample is calcined at 773 K. Basal spacings of the sample heated at various temperatures for 2 h are given in Table 2, along with the corresponding BET and Langmuir surface areas.

The pillared structure seemed to persist without collapsing up to 773 K. Inasmuch as the dehydroxylation of the montmorillonite layers started at $\sim 853$ K, no regular layer spacing

![TGA and DTA curves of the air-dried exchanged-montmorillonites.](image)

**Fig. 1.** TGA and DTA curves of the air-dried exchanged-montmorillonites.

### Table 2. Basal spacings and surface areas of the montmorillonite exchanged with the trinuclear iron complex cation, heated at different temperatures for 2 h.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$d$(001)</th>
<th>$S_g$(m$^2$/g)</th>
<th>BET</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>23·3</td>
<td>138</td>
<td></td>
<td></td>
</tr>
<tr>
<td>623</td>
<td>20·1</td>
<td>215</td>
<td>374</td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>19·6</td>
<td>216</td>
<td>386</td>
<td></td>
</tr>
</tbody>
</table>
Fe(III)-pillared montmorillonites

FIG. 2. XRD patterns of the exchanged-montmorillonite: (a) room temperature; (b) 623 K; (c) 773 K.

could be observed in the XRD analysis of the sample heated at 923 K for 2 h. Notwithstanding, the diffraction peaks corresponding to $\alpha$-Fe$_2$O$_3$ (3.67, 2.69 and 2.50 Å —Brindley, 1961) could already be distinguished at this temperature, and were better defined for the sample heated at 1073 K for 2 h. Similar analysis of the XRD patterns of the sample heated at 623 K for 2 h suggested the existence of a FeOOH phase, due to a broad diffraction peak at about 4.13 Å.

Samples heated at 773 K had the highest surface areas due to the oxidation and further motions of the trinuclear acetate complex in the clay framework.

The sample was pre-heated at 623 K for 2 h before nitrogen adsorption isotherms were obtained. The plots obeyed the BET as well as the Langmuir equation. Multilayer adsorption might have occurred on the outer surface of the sample, but monolayer adsorption more likely occurred in the internal galleries of about 10 Å height opened between the layers of the montmorillonite (Pinnavaia, 1984). This interpretation would explain the higher surface area values determined using the Langmuir equation for monolayer adsorption as compared to those determined with the BET equation for multilayer adsorption. However, there is no evidence of a partially delaminated structure.

The sample heated at 623 K for 2 h was used as reference material for the following sections. It was selected because, after the thermal treatment described, the sample showed high values for basal spacing (20.1 Å) and surface area (215 m$^2$/g) while the structure of the montmorillonite was still preserved. Moreover the intensity of the diffraction peak corresponding to the (001) reflection was affected by the thermal treatment (Fig. 2). This might imply that the number of pores corresponding to the basal spacing decreased with the temperature of treatment. The intensity of the (001) reflection was weaker for the sample heated at 773 K than for that heated at 623 K for 2 h. Therefore, the sample seemed to show the best structural properties at 623 K.
Spectroscopic characterization

**XPS analysis.** Binding-energy data for the main elements in the starting and exchanged montmorillonites are shown in Table 3 along with the values obtained under the same conditions for the trinuclear iron complex.

The binding energies of Al_{2p}, Si_{2p}, and O_{1s} peaks were found to be similar for both the starting and exchanged montmorillonites (RT), suggesting that no effective interaction occurred during the intercalation process. Also, the position of the Al_KLL23L23 Auger peak indicated that the aluminium ions corresponded to the octahedral sites as in the Na-exchanged montmorillonite.

The XPS patterns of the sample heated at 623 K remained nearly unchanged with respect to those of the sample before the thermal treatment. Thus, the environment of the iron ions was apparently unaffected on burning off the acetyl groups of the trinuclear iron complex introduced into the montmorillonite. The binding energy determined for the iron ions in the trinuclear iron complex is in accordance with the value $\text{Fe}_{2p_{3/2}} = 712$ eV found in the acetilacetonate Fe(III) (Wagner, 1983). As the iron ions are octahedrally surrounded by oxygen in the acetilacetonate Fe(III), a similar environment might be postulated for the iron ions in the trinuclear iron complex. Previous XRD analysis indicated the existence of a FeOOH phase in the sample heated at 623 K for 2 h. Regardless of the type of phase present, the iron ions are surrounded by oxygen, and thus no significant shift in binding energy would be expected for the $\text{Fe}_{2p_{3/2}}$ peak in the XPS patterns of the sample before and after the thermal treatment.

Further examination of the O_{1s} peak failed to give an unambiguous differentiation of the oxygen environment of the iron ions in the sample under both conditions. The position of the O_{1s} peak was nearly the same in both spectra obtained for the sample before and after heating at 623 K for 2 h. These values, 532.4 and 532.6 eV, were very likely due to oxygen ions in physically adsorbed water (Harvey & Linton, 1981).

Two carbon peaks, C_{1s}, were observed, as shown in Fig. 3. One was due to carbon contamination in XPS measurements and was observed in every spectrum obtained, and the other was assigned to the carbons in the acetyl groups of the trinuclear iron complex. The latter was clearly observed in the patterns of the air-dried sample but it could hardly be detected in the patterns of the heated sample. These observations confirmed previous results that the thermal treatment was efficient in removing the acetyl groups of the complex introduced in the montmorillonite.

Quantitative data obtained by XPS and atomic absorption are listed in Table 4. As the

| Table 3. Binding and kinetic (Si_KLL and Al_KLL23L23) energies by XPS. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Na_{1s} Fe_{3p} Al_{2p} Fe_{2p_{1/2}} O_{1s} Si_{2p} Si_KLL Al_{KLL23L23} C_{1s} N_{1s} |
| Na-mont. 1073-7 | 74-9 | 727-4 | 713-8 | 532-2 | 103-1 | 1608-8 | 1461-4 | - | - |
| Fe-mont. (RT) - | - | 74-6 | 726-1 | 711-7 | 532-6 | 102-9 | - | 1461-5 | 285-0 | - |
| Fe-mont. (623 K) - | - | 74-7 | 725-8 | 712-2 | 532-4 | 103-2 | - | 1461-2 | 284-8 | - |
| Fe-complex - | 56-5 | 726-0 | 712-4 | - | - | - | 288-8 | 407-3 |
| SiO_{2} - | - | - | - | 533-3 | 103-7 | 1607-6 | - | 284-6 | - |
Fe(II)-pillared montmorillonites

Fe/Al and Fe/Si ratios were higher for bulk analysis by atomic absorption than for XPS surface data, it was concluded that iron is mainly distributed in the interlayer space of the montmorillonite.

Mössbauer spectroscopy. Mössbauer spectra of the trinuclear iron complex and the initial and exchanged montmorillonites at room temperature and calcined at 623 K are presented in Fig. 4.

The initial Na-montmorillonite contained <1% Fe. The Mössbauer parameters determined for this material were characteristic of high-spin iron(III) ions in a distorted octahedral environment and this is compatible with the presence of Fe$^{3+}$ replacing Al$^{3+}$ in the montmorillonite structure.

The presence of at least two different coordination sites may be observed in the iron complex spectra, assigned to a symmetrical octahedral acetate coordinate iron site and two distorted tetrahedral sites in the complex structure (Gmelin, 1906). This allows it to be assigned to the linear configuration rather than to the triangle cluster, against magnetic data (Earnshaw et al., 1966) and Mössbauer spectra (Oldham, 1968), showing evidence for only one type of iron atom in the molecule.

No Fe$^{2+}$ could be detected either in the iron complex or in the Na-montmorillonite. The environment of the Fe$^{3+}$ ions in the clay was determined to be very different from the iron sites in the trinuclear iron complex.

Table 4. XPS and atomic absorption quantitative analyses for the montmorillonite heated at 623 K.

<table>
<thead>
<tr>
<th></th>
<th>Al/Si</th>
<th>Fe/Al</th>
<th>Fe/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic absorption</td>
<td>0.38</td>
<td>2.72</td>
<td>1.02</td>
</tr>
<tr>
<td>XPS</td>
<td>0.31</td>
<td>0.41</td>
<td>0.13</td>
</tr>
</tbody>
</table>
FIG. 4. Mössbauer spectra: (a) Na-montmorillonite; (b) trinuclear iron complex; (c) air-dried exchanged montmorillonite; (d) exchanged montmorillonite, heated at 623 K for 2 h.

The spectra recorded for the air-dried exchanged montmorillonite were fitted to two quadrupole-splitting absorptions of iron(III). However, none of the doublets could be related to the Fe$^{3+}$ ions in the structure of the montmorillonite. As shown in Table 5, the values of the quadrupole splitting and isomer shift were consistent with the trinuclear species being preserved in the clay. This may also indicate that the trinuclear iron centre of the complex was not destroyed at the cation-exchange step in the intercalation process.

The effects of hydrolysis were therefore limited to the removal of acetyl groups from the
Table 5. Mössbauer spectral parameters ($\Delta$: quadrupole splitting mm s$^{-1}$; $\delta$: isomer shift mm s$^{-1}$; $T$: line width at half maximum mm s$^{-1}$; $I$: relative intensity).

<table>
<thead>
<tr>
<th></th>
<th>Doublet I</th>
<th>Doublet II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta$</td>
<td>$\delta$</td>
</tr>
<tr>
<td>Fe$_3$(OCOCH$_3$)$_2$OHNO$_3$</td>
<td>0.52</td>
<td>0.41</td>
</tr>
<tr>
<td>Fe-mont. (RT)</td>
<td>0.54</td>
<td>0.35</td>
</tr>
<tr>
<td>Fe-mont. (623 K)</td>
<td>0.54</td>
<td>0.34</td>
</tr>
<tr>
<td>Na-montmorillonite</td>
<td>0.57</td>
<td>0.16</td>
</tr>
</tbody>
</table>

complex, as previously detected by TGA. The formation of some hydroxylated species due to hydrolysis has been already proposed from XPS results.

No substantial change could be observed in the spectra of the sample calcined at 623 K in relation to those of the Fe-pillared clay at room temperature. The main effect due to the heating is a slight increase in the quadrupole splitting that may be due to changes in the environment of the intercalated iron(III) ions. The values obtained strongly suggest that the iron complex might be only partially decomposed after heating at 623 K for 2 h. Therefore some iron complex preserved in the clay structure could still contribute to the final values in such a way that the most closely related parameters are associated with $\gamma$-FeOOH. This is indeed very peculiar if the nature of the acetate complex and the thermogravimetric data are considered. No Fe$_2$O$_3$ spectral patterns were observed.

CONCLUSIONS

The trinuclear acetato hydroxy-iron (III) cations interacted with the montmorillonite in some partially hydrolysed form. Cation-exchange is the main form of interaction although adsorption of the complex on the outer surface of the montmorillonite has also been observed. The hydrolysis of the trinuclear iron cation is not extensive, and after drying, the main effect of hydrolysis seems to be the removal of acetyl groups from the complex cation. Thus, hydroxylated species are formed without modification of the trinuclear iron structure. On heating up to 623 K, the hydroxy acetate iron(III) cations are not completely decomposed when located in the interlayer montmorillonite space, suggesting that some shielding effect may be exerted on these guest cations which interact weakly with the host structure.

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REFERENCES

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