Large interlayer repeat distances observed for montmorillonites treated by mixed Al–Fe and Fe pillaring solutions

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Raw montmorillonites treated with mixed Al–Fe pillaring solutions, with Fe/(Al + Fe) molar ratio between 0.1 and 1, and heated at 300 °C lead to large *d*-spacings according to XRD which increase from 52 Å for the sample with the lowest iron content to 76 Å for the pure Fe-treated clay sample.

Pillared clay minerals (PILCs) are usually obtained by intercalation of large inorganic polymeric cations which exchange the compensating cations from the clay, then dehydration and dehydroxylation occur upon calcination to give metal oxide clusters which act as pillars. These pillars separate adjacent silicate layers which then increases the interlayer distance and creates a permanent porosity between them.[1]

The synthesis of pillared clays has been investigated extensively in the past two decades as a function of the nature of the clays, the nature of the pillars and the conditions of pillaring. Usually, polyoxo-cations of Al, Zr, Ti, Fe, *etc.* are incorporated as pillars. Many reviews have been published.[2,3] The synthesis of pillared clays from mixed pillaring species is less common and the formation of truly mixed pillars is not easy to confirm when two cationic species are simultaneously intercalated.[4]

In most of the pillared clays reported to date the free height is comparable to the van der Waals thickness of the host layers. The term 'supergallery' has been used previously to describe some pillared clays having high basal spacing and where the thickness of the layer (≈ 10 Å) is smaller than the free interlamellar heights. For example, iron-pillared clays are obtained with basal spacing of *ca.* 23–27 Å[5] and free heights of *ca.* 13–17 Å. In an international patent, McCauley claimed larger basal spacings (>40 Å) of pillared clays obtained by incorporation of various rare earth metals in the trivalent state with aluminium polycations in the clay layers.[6] However claims for gallery heights have never exceeded 40 Å.

In the present work, addition of Al and Fe pillaring solutions, with Fe/(Al + Fe) molar ratio of 0–1 leads to a series of modified Al–Fe-clays with very high distances according to XRD. The products were obtained without incorporation of any non-ionic surfactant or other organic polymeric compounds. The nature of the iron pillaring oligomers is still not well known. In addition, methods for preparing thermally stable Fe-PILCs have not been established.

To study the diffraction patterns of the materials having peaks at very low 2θ angle, proper alignment and calibration of the diffraction instrument is necessary to obtain a good accuracy in the diffraction analysis. To verify that the following obtained results are not an artefact, a low-angle diffraction calibration standard product[7] (silver behenate), considered as a standard which has a set of well-defined (00*l*) diffraction peaks at 2θ angles down to 1.5° with Cu-Kα radiation, was used to calibrate the XRD Siemens D 500 instrument (Fig. 1). The raw Wyoming montmorillonite was received from Comptoir des Minéraux (France). The elemental analyses of this crude montmorillonite obtained by XRF, and corrected by the weight loss which is *ca.* 15%, are: 66.35% SiO_2, 21.61% Al_2O_3, 4.29% Fe_2O_3, 2.70% MgO, 0.02% MnO, 0.21% TiO_2, 2.23% Na_2O, 1.58% CaO, 0.61% K_2O and 0.09% P_2O_5. The cation exchange capacity of this clay was *ca.* 80 mequiv. per 100 g of calcined clay. This material was used without further purification.

The oligomeric pillaring solutions were prepared by the following methods: (i) Al_{13} oligomer: a solution containing hydroxy-Al oligocations with OH : Al ratio of 2.2, was prepared from 0.4 M $AlCl_3 \cdot 6H_2O$ and 0.4 M NaOH. Seven days ageing was carried out at room temperature before use. (ii) Fe oligomer: following the procedure of Rightor *et al.*,[5] Na_2CO_3 powder was added gradually to an aqueous solution of 0.2 M $FeCl_3$, up to a base : Fe ratio of 2. The freshly resulting oligomer was used immediately without ageing.

A 2% suspension of raw clay was prepared by dispersing 2 g of montmorillonite in deionized water. Different amounts of Al and Fe oligomers (Al + Fe = 100%), prepared by the methods described above, were then added simultaneously to this clay slurry to give the ratio of M : clay = 10 mmol (g of clay)$^{-1}$. The suspension was aged for one day at room temperature. The clay products were centrifuged and then washed by successive agitations/centrifugations with deionized water until Cl^- free. Specimens of the clay suspensions were dried on glass slides at room temp. The samples were heated at 300 °C for 3 h. XRD patterns were recorded using Ni-filtered Cu-Kα radiation.

XRD patterns of the various clay samples are shown in Fig. 2. The *d*(001) spacing of the Al-sample is nearly 18 Å [Fig. 2(a)]. This value is similar to those generally reported for Al-PILCs and indicates the success of pillaring. The mixed Al–Fe sample [Fe/(Al + Fe) = 0.1] shows an additional peak at 52 Å which is lower in intensity than the peak at 18 Å. The *d*(004) of this first peak which must appear at nearly 13 Å, could be the origin of the assymetrical behaviour of this reflection [Fig. 2(b)]. The Al–Fe sample [Fe/(Al + Fe) = 0.2] gives two better defined peaks, one at *ca.* 64 Å which indicates that increasing the amount of Fe results in an increase in the *d*-value for the peak appearing at low angle and the other at 16.7 Å with high intensity [Fig. 2(c)]. The position of this second peak coincides with the fourth order (*ca.* 16 Å) of the 64 Å reflection, this again could explain the high intensity of this second peak. The mixed Al : Fe sample [Fe/(Al + Fe) = 0.5] has one peak at 72 Å and a second less intense broad peak centered at *ca.* 15.7 Å [Fig. 2(d)]. In the pure

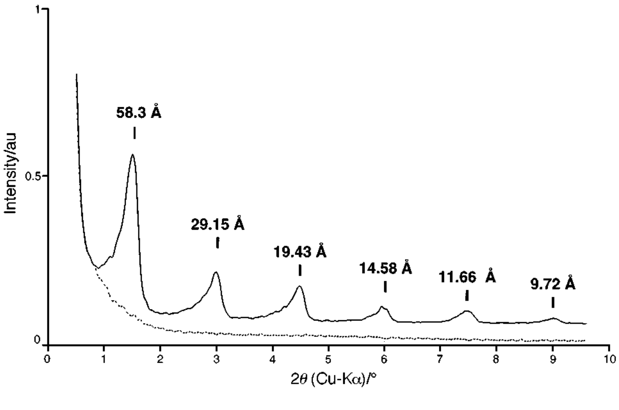

Fig. 1 Low angle XRD pattern of silver behenate powder deposited on glass slide (——) and the glass slide support without sample (- - - -)

Table 1 XRD spacings and textural properties: surface area, porous (V_P) and microporous ($V_{\mu P}$) volumes of the treated montmorillonites (Mt) as a function of Fe/(Al + Fe) molar ratio in the initial solutions, and of the starting raw clay heated at 300 °C. Mesoporous volume (V_{mP}) is obtained by subtracting microporous volume from total porous volume

Clay sample	Fe/(Al + Fe) initial molar ratio	First peak *d*/Å	Specific surface area/ m^2 g^{-1}	V_P/cm^3 g^{-1}	$V_{\mu P}$/cm^3 g^{-1}	V_{mP}/cm^3 g^{-1}
Mt.Al	0	18.3	246	0.18	0.104	0.076
Mt.Al-Fe	0.1	52	230	0.22	0.082	0.138
Mt.Al-Fe	0.2	64	210	0.23	0.047	0.183
Mt.Al-Fe	0.5	72	202	0.24	0.034	0.206
Mt.Fe	1	76	148	0.22	0.002	0.218
raw Mt heated at 300 °C	0	~ 10	18.5	0.06	0.004	0.056

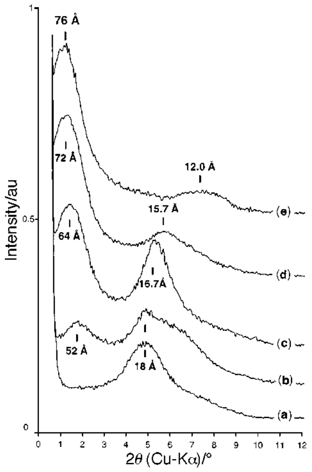

Fig. 2 XRD patterns with oriented specimen, heated at 300 °C, of the clays initially treated by the Al and Fe oligomer solutions in different ratios: (a) Fe/(Al + Fe) = 0; (b) Fe/(Al + Fe) = 0.1; (c) Fe/(Al + Fe) = 0.2; (d) Fe/(Al + Fe) = 0.5 and (e) Fe/(Al + Fe) = 1

Fe sample, the distance of the first peak reaches its maximum at *ca.* 76 Å and the second very broad peak position shifts to a lower distance of *ca.* 12 Å [Fig. 2(e)]. The general observation in all these spectra is that increasing the amount of iron in the initial solutions leads to (i) a shift of the first peak to lower angle and (ii) to a shift of the second peak in the opposite direction with an almost linear decrease in this case of the corresponding basal spacing from 18 to 12 Å.

The high distance observed here for the iron pillared sample was previously suspected by Yamanaka and Hattori,[8] but not shown by XRD. In fact, these authors comparing the adsorption isotherms of different molecules by Al-, Zr- and Fe-PILCs noticed that even though the basal spacings were similar in all these pillared samples, a BET isotherm (presumably, type IV or II) was observed for Fe whereas Langmuir isotherms (type I) were obtained for Zr and Al. From this, they concluded that the pore dimensions of the iron oxide pillared clay are probably larger than those expected from the 16.7 Å obtained basal spacing. They suggested that XRD analysis only reflects the partial well-ordered stacking of the silicate layers, since the remaining disordered parts are not revealed by XRD.

At this stage, the questions are what kind of iron species lead to these high distances of the peaks and do these increasing distances correspond to the interlamellar spaces between the layers? TEM studies are in progress to answer to these questions. In a study on partial hydrolysis of $FeCl_3$, Tchoubar *et al.*[9] have shown in similar experimental conditions that the sizes, which varied with time, of the obtained iron polymers, were centered around 100 Å: thus our *d* values are perhaps not so surprising. However, it is the first time, to our knowledge, that the synthesis of montmorillonites treated by pillaring solutions leading to such unexpectedly large distances of *ca.* 70 Å (XRD) is reported from a regular smectite clay.

The N_2 BET specific surface areas, pore, mesopore and micropore volumes of the treated clays are presented in Table 1. The starting raw montmorillonite clay, heated at 300 °C, exhibits a low surface area of 18.5 m^2 g^{-1}, a low pore volume of 0.06 cm^3 g^{-1} and a microporosity of 0.004 cm^3 g^{-1}. Al-PILC has, as expected, a surface area of 246 m^2 g^{-1}, a pore volume of 0.18 cm^3 g^{-1} and a microporosity of 0.104 cm^3 g^{-1}. With increasing Fe/(Al + Fe) initial ratio, the surface areas of the mixed treated clays decrease and reach 148 m^2 g^{-1} for the pure Fe sample which is still 7 times higher than the surface area of the heated starting clay. Here, the situation is very complex because as shown in our previous studies,[10] some precipitated oxyhydroxide Fe species are retained by the clay outside the interlamellar spaces and the intrinsic surface area is difficult to define. Rather, a comparative global evolution has to be taken into account in these clay materials. Moreover, the total pore volumes of the mixed treated clays remain almost constant, *ca.* 0.23 ± 0.01 cm^3 g^{-1}, while the microporosity of these clays decreases with increased iron content and the residual microporosity value of the iron clay is very low. This indicates that montmorillonite treated with Al–Fe pillared species, creates essentially some mesoporosity between the clay particles, which could be at the origin of these high distances. The pillars may prevent access to the interlamellar spaces and the microporosity decreases to zero, and other unknown species of Al and Fe compounds could be obtained. All these possibilities have to be quantitatively analysed and interpreted from TEM images.

In conclusion, in this work unexpectedly large interlayer distances for montmorillonites treated by mixed Al–Fe and Fe-pillaring solutions are observed by XRD. These distances vary from 52 to 72 Å and reach a maximum at 76 Å in the pure Fe sample. Nevertheless, increasing the amount of iron leads to an increase of mesoporosity instead of microporosity.

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