

# Heterogenation of water-sensitive organometallic catalysts into layered aluminosilicates

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## Abstract

Non-aqueous intercalation of montmorillonite with the water-sensitive species  $[\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_6\text{pyr}_3]$  was achieved with the use of nitromethane as solvent. The adsorption of the complex into the clay was studied photometrically and follows second order kinetics. Thermogravimetric analysis showed that the complex is adsorbed in excess of the CEC of the clay. XRD measurements suggest that the complex is intercalated parallel to the sheets. The surface area of the fired solids is rather low, due the small height of the formed  $\text{MnO}_x$  pillars.

## 1. Introduction

The chemistry of intercalation of various species into smectite clays has received considerable interest during the last 15–20 years, for various reasons. First, the immobilization of metal complex catalysts in the interlamellar space of smectite clays has offered new ways of combining the advantages of both homogeneous and heterogeneous catalysis [1–3]. Apart from these advantages very often the heterogenized homogeneous catalyst shows increased catalytic activity and selectivity as compared to the homogeneous one, due to the limited orientations by which the molecules are forced to accommodate themselves between the aluminosilicate sheets during intercalation [4,5]. Second, by pillaring the smectite clays with thermally stable metal oxides it has been possible to produce high surface area materials that possess a two-dimensional microporosity, and are usually employed as absorbents and/

or heterogeneous catalysts for transformation of various organic molecules [6,7]. As precursors are used poly-hydroxy-cations of metals like Al [8], Zr [9], and many others, which after intercalation between the aluminosilicate layers and calcination, are transformed into oxidic pillars of various height. Pillars which have been introduced in this way include single species like  $\text{NiO}_x$  [10],  $\text{CuO}_x$  [11],  $\text{FeO}_x$  [12] or double/binary oxides like  $\text{LaMO}_x$  ( $\text{M} = \text{Ni}, \text{Co}, \text{Mn}$ ) [13,14],  $\text{AlO}_x$ – $\text{FeO}_y$  [15,16] as well as  $\text{REO}_x$ – $\text{AlO}_x$  [17].

Traditionally, the intercalation of the above chemical species into cationic clays is performed by ion-exchange in aquatic media. The reason for this practice is due mainly to the fact that the swelling of clays in organic solvents and thus the expansion of the interlayer space is usually limited. So in the absence of water it is very difficult for a bulky metal complex or a poly-hydroxy-cation to penetrate between the layers [18]. Some trials for intercalation into non-aquatic media have shown limited percentage of exchange < 20%.

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But very often in the literature, when the presence of organic solvent is necessary, the addition of water accelerates the procedure with better results [18,19], a fact due presumably to the swelling effect of water on the clay.

The question of attempting intercalation of water sensitive chemical species, like multinuclear complexes, by cation exchange into clays has not been addressed up to now according to our knowledge. The probable reason is that suitable solvents, or mixture of solvents, should be employed, satisfying the following requirements: (i) The complex should be easily dissolved in them without decomposition. (ii) The aluminosilicate sheets should be adequately separated to allow insertion of chemical species.

Recently we became interested in intercalating water-sensitive-multinuclear complexes into clay layers. Such complexes are for example  $[\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_6\text{pyr}_3]\text{ClO}_4$  and they have been considered as biomimetic systems, resembling the multimanganese centre of enzymes which decomposes water. This and other similar complexes have been used as homogeneous catalysts for the activation of C–H bond of hydrocarbons in order to obtain oxidation products C–OH [20,21]. In some trials we performed using aqueous or aqueous/organic environment the success was rather limited, because the complex was readily hydrolyzed in the presence even of small quantities of water, resulting in  $\text{MnO}_x$  species of high surface area [22] and catalytic activity [23]. So we had to develop a non-aqueous method of intercalation for the above and other similar water sensitive complexes.

## 2. Experimental

### 2.1. Preparation of the complex

The multinuclear manganese complex used was  $[\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_6(\text{pyr})_3]\text{ClO}_4$  [20]. The method of its preparation is reported in detail in Ref. [20] and it was followed closely in the present case. Briefly, 2.00 g of  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$

(6.15 mmol) were dissolved in a mixture of 20 ml EtOH, 3 ml pyridine and 12 ml glacial acetic acid. In this mixture 1.14 g (3.15 mmol) of  $\text{N-nBu}_4\text{MnO}_4$  were added under intense stirring. Addition of 0.69 g (5.65 mmol) of  $\text{NaClO}_4$  results in precipitation of a brown mass of the complex which was subsequently filtered and washed by acetone. The brown solid obtained was examined for its IR spectra which was found similar to that reported in [20].

### 2.2. Intercalation of the complex into montmorillonite

1 g Na–montmorillonite (CEC = 100 mequiv./100 g) was added to 100 ml of nitromethane and the suspension kept under continuous stirring for one day so that the solvent would penetrate between the aluminosilicate layers. 0.88 g (1 mequiv.) of the complex was then added and the suspension took the dark brown color of the complex. Four days later the color of the suspension became light brown, an indication that the complex had been transferred on the clay. The brown solid was filtered, washed by acetone and dried in air. Yield 1.52 g. We did not notice any desorption of the complex during the washing with acetone. By the same method we also synthesized some other samples with ratios complex (mequiv.)/clay (mequiv. of CEC) varying in the range 0.12–8.00.

### 2.3. Kinetics of adsorption

The kinetic of adsorption was studied photometrically, since during the intercalation the color of the supernatant liquid became weaker due to the transfer of the complex from the liquid phase into the clay layers. The concentration of the dissolved complex as a function of time was followed using a Photometer UV–VIS Spectrotronic 21 Bausch&Lomb at  $\lambda = 500$  nm. Then from the difference from the initial concentration at  $t = 0$  the amount of the adsorbed complex was found. Were studied three samples with ratios complex (mequiv.)/clay (mequiv. of CEC) 1.00, 0.50 and

0.33. In all the samples the initial concentration of the complex was kept constant.

#### 2.4. Thermogravimetric analysis

The obtained solids after drying were examined to establish their thermogravimetric behaviour in a Thermobalance TRDA3H of the Chyo Balance Co. having the ability to record simultaneously the parameters T, TG, DTG and DTA. The heating rate was 5 deg/min and the sample was kept under a flow of dried air 30 ml/min.

#### 2.5. XRD studies

The X-ray diffraction patterns of the obtained materials heated at 130, 300 and 500°C, were obtained by a Siemens Diffractometer (Cu anode,  $\lambda = 1.54$ ). The samples were prepared as oriented films on glass pieces to favor the detection of 001 reflections in X-rays and heated at the above temperatures for 3 h.

#### 2.6. Surface area

The specific surface areas ( $\text{m}^2 \cdot \text{g}^{-1}$ ) of the solids at different temperatures were determined by the single-point BET method of  $\text{N}_2$  adsorption at  $T = 77$  K employing a Carlo Erba 1750 Sorptory equipment.

### 3. Results and discussion

First of all it should be emphasised that the complex is adsorbed within the aluminosilicate layers and not on the external surface of the solid. This was confirmed by washing the intercalated system with warm acetone for long periods without observing any brown colouring of the solvent. Bear in mind that acetone is the typical recrystallization solvent of the trinuclear complex so if it was adsorbed on the external surface it would be easily transferred to the liquid phase. The absence of desorption indicates strong adsorption of the complex within the interlamellar space.

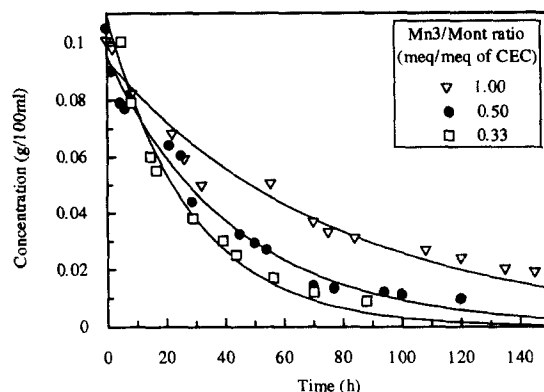


Fig. 1. First order kinetics for the intercalation of the  $\text{Mn}_3$  complex into clay.

#### 3.1. Kinetics of adsorption

The concentration of the complex in the liquid phase as a function of time for the three ratios mequiv. of  $\text{Mn}_3$ :mequiv. of CEC of clay = 1.00, 0.50 and 0.33, is shown in Fig. 1.

As a first approximation, the experimental points of the drop of the concentration of the complex in the liquid phase was considered to obey first order exponential decay:

$$C = C_0 * e^{-kt} \quad (1)$$

where  $C$  is the concentration at time  $t$ ,  $C_0$  is the initial concentration and  $k$  is a constant. It should be noticed that this apparent rate constant  $k$  might be diffusion controlled, but this does not change the following discussion.

Fitting of the experimental points to Eq. (1) for the above ratios gives  $k$  values equal to 0.013, 0.024 and 0.034 ( $\text{h}^{-1}$ ) respectively. Since the  $k$  values increase with the concentration of the complex, or otherwise drop with the concentration of the clay, it seems that the quantity of the clay influences the kinetic of adsorption. So it would be better to assume second order kinetics. Then the reduction of the concentration of the complex in the liquid will be given by the relationship:

$$-\frac{dC_{\text{Mn}_3}}{dt} = k * C_{\text{Mn}_3} * C_{\text{mont}} \quad (2)$$

where  $C_{\text{Mn}_3}$  the concentration of the complex in the liquid phase and  $C_{\text{mont}}$  the concentration of the

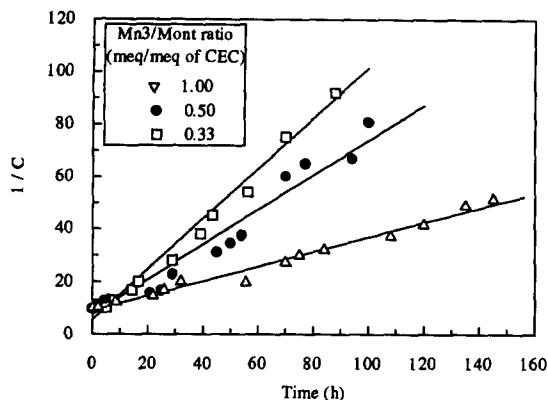


Fig. 2. Second order kinetics for the intercalation of the  $\text{Mn}^3$  complex into clay.

adsorption sites of montmorillonite which are actually reflected in its CEC. For the three ratios used  $C_{\text{Mn}^3}/C_{\text{mont}} = 1.00, 0.50$  and  $0.33$ . As a result Eq. (2) is transformed to:

$$-\frac{dC_{\text{Mn}^3}}{dt} = k_{\text{app}} * C_{\text{Mn}^3}^2 \quad (3)$$

where  $k_{\text{app}} = k, k/0.50, k/0.33$ , for the three different experiments.

Integration of Eq. (3) in the limits  $t = 0$  to  $t$  and  $C = C_0$  to  $C$ , gives the concentration  $C$  of the complex as a function of time  $t$ :

$$\frac{1}{C} = \frac{1}{C_0} + k_{\text{app}} * t \quad (4)$$

So the slope of the line  $1/C = f(t)$  provides the value of the constant  $k$ . The fitting of the experimental points to Eq. (4) is shown in Fig. 2. The  $k$  values for the three ratios have been also calculated and founded almost similar and equal to 2.8, 3.3 and 3.2 ( $1 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ ) respectively. Since the  $k_{\text{app}}$  values are so close to each other and independent of the concentrations, it seems that the second order kinetics assumption is indeed correct and the apparent rate constant of the observed system is  $k = 3.0 \pm 0.2$  ( $1 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ ).

### 3.2. Thermogravimetric analysis

In Fig. 3 the weight loss as well as the DTA curves as a function of temperature for (a) the sample with ratio complex (mequiv.)/clay

(mequiv.) = 1.00 and (b) a sample of pure montmorillonite previously mixed with nitromethane and dried in air, is shown.

The weight loss 20.51% at temperature 250–280°C, accompanied by a strong exothermic effect in Fig. 3(a) shows the adsorption of a significant quantity of the complex by the clay. It refers to the decomposition of the organic matter (pyridine and acetic acid ligands) of the complex, since it does not appear on the pure clay sample. The organic part of the complex that is decomposed is about the 50% of its total weight. So, we can calculate that on 1 g montmorillonite, for initial ratio in the solution equal to 1.00, is intercalated about 0.60 g of the cationic part of the complex  $[\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_6\text{pyr}_3]^+$  ( $\approx 80\%$  of CEC of the clay).

Since the amount of the complex adsorbed can be estimated from the weight loss at 250–280°C, we studied the thermogravimetric behaviour of the other samples intercalated at different ratios complex (mequiv.)/clay (mequiv. of CEC). In Fig. 4(a) the TG curves and in Fig. 4(b) the DTA curves are shown for initial ratios complex (mequiv.)/clay (mequiv.) in the solution, in the range 0.12–8.00.

In Fig. 5 the weight loss of these samples in the temperature range 250–280°C is shown as a function of the ratio complex (mequiv.)/clay (mequiv. of CEC). This curve could be regarded as an adsorption isotherm. A comparison of this

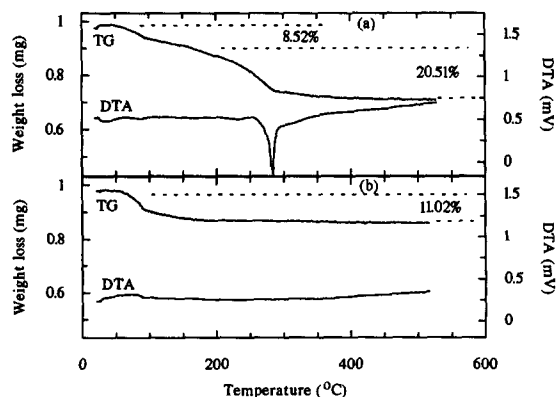


Fig. 3. TG and DTA curves for (a) the sample with initial ratio complex (mequiv.)/clay (mequiv.) 1.00 and (b) pure montmorillonite in nitromethane.

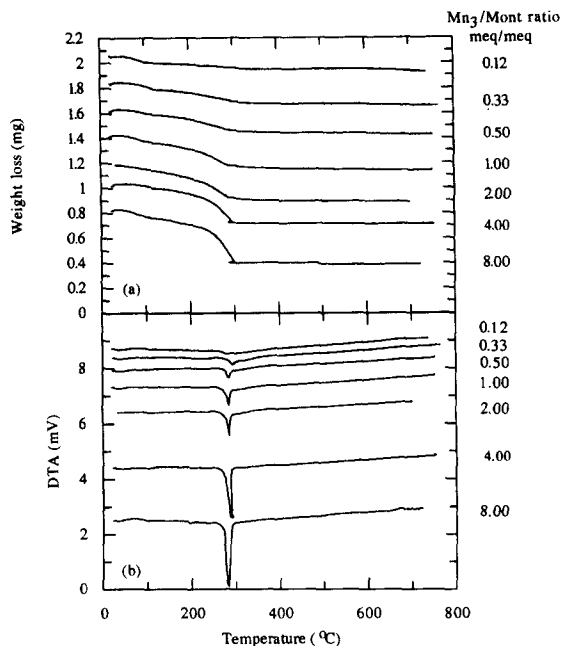


Fig. 4. (a) TG and (b) DTA curves for all the samples prepared with different complex (mequiv.)/clay (mequiv.) ratios.

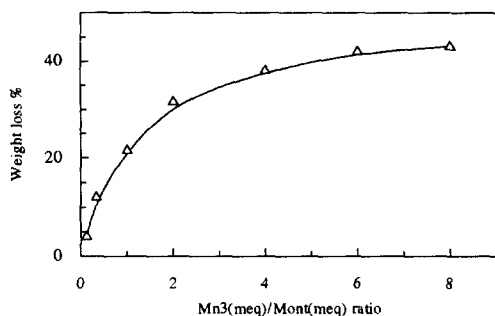


Fig. 5. Weight loss in the temperature range 250–280°C as a function of the complex (mequiv.)/clay (mequiv.) ratio.

curve with the various types of adsorption isotherms given in a classification by Giles et al. [24], gives a Langmuir type mechanism for the adsorption of the cationic part of the complex between the aluminosilicate sheet of the clay. It also assumes the formation of a monolayer.

It is very important also to notice that at high values of ratios complex (mequiv.)/clay (mequiv. of CEC) in the initial suspension, we calculate adsorbed quantities of the complex that exceeding the CEC of the clay. This phenomenon is very well known and has been studied much, for example in the adsorption of organoclays with a large carbon chain  $C_{>10}$  by clays [25]. The

quantity of the complex that is adsorbed on the clay exceeding the CEC of the clay is in the neutral form  $[Mn_3O(CH_3COO)_6(pyr)_3]ClO_4$ . Nevertheless, another distinct possibility for the reduced weight loss at high ratios complex/clay may be the remaining carbon in the form of coke into the clay, apart from  $MnO_3$  species.

### 3.3. XRD studies

In Fig. 6 the XRD patterns in small angles are shown after heating the samples at different temperatures. The samples examined had a ratio complex (mequiv.)/clay (mequiv. of clay) = 1. Pure montmorillonite in nitromethane was also examined as reference. For the intercalated sample heated at 130°C, the  $d_{001}$  distance is 1.24 nm, so if the thickness of the aluminosilicate layer (0.95 nm) is subtracted, it seems that the flat complex is intercalated between the aluminosilicate sheets parallel to them, forming thus props of approximately 0.30 nm height. At 300°C the pillars shrink because of the decomposition of the organic part of the complex, to a height of 0.17 nm. This very small height of the pillars is due to the flat structure of the core  $Mn_3O$  and the parallel orientation that it takes in respect to the sheets. It is very characteristic that at this temperature the pure clay is already collapsed, due to the desorption of the solvent. At 500°C two peaks appear suggesting

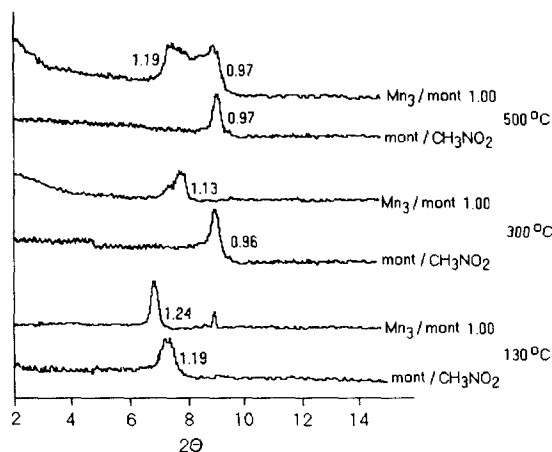


Fig. 6. XRD patterns of montmorillonite intercalated with the complex  $Mn^3$  and pure montmorillonite in nitromethane heated at different temperatures.

Table 1  
Specific surface areas ( $\text{m}^2 \cdot \text{g}^{-1}$ ) of the samples heated at various temperatures

Sample	Temperature/ $^{\circ}\text{C}$					
	200	300	400	500	600	700
$\text{Mn}_3/\text{mont}$ 0.33	12	47	62	45	24	19
$\text{Mn}_3/\text{mont}$ 1.00	14	54	71	47	25	29
$\text{Mn}_3/\text{mont}$ 2.00	21	45	65	51	25	20

that some of the material has collapsed, but some pillars are still present.

### 3.4. Surface area

The specific surface area of three samples with different ratios complex (mequiv.)/clay (mequiv. of CEC) = 0.33, 1.00 and 2.00 at heated at various temperatures are shown in Table 1. The maximum values of the surface area ( $70 \text{ m}^2 \cdot \text{g}^{-1}$ ) appears after heating the solids at temperatures  $400^{\circ}\text{C}$ , where the organic part of the complex is decomposed and the remaining pillars keep the aluminosilicate sheets apart. The values of the surface areas are however small for a pillared clay. But as mentioned before, since the complex is flat and lies parallel to the sheets, the pillars are very low. So a very small region of the interlayer space is open for  $\text{N}_2$  adsorption. As the temperature rises the surface is reduced, due to the collapse of the pillars and the pillared structure.

Perhaps at this point it should be mentioned that before reaching the final decision for the use of nitromethane, as an appropriate intercalation solvent, we made several attempts with other organic solvents, such as acetone, ethanol and methanol. In these experiments we had limited success and the ion exchange never exceeded 10% of the CEC of the clay. So, the questions that emerges are: Why does nitromethane differ so much from the other organic solvents and why does its behaviour as an intercalation solvent more resemble that of water?

Studies on the interactions between organic molecules and clays carried out some time ago by MacEvan [26] show that only nitromethane and

acetonitrile can form 3 molecular layers between the aluminosilicate sheets keeping them apart in an interlayer distance  $>1.0 \text{ nm}$ . All the other organic molecules (ethanol, methanol, acetone, etc.) form 2 or 1 layers and interlayer distance  $<0.8 \text{ nm}$ . It seems that there exist a critical value for the an interlayer distance between  $0.8 \text{ nm}$  and  $1.0 \text{ nm}$  for intercalation. We can also assume that the third intermediate nitromethane molecule, which is not directly attached to the clay surface, is probably easily removable and replaceable by the complex cations. The successful intercalation of the complex into the clay in the case of nitromethane (a) and the unsuccessful case of ethanol (b) are represented schematically in Fig. 7. Of course, it is well known the corresponding values for water is more than 30 molecular layers and more than  $10 \text{ nm}$  interlayer distance. That is the reason why the procedure of intercalation by ion exchange in water usually takes some minutes to complete while the intercalation in nitromethane needs some days. Finally there might be another reason for the successful use of nitromethane as solvent. This might be related to the low donor capacity of nitromethane towards metal ions [27]. Actually it has been well established that the use of nitromethane does not change the electrolytic type of the complexes. Thus the cation  $[\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_6(\text{pyr})_3]^+$  should remain intact in the solvent. The failure to obtain good intercalation results with other solvents can be due by some kind of dissociation or decreased mobility of the complex caused by coordination of the solvent molecules [27].

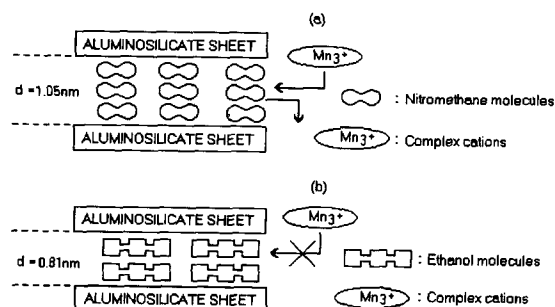


Fig. 7. Model for (a) successful, in the case of nitromethane and (b) unsuccessful attempt in the case of ethanol for intercalation of montmorillonite with complex  $\text{Mn}_3$ .

#### 4. Conclusions

We have developed a method of intercalating water-sensitive complexes into clays by employing non-aquatic media. Nitromethane proved to be an excellent medium for that purpose. The proposed method may find applications either in the immobilization of homogeneous water-sensitive complex catalysts or in the preparation of new pillared materials. Especially as far as the last point is concerned, the variety of the multinuclear complexes of various composition and dimensions can offer new possibilities for the preparation of new technologically important porous materials, supported homogeneous catalysts as well as in controlled released processes.

#### Acknowledgements

Financial support from the programs STRIDE-33 and PENED '91 is acknowledged.

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