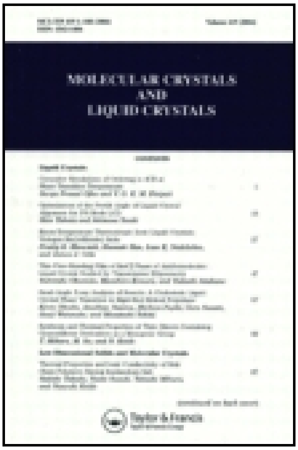

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Umberto Costantino [a], Sara Clementi [a], Morena Nocchetti [a] & Riccardo Vivani [a]

[a] Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 8, 06123, Perugia, ITALY

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Intercalation and Grafting of n-Alkyl Phosphonates into Synthetic Hydrotalcites

UMBERTO COSTANTINO, SARA CLEMENTI, MORENA NOCCHETTI,
and RICCARDO VIVANI.
Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto, 8, 06123,
Perugia, ITALY.

The chloride ions of synthetic hydrotalcite $[Zn_{0.67}Al_{0.33}(OH)_2]Cl_{0.33}\cdot 0.4H_2O$ were fully exchanged with $C_nH_{2n+1}PO_3H^-$ and $C_nH_{2n+1}PO_3^{2-}$ anions (n=0, 1, 2, 3, 4) and the products obtained were characterised for their composition, X-ray diffraction powder patterns, FT-IR absorption spectra and thermal behaviour. n-Alkylphosphonate anions are accommodated in the interlayer region as a monomolecular film with the alkyl-chains almost perpendicular to the layer plane and an odd-even alternation of the interlayer distance, as a function of the number of carbon atoms in the alkyl-chain, is observed. As a consequence of a mild thermal treatment the hydrogenphosphonates react with the hydroxyls and attach themselves to the inorganic layer to produce novel Zn and Al hydroxy alkylphosphonates that are able to intercalate n-alkanols.

Keywords: synthetic hydrotalcites; n-alkylphosphonates intercalation; grafting reactions; Zn and Al hydroxy alkylphosphonates; n-alkanols intercalation.

INTRODUCTION

Hydrotalcite-like compounds (HTlc) form a large class of inorganic layered compounds extensively studied as catalysts, precursors and supports of catalysts, anionic exchangers, additives, .etc. Their general formula is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}$ $[A^{-n}_{x/n}]^{x-}mS$, where M(II) may be Mg, Zn, Ni, etc.; M(III) Al, Cr, Fe, etc.; A^{-n} is the charge compensating anion (CO_3^{2-}, SO_4^{2-}, Cl^-, organic anions); m the mol/mol of the cointercalated solvent, generally water. HTLc are able to intercalate, *via* ion-exchange, a large variety of anions, but little information is available on the exchange of phosphonate anions[1]. The uptake of hydrogen phosphates and phenylphosphonates has already been reported and grafting reactions of these anions with the hydroxyls of the layers have been described[2]. In this paper, we focus our attention on the exchange of hydrogen n-alkylphosphonates and n-alkylphosphonates for chlorides of Zn-Al-HTlc and on the chemical and physico-chemical characterisation of the products obtained. The intercalation of n-alkanols in some grafted materials is also reported.

EXPERIMENTAL

All reagents used were C. Erba RP-ACS except $CH_3PO_3H_2$, $CH_3CH_2PO_3H_2$, $CH_3(CH_2)_2PO_3H_2$, $CH_3(CH_2)_3PO_3H_2$ which were Fluka products.

Zn-Al hydrotalcite was obtained by co-precipitation of Zn(II) and Al(III) hydroxycarbonates from homogeneous solution[2].The carbonate form was converted into the chloride form via ion exchange at pH 5. The solid was washed with CO_2-free distilled water and dried at room temperature over P_4O_{10}.

All the exchanged forms were generally obtained by equilibrating for three days 1 g of chloride form with 50 ml of 0.1 M solution of the sodium salt of the anion to be intercalated. After equilibration the solids were washed with CO_2-free distilled water and dried at room temperature (r.t.) at 75% relative humidity (R.H.). The zinc and aluminium content of the HTLc was determined by standard EDTA titrations. Carbonate and water content were obtained both with C, H elemental analysis and thermogravimetry. Non-carbonate anions were determined by ion chromatography (Dionex 2000). Coupled TG-DTA analyses were performed with a Stanton-Redcroft STA 760 Analyzer at an heating rate of 5°C/min, in air flow. The X-ray powder diffraction (XRPD) patterns were taken with a computer controlled Philips PW 1710 diffractometer, using CuKα radiation (40 KV, 30mA). FT-IR spectra of solid dispersed in KBr, were taken with a Jasco FT-IR-410 spectrometer.

RESULTS AND DISCUSSION

The well crystallised $Zn_{0.67}Al_{0.33}(OH)_2Cl_{0.33}0.4H_2O$ (Zn-Al-Cl) showed a good affinity for the anions derived from the dissociation of the n-alkylphosphonic acids. The complete replacement of the Cl^- anions by $C_nH_{2n+1}PO_3H^-$ and $C_nH_{2n+1}PO_3^{2-}$ anions (n = 0, 1, 2, 3, 4) was achieved simply by equilibrating the solid with solutions containing the chosen phosphonate as a predominant species. Mass and charge balance both in solution and in the solid showed that, within the experimental error, only one type of anion is present in the solid. The intercalation compounds obtained maintain a good degree of crystallinity as indicated in the XRPD patterns shown in Figure 1. Table I lists the composition of the samples, held at r.t. and 75% R.H., their interlayer distance (d_l), the increment (Δd_l) of d_l as n is increasing and the mol of cointercalated water per mol of guest. It may be noted that: a) the intercalates containing monovalent and divalent anions derived by the same acid have similar d_l value; b) for both types of intercalate there is a odd-even alternation of d_l as a function of the number of carbon atoms in the alkyl-chain (n_c); c) the

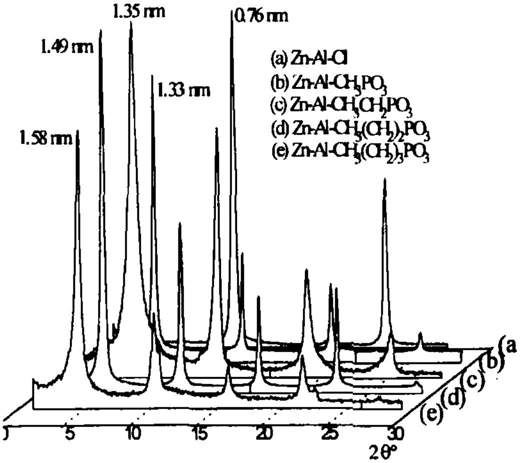

FIGURE 1 XRPD patterns of alkyl phosphonate intercalation compounds.

amount of cointercalated water per mol of monovalent guest anion is 2.5~3 times lower than that found per mol of divalent guest anions. These observations lead to formulate a simple structural model where the brucite-like sheets, 0.44 nm thick, are separated by the n-alkylphosphonates and the $-PO_3H^-$ or $-PO_3^{2-}$ groups, compensating the positive layer charges, lie on the surface of the sheets. The n-alkylchains are in trans-trans conformation, the P-C bond being almost perpendicular to the layer plane to give the observed mean increment, $\Delta d_l/\Delta n_c \sim 0.1$ nm/n_c, consistent with the presence in the interlayer region of a monolayer of extended alkylphosphonates. The alkylchains belonging to phosphonates interacting with the surface of two faced layers can interpenetrate since their cross section (0.19 nm^2) is much lower than the free area available to each monavalent and divalent anions, estimated to be ≈0.50 nm^2 and ≈1 nm^2 respectively.

TABLE I Composition and interlayer distance of intercalation compounds.

Composition	d_l (nm)	Δd_l (nm)	mol H_2O/mol P
$[Zn_{0.67}Al_{0.33}(OH)_2](HPO_3H)_{0.33} \cdot 1.0H_2O$	1.19		3.0
$[Zn_{0.67}Al_{0.33}(OH)_2](CH_3PO_3H)_{0.33} \cdot 1.06H_2O$	1.35	0.16	3.2
$[Zn_{0.65}Al_{0.35}(OH)_2](CH_3CH_2PO_3H)_{0.35} \cdot 1.02H_2O$	1.38	0.03	2.9
$[Zn_{0.65}Al_{0.35}(OH)_2](CH_3(CH_2)_2PO_3H)_{0.35} \cdot 1.03H_2O$	1.50	0.12	2.9
$[Zn_{0.65}Al_{0.35}(OH)_2](CH_3(CH_2)_3PO_3H)_{0.35} \cdot 1.05H_2O$	1.59	0.09	3
$[Zn_{0.67}Al_{0.33}(OH)_2](HPO_3)_{0.165} \cdot 1.1H_2O$	1.10		6.7
$[Zn_{0.67}Al_{0.33}(OH)_2](CH_3PO_3)_{0.165} \cdot 1.27H_2O$	1.33	0.23	7.7
$[Zn_{0.65}Al_{0.35}(OH)_2](CH_3CH_2PO_3)_{0.175} \cdot 1.44H_2O$	1.35	0.02	8.2
$[Zn_{0.65}Al_{0.35}(OH)_2](CH_3(CH_2)_2PO_3)_{0.175} \cdot 1.6H_2O$	1.49	0.14	9.1
$[Zn_{0.65}Al_{0.35}(OH)_2](CH_3(CH_2)_3PO_3)_{0.175} \cdot 1.75H_2O$	1.58	0.09	10

It was interesting to see whether microporosity could be obtained after dehydration. It was indeed found that dehydration of the intercalates, and even their exposure to air for long periods, gives rise to solid state reactions accompanied by a dramatic modification of the XRPD patterns. Fig. 2 shows the modification of the XRPD patterns of the intercalate $[Zn_{0.65}Al_{0.35}(OH)_2](C_2H_5PO_3)_{0.175}\ 1.4H_2O$ when exposed to air for the times indicated. The progressive disappearance of the reflection at d=1.35 nm and the appearance of a reflection at d=2.13 nm of its 2nd, 3th and 4th orders are evident.

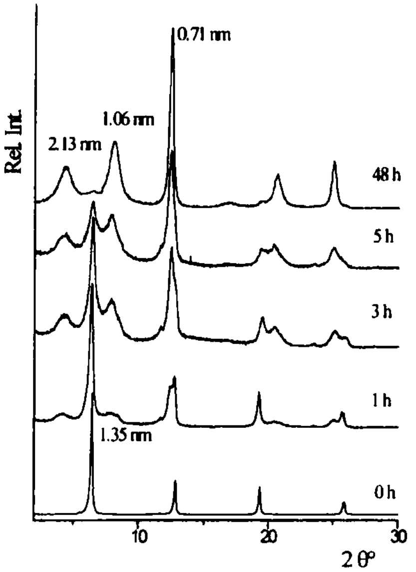

FIGURE 2 XRPD patterns for $ZnAlCH_3CH_2PO_3$ after exposition to air for different times.

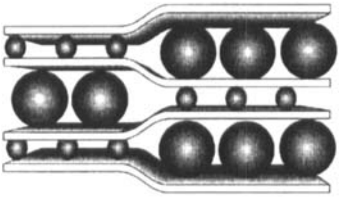

FIGURE 3 Structural model of $ZnAlCH_3CH_2PO_3$ after exposition to air

The identity period is the sum of the interlayer distance of the original intercalate plus that of the HTlc in carbonate form. One explanation of this phenomenon may be that intercalated phosphonate behaves as strong Brønsted base and may deprotonate some co-intercalated water molecules. In the presence of CO_2 the following reaction may occur: $2C_2H_5PO_3^{2-} + H_2O + CO_2 = 2C_2H_5PO_3H^{-} + CO_3^{2-}$. The space filling postulate and the hydrophobic interactions could facilitate the diffusion of the alkylphosphonates to obtain a disposition of the guest similar to that of a stage 2 compound of the Hérol-Daumas domain model[3]. The alternation of guest islands along the c-axis, produces the periodicity observed (see Fig.3). It may be noted that the drying of the samples in a CO_2 free atmosphere generally led the collapse of the layered structure and consequent disorder of the solid. Different behaviour was observed when the intercalation compounds with hydrogen phosphonates are heated at temperatures higher than 50°C. The interlayer distance collapses to lower values and the FT-IR absorption spectrum shows shifting of the phosphate absorption band to lower frequencies. For example the interlayer distance of the intercalate $[Zn_{0.65}Al_{0.35}(OH)_2](CH_3(CH_2)_3PO_3H)_{0.35}\ 1.04H_2O$ collapses from 1.59 to 1.32 nm when the sample is heated at 120°C.

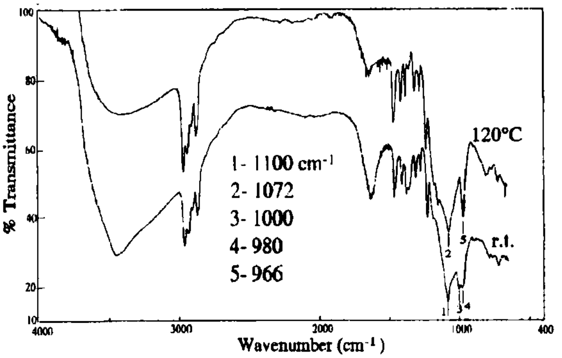

FIGURE 4 FT-IR spectra of $ZnAlCH_3(CH_2)_3PO_3H$ samples at r.t. and after heating to 120°C.

FT-IR spectra of the room temperature and heated samples (Fig. 4) show the shifting of the phosphate absorption band and the two maxima (1072, 966 cm^{-1}), in the high temperature spectrum, could be assigned to the asymmetric and symmetric stretching vibrations of a symmetrically engaged PO_3^{2-} group. These observations could indicate that a grafting reaction has occurred with the formation of new layered Zn and Al hydroxy alkyl phosphonates.

The layered grafted materials are able to intercalate polar species. Preliminary results have been obtained by equilibrating $Zn_{0.65}Al_{0.35}(OH)_{1.65}(C_2H_5PO_3)_{0.35}$ (d_l=1.0 nm) in some pure n-alkanols at r.t. per 1 day. This simple procedure allows to obtain the intercalation compounds with the following interlayer distance: ethanol, 1.61 nm; propanol, 1.75 nm; butanol; 1.89 nm, hexanol, 2.4 nm. The mean increment of the interlayer distance as a function of the number of carbon atoms, in the alkanol chain (0.18 nm/n_c) indicates the formation of a bimolecular film of alkanols into the interlayer region.

Acknowledgement

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