J. Mater. Environ. Sci. 7 (3) (2016) 790-798
ISSN : 2028-2508
CODEN: JMESCN

Study of the properties of intercalation and grafting of phosphonate ions in layered double hydroxides

E. Elkhattabi[1], M. Lakraimi[2], M. Berraho[1], A. Legrouri[3], R. Hammal[4], M. Badreddine[5], L. El Gaini[1]

[1]*Faculté des Sciences Semlalia, Université Cadi Ayyad, BP 2390, Marrakech 40000, Morocco.*
[2]*Ecole Normale Supérieure, Université Cadi Ayyad, BP 2400, Marrakech 40000, Morocco.*
[3]*Al Akhawayn University, PO Box 104, Ifrane 53000, Morocco.*
[4]*Faculté des Sciences, Université Chouaib Doukkali, BP 20, El Jadida 24000, Morocco.*
[5]*Centre Régional des Métiers de l'Education et de la Formation, 40000 Marrakech, Morocco.*

Received: 3 April 2015, Revised 14 Sept 2015, Accepted 20 sept 2015
** Corresponding authors: E-mail:* mlakraimi@yahoo.fr and mberraho@yahoo.fr

Abstract

Layered double hydroxides (LDHs) have been investigated for many years as host materials for a range of anion exchange and intercalation reactions. The ion exchange of phosphonate ion in Zn-Al-chloride layered double hydroxides was investigated. The chloride precursors prepared by coprecipitation at pH 9 preserved their lamellar structure following ion exchange. It was found that the aging time is important in controlling the crystallization of the phosphonate-exchanged compounds. The best phase, in terms of crystallinity, was obtained for an aging time of 3 h at 25°C in 0.01 M phosphonate solution. The grafting of the anion onto the hydroxylated sheets by moderate thermal treatment was confirmed by a combination of several techniques, including powder X-ray diffraction (XRD) and infrared (IR) spectroscopy.

Keywords: Layered double hydroxide (LDH); intercalation; grafting; phosphonate; ion exchange.

1. Introduction

It is known that phosphonic acids, compounds containing the Lewis acid moiety R-CP(O)$(OH)_2$, are characterized by a stable covalent carbon to phosphorous bond. The corresponding anions of the phosphonic acids are called phosphonates.

Phosphonates are a group of chelating agents that are used in high quantities in oil production, cooling water, and desalination systems to inhibit scale formation and corrosion, in the textile industry to stabilize peroxide based bleaching agents, in industrial and household detergent formulations as chelating agents, and in nuclear medicine as bone-seeking carriers for radionuclides [1].

Phosphonates are complexing agents containing one or more C–PO$(OH)_2$ groups [2]. They are effective chelating agents for di- and trivalent metal ions [3], inhibitors of crystal growth and scale formation and are quite stable under harsh chemical conditions. In pulp and paper manufacturing and in textile industry, they are utilized as peroxide bleach stabilizers, acting as chelating agents for metals that could inactivate the peroxide. In detergents, they are used as a combination of chelating agent, scale inhibitor and bleach stabilizers. Around 16,000 tons of phosphonates are used in Europe and 30,000 tons in USA each year [4].

Phosphonates are not biodegraded during wastewater treatment [5] but can be rapidly oxidized in the presence of manganese [6] or are photodegraded by sunlight [7]. Much less is known about the fate and behavior of the corresponding phosphonates in the environment [1,8,9].

The existing reviews are either several years old, and therefore do not cover the newest literature [1], or focus on toxicology and risk assessment based on the limited data that were available at that time [9].

What is missing is an overview of the chemistry of these compounds, which can help understand and predict the environmental behavior of these compounds more accurately and that can be the basis for a refined risk assessment. The aim of this review is therefore to provide an overview of the thermal characterization, spectral and morphostructural LDH-phosphonate phase.

That is why we became interested in this study of intercalation and grafting of phosphonates in LDHs, obtaining thus a new microporous material based on LDHs with permanent pillars layers. These pillars are created by permanent bridging between the hydroxyl layers and phosphonates anions through more stable covalent bonds.

2. Materials and methods

2.1. Materials

All experiments were carried out under a stream of N_2 in order to avoid, or at least minimize, the contamination by atmospheric CO_2.

The [Zn-Al-Cl] precursor was prepared by coprecipitaion at a constant pH. A homogeneous mixture of $ZnCl_2$ and $AlCl_3$ aqueous solution, with a molar ratio of x = 0.33, was slowly introduced under stirring in a reactor which contained 250 mL of freshly decarbonated water. The pH of the solution was maintained constant at a value of 9 by the simultaneous addition of 1.0 M NaOH solution. The precipitate obtained was filtered, washed several times with water and then dried at room temperature.

Exchange reactions were carried out with 100 mg of [Zn-Al-Cl] LDH suspended in 100 mL of 0.1 M phosphonate ions ($COOCH_2PO_3^{3-}$) solution, which was stirred. The pH of the mixture was 9. The anion exchange reaction was achieved at ambient temperature (25°C) with 8 h of aging time. The solids were separated from the solution by centrifugation and then washed several times with water. They were then dried in air at ambient temperature (25°C).

2.2. Methods

XRD equipment used was a XPERT-MPD diffractometer. Samples of unoriented powder were exposed to copper K_α radiation (λ = 0.15415 nm). Measurement conditions were: 2θ range: 5-70°, step size: 0·08° 2θ and step counting time: 4 s. Data acquisition was effected on a DACO-MP microcomputer. Unit cell constants were calculated using a least-squares refinement.

Absorbance IR spectra were recorded on a Perkin-Elmer 16 PC spectrophotometer, at a resolution of 2 cm^{-1} and averaging over 100 scans, in the range 400-4000 cm^{-1}. Samples were pressed into KBr discs.

Samples in the form of a dry powder were sprinkled onto the surface of a very thin adhesive layer for examination in the SEM. They were then coated by vacuum deposition with gold in order to minimize the severe charging effects that proved to be characteristic of the materials examined. They were run on a Cambridge Stereo scan 360 microscope operated at an accelerating voltage of 5 kV.

3. Results and discussion

3.1. LDH material

XRD pattern for the [Zn-Al-Cl] precursor (Figure 1) indicates that the sample, which consists of a single phase, is very well crystallized with its constituting crystallites of large size. This pattern is in agreement with that found for crystallites of the hydrotalcite-like minerals. The XRD powder data, refined on the hexagonal setting with a rhombohedral symmetry (space group: $R(-3)m$), provided the lattice parameters for the sample: **a** = 0.307 nm and **c** = 2.334 nm.

The IR spectrum (Figure 2) indicates the presence of small amounts of the carbonate anion in all compounds despite the precautions taken during the preparation of the solids. This contamination may be explained by the stability of the anion in basic solution and the high selectivity of [Zn–Al] LDHs for the carbonate anion [10].

The chloride precursor was used for the preparation of phosphonate containing LDH by ion exchange. The separate effects of initial phosphonate concentration and aging time were investigated in order to determine the optimum conditions for complete exchange, grafting phosphonates and best crystallized compounds.

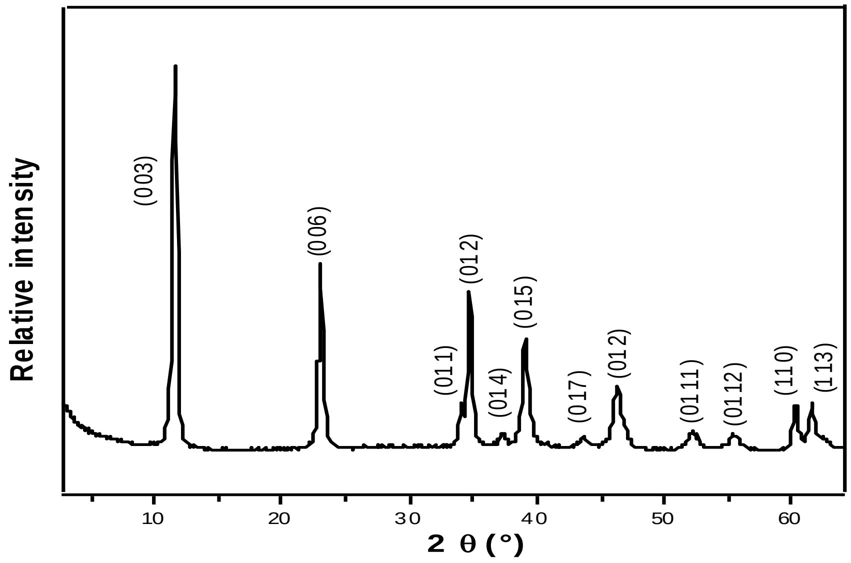


Figure 1: XRD pattern of [Zn-Al-Cl] precursor.

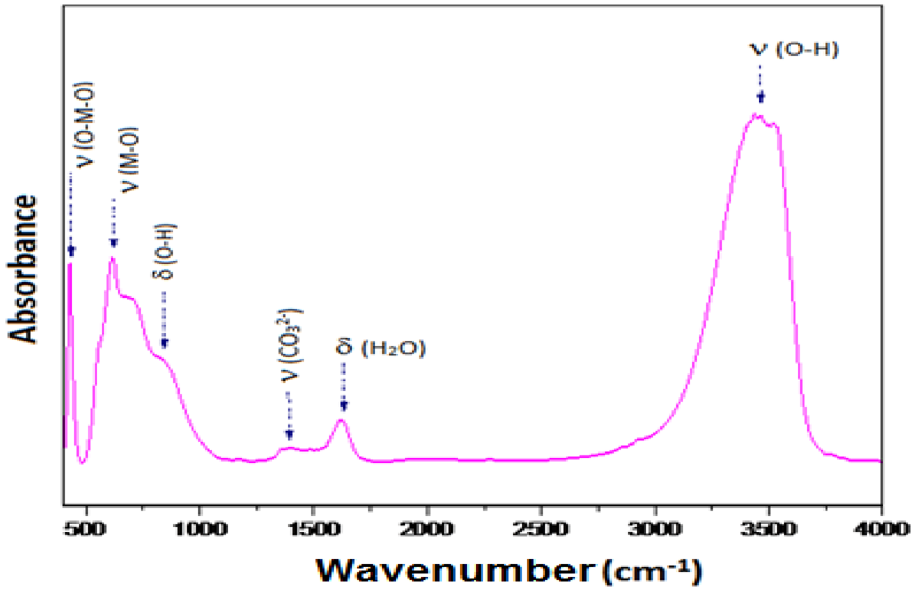


Figure 2: FTIR spectrum of [Zn-Al-Cl] precursor.

3.2. Ion exchange of chloride by phosphonate ions

Effect of concentration

The suspensions were kept at room temperature (25°C) under stirring for 3 h. During the stirring, the suspension is under nitrogen in order to minimize contamination by the carbonate ions exchanged from the CO_2 from the air.

XRD patterns for [Zn-Al-$COOCH_2PO_3$] LDHs prepared with different concentrations are shown in figure 3. The lamellar structure of the material is preserved after exchange. However, the crystallinity is lowered, as attested to be the broadening of the (110) reflection, indicating certain disorder in the layers, and a displacement of (00*l*) lines, denoting an increase in the interlayer space which is due to the exchange of chloride by phosphonate ions.

The study of the effect of phosphonate concentration indicates that the lowering of crystallinity is more pronounced for 0.1 M. Relatively, the best phase in terms of crystallinity, was obtained for a phosphonate concentration of 0.01 M.

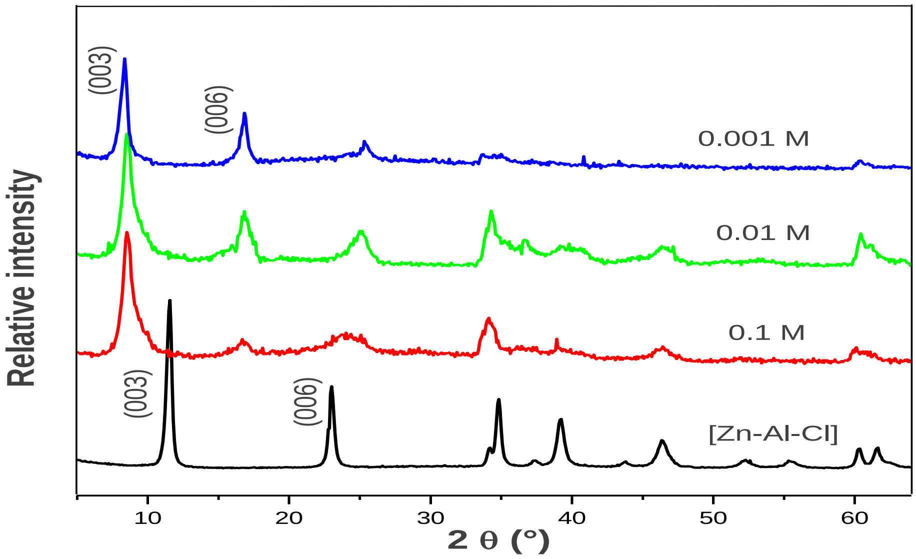


Figure 3: XRD patterns of exchanged phases [Zn-Al-$COOCH_2PO_3$] obtained with different phosphonate concentrations.

Effect of aging time

The effect of aging time was investigated in solutions with a phosphonate concentration of 0.01 M, to determine the optimum conditions for complete exchange reaction and best crystallized compounds.

The change of the stirring time from 30 min to 1 h is accompanied by a relative increase in the crystallinity of the exchanged phase (Figure 4). This is indicated by the increase in intensities of the two lines (003) and (006). The exchange of the chloride ions by phosphonate ions occurs rapidly after 30 min of contact time. The shift of (003) and (006) lines towards higher interlayer distances might be attributed to the anion orientation and to the amount of anions in the interlayer space.

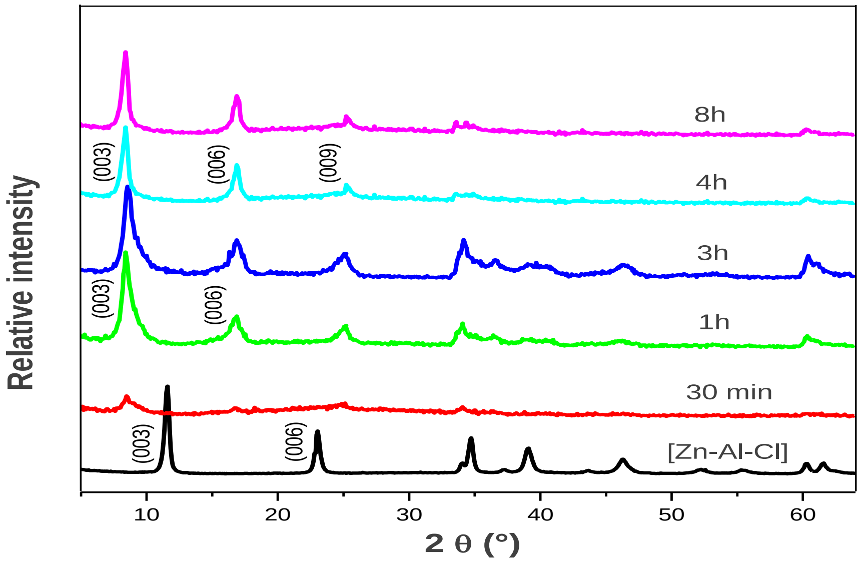


Figure 4: XRD patterns of exchanged phases [Zn-Al-$COOCH_2PO_3$] obtained with different aging time.

These results indicate that the most preferred time for well-crystallized phase formation is within a range of 1–8 h. The best phase, in terms of crystallinity, was obtained for an aging time of 3 h.

The lattice parameters of the well-crystallized compound were refined from the XRD patterns on the hexagonal setting with a rhombohedral symmetry (space group *R*-3*m*). The parameters are **c** = 2.961 nm (**d** = 0,987 nm) and **a** = 0.306 nm. These parameters, compared with those of [Zn-Al-Cl], **a** = 0.307 nm and **c** = 2.334 nm (**d** = 0.778 nm), indicate that the basal periodicity, corresponding to the distance between two neighboring metallic cations, is preserved.

Infrared spectroscopy

The IR spectrum of [Zn-Al-$COOCH_2PO_3$] is illustrated in Figure 5. All stretching and bending vibration modes of the phosphonate anion are observed in the spectrum, besides the absorption bands of the hydroxylated layers. It can be noted that the lattice vibrations are preserved and the new bands imply that the phosphonate anion is present.

The absorption centered at 3460 cm^{-1}, which results from the stretching vibration of hydroxyl groups and water molecules, is appreciably broadened by the presence of the phosphonate anion. This may be attributed to the interaction of the anion with water molecules as well as the interlayer matter disorder [11]. The absorption at 1650 cm^{-1} is assigned to the bending vibration of water.

The proof for the presence of phosphonate groups results from their characteristic vibrations: ν_s(P–O) at 1060 cm^{-1} and ν_{as}(P–O) at 1140 cm^{-1}. ν_s(C–O) at 1380 cm^{-1} and ν_{as}(C–O) at 1600 cm^{-1}.

The ν(P–C) vibration out of the plane appears at 1100 cm^{-1}. The shoulder at about 1210 cm^{-1} is characteristic of the P=O group [12-14].

The band at 1360 cm^{-1}, which increases after exchange, is assigned to the carbonate CO_3^{2-}. Lattice vibrations appear around 425, 560, 620 and 825 cm^{-1}.

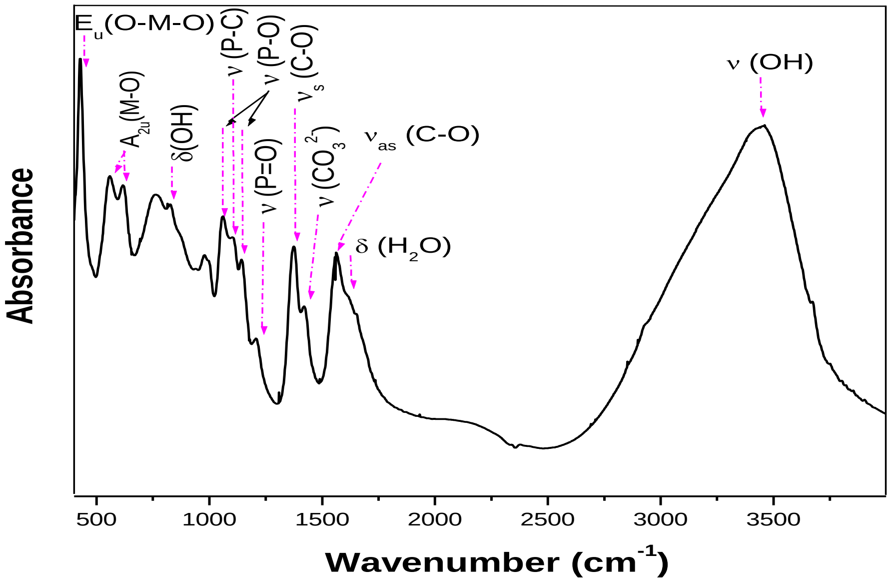
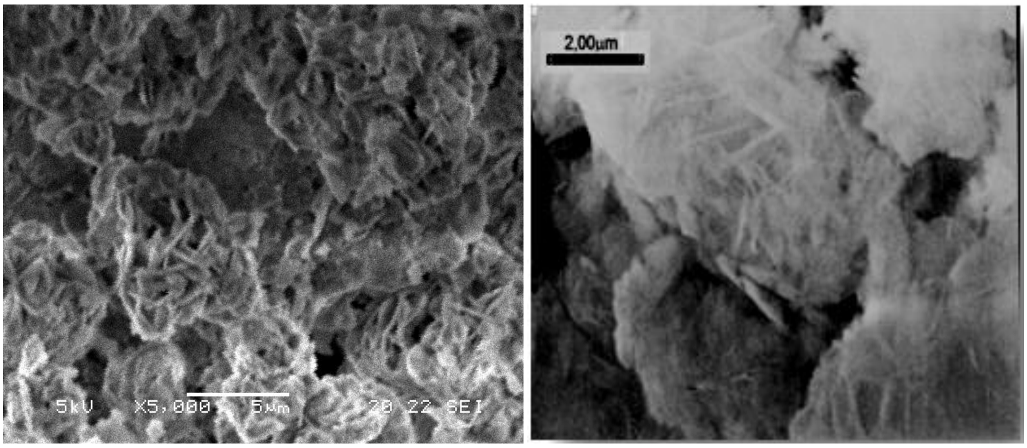


Figure 5: IR spectrum of exchanged phase [Zn-Al-$CO_2CH_2PO_3$].

Scanning Electron Microscopy

The micrograph of the exchange phase [Zn-Al-$CO_2CH_2PO_3$] is shown in Figure 6. The examination of the precursor and phosphonate-intercalated materials by SEM reveals that the crystals present almost the same morphological features.

They tend to result from the superposition of several leaflets with dimensions of the particles being about 5 µm for [Zn–Al–Cl] and 4 µm for [Zn-Al-$CO_2CH_2PO_3$]. The small morphological alteration of the layers, after exchange, can be due to the decrease in crystallinity observed by XRD in the sample.



(a) (b)

Figure 6: SEM photographs of [Zn–Al–Cl] (**a**) [Zn-Al-$CO_2CH_2PO_3$] (**b**).

Thermal Study

The XRD patterns are reported in Figure 7. Compared with the XRD patterns of the starting material, these patterns show the following aspect:

- Between 50 and 165 or 200°C, XRD peaks corresponding to the (00*l*) basal spacing were shifted toward higher diffraction angles (2θ) and became broad and less intense, indicating that the LDH undergoes a certain disorganization on heating.
- Between 200 and 400°C, the LDH phases disappeared and an amorphous phase related to metal oxides emerged, as indicated by the broad bands observed on the XRD pattern of the sample calcined at 200°C. The intensity of these bands increased with increasing temperature.
- At 800°C, the diffractogram revealed a mixture of zinc oxide and the spinel-type phase, $ZnAl_2O_4$.

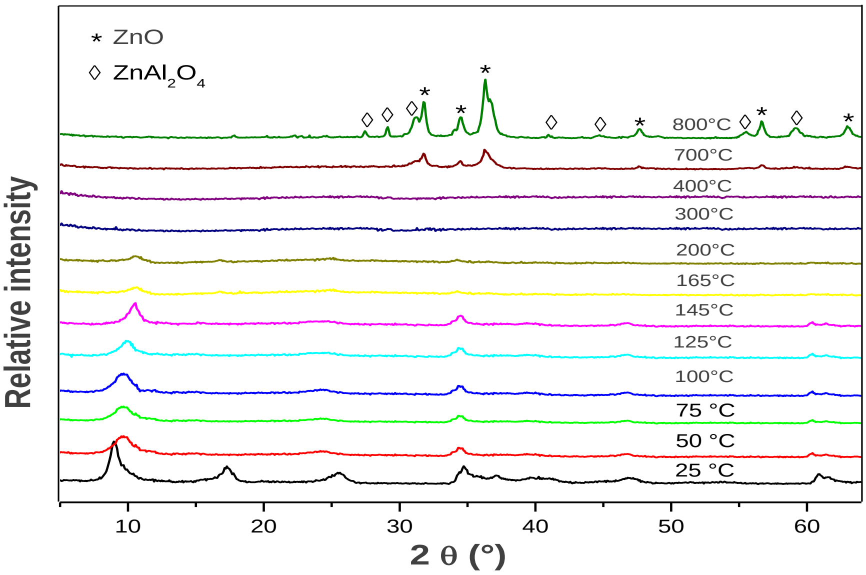


Figure 7: XRD patterns of [Zn-Al-$CO_2CH_2PO_3$] compound calcined at different temperatures.

The cell parameter **a** appears to be independent of the calcination temperature, while the interlayer spacing of [Zn-Al-$CO_2CH_2PO_3$] phase shows a strong change. Figure 8 shows that the basal spacing decreases with increasing temperature. The contraction, which corresponds to an important structural change of the interlayer domain, is related to water loss and dehydroxylation.

Effect of temperature on the parameter ***c***

Despite the large size of the phosphonate anion, the interlayer distance after heating is lower than that observed in [Zn–Al–Cl] (**d** = 0.778 nm). The parameter **c** decrease from 2.961 to 2.22 nm suggests that only one oxygen layer of the anion is located between the sheets. This behavior can be attributed to a grafting of the phosphonate anion to the brucite-like layers [15,16].

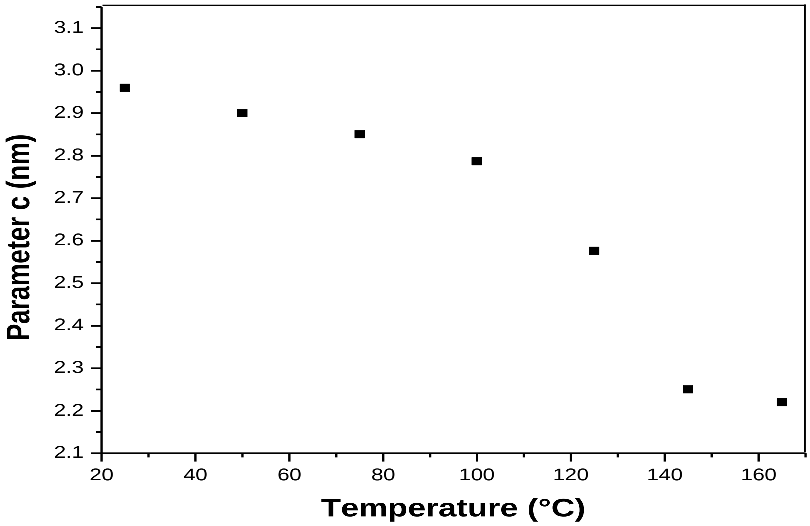


Figure 8: Evolution of the parameter **c** (**c** = 3$\mathbf{d}_{003}$) depending on the temperature.

Infrared spectroscopy

The IR spectroscopy study was limited to the range of temperature where the LDH phase is stable. The overall shape of the spectra is similar to those of LDH. As shown in Figure 9, an increase in the calcination temperature decreases the intensity of ν(OH) and δ(H_2O) bands. This indicates the loss of interlayer water. The attenuation of the band characteristic of the vibration E_u (O-M-O) (438 cm^{-1}) of the crystal lattice may be due to a deterioration of the crystallinity of the host matrix with the heating temperature.

A more significant change is noted in the bands between 600 and 700 cm^{-1} characteristic of stretching vibrations A_{2u} and E_u of M-O.

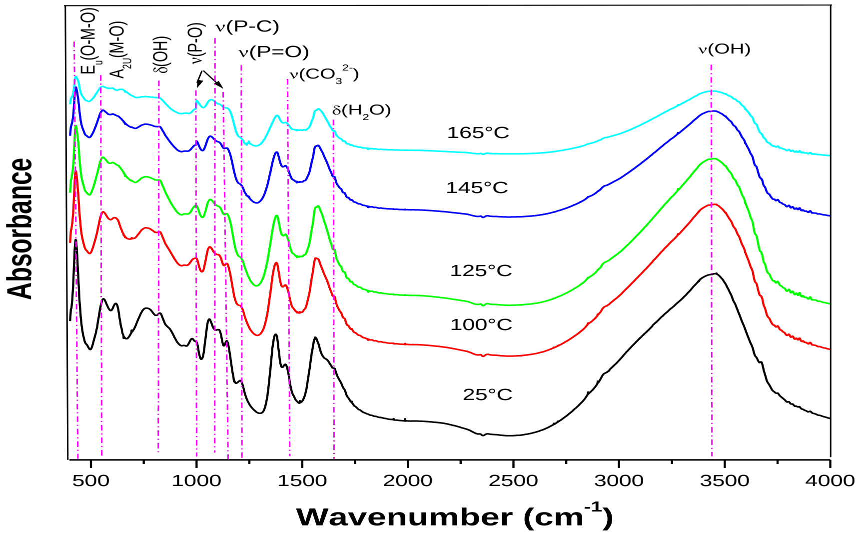


Figure 9: IR spectra of [Zn-Al-$CO_2CH_2PO_3$] phase heated at moderate temperatures.

It is noteworthy that despite the precautions taken during the preparation of the samples, the FTIR spectra exhibit the valence vibrations for the carbonate ion, at 1400 cm^{-1}. This contamination, by atmospheric CO_2, which is more pronounced for the two samples prepared in basic solutions, may be explained by the stability of CO_3^{2-} in basic media and the high selectivity of the LDH for this anion [10]. However, the carbonate is found in the solids in form of traces since no carbonate-phase was detected in the XRD patterns.

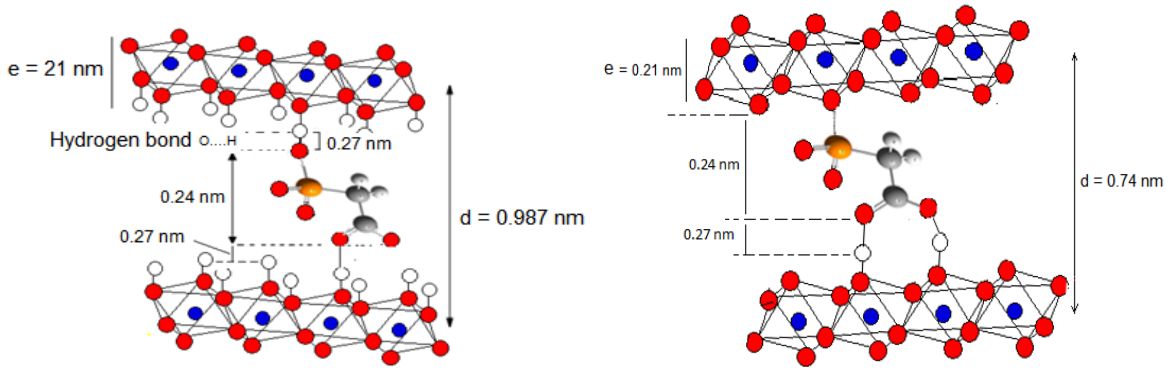
The bands observed at 1080 and 1150 cm^{-1} correspond to the antisymmetric and symmetric vibrations of P-O, respectively.

Structural model

Before proposing an orientation of the phosphonate ion between and the layers, we determined the value of the length of the molecule $CO_2CH_2PO_3$ by molecular orbital semi-empirical method with the Gaussian 03 software, the calculated value for a horizontal position is 0.24 nm. Figure 10 shows the orientation of phosphonate ion grafted to the LDH sheets.

The interlamellar distance of is 0.987 nm, as determined experimentally, suggests a horizontal direction of the anion in the interlayer space:

$$\mathbf{d} = 0.21 + 0.27 + 0.27 + 0.24 = 0.99 \text{ nm} \sim 0.987 \text{ nm}.$$



(a) (b)

Figure 10: Structural model of the phosphonate anion non-grafted (**a**) and grafted (**b**) to the LDH sheets.

Recent studies on LDH interspersed with monofunctional organic anions show no grafting process by the carboxylate group [17-20]. We believe that, for the grafted phase, the phosphonate anion will keep the same orientation in the interlamellar space with exchange of the hydroxyl group of the sheet by the oxygen of the phosphonate group. The expected interlayer distance is equal to the distance obtained from the phase obtained at room temperature (not grafted) minus the distance of a hydrogen bond (0.27 nm), giving a new distance **d'** = 0.987 - 0.27 = 0.717 nm, with **c'** = 3**d'** = 2.16 nm. The latter value is comparable to that obtained experimentally in the range of 2.22 nm (Figure 10).

Sabbar et al [21] have proposed an alternative orientation of the same anion in the interlayer space by directing both carboxylate and phosphonate functions to the same sheet. These authors have not reported grafting by heating this phase, which may be probably due to that the carboxylate groups that did not produce a grafting process, as was noted above, and their orientation influence phosphonate groups not grafted to the sheets. The moderate heat treatment resulted in a small contraction in the interlayer space of 0.14 nm, which can only be due to the loss of interlayer water.

By against our exchange phase and given the contraction value of the parameter **c**, we can only be in accordance with a provision of the phosphonate anion parallel to the sheets with two groups, carboxylate $-CO_2^-$ and phosphonate $-PO_3^-$ are each directed to a sheet and form hydrogen bonds with these two sheets.

Similar results were reported by other authors regarding either the grafting of sulfonate ions with host matrices based on Zn-Al or Cu-Cr after heating at around 80°C [22] or grafting phosphate ions on a matrix based on Mg-

Al [23]. The interlayer phosphate is grafted to the layer by the formation of direct bonding to metal cations in the layer, accompanied by a change in polytype of the crystalline structure. The grafted phosphate becomes immobilized and cannot be removed by anion-exchange with 1-octanesulfonate. At the same time, the XRD pattern clearly shows a decrease of the basal spacing according to the contraction process which could be interpreted as a progressive organic molecule condensation onto the inorganic layers via iono-covalent bonds.

Conclusion

The study of the influence of some parameters on the intercalation of phosphonate ions in LDH and characterization of phases obtained by X-ray diffraction of the interlayer space, followed by IR spectroscopy showed that the total exchange of the chloride ion by the phosphonate ions is obtained at pH 9 using a 0.01 M in phosphonate solution under stirring for 3 hours.

The interlayer distance increases from 0.778 nm for the host matrix to 0.987 nm after exchange.

Heat treatment of the [Zn-Al-$CO_2CH_2PO_3$] phase showed that there is a grafting phenomenon of phosphonate ions to the LDH sheets and preservation of the layered structure of the phase heated at 165°C. Above 200°C, the layered structure disappears in favor of an apparent amorphization that persists up to 400°C. Calcination at 800°C results in an improvement of the crystallinity of ZnO and a crystallization of the spinel phase, $ZnAl_2O_4$.

References

1. Gledhill W.E., Feijtel T.C.J., *Handb. Environ. Chem.* 3 (1992) 261.
2. Nowack B., *Water Res.* 37 (2003) 2533.
3. Lacour S., Deluchat V., Bollinger J.C., Serpaud B., *Talanta*, 46 (1998) 999.
4. Nowack B., Van Briesen J.M., *J. Am. Chem. Soc.* 910 (2005) 1.
5. Horstmann, B., Grohmann, A., *Vom Wasser*, 70 (1988) 163.
6. Nowack B., Stone A.T., *Environ. Sci. Technol.* 34 (2000) 4759.
7. Lesueur C., Pfeffer M., Fuerhacker M., *Chemosphere*, 59 (2005) 685.
8. Knepper T.P., Weil H., *Vom Wasser*, 97 (2001) 193.
9. Jaworska J., Van Genderen-Takken H., Hanstveit A., Van de Plasche E., Feijtel T., *Chemosphere*, 47 (2002) 655-665.
10. Miyata S., *Clays Clay Miner.* 28 (1980) 50.
11. Bish D.L., Brindley G.W. *Am. Mineral.* 62 (1977) 458.
12. Corbridge D.E.C, Lowe E.J., *J. Chem. Soc.* 493 (1954) 4555.
13. Rulmont A., Cahy R., Liegois-Duykaerts M., Tarte P., *Eur. J. Solid State Inorg. Chem.* 28 (1990) 207.
14. Carlino S., Hudson M.J., Wafik Husain S., Knowles J.A., *Solid State Ionics*, 84 (1996) 117.
15. Depège C., El Metoui F.Z., Forano C., De Roy A., Depuis J., Besse J.P., *Chem. Mater.* 8 (1996) 952.
16. Costantino U., Casciola M., Massinelli L., Nocchetti M., Vivani R., *Solid State Ionics*, 97 (1997) 203.
17. Sato T., Okuwaki A., *Solid State Ionics*, 45 (1991) 43.
18. Prevot V., *Doctorat de l'Université,* Université Blaise Pascal, Clermont Ferrand, France, 1999.
19. Lakraimi M., Legrouri A., Barrooug A., De Roy A. et Besse J.P., *J. Mater. Chem.* 10 (2000) 1007.
20. Lakraimi M., *Thèse d'Etat,* Université Cadi Ayyad, Marrakech, Morocco, 2002.
21. Sabbar E., De Roy M.E., Leroux F., *J. Phys. Chem. Solids,* 67 (2006) 2419.
22. Fleutot S., Dupin J.C., Renaudin G., Martinez H., *Phys. Chem. Chem. Phys.* 13 (2011) 17564.
23. Shimamura A., Kanezaki E., Jones M.I., Metson J.B., *J. Solid State Chem.* 186 (2012) 116.