INFLUENCE OF pH ON PHOSPHATE INTERCALATION
IN ZINC–ALUMINUM LAYERED DOUBLE HYDROXIDE

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The exchange of chloride ion by phosphate ions in [Zn–Al–Cl] layered double hydroxide was inves-
tigated using X-ray diffraction and infrared spectroscopy. The effects of the pH of the solution con-
taining the phosphate ions on the ion exchange was studied. The best sample in terms of crystallinity,
was obtained at pH 8. This sample was further characterized by scanning electron microscopy and
microanalysis.
Key words: Layered double hydroxides; Ion exchange; Hydrotalcite phase; Phosphates.

Layered double hydroxides (LDH)s, also called anionic clays or hydrotalcite-like com-
pounds[1], are layered solids which have a stacking of positively charged octahedral
sheets. The net positive charge, which is due to substitution of trivalent by divalent
metal ions in the brucite-like metal hydroxide $M(OH)_2$, is balanced by an equal nega-
tive charge of the interlayer solvated anions. The LDH compounds can be represented
by the general formula[2]:

$[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}[X_{x/m}^{m-}·n\ H_2O]^{x-}$ symbolized by $[M^{II}–M^{III}–X]$,

where $M^{II} = Mg^{2+}$, Zn^{2+}, Mn^{2+},...; $M^{III} = Al^{3+}$, Cr^{3+}, Fe^{3+},...; $X^{m-} = Cl^-$, NO_3^-, CO_3^{2-}, ...
and x varies between 0.20 and 0.33 (refs[3,4]).

These materials have received considerable attention in recent years due to their potential
technological applications in various domains such as catalysis, electrochemistry,
separation technology, and medicine[5–11]. This attention results from the layered struc-

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ture of these materials and their high anion exchange capacity. In fact, the interlayer solvated anions are exchangeable, which leads to important variations in the interlamellar distance[12,13].

A bibliographical study indicated that the LDHs intercalated by the phosphate ions are difficult to synthesize with good crystallinity, because the coprecipitation of metallic salts in the presence of phosphates leads to metal phosphates. This study forms part of a wider investigation undertaken on the intercalation of phosphate ions in the [Zn–Al] LDH by ion exchange. The effects of the anion concentration in solution, the aging time, and temperature were studied in order to determine the optimum conditions under which an intercalated clay is obtained with good crystallinity and high exchange rate[14]. We report here on the effect of the pH of the solution containing the phosphate ions on the ion exchange. Both the [Zn–Al–Cl] precursor and the phosphate-exchanged phases prepared at different pH values were characterized by powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (IR). The best sample, in terms of crystallinity, obtained in the series was subjected to further characterization by scanning electron microscopy (SEM) and microanalysis.

EXPERIMENTAL

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 the method of coprecipitation at constant pH (ref.[15]). Aqueous solutions containing $ZnCl_2$ (50 mmol) and $AlCl_3 \cdot 6\ H_2O$ (25 mmol) ($[Zn^{2+}]/[Al^{3+}] = 2$) was slowly introduced under stirring in reactor which contains 250 ml of freshly deionized water. The pH was maintained constant at pH 9 by the simultaneous addition of 1.0 M NaOH solution. The resulting slurry was then left under stirring for 37 h. The precipitate was filtered, washed several times with water, and then dried on air at 30 °C.

Exchange reactions were carried out with 200 mg of the [Zn–Al–Cl] LDH suspended in 200 ml of 0.01 M sodium hydrogenphosphate (Na_2HPO_4) solutions which were stirred[16,17]. The pH of the mixture was adjusted either by acidification with 2 M H_3PO_4 solution or by addition of 2 M NaOH solution. The anion exchange reaction was achieved at ambient temperature (30 °C) with 5 h of aging time. The solids were separated from the solution by centrifugation and then washed several times with water. They were then dried on air at ambient temperature (30 °C).

Methods

The XRD equipment used was a Siemens D 501 diffractometer. Samples of unoriented powder were exposed to CuKα radiation ($\lambda = 0.15415$ nm). Measurement conditions were: 2θ range 2–65°, step size 0.08° 2θ, step counting time 4 s. Data acquisition was effected on a DACO-MP microcomputer. Unit cell constants were calculated using a least-squares refinement.
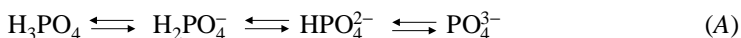
Fourier-transform IR spectra were recorded on a Perkin–Elmer 16 PC spectrophotometer at a resolution of 2 cm^{-1} and averaging over 100 scans in the range 400–4 000 cm^{-1}. Samples were pressed into KBr disks.

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 Stereoscan 360 microscope operated at an accelerating voltage of 20 kV.

X-Ray microanalysis was carried out on a Pentafet Oxford apparatus. For homogeneity, the samples were pressed into small disks and mounted on the sample holder. The results obtained constitute a mean of several analyses done on different points of the disk.

RESULTS AND DISCUSSION

Before disclosing the results of this study, let us recall that according to the pH of the solution the possible predominant equilibria for the phosphate ions are:

$$H_3PO_4 \longleftrightarrow H_2PO_4^- \longleftrightarrow HPO_4^{2-} \longleftrightarrow PO_4^{3-} \qquad (A)$$

with $pK_{a1} = 2.15$, $pK_{a2} = 7.20$, and $pK_{a3} = 12.33$ (ref.[18]).

Table I summarizes the composition of 0.010 M phosphate buffer as a function of the pH value. The choice of pH values is based on two main facts: (i) Too much acidic solutions were avoided in order to prevent dissolution of the matrix. (ii) The pH was varied in an interval where the predominant species are $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}.

X-Ray Diffraction

The XRD pattern for the precursor (Fig. 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[15]. The XRD powder data, refined on the hexagonal setting with a rhombohedral symmetry (space group: $R\bar{3}m$, No. 166), provided the lattice parameters for the sample: $a = 0.3077(2)$ nm and $c = 2.323(2)$ nm.

XRD patterns for the samples obtained upon exchange of the chloride ion by the phosphate ion at different pH values present some common features (Fig. 1). The la-

TABLE I
Composition of 0.010 M sodium phosphate buffer solution (in %) at different pH values

Anion	pH				
	6.5	8	9	11	12.5
$H_2PO_4^-$	83.3	13.7	1.4	$1.52 \cdot 10^{-2}$	$2.0 \cdot 10^{-4}$
HPO_4^{2-}	16.6	86.2	98.5	95.53	40.3
PO_4^{3-}	$2.5 \cdot 10^{-7}$	$4.0 \cdot 10^{-5}$	$4.6 \cdot 10^{-4}$	4.45	59.6

mellar structure of the material is preserved upon intercalation. However, the crystallinity is lowered, as attested by the broadening of the lines and the decrease in their intensity. In addition, intercalation is observed to cause a broadening of the (110) reflection indicating certain disorder in the layers and a displacement of the (003) line, denoting an increase in the interlamellar space which is due to the exchange of the chloride by the phosphate[16,19–21].

The lowering of crystallinity is more pronounced for low pH values. This might be explained by partial dissolution of the LDH in the acidic solutions. The interlamellar space was observed to decrease with increasing pH (Fig. 2). This decrease can be explained by the fact that when the pH increases, the size of the predominant phosphate species present in the solution decreases, and their charge increases, leading to stronger attractions between the anions and the positively charged layers. However, as expected, the lattice parameter a, which is related to the metal–metal interatomic distance within the layers, is very little affected by the pH variation.

Infrared Spectroscopy

The IR spectrum of the starting material [Zn–Al–Cl] (Fig. 3) presents a profile which resembles those exhibited by all hydrotalcite-like phases[15]. Typical of this spectrum are
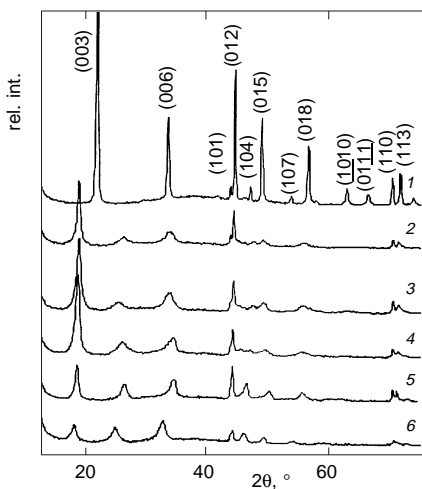

FIG. 1
XRD patterns of [Zn–Al–Cl] and phosphate-exchanged phases obtained at different pH values. [Zn–Al–Cl] (*1*); pH: 12.5 (*2*), 11.0 (*3*), 9.0 (*4*), 8.0 (*5*), 6.5 (*6*)
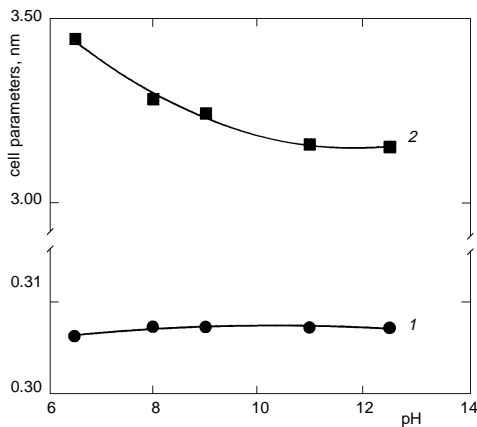
FIG. 2
Evolution of the cell parameters, a (*1*) and c (*2*), with the pH of the solution in which the exchange was carried out

the large band at 3 490 cm^{-1}, the band at 1 620 cm^{-1}, and the small shoulder at 830 cm^{-1} which correspond to the valence vibration of hydroxy groups, the bending vibration of water $\delta(H_2O)$, and the planar lattice vibration of hydroxy groups $\delta(OH)$, respectively. The bands observed in the low-frequency region of the spectrum correspond to the lattice vibration modes and can be attributed to M–O (841 and 647 cm^{-1}) and O–M–O (435 cm^{-1}) vibrations.

In addition to the bands observed for the precursor, the IR spectra of the exchanged phases at different pH values (Fig. 3) present some characteristic bands of the ortho-phosphate around 1 220, 1 050, 870, and 550 cm^{-1} corresponding to $\delta(P-OH)$, $\nu_3(PO_4^{3-})$, $\nu_1(PO_4^{3-})$, and $\nu_4(PO_4^{3-})$ vibrations, respectively[22,23]. On the other hand, the band characteristic of hydroxy groups underwent some broadening and became non-symmetrical. This can be explained by the establishment of hydrogen bonding between the phosphate groups and water or hydroxy groups.

When the pH of the solution was increased, the following phenomena were noted: (i) The appearence of an intensity increase in the valence vibrations for the carbonate ion, situated at about 1 400 and 870 cm^{-1}. This contamination by atmospheric CO_2, despite the precautions taken during the exchange, may be explained by the stability of CO_3^{2-} in basic solution and the high selectivity of LDH for this anion[24]. (ii) The reduction of the intensity of the band situated at about 1 200 cm^{-1}, which is characteristic of the $\delta(P-OH)$ deformation vibration, and the increase in the intensities of the bands situated at about 560 and 780 cm^{-1}, which are attributed to the $\nu_4(PO_4^{3-})$ and $\nu_1(PO_4^{3-})$ valence vibrations, respectively. These latter observations are in good agreement with the fact that when the pH increases, the concentration of the phosphate ion PO_4^{3-} in the solution increases at the expense of the hydrogenphosphate ions (HPO_4^{2-} and $H_2PO_4^{-}$).
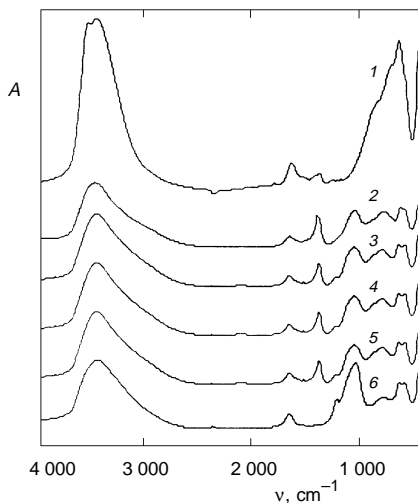

FIG. 3
IR spectra of [Zn–Al–Cl] and phosphate-exchanged phases obtained at different pH values. [Zn–Al–Cl] (*1*); pH: 12.5 (*2*), 11.0 (*3*), 9.0 (*4*), 8.0 (*5*), 6.5 (*6*)

It can be concluded from XRD and IR investigations that the best exchanged phase can be obtained at pH 8. Therefore, this phase was further characterized by SEM and microanalysis.

Scanning Electron Microscopy and Microanalysis

The examination of the parent and the phosphate-intercalated materials by SEM (Fig. 4) revealed that the crystals present almost the same morphological features. They look to result from the superposition of several leaflets with the dimensions of the particles being of about 7 µm for [Zn–Al–Cl] and 5 µm for [Zn–Al–HPO$_4$]. These particles are constituted of crystallites which sizes are of approximately 2×0.8 and 1.4×0.4 µm, respectively. The small morphological alteration of the layers, upon exchange, can be due to the decrease in crystallinity observed by XRD in the sample.

The microprobe analysis of the sample before and after exchange was carried out on different crystals and for separate points in the same crystal for each phase. The spectrum of the parent material exhibits characteristic emissions for zinc, aluminum, and chlorine, while that of the intercalated sample presents, in addition to the emissions of

TABLE II
Elemental microanalysis (in mole %) for the [Zn–Al–Cl] LDH and the phosphate-intercalated phase

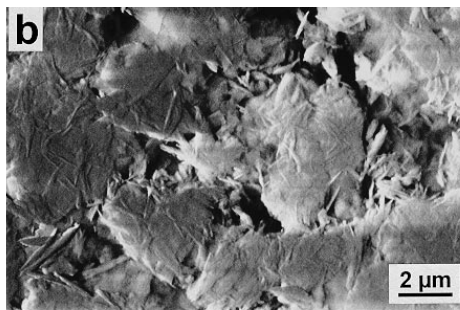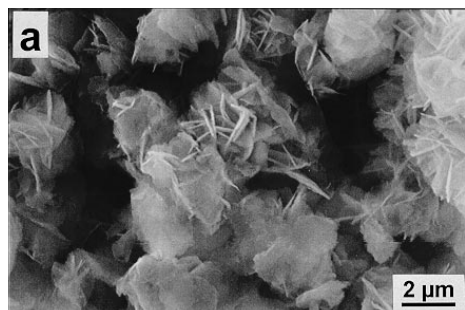| Phase	Element			
	Zn	Al	Cl	P
[Zn–Al–Cl]	48.0	22.4	27.1	–
[Zn–Al–HPO$_4$]	54.5	29.7	–	15.8

FIG. 4
SEM photographs of [Zn–Al–Cl] (a) and the phosphate-exchanged phase obtained in the solution of pH 8 (b)

zinc and aluminum, only that of phosphorus (Fig. 5) confirming the chloride–phosphate ion exchange. This characterization also suggests that the samples have a homogeneous composition the average of which is given in Table II.
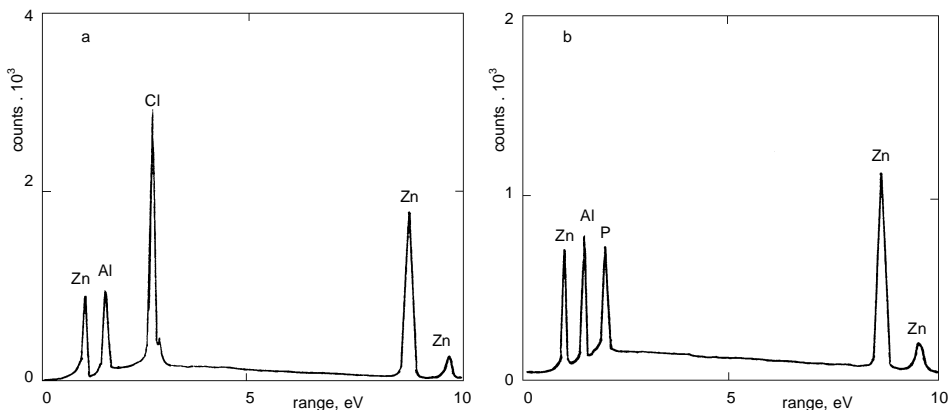

FIG. 5

X-Ray microanalysis spectra of [Zn–Al–Cl] (a) and the phosphate-exchanged phase obtained in the solution of pH 8 (b)

CONCLUSIONS

Phosphate-intercalated [Zn–Al] LDH phases were prepared from a chloride precursor, which was obtained by coprecipitation method at constant pH, by exchange reaction in a phosphate-containing solution. The effects of the pH of the anion-containing solution on the exchange was studied in order to determine the optimum pH under which the intercalated clay is obtained with a good crystallinity and high exchange rate. XRD and IR revealed that, in all cases, the crystallinity of [Zn–Al–HPO$_4$] phases is lower than that of the precursor. Intercalation was also observed to cause certain disorder in the layers without destruction of the lamellar structure of the material. The best crystalline material, with high exchange rate, was obtained by carrying out the exchange at pH 8. SEM observation of the parent material and the sample obtained upon intercalation at pH 8 showed that the morphology of the crystals did not undergo a large modification following the ion exchange. Microanalysis of the samples showed that these possess a homogeneous composition and confirmed the phosphate intercalation. Further investigations are under way to examine the reactivity of the phosphate ion inside the interlamellar domain, following thermal treatment.

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