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# Intercalation of vanadate in Ni, Zn layered hydroxyacetates

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## Abstract

Interlayer acetate anions in layered double hydroxyacetates of $Ni^{2+}$ and $Zn^{2+}$ have been exchanged by oxovanadates following three synthetic routes (at 60°C, under hydrothermal conditions and after preswelling with caprylate anions) and different pH; direct exchange at room temperature was not successful. Complete exchange was achieved under adequated conditions, and the precise nature of the interlayer anion depends on the pH during exchange: at low pH (4.5), the presence of $\alpha$-$VO_3$ chains, with anchoring (grafting) of the species to the hydroxide layers, is proposed. At higher pH (9.5) $V_2O_7^{4-}$ species are present in the interlayer. Thermal decomposition of these vanadate-intercalated products leads to formation of orthorhombic $Ni^{2+}$ and $Zn^{2+}$ vanadates, together with NiO.

*Keywords:* Layered compounds; Host-guest systems; Polyoxometalates; Hydroxyacetates

## 1. Introduction

Anion exchanged layered compounds have been extensively studied in the last years, due to their potential ability as ion exchangers with organic and inorganic anions. The most widely studied anion exchanged layered materials are the double layered hydroxides (LDH) family of materials [1–3], which consist of positively charged hydroxide layers and interlayered anions. In addition to this family, anion exchangeable layered mixed basic salts have been recently synthesized through the hydrothermal decomposition of mixed aqueous solutions of zinc and nickel acetates, and tested as anion exchangers [4–6]. These materials are known as layered double acetates (LDA), and their structure can be described from brucite-like $Ni(OH)_2$, where up to 25% of $Ni^{2+}$ cations have been removed from the octahedral holes, and substituted by $Zn^{2+}$ cations which are located outside the layers, coordinated to three hydroxyl groups and completing a tetrahedral coordination with water molecules and/or interlayer acetate anions, as depicted in Fig. 1. The formula can be written as $Ni_{1-x}Zn_{2x}(OH)_2(CH_3COO)_{2x}\cdot nH_2O$. Two main differences exist between LDHs and LDA: (i) in LDHs, cations with different formal charges exist, while in LDA both cations are divalent, and (ii) while in LDHs the cations are sandwiched between two layers of hydroxyl groups, in LDAs the Zn cations are located outside these sandwiches, outside the hydroxyl layers.

Some of the most interesting anions to be intercalated in these materials are polyoxometalates, because the experimental conditions during synthesis (specially pH) determine the specific nature of the intercalated anion, as the polymerization degree is pH-dependent [7]. As previously shown [8], layered materials with different gallery heights are thus obtained, as a consequence of the different size of polyoxometalates with varying polymerization degree. As a result, these materials can show molecular sieve properties. In addition, they lead, upon thermal decomposition, to homogeneously dispersed mixed oxides, which are useful as heterogeneous catalysts [9,10].

Following previous works on intercalation of polyoxovanadates into LDHs [8,11–16], here we report on the intercalation of decavanadate under different experimental conditions in the interlayer space of a

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Ni- and Zn-layered hydroxyacetate, whose preparation and characterization have been reported elsewhere [6].

## 2. Experimental

### 2.1. Synthesis of the samples

All reagents (p. a.) were from Fluka (Switzerland).

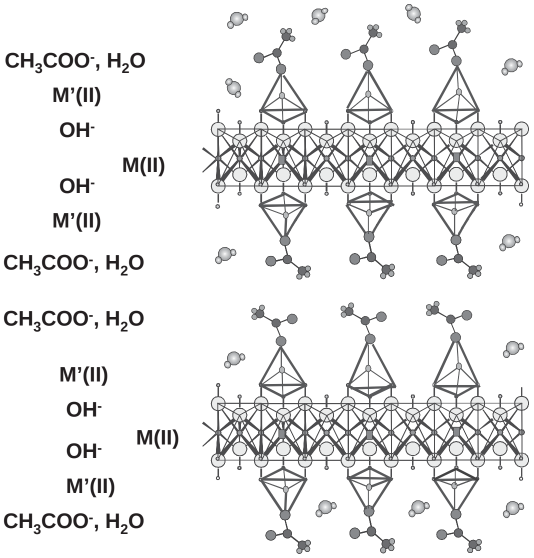

Fig. 1. Schematic representation of a Ni, Zn, double-layered hydroxyacetate.

### 2.2. Parent Ni–Zn hydroxyacetate

This was synthetised under hydrothermal conditions [4,6]. Briefly, aqueous solutions of Ni$^{2+}$ and Zn$^{2+}$ acetates (Zn/Ni atomic ratio 0.5) were mixed; the solution was submitted to hydrothermal treatment in a teflon lined stainless steel bomb at autogenous pressure at 120°C for 24 h. The solid was separated by centrifugation and it was repeatedly washed with distilled water, and dried at room temperature in a vacuum dessicator over silica gel.

### 2.3. Vanadate intercalates

Intercalation of vanadate was carried out following different routes, as summarized in Fig. 2.

### 2.4. Route 1. Anion exchange of hydroxyacetate at room temperature

A solution containing 1.2 g of NaVO$_3$ in 50 mL of previously boiled water (pH adjusted at 4.5) was added to 1 g of a Ni, Zn, hydroxyacetate slurry (ca. 1 g solid/100 mL solution). Once the addition was completed, the mixture was magnetically stirred for 2 h at room temperature and the pH was adjusted to 4.5, 8.5, or 9.5 by adding HCl or NaOH (pH meter Metrohm 691 with an automatic 725 Dosimat dispenser from Metrohm). The solid was separated by centrifugation (Sorvall Super T21) at 10,000 rpm and washed with

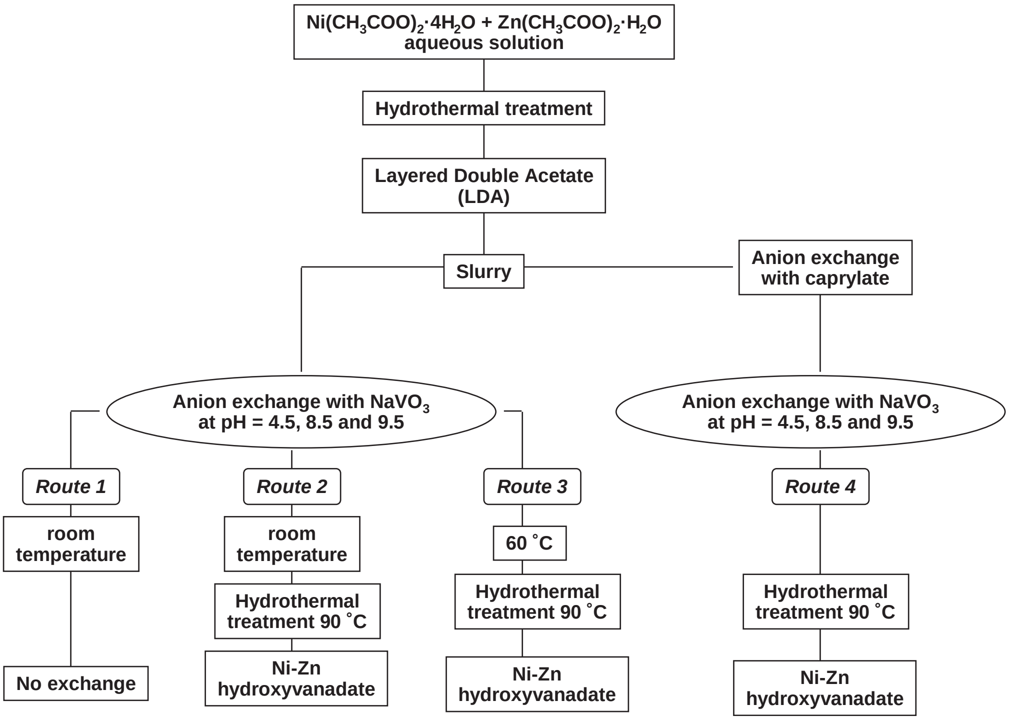

Fig. 2. Scheme of the synthesis routes used in this work.

boiled water and dried under vacuum at room temperature.

### 2.5. Route 2. Anion exchange with hydrothermal treatment

The same method described for route 1 was followed, but prior to centrifugation and separation, the product was submitted to hydrothermal treatment at autogenous pressure at 90°C for 24 h.

### 2.6. Route 3. Anion exchange of hydroxyacetate at 60°C and hydrothermal treatment

The procedure described in route 2 was followed, but the exchange was carried out at 60°C instead of room temperature.

### 2.7. Route 4. Anion exchange with preswelling with caprylate

The hydroxyacetate was first exchanged with caprylate anions, which were in turn exchanged with the vanadate anions; the pH was adjusted to 4.5, 8.5 or 9.5. The product was submitted to hydrothermal treatment at 90°C for 24 h. The solid was separated by centrifugation and washed with previously boiled water and air dried at room temperature.

### 2.8. Experimental techniques

Powder X-ray diffraction (XRD) was performed in a Siemens D-5000 instrument, using Cu*K*α radiation ($\lambda = 1.54050$ Å) at 40 kV and 30 mA at a scanning speed of 2° ($2\theta$)/min.

The FT-IR spectra were recorded following the KBr pellet technique (1% weight sample: KBr) in a Bomen MB-100 Fourier Transform instrument.

Elemental chemical analyses for Ni, Zn, and V were carried out by atomic absorption spectrometry in an AA-3100 instrument from Perkin Elmer. Samples were dissolved in HCl.

Thermogravimetric (TG) and Differential Thermal Analyses (DTA) were carried out in TG7 and DTA7 instruments, respectively, from Perkin Elmer, in flowing oxygen (from L'Air Liquide, Spain) at a heating rate of 10°C/min.

## 3. Results and discussion

### 3.1. Layered hydroxyacetate

The pale green Ni–Zn hydroxyacetate is characterized by a sharp, intense, XRD line close to 13 Å (Fig. 3), together with some other extremely weak peaks, confirming the layered structure (hexagonal H1 cell, $a = 6.163$ Å, $c = 12.93$ Å). The Zn/Ni molar ratio was

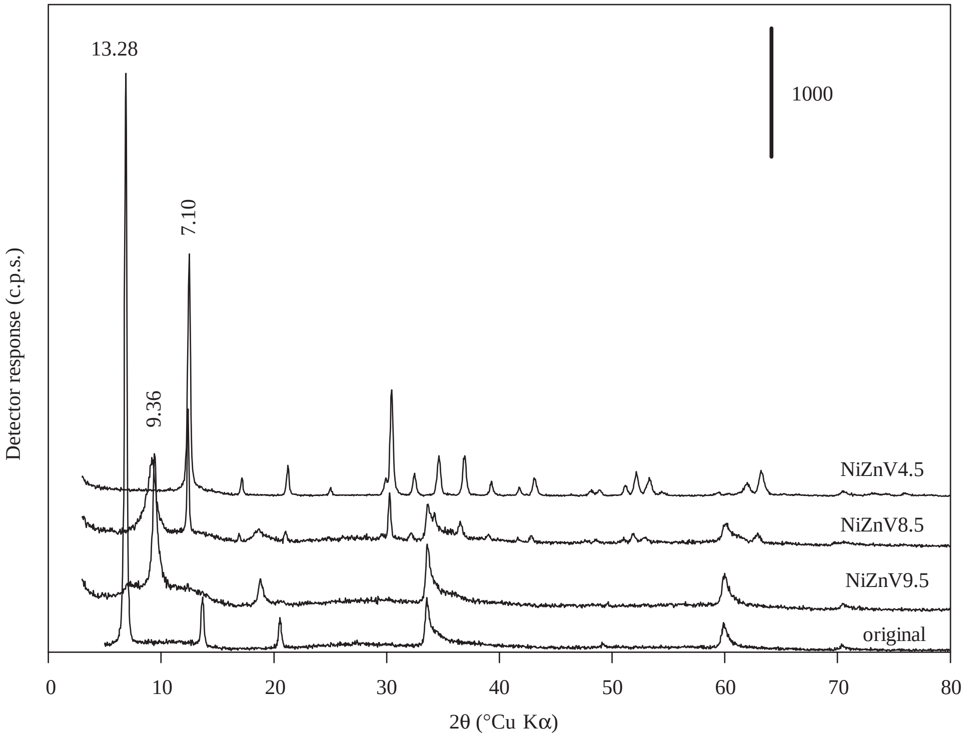

Fig. 3. XRD diagrams of parent hydroxyacetate and of the samples prepared at pH 4.5 following route 3 and for pH 8.5 and 9.5, following route 2.

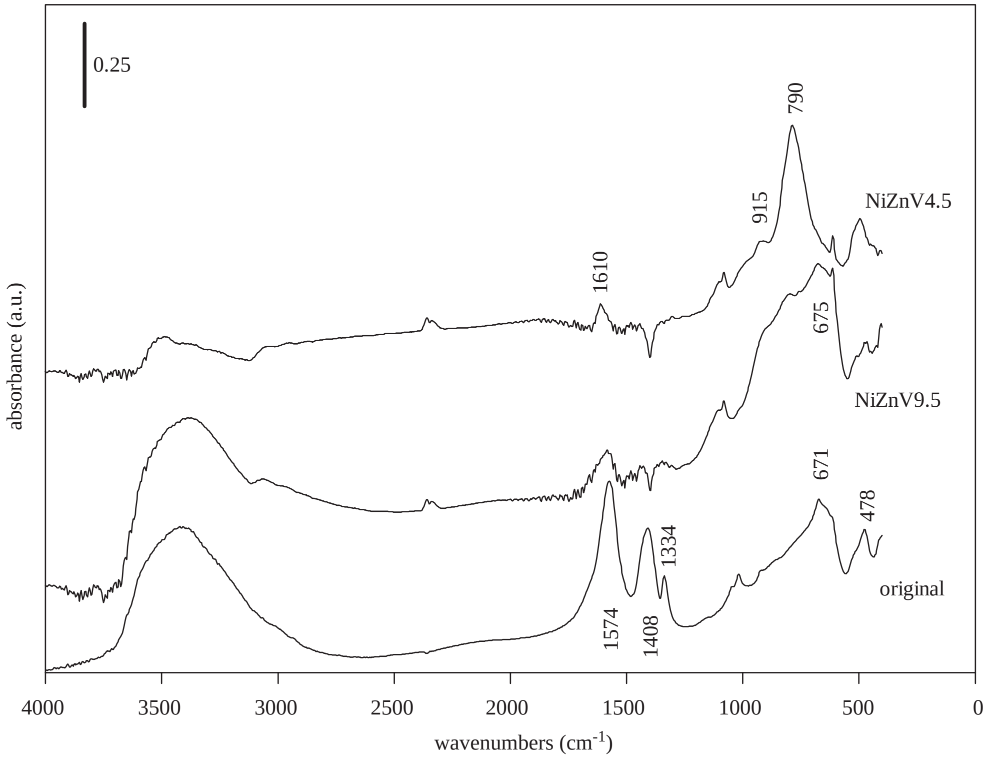

Fig. 4. FT-IR spectra of parent hydroxyacetate and of the samples prepared at pH 4.5 and 9.5.

0.5, equivalent to $x = 0.2$. The FT-IR spectrum (Fig. 4) shows a broad absorption band centered at 3400 cm$^{-1}$ [$\nu$(OH)], together with absorptions at 1574 and 1408 cm$^{-1}$ [$\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively], 1334 cm$^{-1}$ [$\delta(CH_3)$] and 671 and 478 cm$^{-1}$ [$\rho(H_2O)$ and $\delta(COO^-)$] [4,6]. Curling of the particle borders, as observed by TEM (not shown), is indicative of their extremely small thickness.

### 3.2. Layered hydroxyvanadates

As mentioned above, vanadate exchange has been carried out at pH 4.5, 8.5 and 9.5. Route 1 was unsuccessful to obtain an exchanged material whichever the pH used; in all three cases the product contained acetate in the interlayer, as it was concluded from XRD results (a single phase with spacing 12.6 Å) and FTIR spectra (characteristic acetate bands at 1580, 1412, and 1337 cm$^{-1}$).

However, all other three routes used led to successful results: both exchange with hydrothermal treatment at room temperature or at 60°C, or preswelling of the pristine material with a bulk anion (caprylate) led to formation of analogous yellowish-green solids in all three cases. As in the case of the hydroxyacetate, the TEM micrographs showed formation of extremely thin hexagonal particles, which are easily broken. This is the same shape shown by the original hydroxyacetate material, suggesting a topotactic exchange in the acetate/vanadate system; XRD results, Fig. 3, also demonstrate formation of a layered material, similar to the parent hydroxyacetate, but with different spacings (see below). For the sake of brevity, results will be shown only for materials prepared following route 2 (at pH 8.5 and 9.5) and route 3 (at pH 4.5), as similar results were obtained when the other routes were followed. The solids will be named as NiZnVY, where Y stands for the pH used during synthesis.

The XRD diagrams of solids obtained at pH 4.5 following route 3 and pH 8.5 and 9.5 following route 2 are included in Fig. 3. That for sample NiZnV4.5 corresponds to a crystalline phase which has been indexed assuming an hexagonal cell (Table 1). The cell parameters obtained are $a = 5.9778$ Å and $c = 7.133$ Å (Table 2). The basal spacing $d_{001} = 7.10$ Å corresponds to a gallery height of 2.3 Å according to the presence of $\alpha$-$VO_3^-$ chains [12], as confirmed (see below) by FT-IR spectroscopy. At pH 9.5 a single phase is also formed, with a basal spacing of 9.36 Å, very similar to that observed when vanadate species are intercalated in layered double hydroxides at the same pH [8]. This spacing is consistent with the presence of $V_2O_7^{4-}$ species in the interlayer. The exchange carried out at intermediate pH, 8.5, gives rise to the formation of two phases, characterized by basal planes close to 9.36 and 7.10 Å, indicating the simultaneous presence of the two phases above mentioned. The asymmetry observed in the XRD diagrams of samples NiZnV8.5 and NiZnV9.5

Table 1
Experimental (*d*-exp) and calculated (*d*-cal) peak positions (Å) and relative intensities ($I/I_0$ exp) from NiZnV4.5 and NiZnV9.5 XRD diagrams

| NiZnV4.5 | | | | NiZnV9.5 | | | |
|---|---|---|---|---|---|---|---|
| *hkl* | *d*-exp | *d*-cal | $I/I_0$ exp | *hkl* | *d*-exp | *d*-cal | $I/I_0$ exp |
| 0 0 1 | 7.093 | 7.133 | 100 | 0 0 1 | 9.36 | 9.40 | 100 |
| 1 0 0 | 5.152 | 5.177 | 8 | 0 0 2 | 4.71 | 4.70 | 21 |
| 1 0 1 | 4.181 | 4.189 | 13 | 0 2 0 | 2.66 | 2.67 | 38 |
| 0 0 2 | 3.556 | 3.567 | 4 | 2 2 0 | 1.541 | 1.541 | 23 |
| 1 1 0 | 2.9957 | 2.9888 | 6 | 0 4 0 | 1.335 | 1.334 | 6 |
| 1 0 2 | 2.9312 | 2.9372 | 44 | | | | |
| 1 1 1 | 2.7551 | 2.7567 | 10 | | | | |
| 2 0 0 | 2.5874 | 2.5884 | 17 | | | | |
| 2 0 1 | 2.4315 | 2.4332 | 17 | | | | |
| 1 1 2 | 2.2903 | 2.29091 | 6 | | | | |
| 1 0 3 | 2.1596 | 2.1609 | 4 | | | | |
| 2 0 2 | 2.0951 | 2.0950 | 8 | | | | |
| 2 1 1 | 1.8886 | 1.8887 | 3 | | | | |
| 1 1 3 | 1.8610 | 1.8609 | 3 | | | | |
| 0 0 4 | 1.7831 | 1.7834 | 5 | | | | |
| 2 0 3 | 1.7512 | 1.7512 | 10 | | | | |
| 2 1 2 | 1.7160 | 1.7155 | 8 | | | | |
| 1 0 4 | 1.6833 | 1.6862 | 2 | | | | |
| 3 0 2 | 1.5535 | 1.5534 | 2 | | | | |
| 1 1 4 | 1.5325 | 1.5315 | 1 | | | | |
| 2 2 0 | 1.4957 | 1.4944 | 6 | | | | |
| 2 0 4 | 1.4688 | 1.4686 | 11 | | | | |
| 3 1 2 | 1.3338 | 1.3319 | 3 | | | | |
| 4 0 0 | 1.2919 | 1.2940 | 2 | | | | |
| 4 0 1 | 1.2736 | 1.2734 | 1 | | | | |

Table 2
Elemental chemical analysis data and crystallographic parameters and V/Zn ratio for selected samples[a]

| Sample | Ni[b] | Zn[b] | V[b] | *x* | V/Zn molar ratio | *c* (Å) | *a* (Å) |
|---|---|---|---|---|---|---|---|
| NiZnV4.5 | 22.95 | 14.55 | 18.94 | 0.22 | 1.66 | 7.133 | 5.9778 |
| NiZnV9.5 | 32.46 | 23.71 | 8.22 | 0.25 | 0.44 | 9.408 | 6.1631 |
| $Ni_{1-x}Zn_{2x}(OH)_2(A^-)_{2x} \cdot nH_2O$ | | | | | | | |

[a] All values have been rounded to two figures.
[b] Weight percentage.

in the peaks close to 2.66 and 1.54 Å ($2\theta$ ca. 33 and 60°, respectively) (Fig. 3), also present in the XRD diagram of the hydroxyacetate, has been attributed to a disordered stacking of the layers (*c*-axis turbostraticity) [17]. The XRD diagram of sample NiZnV4.5 is quite different, with sharper and symmetric peaks, indicating a more ordered structure. This difference can be related with the anchoring of vanadate species in the hydroxide layers at low pH (see below). Due to the presence of two crystalline mixed phases in sample NiZnV8.5, this will not be included in the discussion below.

Differences between the FTIR spectra of the vanadates prepared at low and high pH can be also observed in Fig. 4. In all cases the bands of the acetate anion (the spectrum of the corresponding sample is also included for comparison) are absent, confirming that the exchange has been complete. Above 1500 $cm^{-1}$ the spectra are very similar for all NiZn vanadates, with a broad band centered around 3422 $cm^{-1}$ due to the $\nu(OH)$ mode of interlayer water molecules and of the layer hydroxyl groups (the intensity of this band is weaker for sample NiZnV4.5 than in that for sample NiZnV9.5, in agreement with a lower water content in this last sample, as concluded from the TG measurements); the band close to 1600 $cm^{-1}$ is due to the bending mode of interlayer water molecules; bands below 800 $cm^{-1}$ are due to the same vanadate species and lattice vibrations. The most intense band in the spectrum of NiZnV4.5, centered at 790 $cm^{-1}$, can be ascribed to the $\nu(VO_2)_{asym}$ mode [17,18] and the small bands at 915 and 614 $cm^{-1}$ may be attributed to $\nu(VO_2)_{sym}$ and $\nu(V\text{–}O\text{–}V)_{sym}$ modes, respectively. The spectrum of sample NiZnV9.5, also included in the same figure, shows bands characteristic of species formed by corner-sharing [$VO_4$] tetrahedra at 915 cm$^{-1}$, $\nu(VO_2)_{sym}$, 796 cm$^{-1}$ $\nu(VO_2)_{asym}$, 675 cm$^{-1}$ $\nu$(V–O–V)$_{asym}$, and 614 cm$^{-1}$, $\nu$(V–O–V)$_{sym}$ [18].

Elemental chemical analysis for the samples prepared are given in Table 2, together with the molar V/Zn ratios and $x$ values. Almost the same $x$ value has been obtained for both samples ($x = 0.23-0.25$), very close to that of the acetate precursor; the small deviation for sample NiZnV4.5 may be due to a partial, selective dissolution of the layers because of the rather low pH used during synthesis. These results indicate that the composition of the layers is roughly the same before and after the treatment with vanadate, suggesting the exchange has been topotactic. However, the vanadium content decreases as the pH during exchange is increasing and, consequently, the V/Zn molar ratio also decreases. As the vanadate anion is balancing the positive charge due to incorporation of Zn cations, this means that different oxovanadates (i. e., with a different polymerization degrees and different vanadium-to-charge ratios) exist in the interlayer of the different samples. This polymerization degree depends on the equilibrium pH [19]: roughly speaking, the lowest the pH, the largest the nuclearity of the oxovanadate. In most cases, when a single phase is present, an approximate idea about the nature of the interlayer anion can be then obtained from the V/Zn stoichiometry. For example, the experimental value for V/Zn ratio in sample NiZnV9.5 is 0.44 (Table 2), very close to that calculated for the presence of species $V_2O_7^{4-}$ as interlayer anions (theoretical value equal 0.5). For sample NiZnV4.5, where the graftting process takes place, the value of the V/Zn ratio could deviate from the theoretical value. So, the value 1.66 (Table 2) is higher than that expected for the presence of $\alpha$-$VO_3$ chains in the interlayer space for this last compound (theoretical value equal 1). This difference will be explained below.

The presence of anions in the interlayer with different nuclearity and, consequently, with a different size, leads to different spacings for the XRD peaks originated by the basal planes. For non-spherical anions, the different orientation of the anions can give also rise to different spacings. So, the height for $V_2O_7^{4-}$ in a flat orientation (the line joining the center of both tetrahedra parallel to the hydroxide layers) is 4.7–5 Å [19] and, assuming a value of 4.8 Å for the width of the nickel hydroxide-like layer (similar to the value reported for the width of the brucite-like layers in hydrotalcites) [19,20] would give rise to a value of 9.5–9.8 Å for parameter $c$, very close to the experimental value calculated from the XRD diagram for sample NiZnV9.5 (9.36 Å). The experimental value of parameter $c$ for sample NiZnV4.5 is 7.11 Å and, assuming again a width of 4.8 Å for the nickel hydroxide-like layer, this leaves only 2.31 Å for the interlayer anions. The height of the interlayer in the last compound is too small to accommodate any other oxovanadate except $(VO_3)_n^{n-}$ chains (2.5 Å).

An explanation for these experimental results can be found taking into account the grafting of the interlayer anions to the nickel hydroxide-like layers, in a similar way to what has been previously observed by different authors when intercalating vanadates or chromates in the interlayer space of different hydrotalcite-like materials [21,22]. Such a process consists in substitution of one hydroxyl group of the nickel hydroxide-like layer by one oxide anion from the interlayer oxometalate. In this way, the oxometalate becomes anchored to the hydroxide layer, decreasing the room required to accommodate the oxometalate. Such a process is favoured at low pH values (as that used to prepare sample NiZnV4.5), probably through a partial dissolution of the layer in acidic conditions. FT-IR results also support such a grafting, as the intensity of the band at 675 cm$^{-1}$ recorded in the spectrum of sample NiZnV9.5 and due to (V–O–V)$_{asym}$, decreases in the spectrum of sample NiZnV4.5, as well as the band at 614 cm$^{-1}$, probably because grafting makes difficult the mobility of the species [17].

Grafting can be experimentally checked from ion exchange studies: while in non-grafted samples the interlayer anions can be substituted by others [6], exchange is hindered if the interlayer anion is strongly bonded (i.e., grafted) to the layer. In order to check grafting, we tried to exchange vanadate for carbonate in sample NiZnV4.5, as it is well known the high affinity of this sort of materials for carbonate anions. A portion of this sample was kept under vigorous magnetic stirring with a 0.5 M $K_2CO_3$ aqueous solution for 48 h at room temperature. After washing with distilled water and drying, the XRD diagram and the FTIR spectra were coincident with those of sample NiZnV4.5, indicating that exchange did not take place, i.e., vanadate was strongly bonded to the nickel hydroxide-like layers in a grafted mode.

Previous studies applying XAS techniques to hydrotalcites with interlayer oxovanadates [15,16] have demonstrated the presence of $V_{10}O_{28}^{6-}$ species in these compounds when the intercalation is carried out at pH 4.5, and so, the presence of decavanadate in the interlayer space of our hydroxyacetates should not be discarded beforehand. However, for the rather small room left to accomodate this species in sample NiZnV4.5, one could argue that the rather high electric density of decavanadate anions should introduce some sort of unstability, as each decavanadate has to balance 10 Zn(II) cations located outside the nickel hydroxide-like layer; under such circumstances the decavanadate unit would be located rather far away from most of these Zn(II) cations. Consequently, the presence of $(VO_3)_n^{n-}$ could be more favored in the case of the hydroxyacetates at the same pH.

### 3.3. Thermal decomposition

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for samples NiZnV4.5 and NiZnV9.5 are shown in Fig. 5. Two consecutive weight losses are observed in both cases, although from the DTG curves some of the weight losses may be composed of two consecutive steps.

The first weight loss is completed at ca. 200°C and is composed of a single, strong weight loss amounting ca. 8–9% of the initial sample weight, centered at ca. 84°C and 134°C, the precise position depending on the sample, and should correspond to removal of interlayer water molecules. Previously to this loss, a minor weight loss can be concluded from the DTG curves, which should correspond to removal of weakly held water molecules, probably adsorbed on the external surface of the crystallites. The second weight loss is completed at 450°C and above this temperature only a small weight loss around 700–800°C can be observed in both cases.

The weight loss corresponding to the first step has been used to calculate the amount of water in the interlayer, assuming the chemical composition of the layers is not modified upon dehydration and that this dehydration is complete. The corresponding formulas have been included in Table 3. These formulas have been calculated on the basis of elemental chemical analysis data included in Table 2, the first weigth loss obtained from Fig. 5 and X-ray information from Fig. 3, which permits to propose the nature of the interlayer anion. The formula for NiZn4.5 has been obtained taking as reference the calculation of Delmas et al. in grafted layered double hydroxides [18], viz., if all vanadium ions present were non-grafted $(VO_3)_n^{n-}$ chains, the achievement of the charge balance would require the presence of one vanadium ion per zinc ion. However, if grafting takes place by release of $OH^-$ ions in the acidic medium, the corresponding charges need then been compensated by the intercalation of additional vanadate species. In this

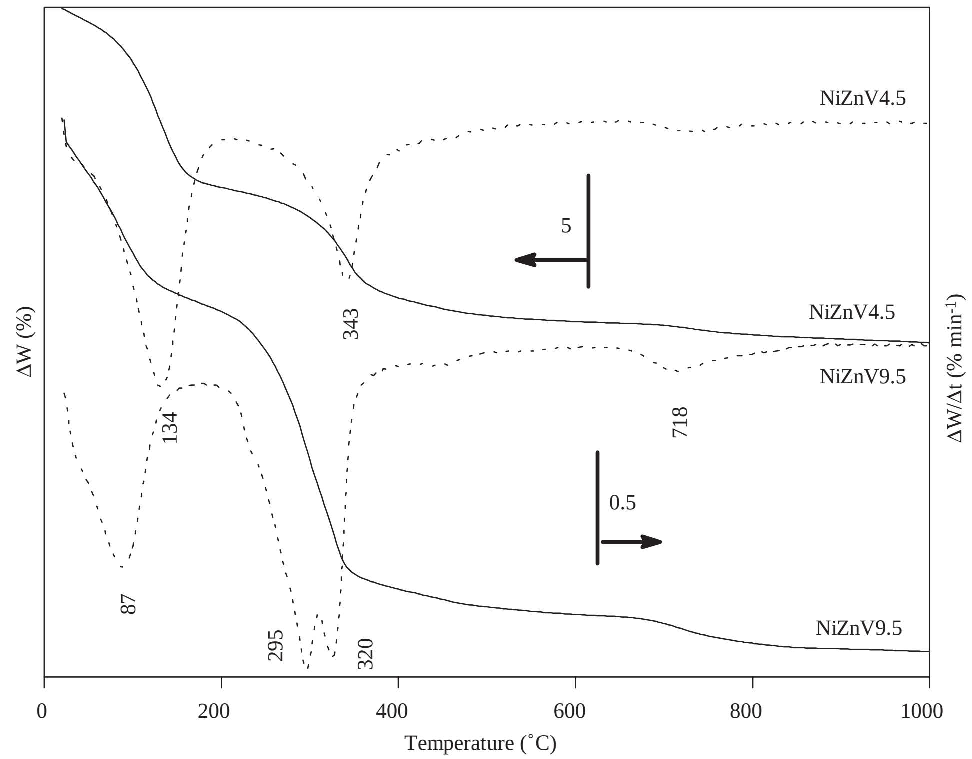

Fig. 5. TG (solid lines) and DTG (dotted lines) of hydroxyvanadates ZnNiV4.5 and ZnNiV9.5.

Table 3
Weight losses and formulas of the solids prepared

| Sample | Weight loss (%) | | Formula |
|---|---|---|---|
| | 20–200°C | 200–450°C | |
| NiZnV4.5 | 8.1 | 5.4 | $Ni_{0.78}Zn_{0.44}(OH)_{1.71}(VO_3)_{0.73} \cdot 0.86\ H_2O$ |
| NiZnV9.5 | 8.5 | 12.0 | $Ni_{0.75}Zn_{0.49}(OH)_2(V_2O_7)_{0.11} \cdot 0.69\ H_2O$ |

case, the experimental V/Zn ratio of 1.66 could be justified.

The second weight loss takes place between 200°C and 450°C. Total weight losses for the samples coincide within experimental error with the calculated values from the formula included in Table 3; weight percentages of the residue after calcination were 84.9% (calculated 82.3%) for sample NiZnV4.5 and 78% (79.5%) for sample NiZnV9.5.

While the first weight loss represents 8–9% in both cases, the second weight loss, due to removal of layer hydroxyl groups, corresponds to 13% for sample NiZnV9.5, but only 5.4% for sample NiZnV4.5; the lower weight loss in this last case may be tentatively related to the lower hydroxyl concentration in this sample because of vanadate grafting, as concluded from the elemental chemical analysis and XRD results discussed above.

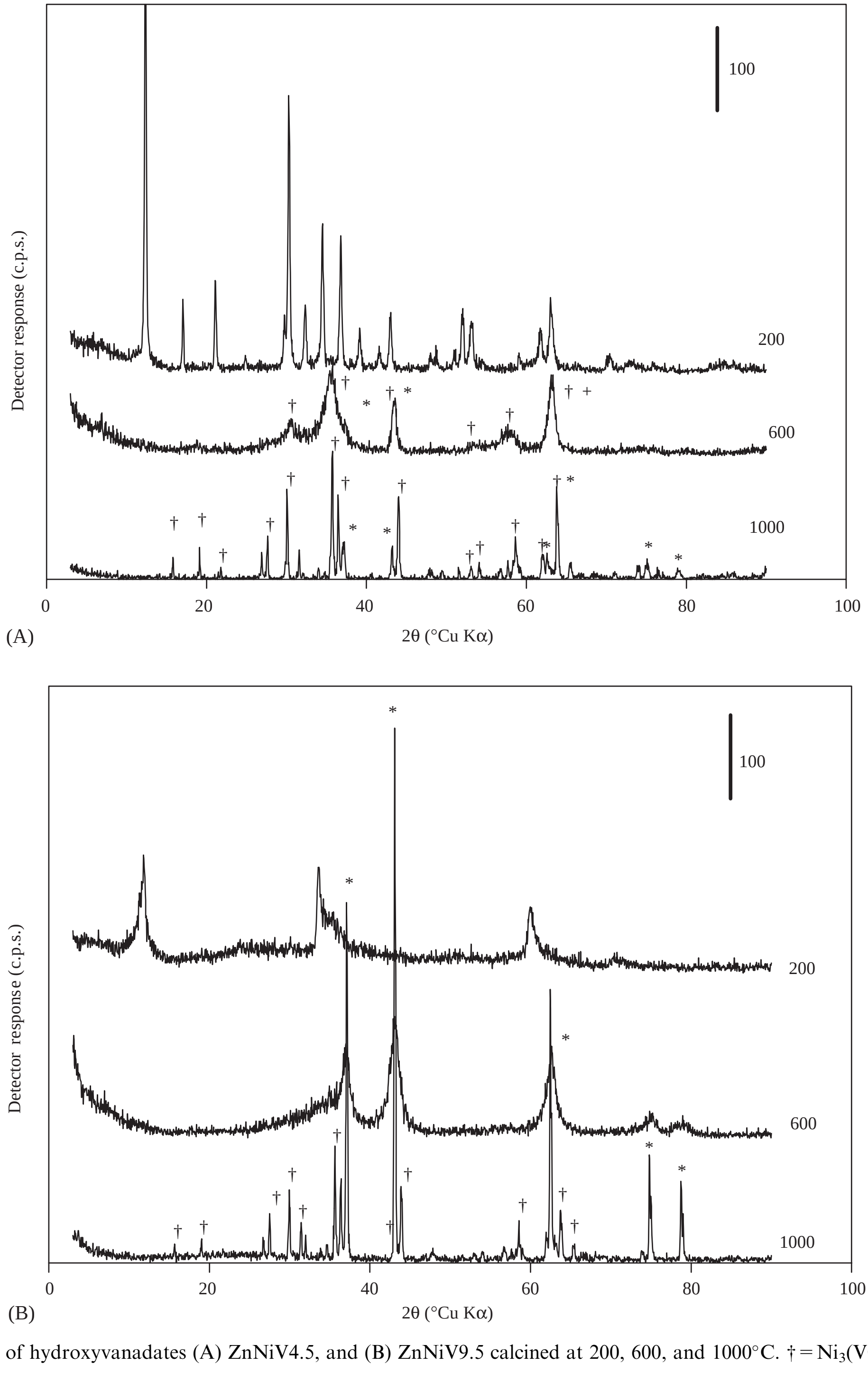

Fig. 6. XRD diagrams of hydroxyvanadates (A) ZnNiV4.5, and (B) ZnNiV9.5 calcined at 200, 600, and 1000°C. † = $Ni_3(VO_4)_2$ and/or $Zn_3(VO_4)_2$; * = NiO.

XRD diagrams have been recorded for the solids calcined for 3 h in air at singular temperatures in the TG curves, i.e., 200°C (after the first weight loss, corresponding to interlayer water removal), 600°C (after the second weight loss), and 1000°C, where formation of well crystallized species is expected. The diagrams are shown in Fig. 6.

After calcination at 200°C the solids maintain a greenish-yellow colour, as the original samples; no major changes are observed in the XRD diagram of sample NiZnV4.5, only changes in the relative intensities of some of the diffraction maxima, but the position of the first maximum remains in the same position, indicating that the layered phase is stable up to 200°C. The peaks become broader for sample NiZnV9.5, and a decrease in the spacing, from 9.36 to 7.4 Å, is observed; this value is close to that reported elsewhere for hydrotalcite-like compounds (it should be stressed that the width of the layers is almost coincident in hydrotalcites and in the hydroxyacetates here studied) with grafted interlayer $V_2O_7^{4-}$ species [21].

Calcination at 600°C leads to destruction of the layered structure, and only a few broad peaks are recorded, suggesting the low crystallinity of the phases formed. The positions of the maxima for sample NiZnV4.5 correspond to the most intense diffraction maxima of orthorhombic $Ni_3(VO_4)_2$ and $Zn_3(VO_4)_2$ (JCPDS files 37-353 and 34-378, respectively) and the presence of NiO is also detected (JCPDS file 44-1159). However, only peaks due to NiO are recorded for sample NiZnV9.5 calcined at 600°C. The difference can be due to the different contents of Ni and V in both samples: the larger content of V in sample NiZnV4.5 favors formation of the corresponding vanadates, while for sample NiZnV9.5 the lower V and higher Ni content might lead to formation of the vanadates, but the Ni in excesss forms NiO.

Calcination at 1000°C leads to crystallization of the mostly amorphous phases detected after calcination at 600°C, together with development of new diffraction maxima, confirming the presence of such phases. So, for sample NiZnV4.5, in addition to peaks of the vanadate salts (the maxima for the Ni and Zn salts are extremely close ones to the others, and formation of mixed Ni–Zn vanadates cannot be ruled out), weak peaks due to crystallization of NiO can be detected. On the contrary, for sample NiZnV9.5, although the NiO peaks remain the most intense ones, new peaks due to the vanadates develop.

## 4. Conclusions

Interlayer acetate anions in layered double (nickel, zinc) hydroxyacetates can be easily exchanged topotactically by oxovanadates upon heating, hydrothermal treatment or preswelling with bulk organic anions; direct exchange at room temperature was not possible. The nature (polymerisation degree) of the interlayer oxovanadate depends on the pH during exchange and, under acidic pH conditions, grafting of the vanadate to the hydroxyl layers is favoured, probably because of partial dissolution of the layers. The solids obtained are stable up to ca. 250°C. Calcination at higher temperatures leads to mixtures of nickel oxide and orthorhombic nickel and zinc vanadates; for intermediate calcination temperatures (600°C) the nature of the crystalline phases depends on the nature of the interlayer oxovanadate.

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