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Chromate intercalation in Ni-Zn layered hydroxide salts

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A R T I C L E I N F O

ABSTRACT

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1. Introduction

There is an increasing interest in their use of layered double hydroxides (LDHs) in many fields (catalysis, environmental remediation, pharmaceutics, etc.) (Vaccari, 1999; Rives, 2002; Wypych and Satyanarayana, 2004; Del Hoyo, 2007). On the other hand, the literature regarding layered hydroxide salts (LHSs), is scarce (Meyn et al, 1993; Newman and Jones, 1999; Arizaga et al., 2007). This last group of solids presents layer compositions and structures different from LDHs. LHSs are classified by their structure: compounds with a botallackite-like structure, with general formula $M^{2+}(OH)_{1-x}A^{m-}_{x/m}$. nH_2O , where $M^{2+} = Cu^{2+}$, Ni^{2+} and A^{m-} is the interlayer anion (Park and Lee, 2005; Poul et al., 2000) and compounds with a hydrozincite-like structure, with general formula $M_5^{2+}(OH)_8 A_{2/m}^{m-}$. nH_2O , where $M^{2+} = Zn^{2+}$, Co^{2+} , etc. (Newman and Jones, 1999; Poul et al., 2000). They can be also classified according to their layers composition: simple, if only one metal cation is forming the layers; double, if more than a metal cation is present.

Ni–Zn layered hydroxide salts (Ni–Zn–LHSs) can be classified as double, hydrozincite-like compounds. They present a rising interest (Nishizawa and Yuasa, 1998; Rojas et al., 2002) because of their complex structure (that combines intercalation and coordination chemistry) (Choy et al., 1998), and their high and variable ion exchange capacity. As a consequence, they are investigated as adsorbents, catalysts, etc. (Kozai et al., 2002; Arulraj et al., 2007; Sicard et al., 2009).

a rather large oxometalate concentration, which almost completely balanced the positive charges of the layers, as concluded from element chemical analysis, powder X-ray diffraction, and FT-IR spectroscopy results. Thermal decomposition of the solid led to dehydration and chromate anion grafting, followed by dehydroxylation of the host and reduction of the chromate anions. The solid then lost the layer structure

An acetate-intercalated Ni–Zn layered hydroxide salt (LHS) was exchanged with chromate anions, achieving

dehydroxylation of the host and reduction of the chromate anion. The solid then lost the layer structure, forming solids with large micro and mesoporosity, which corresponded to poorly crystallized (Zn, Ni)–Cr spinels, as well as nickel and zinc oxides.

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Ni–Zn–LHSs structure is based on Ni(OH)₂ brucite-like layers where a non stoichiometric amount of the Ni²⁺ ions located in octahedral sites are removed and the positive charge recovered by two Zn²⁺ ions placed in tetrahedral sites outside the layers, on both sides of each Ni²⁺ vacancy (Rojas et al., 2002). The layers present a positive charge excess, which is balanced by the introduction of anions in the interlayer space, where also solvent molecules (usually water) are placed. The interlayer guests also coordinate Zn²⁺ ions, which attain then a tetrahedral coordination, the other positions being occupied by three hydroxyl groups from the layers. The general formula of these compounds can be written as Ni_{1-x}Zn_{2x}(OH)₂A^{m–}_{2x/m}·nH₂O. In these solids the interlayer anions can also be exchanged under mild reaction conditions, allowing modification of their composition and extending their applications.

Thus, the incorporation of metal chelates (Rojas et al., 2008) and polyoxometalates (Ballesteros et al., 2008) permits the incorporation of metal ions that do not fit in the structure of the layers because of their size and/or formal charge (Rojas et al., 2004). Chromium cannot be incorporated into the layers of Ni–Zn–LHSs as their structure do not allow incorporation of trivalent ions, but it can be expected that chromate and/or dichromate can be intercalated between the layers, as they do in LDHs (Miyata and Okada, 1977; Rives and Ulibarri, 1999; Malherbe and Besse, 2000; Prasanna et al., 2007). Both anions are formed by [CrO₄] tetrahedra that, in the case of dichromate, are bridged by an O–Cr–O bond with an angle close to 120°. Chromate [CrO₄^{2–}] is the main form above pH = 8, but, as pH is lowered, both HCrO₄⁻ and dichromate anions (Cr₂O₇^{2–}) are in equilibrium between pH 6 and 2.

Chromate/dichromate intercalation in Ni–Zn–LHSs will increase the solids versatility and their potential use as catalysts and catalyst precursors. Nickel oxides and their derivatives (e.g., by mixing or forming solid solutions with other oxides) are used in many catalytic

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processes, such as methane reforming (Tsyganok et al., 2001) and partial oxidation of propane (Schulze et al., 2001). Chromate anions also present many catalytic applications: benzylic and alylic oxidations are accelerated by the presence of chromate anions (Arends and Sheldon, 2001). Finally, chromium-containing metal oxides obtained by calcination of chromate-intercalated LDHs have been investigated for the activation of the aldolic condensation reaction between formaldehyde and ketone (Suzuki and Ono, 1988) and ethane dehydrogenation (Tsyganok et al., 2007).

In this study we report the synthesis of an acetate-containing Ni– Zn–LHS that is then exchanged with chromate ions.

2. Experimental

2.1. Samples preparation

All reagents (a. p.) were from PANREAC (Spain) and were used without further treatment. Nitrogen was supplied by Air Liquide (Spain) and presented a sufficiently high nominal purity (4.6 or 99.996%). Water used in the synthesis procedure was previously boiled and purged with N_2 to prevent CO₂ presence.

The acetate-intercalated sample was prepared by coprecipitation induced by hydrothermal treatment, as previously described (Rojas et al., 2002). A 200 ml aqueous solution containing both Ni^{2+} and Zn^{2+} acetates was prepared with a Ni/Zn molar ratio of 2 and 1 M total concentration in an autoclave and submitted to hydrothermal reaction at 150 °C for 24 h. The light green solid obtained was isolated by centrifugation at 10,000 rpm (Sorvall Super T21), repeatedly washed with distilled water and finally dried at room temperature in a desiccator over silica gel.

Chromate intercalation into Ni–Zn–LHS was performed by anion exchange. 1 g of the dried sample was dispersed in 100 ml of decarbonated water and was magnetically stirred for 24 h to reach a maximum dispersion of the particles and a complete hydration of the interlayer space. The pH of the slurry was then adjusted to the desired value by addition either of 0.5 M HCl or NaOH aqueous solutions (pH meter Metrohm 691 with an automatic 725 Dosimat dispenser from Metrohm). Next, a 50 ml solution containing 2.7 g K₂Cr₂O₇ was added drop wise to the dispersion while pH was maintained at a constant value by the addition of NaOH. Once the addition was complete, the resulting dispersion was maintained under stirring for 2 h and then submitted to hydrothermal reaction at 90 °C for 24 h. The solid was separated, washed, and dried at room temperature in a desiccator over silica gel.

2.2. Experimental techniques

Element chemical analyses of the metal ions were performed by atomic absorption spectrometry in an AA-3100 instrument from Perkin Elmer. Elemental chemical analyses of C and N were performed in a Euro Elemental Analyze Eurovector instrument while the water content of the samples was calculated from the first mass loss obtained in the thermogravimetric analysis of the samples (see below). Powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D-5000 instrument, using CuK α radiation ($\lambda = 1.5405$ Å) at 40 kV and 30 mA at a scanning speed of 2° (2 θ)/min. The FT-IR spectra (KBr pellet technique, 1% sample:KBr mass ratio) were recorded in a Spectrum One Perkin Elmer Fourier Transform Instrument, averaging 100 scans at a nominal resolution of 4 cm^{-1} to improve the signal-tonoise ratio. The scanning electron microscope (SEM) images were obtained in a JEOL6300 instrument from samples prepared by deposition of a sample dispersion drop on a Cu sample holder, afterwards covered with an Au layer in a Baltec SCD005 apparatus. Thermogravimetric (TG) and Differential Thermal Analyses (DTA) were carried out in a SETARAM Setsys Evolution 16/18 instrument, in flowing air (20 ml/min) at a heating rate of 5 °C/min. Analysis of gases evolved during thermal decomposition (EGA) was carried out in a Pfeiffer Vacuum OmniStar mass spectrometer directly connected to the thermal analyzer. Nitrogen adsorption isotherms of the samples at liquid nitrogen temperature were recorded on a Micromeritics ASAP 2101 instrument. Before the experiments, the samples were outgassed (residual pressure 10 mbar) at 150 °C for 4 h as, according to the thermal analysis results, this temperature was high enough to remove interlayer water without disturbing the interlayer anions or the layer structure. The specific surface area was determined by the BET method, while the external specific surface area and the microporous volumes were determined by the *t*-method.

3. Results and discussion

Although several synthesis routes at different pH values were attempted to intercalate both chromate and dichromate in Ni–Zn–LHSs, the intercalation of the latter anion was not achieved. At high pH values dichromate anions were absent in the solution, while at lower pHs the instability of the Ni–Zn–LHS layers led to the loss of the bidimensional structure of these solids, obtaining a well crystallized phase, with a three-dimensional structure.

On the other hand, inclusion of chromate anions was accomplished successfully at pH values above pH=7.5, although the maximum exchange was reached at pH=9.5. The sample prepared at pH=9.5 was selected for its structural and morphological characterization and will be referred to as LHS-[Ni-Zn-CrO₄], while the acetate-intercalated precursor will be named as LHS-[Ni-Zn-AcO].

The element chemical analysis results for both samples are included in Table 1. The parameter x (that characterizes the layer composition) remained almost constant, indicating that the Ni–Zn–LHS layers remained unaffected during the exchange process, which probably indicated a topotactic mechanism. The molar Cr/Zn ratio was close to 0.5, which was near to the calculated value for a Ni–Zn–LHS fully intercalated with chromate ions.

The PXRD patterns of both samples (Fig. 1) corresponded to a single crystalline phase with a hexagonal structure typical of Ni-Zn-LHSs (Choy et al., 1998; Rojas et al., 2002). For LHS-[Ni-Zn-CrO₄], the (001) reflection shifted to higher 2θ values. Above $2\theta = 30^{\circ}$ both patterns were very similar, as the reflections recorded in this range corresponded to reflections in the *a*–*b* plane. Indexing was performed by the least square method. The calculated lattice parameters were c = 12.9 Å and a = 6.16 Å for the acetate-intercalated sample and c = 9.1 Å and a = 6.16 Å for LHS–[Ni–Zn–CrO₄]. The large difference between the *c* parameters is due to the double layer arrangement of acetate anions, while chromate anions are disposed in a single layer. The c parameter obtained for LHS-[Ni-Zn-CrO₄] is in good agreement with those at the literature for chromate-intercalated LDHs (between 8.3 and 10 Å, depending on the water content of the interlayer space) (Rives, 2002). No reflections were observed close to 12.9 Å in the chromate-intercalated sample, which indicated the absence of acetate impurities. However, a wide, low intensity reflection was obtained at $2\theta = 10^{\circ}$ approximately. This reflection may be due to a partially dehydrated or even grafted chromate LDH phase (see the PXRD patterns of calcined samples).

Table 1	
Chemical composition, molar ratios	and calculated formula of Ni-Zn-LHSs.

Sample	Ni ^a	Zn ^a	Cr ^a	x ^b	Cr/Zn	Formula
LHS-[Ni-Zn-AcO]	36.0	17.0	-	0.20	-	[Ni _{0.8} Zn _{0.4} (OH) ₂] (CH ₃ COO) _{0.4} 0.94H ₂ O
LHS-[Ni-Zn-CrO ₄]	32.8	21.0	8.1	0.22	0.48	[Ni _{0.78} Zn _{0.44} (OH) ₂] (CrO ₄) _{0.21} 0.71H ₂ O

^a Mass percentage.

^b x in the formula: $Ni_{1-x}Zn_{2x}(OH)_2X^{m-}_{2x/m} \cdot nH_2O$.



Fig. 1. PXRD patterns of LHS-[Ni-Zn-AcO] (a) and LHS-[Ni-Zn-CrO₄] (b).

The FT-IR spectra of both acetate and chromate-intercalated samples showed broad bands between 4000 and 2000 cm⁻¹ (not shown) corresponding to stretching vibration modes of hydroxyl anions of the layers (Choy et al., 1998; Rojas et al., 2002) while bands assigned to lattice vibration modes were registered at wavenumbers below 700 cm⁻¹. In the range shown in Fig. 2, bands corresponding to the intercalated anion were detected: ν (COO)_{asym} and ν (COO)_{sym} stretching modes and to the δ (CH₃) mode of the acetate anion were recorded at 1574, 1408 and 1335 cm⁻¹, respectively, in the spectrum of parent sample LHS-[Ni–Zn–AcO] sample while, for the chromate-intercalated sample, specific bands were obtained at 911 and 870 cm⁻¹.

In aqueous solution, free chromate ions show a tetrahedral symmetry and possess two IR active (846 and 349 cm⁻¹) and two Raman active (890 and 378 cm⁻¹) vibration modes (Nakamoto, 1986). Intercalation of the anions lowered their symmetry. Consequently, the stretching vibration mode ν_3 , triply degenerated in tetrahedral symmetry, became undegenerated (Miyata and Okada, 1977). Thus, two bands were registered for LHS–[Ni–Zn–CrO₄]. The



Fig. 2. FT-IR spectra of LHS–[Ni–Zn–AcO] (a) and LHS–[Ni–Zn–CrO₄] as prepared (b) and calcined at 200 $^\circ C$ (c).

presence of only two bands and the small separation between them can be an indication that chromate anions were not directly coordinated to the Zn^{2+} ions of the layers and water molecules completed the coordination sphere of the Zn^{2+} ions.

A SEM image of LHS–[Ni–Zn–CrO₄] (Fig. 3) showed plate-like particles, similar to those of the parent acetate-containing Ni–Zn–LHS (Rojas et al., 2004). The particle size was not uniform, ranging between 0.5 and 5 μ m. Stacking led to development of interparticle holes and pores with a slit shape that will have an important effect on the surface properties of the solid.

The nitrogen adsorption isotherm of LHS–[Ni–Zn–CrO₄] sample (Fig. 4a) was similar to that obtained for layered compounds as clay



Fig. 3. SEM image of LHS-[Ni-Zn-CrO₄] as prepared (a) and calcined at 400 °C (b and c).

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Fig. 4. N2 adsorption isotherms of LHS-[Ni-Zn-CrO4] (a) and calcined at 400 °C (b).

minerals (Rouquerol et al., 1999). According to the IUPAC classification (Sing et al., 1985), the isotherm corresponded to type II, indicating adsorption in macroporous and/or non-porous materials, although the adsorption capacity was rather low. The shape of the isotherm and the presence of a hysteresis loop suggested the presence of mesopores. The shape of this hysteresis loop is characteristic of a non-limited adsorption at high relative pressures and is observed for aggregates of plate-like particles, which give rise to slit shaped mesopores (Sing and Gregg, 1982). The hysteresis loop shape can be also affected by other factors such as pore radius distribution (Taylor and Sermon, 1995). In this case, the narrow separation between the adsorption and desorption branches indicated the presence of pores with regular geometry and a wide radii range. Nevertheless, the maximum N₂ volume adsorbed by this solid (42.8 cm³/g SPT), indicated a poor surface development, and the sample cannot be properly considered as mesoporous. The curve was similar to those previously reported for Ni-Zn-LHSs (Rojas et al., 2008) and LDHs (Malherbe et al., 1997; Carja et al., 2001).

The specific surface areas measured by the BET method (S_{BET}) and the *t*-method (S_t) as well as the micropore equivalent area (A_{μ}) are reported in Table 2. The BET area and pore volume were low and, according to the *t*-plot, micropores were absent.

Three processes were detected in the DTA curves (previously reported) of acetate-containing samples: dehydration of the interlayer space (endothermic), dehydroxylation of the layers (endothermic) and loss of the intercalated acetate ions by oxidation (exothermic). Chromate-intercalated samples (Fig. 5) showed only two endothermic peaks: the first peak at 126 °C was assigned to the loss of weakly bound interlamellar water, while that at higher temperature (372 °C) was assigned to dehydroxylation of the layers, destroying the layer structure. This process overlapped with that corresponding to the reduction of chromate to Cr^{3+} , which remained in the structure of the

Table 2

Specific surface area and porosity parameters of chromate-intercalated LHS and its calcinations products at 400 °C, using the BET and the *t*-plot method.

Sample	$S_{\rm BET}^{\rm a}$	St ^b	A _µ ^c
LHS-[Ni-Zn-CrO ₄]	17	22	-
LHS-[Ni-Zn-CrO ₄] 400 °C	217	23	194

^a BET specific surface area, in m²/g.

^b *t*-method external specific surface area, in m^2/g .

^c *t*-method specific micropore area, in m^2/g .



Fig. 5. TG and DTA diagrams of LHS–[Ni–Zn–CrO₄] and mass spectrometry analysis of the gases evolved during the thermal decomposition.

metal oxide after calcination. The positions of the peaks in the DTA curve were similar to those recorded for Ni–Zn–LDHs intercalated with other divalent anions, specially carbonate (Rojas et al., 2002) and pyrovanadate (Rojas et al., 2004), although the temperature was slightly higher than those for sulfate-containing samples, despite chromate and sulfate have the same formal charge (-2) and symmetry (T_d) .

The TG-curve (Fig. 5) showed two mass losses associated to the corresponding thermal effects in the DTA curve. The first one extended between 25 and 200 °C and corresponded to a loss of 8.7% of the initial sample mass. The second mass loss was retarded (it took place between 250 and 550 °C) and the mass loss was larger (16.4%) and close to that calculated from the chemical formula of the compound, considering that, at T = 1000 °C, the obtained phases were only the corresponding metal oxides. Mass spectrometry analysis of the gases evolved during the thermal decomposition of the sample is also shown in Fig. 5 (bottom). The TG and DTA curves in nitrogen were experimentally identical to those recorded in an oxidizing atmosphere, as no oxidation process was involved. Analysis of the gases indicated evolution of water during the dehydration and dehydroxylation processes and of oxygen during chromate reduction.

The structure and morphology of solids after calcination of LHS-[Ni-Zn-CrO₄] were observed at three temperatures, chosen from the TG/DTA analyses: (i) 200 °C (corresponding to removal of interlayer water), (ii) 400 °C (after destruction of the lamellar structure, with maximum specific surface area) and (iii) 1000 °C (formation of well crystallized oxides). The PXRD patterns recorded for these samples are shown in Fig. 6. To detect grafting processes (anion anchoring to the layers, replacing one hydroxyl anion), the PXRD diagrams of samples calcined up to 200 °C were also recorded, and the value of lattice parameter *c* and full width at half maximum (FWHM) for the 001 reflection are reported in Table 3. Below 100 °C, the parameter *c* decreased from 9.1 to 7.8 Å, and the reflection width was considerably increased, suggesting an increased disorder of the solid. Removal of some hydroxyl groups was produced above 100 °C, leading to chromate grafting, a process which further decreased the lattice parameter c to 7.1 Å. This process was accompanied by a sharpening

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Fig. 6. PXRD patterns of LHS-[Ni-Zn-CrO₄] calcined at 200, 400 and 1000 °C.

of the reflection, suggesting an increasing order of the solid. These findings are similar to those previously reported for chromateintercalated Cu–Al–LDHs (Forano et al., 1997) and vanadate intercalated Ni–Zn–LHSs (Rojas et al., 2004).

The IR-spectrum of LHS–[Ni–Zn–CrO₄] sample calcined at 200 °C (Fig. 2c) showed three bands (939 (sh), 909 and 867 cm⁻¹), assigned to the v_3 vibration mode, triply degenerated for the free chromate anion. This indicated that the symmetry loss was more pronounced after dehydration, probably due to the grafting process. A similar IR bands splitting was recorded for Cu–Cr–LDHs with chromate anions grafted to the layers (Depegè et al., 1994).

Above temperature of the layer dehydroxylation the sample lost its lamellar structure. Thus, the 00l reflections at low 2θ completely vanished after calcination at 400 °C, while reflections corresponding to poorly crystallized NiO phases were recorded (JCPDS file 44-1159). No reflections of zinc oxide, chromium oxide or chromate salts were observed, indicating that Cr^{3+} ions were well dispersed in the NiO phase or forming an amorphous phase.

At higher temperatures more reflections were recorded and all of them became sharper. Narrow reflections of NiO phases were observed in the PXRD pattern recorded after calcination at 1000 °C, and also crystalline ZnO (JCPDS file 05-0664) and chromium spinel phases seemed to be present. The JCPDS filed PXRD diagrams of Ni–Cr (NiCr₂O₄, 23–1271) and Zn–Cr (ZnCr₂O₄, 22–1107) showed reflections in very close positions, and consequently they cannot be differentiated using PXRD; the obtained spinel phase may contain either Zn²⁺, Ni²⁺ or both.

The nitrogen adsorption isotherm for the sample calcined at 400 °C (Fig. 4) showed a shape very different from the uncalcined sample. The nitrogen adsorption was considerably enhanced and, at low relative pressures, an almost vertical section was registered, which was associated to condensation in micropores (isotherm type I, according to the IUPAC classification). As the relative pressure further increased, the slope of the curve decreased, and according to its shape, the isotherm was ascribed to type II, but with a contribution of a type IV and a H3 type hysteresis loop.

Table 3

c parameter and FWHM data for calcined LHS-[Ni-Zn-CrO₄].

Calcination temperature (°C)	<i>c</i> (Å)	FWHM ^a (001) (°20)
25	9.1	0.20
75	8.2	0.87
100	7.8	1.01
135	7.4	0.85
180	7.3	0.58
200	7.1	0.33

^a Full width at half maximum.

The change observed in the shape of the isotherm was in agreement with the specific surface area (Table 2). The BET area largely increased compared to the uncalcined sample, due to the increase of the micropore area, while the external surface remained low, as concluded from the application of the *t*-method. The sample showed high microporosity due to the formation of thin channels in the Ni–Zn–LHSs during the thermal decomposition, when gaseous compounds escape from the solid. This process was previously described for LDHs (Reichle, 1985).

Fig. 3b and c shows SEM images at two different magnifications of LHS–[Ni–Zn–CrO₄] calcined at 400 °C. Irregularly shaped particles were formed by stacking of broken, uneven layers. The particle size was similar to that of the uncalcined particles, which explains the similar external specific surface area at both temperatures. Dehydroxylation and interlayer anion decomposition processes destroyed the layer structure, but not the plate-like shape of the particles.

4. Conclusions

Intercalation of chromate by anion exchange in Ni–Zn–LHSs was studied. Dichromate anions could not be intercalated. Chromate-intercalated Ni–Zn–LHS showed a lower basal spacing than the acetate-intercalated precursor. FT-IR spectrum indicated that the chromate anions were not directly coordinated to the layer Zn²⁺ ions. The sample showed a similar morphology as the precursor, with large plate-like particles with a poor surface development and slit shaped mesopores with a wide range of pore radii.

The thermal decomposition of the sample took place in two endothermic steps: loss of interlayer water overlapping with chromate grafting, and dehydroxylation of the layers accompanied by the reduction of the intercalated chromate with oxygen evolution. The first process produced decreased basal spacing. At higher temperatures chromate grafting increased the layer ordering. The second process led to the collapse of the layer structure and amorphous metal oxide phases were formed with low external specific surface area and moderate microporosity. Calcination at higher temperatures increased their crystallinity, allowing the identification of NiO and ZnO phases as well as chromium spinels either with Zn^{2+} or Ni²⁺ ions in their structures.

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