

Article

# 30 Years of Vicente Rives' Contribution to Hydrotalcites, Synthesis, Characterization, Applications, and Innovation

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**Abstract:** Hydrotalcite is the name of a mineral discovered in Sweden in 1842 whose formula is  $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$  and presents a layered crystal structure that consists of positively charged hydroxide layers neutralized by interlayer anions as carbonate, also containing water molecules. The ease of their synthesis and the possibility of incorporating other layer cations and interlayer anions have made this type of layered double hydroxides (LDH) a group of very interesting materials for industry. In addition to LDH and due to the name of the most representative mineral, this group of compounds is commonly called hydrotalcite-like materials, or simply hydrotalcites. Another way of referring to them is as anionic clays because of their layered structure but, unlike classical clays, their layers are positive and their interlayers are anionic. The main fields of application of these solids comprise catalysis, catalyst support, anion scavengers, polymer stabilizers, drug carriers, or adsorbents. This paper briefly summarizes some of the work carried out by Professor Rives over more than thirty years, focused, among other topics, on the study of the synthesis, characterization, and applications of hydrotalcites. This research has led him to train many researchers, to collaborate with research groups around the world and to publish reference papers and books in this field. This contribution, written to be included in the Special Issue "A Themed Issue in Honor of Prof. Dr. Vicente Rives", edited on the occasion of his retirement, only shows a small part of his scientific research and intends to value and recognize his cleverness and his enormous scientific and human quality.

**Keywords:** hydrotalcite; LDH (layered double hydroxide); synthesis of hydrotalcites; hydrotalcites as catalysts; hydrotalcites as adsorbents



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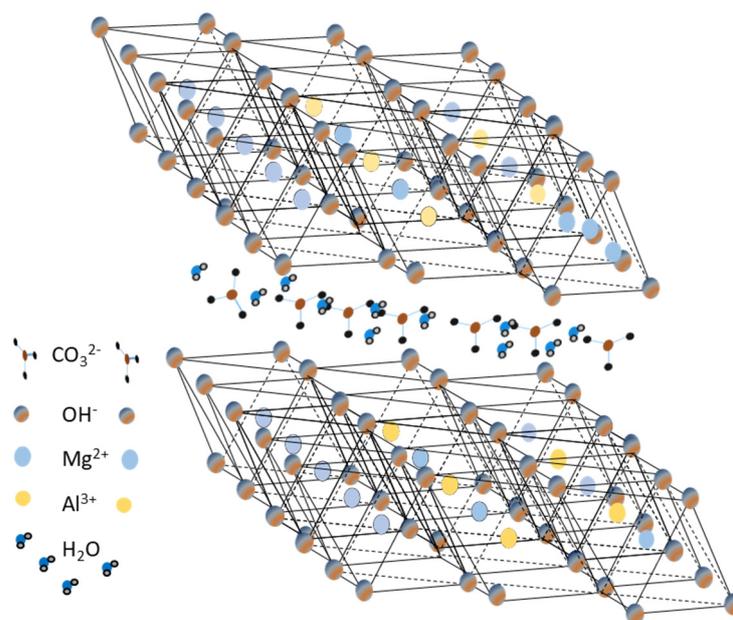


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## 1. Introduction

Hydrotalcite-like compounds (HT), so-called "anionic clays", are layered double hydroxides with general formula  $[M_{1-x}M'_x(OH)_2]^{x+}(X)_{x/m} \cdot nH_2O$ , where  $M = Mg(II), Zn(II), Ni(II), \dots$ ,  $M' = Al(III), Fe(III), \dots$  and  $X = CO_3^{2-}, NO_3^-, SO_4^{2-}, \dots$  [1]. This is the sentence that, in 1991, started a new line of research for Professor Rives' research group at the Universidad de Salamanca. It can be said that it was "the principle of a beautiful friendship" with these solids for Prof. Rives and for many people that were a part of his team during this time. The study of these layered double hydroxides (LDH) has led to the collaboration of Prof. Rives with researchers from all over the planet. These collaborations implied a great advance in the knowledge of this group of compounds.

As indicated, hydrotalcite-like compounds or hydrotalcites (HT), layered double hydroxides (LDH), or anionic clays, are the common names for these kinds of materials. The first name is an extension of that of the mineral found in Snarum, Norway [2,3], extended for designating the large family of solids, mainly synthetic, with its structure. As these solids have, contrary to the natural clays, their layers positively charged and so, their interlayer space occupied by exchangeable anions, they are also known as anionic clays. Finally, attending to their layered structure and chemical composition, they belong to the family of the layered double hydroxides (Figure 1).



**Figure 1.** Structure of Mg–Al–carbonate hydrotalcite.

The formula of this mineral was first given by the Italian mineralogist Ernesto Manasse in 1915 [4], and so manasseite is another name used for this solid, although it slightly differs from hydrotalcite in its chemical composition. In 1942, two Swiss scientists, Feitknecht and Gerber, described for the first time the synthesis of this compound [5]. During the second half of the 20th century, a great number of researchers have reported on its crystal structure [6–8]. All these aspects, together with the synthesis methods and the large number of possible applications, were largely commented on in the first book entirely dedicated to these compounds, edited by Prof. Rives in 2001 [9]. The entire book has been cited more than 1400 times, according to GoogleScholar, even more, if considering the separate chapters. The high interest in hydrotalcites has given rise to the publication of thousands of scientific articles and bibliographic review papers (9300 documents when looking for “hydrotalcite” at Web of Science™). One of the most important revision papers is that published by Rives and Ulibarri in 1999, which reviewed the scientific articles published up to that date on the synthesis, properties, and applications of hydrotalcite-like materials containing intercalated anions constituted by metal complexes or oxometalates [10] (cited 770 times according to Web of Science and 1000 times according to GoogleScholar). This review described the role of catalysts, sensors, electrodes, etc., that these materials can play, as obtained or after thermal treatments.

The aim of this work is to summarize the scientific works dedicated to the knowledge of LDH that Professor Rives has carried out and shared, together with his collaborators, with the entire scientific community. Another no less important purpose of this paper is to acknowledge the time dedicated and the will, kindness, good work, and brilliance with which Professor Rives has been able to teach and supervise all the research students that have had the luck of working with him.

## 2. Synthesis and Characterization

Rives et al. reported for the first time, in 1991, the synthesis and characterization of the solid obtained after thermal treatments of Co,Al-hydroxycarbonate compound containing Co(II) cations with a hydrotalcite structure [1]. In the same year, they described the synthesis by the coprecipitation method of layered double hydroxides, also with the hydrotalcite-like structure and containing carbonate as interlayer anion and Ni(II) and Al(III) cations in the layers [11]. Several solids with different Ni/Al ratios were prepared and studied by means of FT-IR and V-UV/DR spectroscopies. The local environment of the Ni(II) cations was found to be octahedral in all cases, but the orientation of the interlayer

carbonate anions varied depending on the Ni/Al ratio. Although the synthesis of this type of hydrotalcite had been previously reported by Reichle [12], its behavior upon aging treatments was not clear. Rives et al. studied in-depth for the first time the Co(II)/Co(III) oxidation in these compounds, linked to the synthesis and aging treatment experimental conditions. Aging was carried out by thermal treatments, and so the same authors, in 1992, continued their study by analyzing the effect of hydrothermal treatments on the nature of the hydrotalcites when varying the time and temperature [1]. Consequently, they also examined the physicochemical properties of MgAl hydrotalcites synthesized by the coprecipitation method and they established the bases that explained the variation of the crystallinity with the temperature, time, and type of aging treatment [13,14]. The Mg/Al ratio increased, and the specific surface area and the water content decreased, when the hydrothermal treatment was prolonged.

To explain the importance of these materials for their use in catalysis, a study of their acid/base properties was conducted in 1993 on a MgAl-HT and on their calcination products [15]. The adsorption of pyridine to measure the acidity, and formic acid to study the basicity on the surface of the HT was carried out by using FT-IR spectroscopy. The acid and basic sites of these solids were described and the authors confirmed that Lewis acid sites were linked to Al(III) ions and the basic ones were correlated to isolated surface hydroxyl groups. More recently a wide study of the control of the synthesis conditions to obtain hydrotalcite-like materials with tuned properties has been done on MgAl hydroxycarbonates [16]. In this work, the authors tried to find the optimal conditions to prepare samples with pre-designed structural and textural properties. They found that a sample obtained after 48 h of conventional hydrothermal treatment can be synthesized by aging only 10 h under microwave irradiation. Hydrothermal treatment under microwave irradiation needed shorter treatment times and, thus, lower energy consumption, leading to hydrotalcites with higher crystallinity than conventional hydrothermal treatments. This last work was based on the studies previously carried out on the incidence of microwave thermal treatments, in which the changes in the crystallinity, the textural and structural characteristics, or the porosity of different hydrotalcites were explored [17–19].

The research in HT containing oxidizable cations continued with the report for the first time of the synthesis of an LDH containing V(III) cations in the layers [20]. To avoid vanadium (III) oxidation, the synthesis was carefully designed; the preparation of an Mg-V-carbonate HT was carried out under a nitrogen atmosphere using Schlenk techniques. Characterization results using powder X-ray diffraction (PXRD) infrared spectroscopy with Fourier Transform (FT-IR) and extended X-ray absorption fine structure (EXAFS), among other techniques, confirmed the formation of hydrotalcites with Mg(II) and V(III) cations in the layers,  $\text{CO}_3^{2-}$  as an interlayer anion, and with a well-ordered layered structure. Subsequently, Labajos et al. described different ways of obtaining and aging Mg(II)-V(III)-HT with carbonate as interlayer anion, widely studying the effect of drying under air or under vacuum and the incidence of the hydrothermal treatment in the as-synthesized samples and its calcination products [21] was tested. The use of vacuum for drying and hydrothermal treatment after synthesis gave rise to better-crystallized samples. The first description in the literature of the synthesis and characterization of Ni(II)-V(III) hydrotalcites with different Ni/V molar ratios and the study of their calcination products was carried out by Rives's research group in 1999 [22]. The synthesis of this system was similar to the previously reported to avoid the V(III) oxidation [21,22], obtaining well-crystallized hydrotalcite with Ni(II) and V(III) in the brucite-like layers, and carbonate with the plane parallel to the brucite-like layers as interlayer anion [22].

The characterization of this type of layered solids by different thermal techniques, namely thermogravimetry (TG) Differential Thermal Analysis (DTA), and Temperature Programmed Reduction (TPR), has been largely implemented along to improve the knowledge of the properties of the HT [9,23]. TG and DTA analysis were demonstrated to be essential to analyzing the nature and the strength of the bond of interlayer anions and molecules, and also the number of volatile species. Thus, Labajos and Rives investigated the thermal evo-

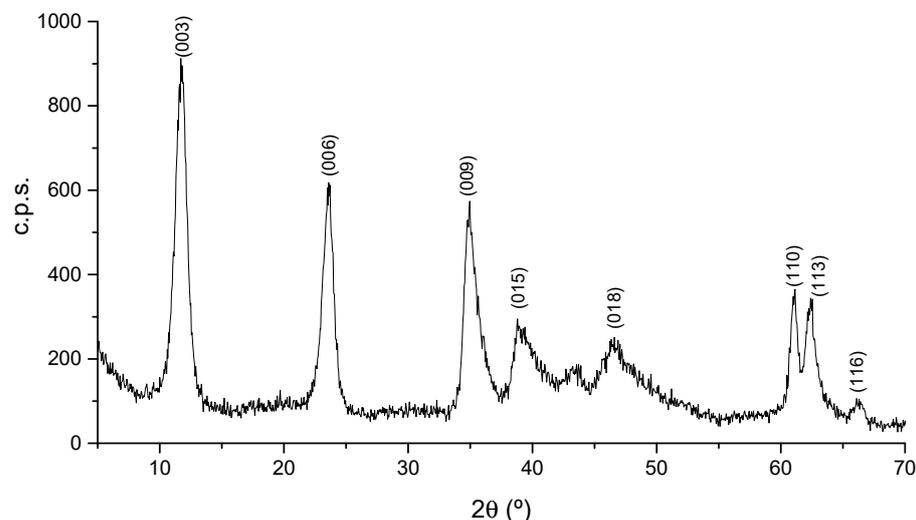
lution of the layer Cr(III) cations of HT compounds [23]. The presence of chromate species after calcination at medium temperatures in MgCr and NiCr of HT was recognized by TPR analysis of the samples [23]. TPR analysis of a series of carbonate-HT with reducible cations such as Co(II)-Fe(III), Ni(II)-Cr(III), Mg(II)-Mn(III), and MgAl-vanadate were carried out. The results proved the ability of these techniques to complete the characterization of these solids, mainly focusing on their applicability as catalysts and/or catalyst precursors. [24].

The interest in HT containing cations with redox properties increased because of their potential as oxidation or photooxidation catalysts. Thus, a comparative study of vanadate exchanged MgAl, MgCr, NiAl, and NiCr-HT obtained by means of different synthesis methods was reported in 1994–1995 [25–27]. The synthesis procedures tested to introduce the vanadate anions in the interlayer were direct coprecipitation, direct or indirect reconstruction, and pre-swelling with glycerol, among others. These preparations were also done to compare the results with those of hydrotalcites previously synthesized containing vanadium (III) within the layers [24]. The different synthesis procedures gave solids with similar composition and layered structure but with differences in the crystallinity degree and specific surface area and porosity. These kinds of differences are interesting to obtain final materials with specific properties in catalytic reactions [28–33]. The use of alternative routes to synthesize hydrotalcite-like materials with decavanadate in the interlayer was also assessed. For this, the application of an ultrasonic method was used to obtain MgAl-decavanadate by means of anionic exchange between carbonate and decavanadate. This anionic exchange was achieved by submitting a suspension of MgAl-carbonate LDH precursor in a vanadate solution to ultrasonic treatment. The exchange was easily achieved, and the crystallinity of the final solid was higher than that of the precursor [34]. The synthesis of polyoxovanadate pillared systems of ZnAl-HT was also tested and in this case, the structural characterization was implemented by an X-ray absorption and diffraction study [35]. The inclusion of anions other than vanadate in the interlayer space was successfully achieved as Zn,Al-HT interlayered with hexacyanoferrate(II) and hexacyanoferrate(III) anions were synthesized by reconstruction of the solid obtained by calcination of the carbonate form at 500 °C, anionic exchange of nitrate- and terephthalate-containing HT, and also direct synthesis [36].

Anions other than carbonate or decavanadate, such as oxalate, borate, or silicate anions, have also been used as interlayer anions that compensate for the layer charge, and the synthesis procedure gave perfectly characterized solids having the hydrotalcite-like structure. The layered solids were synthesized by using two different procedures [37,38]. The first one was the anion exchange method by changing the nitrate anion of a MgAl-nitrate HT for the different anions, borate, silicate, or  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ . The reconstruction method of Mg-Al-carbonate calcined HT was also used for obtaining the Mg,Al layered double hydroxide with  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  anions in the interlayer. All solids obtained showed PXRD patterns typical of layered solids with a hydrotalcite-like structure (Figure 2).

The effect of the Mg/Al molar ratio on the disposition and number of anions in the interlayer spacing was thoroughly studied. The interlayer spacing value depended on this ratio, and thus also depended on the precise orientation of the interlayer anions [37,38]. In this sense, the “memory effect” is a very interesting property of this kind of compound that is based on the ability of the oxides derived from the calcination of HT in reconstructing the layer structure when rehydrated in the presence of anions. This effect was also widely depicted in 1999 by submitting to rehydration the oxides obtained after calcining the original solids at increasing temperatures [39]. The crystalline phases formed were assessed by means of PXRD and the Al cations environment by  $^{27}\text{Al}$  MAS NMR. It was observed that the reconstruction could be complete when the calcination temperature was below 550 °C and the time of rehydration 24 h. When samples were calcined at 750 °C, a rehydration time of 3 days was necessary. Finally, after calcination at 1000 °C, only a partial reconstruction was possible. However, the NMR results indicated that some of the Al(III) cations remained in tetrahedral sites [39]. This work aroused the interest of many researchers and has been widely cited (more than 190 times according to Web of Science<sup>TM</sup>, and more than 250 times

according to GoogleScholar) in different HT research publications. Recently, it was cited in a review that summarizes the effect of aluminum content on optical, electrical, and dielectric properties of mixed metal oxides obtained by calcination of Mg-Al-nitrate HT [40].



**Figure 2.** PXRD of a Mg–Al–carbonate hydroxalcite obtained by the coprecipitation method. The Miller indices are assigned according to the JCPDS 22-700.

The calcination products of all these LDH have always shown a high interest because of the possibility of obtaining double, ternary, or quaternary mixed oxides with high specific surface area and dispersion degree, and so suitable for catalysts reactions. Countless LDH have been prepared to improve the synthesis methods and also the characterization procedures of the solids derived from their calcination [41–43]. Ulibarri et al. studied the synthesis of hydroxalcites with oxidable cations in the layers, such as Ni and Mn, and their incidence in the mixed oxides obtained from their calcination at different temperatures [43]. Fernández et al. synthesized Mg-Al-Fe hydroxalcites with different Al/Fe molar ratios to test the effect of iron content on the crystalline phases formed upon thermal decomposition [44]. Trujillano et al. described the synthesis and characterization of Co-Fe-carbonate HT and their calcination products. The formation of  $\text{Co}_x(\text{II})\text{-Co}_y(\text{III})\text{-Fe}_z(\text{III})$  oxides with spinel-like structure and different cation molar ratios, depending on the temperature and time of calcination, was widely studied [45,46]. A Ni-Fe-carbonate HT was prepared by testing two different aging treatments and calcining temperatures to each original sample [47]. X-ray absorption results for calcined samples showed that Ni(II) cations were located in octahedral sites, while Fe(III) cations were in octahedral and tetrahedral sites in the same proportion. Coordination parameters at the first and second shells of Ni(II) and Fe(III) cations for the sample calcined at 750 °C coincided with those expected for a mixture of NiO and the  $\text{NiFe}_2\text{O}_4$  spinel, phases detected by X-ray diffraction [47]. For the sample calcined at 450 °C, although PXRD only detected crystalline NiO, X-ray absorption measurements also indicated that Fe(III) ions were forming an amorphous phase. This study also allowed us to know that the reducibility of cations in the sample calcined at 450 °C depended on the synthesis method and the formation of the spinel phase. This article has also received large attention (109 Web of Science citations, and 148 GoogleScholar citations up to May 2022). Recently, it has been used as a reference in a review dealing with the use of hydroxalcite as adsorbents for the removal of heavy metal anions as water contaminants [48].

To study systems with more than two cations in the layer and to test the nature of derived mixed oxides containing yttrium obtained by its calcination, a new Mg,Al,Y-LDH with the hydroxalcite-like structure as a precursor of mixed oxides was prepared. This study was based on industry interest in yttrium garnets as gemstones and as magnetic materials. The synthesis was carried out by coprecipitation of Mg(II), Al(III), and Y(III) cations

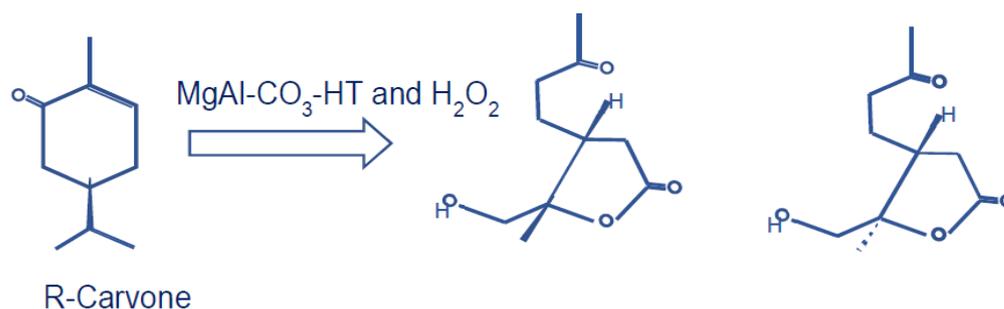
in alkaline solutions. The nature of mixed oxides obtained by calcination at increasing temperatures was assessed mainly by X-ray diffraction [49].

Other type of LDH is the so-called hydrocalumite, which contains Ca (II) and Al (III) as layer cations and chloride as interlayer anion. For the synthesis of this compound, Al was recovered from a saline slag generated during the recycling of this element, trying to minimize the contamination and valorize this residue [50]. The synthesis of hydrocalumite was favored by using microwave radiation. The optimum aging temperature under MW irradiation was 125 °C, as it allowed to obtain pure hydrocalumite, with high crystallinity and composed of LDH-type aggregates of regular hexagonal particles. The high crystallinity of the solids justified their low  $S_{\text{BET}}$  values. Globally, solids with textural properties comparable to those prepared from pure commercial reagents, can be prepared by using the aluminum slag, which supposes a high added value for this residue. [50]. Depending on the conditions, hydrocalumite was accompanied by impurities of calcite and katoite, the thermal behavior of this system has been studied in detail by a combination of TG, DTA, and analysis of the evolved gases (EGA) by means of mass spectrometry (MS) [51].

### 3. Applications

The catalytic activities for acetaldehyde self-condensation and 2-methylbut-3-yn-2-ol conversion of both Mg-Al and Li-Al HT with carbonate, chloride, nitrate, or vanadate as anions were studied by Rives et al. [52]. The solids were tested as-synthesized and after calcination at different temperatures. The authors concluded that the surface acidity that was measured using Hammett indicators depended on the nature of the anions. Another conclusion was that the host matrix had no major effect on the acidity or the catalytic activity, although the MgAl materials showed higher thermal stability. They also confirmed that the activity was related mostly to the nature of the interlayer anion, and higher catalytic activity was found for the solids containing vanadate.

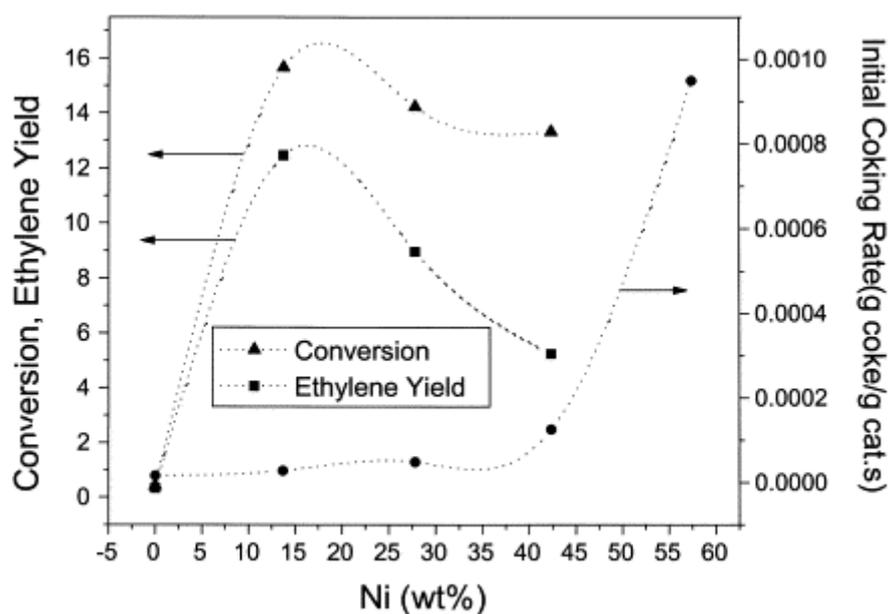
As hydrotalcite-like solids act as catalysts precursors, some catalytic reactions have been tested using the mixed oxides obtained upon calcination of synthetic LDH. In 1997, MgCr-, NiCr- and NiAl-Vanadate hydrotalcites with decavanadate as interlayer anion were prepared. The original solids were calcined and then the surface acidity was studied by monitoring the adsorption of pyridine by FT-IR spectroscopy and tested for 2-propanol oxidative dehydrogenation. The samples NiAl-vanadate presented the highest acidity while the selectivity to the oxidative dehydrogenation was larger on the MgCr- Vanadate, and NiCr- Vanadate samples calcined at 300 °C [53]. The isopropanol oxidation reaction on calcined LDH with different interlayer anions (carbonate, nitrate, silicate, and borate), was studied in 2001 [53]. The original solids were submitted at 600 °C and their surface acidity was determined by ammonia adsorption; surface Lewis acid sites and Brönsted basic sites were studied. The samples derived from carbonate and nitrate hydrotalcites showed the highest activity for acetone formation due to their surface acidity and basicity. In contrast, samples derived from silicate- or borate-HT showed lower activity due to the lack of surface basic sites [54]. MgAl HT was also used in a new and green methodology of synthesis of two chiral building blocks. This synthesis implied a regioselective Baeyer-Villiger reaction and can be considered a green procedure because hydrogen peroxide was the only oxidant used and the catalyst was a non-contaminant MgAl-carbonate HT [55]. Furthermore, the use of carvone, a cheap commercial compound, enhances the value of this methodology (Figure 3).



**Figure 3.** Green synthesis of two chiral building blocks by using hydrotalcites as catalysts.

A wide catalytic study was centered on the influence of Zn content of Ni–Cr–Al mixed-oxide catalysts with a spinel-like structure on the catalytic performance in acetylene hydrogenation. The physicochemical properties of these oxides were also analyzed. The catalysts derived from the calcination of several HT with different cationic molar ratios and formula  $(\text{Zn}_x\text{Ni}_y\text{Al}_z\text{Cr}_t(\text{OH})_2(\text{CO}_3)_{z+t/2}m\text{H}_2\text{O})$ , and the joint action of ZnO and  $\text{Cr}_2\text{O}_3$ , as activity modifier and support modifier, respectively, was tested [56–58].

Continuing with the use of calcined HT for the acetylene hydrogenation reaction, Monzón et al. compared the previous catalysts but doped with Fe(III) instead of Cr(III) [59]. The researchers tested the effect of the Ni/Zn molar ratio on the activity, selectivity, and coke formation of NiO–ZnO– $\text{Al}_2\text{O}_3$  catalysts depending on the Fe/Al cationic molar ratio. They concluded that Ni was not the only one responsible for the performance of the catalyst and that the presence of ZnO gave rise to a significant decrease in the coke formation (Figure 4). The same effect was observed when the catalysts contained Cr(III) instead of Fe(III).



**Figure 4.** Conversion and ethylene yield (left) and initial rate of coke formation (right), versus the Ni loading in the different catalysts derived from calcined HT. Reprinted from Appl. Clay Sci. 1998, 13, 363–379. Copyright (1998) with permission from Elsevier.

In these works, the authors assessed that the calcination of HT was a successful method to obtain highly dispersed mixed oxides. On the other hand, they concluded that the selectivity in the hydrogenation of acetylene, a structure-sensitive reaction, and the coke formation, can be easily modified by varying the chemical composition of the catalysts [59]. Otherwise, the influence of the Ni/Mg cationic molar ratio on the precursor HT was linked with the variation of the selectivity, the activity, and coke formation of NiO–MgO– $\text{Al}_2\text{O}_3$  catalysts modified with Cr(III) for acetylene hydrogenation [60]. An optimal

Ni/Mg molar ratio was found, also observing that the addition of MgO can modulate the catalytic properties of Ni because the conversion, selectivity, and yield to ethylene increased when the Mg/Ni ratio increased, and coke formation simultaneously decreased.

Another catalytic reaction tested using hydrotalcite-derived catalysts was hydroxylation of phenol. For this purpose, Rives et al. synthesized CuCoAl ternary HT with (Cu + Co)/Al atomic ratio of 3.0 and different Cu/Co atomic ratios from 80:20, to 20:80 [61]. The original solids were obtained by the coprecipitation method under low supersaturation. These solids showed a layered hydrotalcite-like structure and their crystallinity increased with the copper concentration. Another remarkable aspect was the increase in the total pore volume and the specific surface area with cobalt content. Calcination of the original hydrotalcites at 500 °C gave rise to the solids whose PXRD patterns corresponded with those of the tenorite and spinel phases. These oxides were tested in the liquid phase hydroxylation of phenol using H<sub>2</sub>O<sub>2</sub> as an oxidant. The higher activity was presented by the calcined solid with a Cu/Co atomic ratio of 75:25. It was also concluded that an increase in substrate/catalyst ratio enhanced the conversion of phenol. Using oxidants other than H<sub>2</sub>O<sub>2</sub> and solvents other than water did not show measurable conversion of phenol. The authors confirmed the influence of the presence of cobalt and of the surface properties on the activity of copper in the control of the development of the reaction [61].

Mg-V-hydrotalcites were synthesized with different Mg/V molar ratios and then calcined at 800 °C to be tested for oxidative dehydrogenation of propane and n-butane. The relative amounts of Mg<sub>3</sub>(VO<sub>4</sub>) and MgO determined the formation of different vanadates, which influenced the performance of the oxides obtained in oxidative dehydrogenation of propane and n-butane [62].

Thanks to their high specific surface area, another application of the HT and their calcination products is the adsorption and removal of pollutant compounds. Thus, Trujillano et al. used HT solids to eliminate the salts responsible for the degradation of the stones of the cultural heritage as well as for their cleaning [63]. In this work, the authors used the MgAl calcined hydrotalcite as an absorbent of anionic contaminants of the stone as a complement of the conventional clays (sorbents of cationic contaminants) that were used by the same research group as sorbents of cationic pollutants and salts [64]. Both surveys demonstrated the possibility of using effective, cheap, non-aggressive, and green procedures to remove pollutants and salts. The authors proved that hydrotalcites and conventional clays are highly effective agents for cleaning stone material in an easy way. This investigation was part of a European scientific and multidisciplinary collaboration project between researchers from a consolidated research unit formed by the Instituto de Recursos Naturales y Agrobiología at Salamanca (IRNASA-CSIC) and the University of Salamanca, dedicated to the cleaning and protection of the artistic heritage in stone, and the Spanish research team was headed by Professor Rives.

Owing to their wide range of chemical composition, HT can show a wide range of colors after calcination. It is well known that on heating the hydrotalcites decompose forming mostly amorphous species when calcining at low temperatures. When the calcination temperature increases, the crystallization of the divalent oxide is first observed, and at higher temperatures segregation of spinel takes place. If the mixed oxides obtained contain transition metal cations, they can be applied as ceramic pigments [65]. With the purpose of starting a study on the use of HT as pigments, a series of MgAl-carbonate HT with Mg/Al molar ratios of 4/1, 2/1,  $\frac{1}{2}$ , and 1/4 were prepared by the coprecipitation method to ascertain the different steps of the degradation of this kind of solids under calcination depending on their composition. The solids obtained had as formula  $[Mg_xAl_{1-x}(OH)_2](CO_3^{2-})_{(x/2)} \cdot nH_2O$  and the optimum x value for hydrotalcite formation was between 0.20 and 0.35. The thermal decomposition of the solids obtained was systematically studied by following the amount of Al in tetrahedral positions and the inversion degree of the spinel obtained at each temperature was determined to be higher as the temperature of calcination increased [65].

Other hydrotalcites prepared by precipitation at constant pH to be used as pigments were those containing Mg (II) and Al(III), doped with 0.5%, 1%, 2%, or 3% of Cr(III) and Y(III) [66]. The solids were calcined at 1200 °C for 5 h in air to give solids with a mixed structure (spinel and rock salt for MgO). Their color was pink, which made these solids suitable for being used as ceramic pigments. The incorporation of Cr in the structure of the spinel modified somewhat the chromaticity coordinates, but quantitative changes follow different trends. Nevertheless, these changes were qualitatively like those observed for the original LDH, so the authors found it easy to predict the expected color of the calcined solids by monitoring the color of the uncalcined precursors [66].

To test the incidence of the preparation method in the final color of the pigments obtained by calcination of HT, nickel-aluminum HT was prepared by conventional coprecipitation and by coprecipitation in the presence of a surfactant. Larger and better-ordered crystals were obtained when the synthesis method was the inverse micelles route [67]. Calcination of the original samples gave rise to the formation of homogeneously dispersed mixed oxides. The lightness and chromaticity coordinates of the solids (HT precursors and calcined solids) were analyzed to ascertain if the preparation procedure influenced the final color. Both the preparation method and the calcination treatment had a little effect on the precise chromaticity coordinates (green/red and blue/yellow) and an important effect on the luminosity (whiteness/darkness) of the solids. The color coordinates of these solids showed that an enhancement of the green color was observed when the HT was prepared in an organic medium. After calcination, this solid also showed a larger luminosity than the solid derived from the HT prepared by conventional coprecipitation [67].

As the thermal decomposition of HT leads to highly dispersed mixed oxides, the precise color of the final oxides can be tuned by controlling the precise chemical composition of LDH precursors containing transition metal cations in the layers. Rives et al. synthesized hydrotalcites containing Co(II) and Cr(III) cations with Co/Cr molar ratios ranging from 2 to 0.5, which were tested as pigments upon calcination. The authors developed the synthesis of some selected samples whose colors were of better quality than two commercial black pigments [68].

The preparation of HT-containing lanthanide cations has also been reported. A series of Mg-Al-carbonate HT with 4% loading of different lanthanide cations in the brucite-like layers was reported [69]. All the original mixtures had an M(II)/M(III) molar ratio of 3, and among the trivalent cations, different Ln/Al molar ratios were considered: 4/96 for Tb-Al, Er-Al, and Yb-Al HT, and 2/2/96 for Er-Yb-Al HT. The as-synthesized solids showed the hydrotalcite-type structure, without contaminating phases and they were calcined at 1000 °C forming perfectly dispersed mixed oxides, with the MgO and the MgAl<sub>2</sub>O<sub>4</sub> spinel structure and without any differentiated phase containing lanthanide ions. All samples prepared and their calcined products were white, except the Er (III)-containing samples, which revealed a weak pink color. The analysis of the color of all the samples was made by determining the colorimetric coordinates L\*a\*b\* of the CIE system (International Commission on Illumination). All the samples containing Tb(III) were submitted to luminescence studies, exhibiting green fluorescence under irradiation of 254 and 365 nm. The emission spectra showed a series of narrow lines ascribed to Tb(III) transitions. The decay curves monitored at 543 nm indicated the presence of a single local Tb(III) environment in the parent and calcined samples. For the calcined samples, the photoluminescence evidence supported the insertion of Tb(III) in MgAl<sub>2</sub>O<sub>4</sub> rather than in MgO [69].

The synthesis, structural characteristics, and applications of some Cu(II)-containing HT were also depicted. Originally, due to the difficulty in the obtaining of hydrotalcites with Cu (II) as the only divalent cation, ethylene glycol was used to reduce the divalent cations of a CuAl-LDH and a NiAl-LDH by means of the so-called polyol process. In this test, it was found that the degree of reduction of both cations to their metallic forms depended on the nature of the interlayer anions as well as on the time and temperature of treatment of the reaction mix [70]. The synthesis, structural and textural characteristics, and the catalytic

performance on the hydroxylation of phenol of CuNiAl and CuCoAl hydrotalcites were described by Kannan and Rives, together with other researchers [71–73]. These authors also studied the transformation of Cu-rich hydrotalcites (Cu + M(II))/Al (with M(II) = Co, Ni, or Mg) when calcined at high temperatures, observing considerable differences in the thermal change temperatures of these samples depending on the co-divalent metal cations [61].

The synthesis under several procedures of NiGa, NiAl, CuAl, or CuAlFe hydrotalcites with carbonate or surfactants as interlayer anions was reported trying to establish a relationship between their properties and the preparation method. The surfactants used were alkyl sulfonates of organic chains with different lengths or alkyl-benzene sulfonates. These materials were submitted to calcination and the thermal effects at increasing temperatures and the solids formed were defined [74–79]. The magnetic properties of CuAl LDH with carbonate or anionic surfactant were also investigated [78], and low oxidation states of copper (Cu<sub>2</sub>O or Cu) were obtained over a mixed oxide phase when Cu(II)Al (III)-LDH containing organic sulfonates in the interlayer were calcined. This reduction of Cu(II) was not possible when the interlayer anion was carbonate, and this process was not observed for cations other than Cu(II) [79]. Ternary hydrotalcite containing Ni, Cu, and Al cations with different cationic molar ratios were also synthesized to measure the effect of copper on the reaction of isomerization of eugenol, observing a decrease in the activity when increasing the amount of copper [80].

The use of hydrotalcites as drug carriers for controlled release is a research line that V. Rives began to study at the beginning of this century. In 2004, MgAl LDH with naproxen in the interlayer was prepared by using two synthetic procedures: reconstruction and coprecipitation. From the X-ray results discussion, the authors concluded that the drug was incorporated in the interlayer of the solids with a tilted bilayer orientation with the carboxylate groups linked to the brucite-like sheets [81].

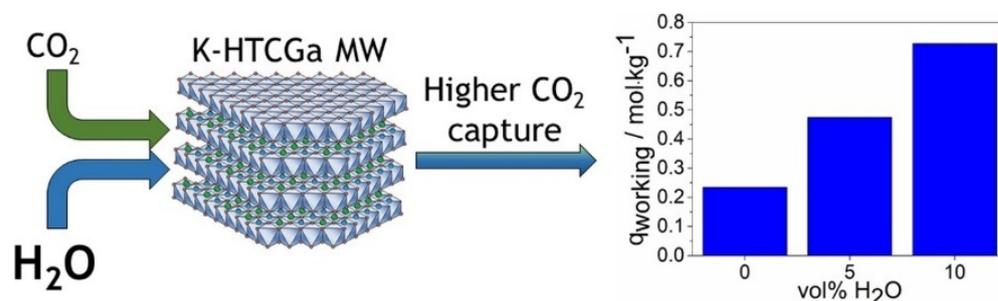
The intercalation of naproxen in LDHs by coprecipitation and anion-exchange was also studied on Mg-Al-Fe HT [82]. The drug release rate was tested *in vitro*, to ascertain if the LDH can act as an additive or as a matrix. The intercalation of the drug forming bilayers and the possibility of its exchange in the biological medium led to a release much slower than when the LDH was only physically mixed with the drug [82]. Later, Rives et al. collected the existing literature on hydrotalcites–drugs interactions in two bibliographic reviews, published in 2013 and 2014, respectively [83,84].

The studies on CO<sub>2</sub> sorption on hydrotalcites started by using calcined HT as sorbents, research done in collaboration with researchers from the Universidade de Porto (Portugal). In this case, the preoccupation with the production of huge amounts of CO<sub>2</sub> from the combustion of fossil fuels, and the greenhouse effect of this gas, justified the use of calcined hydrotalcites as CO<sub>2</sub> adsorbents, finding high efficiency. This suitability was due to the ability of these solids to operate in the temperature interval found in both post- and pre-combustion streams (i.e., 200–400 °C) [85–88].

So as to ascertain the incidence of water in the CO<sub>2</sub> capture, a calcined Mg-Al-Ga HT impregnated with K, aged under microwave irradiation was checked (Figure 5). It was observed that the presence of water significantly increased the CO<sub>2</sub> capture. So did higher total pressures and temperatures. Finally, Energy-dispersive X-ray spectroscopy results showed that under wet conditions potassium and gallium were mobilized towards the sorbent surface and this fact contributed to enhancing the sorbent behavior of the HT.

Different procedures of synthesis, the characterization results, and the thermal properties of composites having hydrotalcites as nanofillers can be found in the literature of this research group [89–94]. The preparation by *in situ* polymerization was tested with the synthesis of a polyethylterephthalate-hydrotalcite by using polyethylterephthalate and different amounts of a hydrotalcite with dodecylsulphate as interlayer anion. The characterization results permitted conclude that the maximum amount of inorganic additive that could be well dispersed was between 2–10%, while higher loadings did not allow a complete dispersion and formed agglomerates [90]. The *in-situ* polymerization method was proved to be the best one to obtain PET-LDH composites with low contents of

LDHs. The PET-LDH composites thus prepared were thermally more stable than similar composites prepared by blending [90].



**Figure 5.** CO<sub>2</sub> sorption experiments over Mg–Al–Ga HT. Reprinted from J. Ind. Eng. Chem. 2019, 72, 491–503. Copyright (2019) with permission from Elsevier.

To evaluate the influence of the hydrotalcite as nanofillers in a polyester resin, two LDH with organic interlayer anions, adipate-LDH and 2-methyl-2-propene-1-sulfonate-LDH were synthesized and characterized. Flexural tests showed that incorporation of organo-LDH in the resin reduced the flexural strength of the resin. The study of fire reaction properties indicated up to 46% reduction in the polyester flammability [90]. Polyamide6.6/Mg,Al/adipate-LDH nanocomposites were prepared by solid state polymerization [92] and the structural characterization and thermal measurements results led to the conclusion that the best dispersion and the best thermal stability of the nanocomposites were achieved for the composite with 0.1% LDH content, and it was higher than that of pure polyamide [92].

The interest in the synthesis of hydrotalcites for the remediation of soils and groundwater contamination was evidenced by the research in the synthesis of MgAl and CaAl HT labeled with fluorescein by intercalation of this molecule [95,96]. These fluorescent solids can act as tracer particles for in situ remediation strategies. Their particle size was tuned by varying the synthesis conditions and aging time with an easy and economic synthesis method. If co-injected with reactive particles showing similar properties, the reactants could easily be detected, thanks to the fluorescent particles, in the subsurface, and their potential movement and spreading rate, caused by groundwater flow, could be followed [95,96].

Hydrotalcites with intercalated oxidizing agents have been proved to act as reactants for remediation strategies because HT serves as supports for the oxidizing agents during their injection to penetrate aquifers. So, the efficiency of LDH intercalated with permanganate and peroxydisulphate anions was tested in batch experiments using trichloroethene or 1,1,2-trichloroethane as the target contaminants. The oxidation processes produced by the intercalated oxidizing agents gave rise to the degradation of the contaminants by the HT-based solids [97].

Hydrotalcite-like compounds treated with acetone to modify their surface area and particle aggregate can be used as sorbents of ecosystems pollutants as chlorinated hydrocarbons [98] or other toxic chemicals such as perfluorooctane sulfonate and perfluorooctanoate [99]. These tuned solids have proved to be powerful and interesting toxic sorbents because of their high anion exchange capacity and high specific surface area [100].

Different ways of preparing hydrotalcite and the phenomena occurring during their synthesis continue being studied [100–102]. So, the synthesis of ZnAl-nitrate LDH has recently been carried out in the presence of methylamine, dimethylamine, and trimethylamine, and under microwave hydrothermal treatment. Solids with high crystal sizes and low particle size distributions were obtained [100]. ZnAl-carbonate HT and the oxides obtained from their calcination have also been proved to be efficient in the photodegradation of 4-nitrophenol, one of the most common contaminants in industrial waters [102]. The catalysts were tested as prepared and after calcination at 650 °C, a treatment that

gave rise to the formation of a ZnO phase dispersed on an Al<sub>2</sub>O<sub>3</sub> amorphous phase. The best performance was found for the calcined solid, which removed the contaminant by adsorption-degradation. The high specific surface area of the solid led to a high adsorption capacity and the high dispersion of its active form allowed a higher degradation power than commercial ZnO that was tested as reference.

#### 4. Conclusions

The work on hydrotalcites done by Professor Rives and the research team that has worked with him is not easy to summarize. Innovation in hydrotalcite synthesis methods has resulted in the knowledge of procedures that lead to obtaining hydrotalcites tailored to the final application. This fact is demonstrated by the extensive and detailed characterization work carried out for more than thirty years. Likewise, the usefulness of these solids as catalysts, catalyst supports, contaminant adsorbents, etc., has been constantly verified. The contribution to the improvement of synthesis procedures of solids that allow for reducing pollution and energy expenditure has been constant in the research projects on hydrotalcites. Such work has been published in several scientific journals and the publications have been widely studied and cited by researchers around the world.

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#### References

1. Ulibarri, M.A.; Fernández, J.M.; Labajos, F.M.; Rives, V. Synthesis and characterization of [Co<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>2</sub>](CO<sub>3</sub>)<sub>x/2</sub>·nH<sub>2</sub>O]. *Chem. Mater.* **1991**, *3*, 626–630. [\[CrossRef\]](#)
2. Hochstetter, C. Untersuchung Über Die Zusammensetzung einiger Mineralien. *J. Prakt. Chem.* **1842**, *27*, 375–378. [\[CrossRef\]](#)
3. Caillère, S. Sur l'hydrotalcite de Snarum (Norvège). *Bull. Soc. Miner.* **1944**, *67*, 411–419. [\[CrossRef\]](#)
4. Manasse, E. Idrotalcite e piroaurite. *Atti Soc. Toscana Sc. Nat. Proc. Verb.* **1915**, *24*, 92–97.
5. Feitknecht, W.; Gerber, M. Zur Kenntnis der Doppelhydroxyde und basischen Doppelsalze III. Über Magnesium-Aluminiumdoppelhydroxyd. *Helv. Chim. Acta* **1942**, *25*, 131–137. [\[CrossRef\]](#)
6. Allmann, R. The crystal structure of pyroaurite. *Acta Cryst. B* **1968**, *24*, 972–977. [\[CrossRef\]](#)
7. Taylor, H.F.W. Segregation and Cation-Ordering in Sjögrenite and Pyroaurite. *Mineral Mag.* **1969**, *37*, 338–342. [\[CrossRef\]](#)
8. Ross, G.J.; Kodama, H. Properties of a Synthetic Magnesium-Aluminum Carbonate Hydroxide and its Relationship to Magnesium-Aluminum Double Hydroxide, Manasseite and Hydrotalcite. *Am. Mineral.* **1967**, *752*, 1036–1047.
9. Rives, V. (Ed.) *Layered Double Hydroxides: Present and Future*; Nova Science Publishers: New York, NY, USA, 2001.
10. Rives, V.; Ulibarri, M.A. Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. *Coord. Chem. Rev.* **1999**, *181*, 61–120. [\[CrossRef\]](#)
11. Labajos, F.M.; Rives, V.; Ulibarri, M.A. A FT-IR and V-UV Spectroscopic Study of Nickel-Containing Hydrotalcite-Like Compounds, [Ni<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>2</sub>](CO<sub>3</sub>)<sub>x/2</sub>·nH<sub>2</sub>O. *Spectrosc. Lett.* **1991**, *24*, 499–505. [\[CrossRef\]](#)
12. Reichle, W.T. Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). *Solid State Ion.* **1986**, *22*, 135. [\[CrossRef\]](#)
13. Rives, V.; Labajos, F.M.; Ulibarri, M.A. Effect of hydrothermal and thermal treatments on the physicochemical properties of Mg-Al hydrotalcite-like materials. *J. Mat. Sci.* **1992**, *27*, 1546–1552.
14. Arco, M.; Rives, V.; Trujillano, R. Surface and textural properties of hydrotalcite-like materials and their decomposition products. *Stud. Surf. Sci. Catal.* **1994**, *87*, 507–515.
15. Arco, M.C.; Martín, C.; Martín, I.; Rives, V.V.; Trujillano, R. A FTIR spectroscopic study of surface-acidity and basicity of mixed Mg,Al-oxides obtained by thermal-decomposition of hydrotalcite *Spectrochim. Acta* **1993**, *49*, 1575–1582.
16. Trujillano, R.; González-García, I.; Morato, A.; Rives, V. Controlling the synthesis conditions for tuning the properties of hydrotalcite-like materials at the nano scale. *Chem. Eng.* **2018**, *2*, 31. [\[CrossRef\]](#)
17. Benito, P.; Labajos, F.M.; Rocha, J.; Rives, V. Influence of microwave radiation on the textural properties of layered double hydroxides. *Micropor. Mesopor. Mat.* **2006**, *94*, 148–158. [\[CrossRef\]](#)
18. Benito, P.; Labajos, F.M.; Rives, V. Microwave-assisted synthesis of layered double hydroxides. In *Solid State Chemistry Research Trends*; Buckley, R.W., Ed.; NOVA Sci. Pub. Inc.: New York, NY, USA, 2007; pp. 173–225.

19. Herrero, M.; Benito, P.; Labajos, F.M.; Rives, V. Change in microporosity of granitic building stones upon stabilisation of  $\text{Co}^{2+}$  in LDH by microwave assisted ageing. *J. Solid State Chem.* **2007**, *180*, 873–884. [[CrossRef](#)]
20. Rives, V.; Labajos, F.M.; Ulibarri, M.A.; Malet, P. A New Hydrotalcite-like Compound Containing V(III) Ions in the Layers. *Inorg. Chem.* **1993**, *32*, 5000–5001. [[CrossRef](#)]
21. Labajos, F.M.; Rives, V.; Malet, P.; Centeno, M.A.; Ulibarri, M.A. Synthesis and characterisation of hydrotalcite-like compounds containing V(III) in the layers, and of their calcination products. *Inorg. Chem.* **1996**, *35*, 1154–1160. [[CrossRef](#)]
22. Labajos, F.M.; Sastre, M.-D.; Trujillano, R.; Rives, V. New layered double hydroxides with the hydrotalcite structure containing Ni(II) and V(III). *J. Mater. Chem.* **1999**, *9*, 1033–1039. [[CrossRef](#)]
23. Labajos, F.M.; Rives, V. Thermal evolution of Cr(III) ions in hydrotalcite-like compounds. *Inorg. Chem.* **1996**, *35*, 5313–5318. [[CrossRef](#)]
24. Rives, V.; Ulibarri, M.A.; Montero, A. Application of temperature-programmed reduction to the characterization of anionic clays. *Appl. Clay Sci.* **1995**, *10*, 83–93. [[CrossRef](#)]
25. Ulibarri, M.A.; Labajos, F.M.; Rives, V.; Trujillano, R.; Kagunya, W.; Jones, W. Comparative Study of the Synthesis and Properties of Vanadate-Exchanged Layered Double Hydroxides. *Inorg. Chem.* **1994**, *33*, 2592–2599. [[CrossRef](#)]
26. Kooli, F.; Rives, V.; Ulibarri, M.A. Preparation and Study of Decavanadate-Pillared Hydrotalcite-like Anionic Clays Containing Transition Metal Cations in the Layers. 1. Samples Containing Nickel-Aluminum Prepared by Anionic Exchange and Reconstruction. *Inorg. Chem.* **1995**, *34*, 5114–5121. [[CrossRef](#)]
27. Ulibarri, M.A.; Labajos, F.M.; Rives, V.; Trujillano, R.; Kagunya, W.; Jones, W. Effect of intermediates on the nature of polyvanadate-intercalated layered double hydroxides. *Mol. Cryst. Liq. Cryst.* **1994**, *244*, 167–172. [[CrossRef](#)]
28. Kooli, F.; Rives, V.; Ulibarri, M.A. Preparation and Study of Decavanadate-Pillared Hydrotalcite-like Anionic Clays Containing Transition Metal Cations in the Layers. 2. Samples containing Magnesium-Chromium and Nickel-Chromium. *Inorg. Chem.* **1995**, *34*, 5122–5128. [[CrossRef](#)]
29. Crespo, I.; Barriga, C.; Ulibarri, M.A.; González-Bandera, G.; Malet, P.; Rives, V. An X-ray diffraction and absorption study of the phases formed upon calcination of Zn-Al-Fe hydrotalcites. *Chem. Mat.* **2001**, *15*, 1518–1527. [[CrossRef](#)]
30. Kooli, F.; Rives, V.; Ulibarri, M.A.; Jones, W. Pillaring of layered double hydroxides possessing variable layer charge with vanadate polyoxoanions. In *Advances in Porous Materials*; Materials Research Society, Sympisum Proceedings; Komarneni, S., Smith, D.M., Beck, J.S., Eds.; Cambridge University Press: Cambridge, UK, 1995; Volume 371, pp. 143–149.
31. Arco, M.; Galiano, M.V.G.; Rives, V.; Trujillano, R.; Malet, P. Preparation and study of decavanadate-pillared hydrotalcite-like anionic clays containing cobalt and chromium. *Inorg. Chem.* **1996**, *35*, 6362–6372. [[CrossRef](#)]
32. Arco, M.; Rives, V.; Trujillano, R.; Malet, P. Thermal behaviour of Zn, Cr layered double hydroxides with the hydrotalcite-like structure containing carbonate or decavanadate. *J. Mat. Chem.* **1996**, *6*, 1419–1428. [[CrossRef](#)]
33. Kooli, F.; Holgado, M.; Rives, V.; San Román, M.; Ulibarri, M.A. A simple conductivity study of decavanadate intercalation in hydrotalcite. *Mat. Res. Bull.* **1997**, *32*, 977–982. [[CrossRef](#)]
34. Kooli, F.; Jones, W.; Rives, V.; Ulibarri, M.A. An alternative route to polyoxometalate-exchanged layered double hydroxides: The use of ultrasounds. *J. Mat. Sci. Lett.* **1997**, *16*, 27–29. [[CrossRef](#)]
35. Barriga, C.; W Jones, W.; Malet, P.; Rives, V.; Ulibarri, M.A. Synthesis and characterisation of polyoxovanadate-pillared Zn, Al layered double hydroxides: An X-ray absorption and diffraction study. *Inorg. Chem.* **1998**, *37*, 1812–1820. [[CrossRef](#)]
36. Crespo, I.; Barriga, C.; Rives, V.; Ulibarri, M.A. Intercalation of iron hexacyano complexes in Zn,Al hydrotalcite. *Solid State Ion.* **1997**, *101*, 729–735. [[CrossRef](#)]
37. Arco, M.; Gutierrez, S.; Martin, C.; Rives, V.; Rocha, J. Effect of the Mg/Al ratio on borate (or silicate)/nitrate exchange in hydrotalcite. *J. Solid State Chem.* **2000**, *151*, 272–280. [[CrossRef](#)]
38. Arco, M.; Gutierrez, S.; Martin, C.; Rives, V. Intercalation of  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  complex in Mg,Al layered double hydroxides. *Inorg. Chem.* **2003**, *42*, 4232–4240. [[CrossRef](#)] [[PubMed](#)]
39. Rocha, J.; Arco, M.; Rives, V.; Ulibarri, M.A. Reconstruction of layered double hydroxides from calcined precursors: A powder XRD and  $^{27}\text{Al}$  MAS NMR study. *J. Mater. Chem.* **1999**, *9*, 2499–2503. [[CrossRef](#)]
40. Lahkale, R.; Sadik, R.; Elhatimi, W.; Bouragba, F.Z.; Assekouri, A.; Chouni, K.; Rhalmi, O.; Sabbar, E. Optical, electrical and dielectric properties of mixed metal oxides derived from Mg-Al Layered Double Hydroxides based solid solution series. *Phys. B Cond. Matt.* **2022**, *626*, 413367. [[CrossRef](#)]
41. Barriga, C.; Kooli, F.; Rives, V.; Ulibarri, M.A. Layered hydroxycarbonates with the hydrotalcite structure containing Zn, Al and Fe. In *Synthesis of Porous Materials*; Ocelli, M.L., Kessler, H., Eds.; Marcel Dekker Inc.: New York, NY, USA, 1996; pp. 661–674.
42. Fernández, J.M.; Barriga, C.; Ulibarri, M.A.; Labajos, F.M.; Rives, V. Preparation and thermal-stability of manganese-containing hydrotalcite,  $[\text{Mg}_{0.75}\text{Mn(II)}_{0.04}\text{Mn(III)}_{0.21}(\text{OH})_2](\text{CO}_3)_{0.11}\cdot\text{NH}_2\text{O}$ . *J. Mat. Chem.* **1994**, *4*, 1117–1121. [[CrossRef](#)]
43. Barriga, C.; Fernández, J.M.; Ulibarri, M.A.; Labajos, F.M.; Rives, V. Synthesis and characterisation of new hydrotalcite-like compounds containing Ni and Mn in the layers and of their calcination products. *J. Solid State Chem.* **1996**, *124*, 205–213. [[CrossRef](#)]
44. Fernández, J.M.; Ulibarri, M.A.; Labajos, F.M.; Rives, V. The effect of iron on the crystalline phases formed upon thermal decomposition of Mg-Al-Fe hydrotalcites. *J. Mat. Chem.* **1998**, *8*, 2507–2517. [[CrossRef](#)]
45. Arco, M.; Trujillano, R.; Kassabov, S.; Rives, V. Spectroscopic properties of Co-Fe hydrotalcites. *Spectrosc. Lett.* **1998**, *31*, 859–869. [[CrossRef](#)]

46. Arco, M.; Rives, V.; Trujillano, R. Cobalt-iron hydroxycarbonates and their evolution to mixed oxides with the spinel structure. *J. Mater. Chem.* **1998**, *8*, 761–767. [[CrossRef](#)]
47. Arco, M.; Malet, P.; Trujillano, R.; Rives, V. Synthesis and Characterization of Hydrotalcites Containing Ni(II) and Fe(III) and Their Calcination Products. *Chem. Mater.* **1999**, *11*, 624–633. [[CrossRef](#)]
48. Dong, Y.; Kong, X.; Luo, X.; Wang, H. Adsorptive removal of heavy metal anions from water by layered double hydroxide: A review. *Chemosphere* **2022**, *162*, 134685. [[CrossRef](#)]
49. Fernández, J.M.; Barriga, C.; Ulibarri, M.A.; Labajos, F.M.; Rives, V. New hydrotalcite-like compounds containing yttrium. *Chem. Mat.* **1997**, *9*, 312–318. [[CrossRef](#)]
50. Jiménez, A.; Misol, A.; Morato, A.; Rives, V.; Vicente, M.A.; Gil, A. Optimization of hydrocalumite preparation under microwave irradiation for recovering aluminium from a saline slag. *Appl. Clay Sci.* **2021**, *212*, 10621. [[CrossRef](#)]
51. Jiménez, A.; Rives, V.; Vicente, M.A. Thermal study of the hydrocalumite–katoite–calcite system. *Thermochim. Acta* **2022**, *713*, 179242. [[CrossRef](#)]
52. Chisem, I.; Jones, W.; Martín, C.; Martín, C.; Rives, V. Probing the surface acidity of lithium aluminum and magnesium aluminum layered double hydroxides. *J. Mater. Chem.* **1998**, *8*, 1917–1926. [[CrossRef](#)]
53. Kooli, F.; Martín, C.; Rives, V. FT-IR spectroscopy study of surface acidity and iso-propanol decomposition on mixed oxides obtained upon calcination of layered double hydroxides. *Langmuir* **1997**, *13*, 2303–2306. [[CrossRef](#)]
54. del Arco, M.; Gutiérrez, S.; Martín, C.; Rives, V. FTIR study of isopropanol reactivity on calcined layered double hydroxides. *Phys. Chem. Chem. Phys.* **2001**, *3*, 119–126. [[CrossRef](#)]
55. Rodilla, J.M.; Neves, P.P.; Pombal, S.; Rives, V.; Trujillano, R.; Díez, D. Hydrotalcite catalysis for the synthesis of new chiral building blocks. *Nat. Prod. Res.* **2016**, *30*, 834–840. [[CrossRef](#)] [[PubMed](#)]
56. Rives, V.; Labajos, F.M.; Trujillano, R.; Romeo, E.; Royo, C.; Monzón, A. Acetylene hydrogenation on Ni–Al–Cr oxide catalysts: The role of added Zn. *Appl. Clay Sci.* **1998**, *13*, 363–379. [[CrossRef](#)]
57. Romeo, E.; Royo, C.; Monzón, A.; Trujillano, R.; Labajos, F.M.; Rives, V. Study of mixed oxides prepared from hydrotalcite-type precursors as hydrogenation catalysts. In *Actas del 16 Simposio Iberoamericano de Catálisis*; Centeno, A., Giraldo, S.A., Páez Mozo, E.A., Eds.; Universidad Industrial De Santander (UIS): Bucaramanga, Colombia, 1998; pp. 567–572.
58. Monzón, A.; Romeo, E.; Royo, C.; Trujillano, R.; Labajos, F.M.; Rives, V. Desarrollo de óxidos mixtos de ni como catalizadores de hidrogenación selectiva (Development of Ni mixed oxides as catalysts for selective hydrogenation). *Av. Ing. Química* **1998**, *8*, 24–27.
59. Monzón, A.; Romeo, E.; Royo, C.; Trujillano, R.; Labajos, F.M.; Rives, V. Use of hydrotalcites as catalytic precursors of multimetallic mixed oxides. Application in the hydrogenation of acetylene. *Appl. Catal. A Gen.* **1999**, *185*, 53–63. [[CrossRef](#)]
60. Romeo, E.; Royo, C.; Monzón, A.; Trujillano, R.; Labajos, F.M.; Rives, V. Preparation and characterisation of Ni–Mg–Al hydrotalcites as hydrogenation catalysts. *Stud. Surf. Sci. Catal.* **2000**, *130*, 2099–2104.
61. Rives, V.L.; Dubey, A.; Kannan, S. Synthesis, Characterization and catalytic hydroxylation of phenol over CuCoAl ternary hydrotalcites. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4826–4836. [[CrossRef](#)]
62. Holgado, M.J.; Labajos, F.M.; Montero, M.J.S.; Rives, V. Thermal decomposition of Mg/V hydrotalcites and catalytic performance of the products in oxidative dehydrogenation reactions. *Mat. Res. Bull.* **2003**, *38*, 1879–1891. [[CrossRef](#)]
63. Trujillano, R.; Vicente, M.A.; Rives, V. Utilización de arcillas catiónicas y aniónicas en la limpieza y desalado del patrimonio artístico (The use of cationic and anionic clays for cleaning and salt removal of cultural heritage). In *Actas del IV Congreso de Rehabilitación del Patrimonio Arquitectónico y Edificación*; Fernández Matrán, M.-A., Castro Castellano, J., Eds.; Centro Internacional para la Conservación del Patrimonio (CICOP España): La Habana, Cuba, 1998; pp. 192–193.
64. Trujillano, R.; García-Talegón, J.; Iñigo, A.C.; Vicente, M.A.; Rives, V.; Molina, E. Removal of salts from granite by sepiolite. *Appl. Clay Sci.* **1995**, *9*, 459–463. [[CrossRef](#)]
65. Nebot-Díaz, I.; Rives, V.; Rocha, J.; Carda, J.B. Thermal decomposition study of hydrotalcite-like compounds. *Bol. Soc. Esp. Ceram.* **2002**, *41*, 411–414.
66. García-García, J.M.; Pérez-Bernal, M.E.; Ruano-Casero, R.J.; Rives, V. Chromium and yttrium-doped magnesium aluminum oxides prepared from layered double hydroxides. *Solid State Sci.* **2007**, *9*, 1115–1125. [[CrossRef](#)]
67. Pérez-Bernal, M.E.; Ruano-Casero, R.J.; Benito, F.; Rives, V. Nickel–aluminum layered double hydroxides prepared via inverse micelles formation. *J. Solid State Chem.* **2009**, *182*, 1593–1601. [[CrossRef](#)]
68. Rives, V.; Pérez-Bernal, M.E.; Ruano-Casero, R.J.; Nebot-Díaz, I. Development of a black ceramic pigment from non-stoichiometric hydrotalcites. *J. Eur. Ceram. Soc.* **2012**, *32*, 975–987. [[CrossRef](#)]
69. Vicente, P.; Pérez-Bernal, M.E.; Ruano-Casero, R.J.; Ananias, D.; Almeida-Paz, F.A.; Rocha, J.; Rives, V. Luminescence properties of lanthanide-containing layered double hydroxides. *Micropor. Mesopor. Mat.* **2016**, *226*, 209–220. [[CrossRef](#)]
70. Kooli, F.; Rives, V.; Jones, W. Reduction of Ni(II)–Al(III) and Cu(II)–Al(III) layered double hydroxides to metallic Ni(0) and Cu(0) via polyol treatment. *Chem. Mat.* **1997**, *9*, 2231–2235. [[CrossRef](#)]
71. Rives, V.; Kannan, S. Layered double hydroxides with the hydrotalcite-type structure containing Cu<sup>2+</sup>, Ni<sup>2+</sup> and Al<sup>3+</sup>. *J. Mat. Chem.* **2000**, *10*, 489–495. [[CrossRef](#)]
72. Dubey, A.; Rives, V.; Kannan, S. Catalytic hydroxylation of phenol over ternary hydrotalcites containing Cu, Ni and Al. *J. Molec. Catal. A Gen.* **2002**, *181*, 151–160. [[CrossRef](#)]

73. Kannan, S.; Rives, V.; Knözinger, H. High-temperature transformations of Cu-rich hydrotalcites. *J. Solid State Chem.* **2004**, *177*, 319–331. [[CrossRef](#)]
74. Alvarez, A.; Trujillano, R.; Rives, V. Differently aged gallium-containing layered double hydroxides. *Appl. Clay Sci.* **2013**, *80*, 326–333. [[CrossRef](#)]
75. Trujillano, R.; Holgado, M.J.; Rives, V. Alternative synthetic routes for NiAl layered double hydroxides with alkyl and alkylbenzene sulfonates. *Stud. Surf. Sci. Catal.* **2002**, *142*, 1387–1394.
76. Klopogge, J.T.; Hickey, H.; Trujillano, R.; Holgado, M.J.; San Roman, M.S.; Rives, V.; Martens, W.N.; Frost, R.L. Characterization of intercalated Ni/Al hydrotalcites prepared by the partial decomposition of urea. *Cryst. Growth Des.* **2006**, *6*, 1533–1536. [[CrossRef](#)]
77. Trujillano, R.; Holgado, M.J.; González, J.L.; Rives, V. Cu-Al-Fe layered double hydroxides with  $\text{CO}_3^{2-}$  and anionic surfactants with different alkyl chains in the interlayer. *Solid State Sci.* **2005**, *7*, 931–935. [[CrossRef](#)]
78. Trujillano, R.; Holgado, M.J.; Pigazo, F.; Rives, V. Preparation, physicochemical characterisation and magnetic properties of Cu-Al layered double hydroxides with  $\text{CO}_3^{2-}$  and anionic surfactants with different alkyl chains in the interlayer. *Physica B* **2006**, *373*, 267–273. [[CrossRef](#)]
79. Trujillano, R.; Holgado, M.J.; Rives, V. Obtention of low oxidation states of copper from  $\text{Cu}^{2+}$ -Al<sup>0</sup> layered double hydroxides containing organic sulfonates in the interlayer. *Solid State Sci.* **2009**, *11*, 688–693. [[CrossRef](#)]
80. Jinesh, C.M.; Rives, V.; Carriazo, D.; Antonyraj, C.A.; Kannan, S. Influence of copper on the isomerization of eugenol for as-synthesized NiCuAl ternary hydrotalcites: An understanding through physicochemical study. *Catal. Lett.* **2010**, *134*, 337–342. [[CrossRef](#)]
81. Arco, M.; Gutiérrez, S.; Martín, C.; Rives, V.; Rocha, J. Synthesis and characterization of layered double hydroxides (LDH) intercalated with non-steroidal anti-inflammatory drugs (NSAID). *J. Solid State Chem.* **2004**, *177*, 3954–3962. [[CrossRef](#)]
82. Del Arco, M.; Fernández, A.; Martín, C.; Rives, V. Release studies of different NSAIDs encapsulated in Mg, Al, Fe-hydrotalcites. *Appl. Clay Sci.* **2009**, *42*, 538–544. [[CrossRef](#)]
83. Rives, V.; Arco, M.; Martín, C. Layered double hydroxides as drug carriers and for controlled release of non-steroidal anti-inflammatory drugs (NSAIDs): A review. *J. Controll. Rel.* **2013**, *169*, 28–39. [[CrossRef](#)]
84. Rives, V.; Arco, M.; Martín, C. Intercalation of drugs in layered double hydroxides and their controlled release: A review. *Appl. Clay Sci.* **2014**, *88–89*, 239–269. [[CrossRef](#)]
85. Silva, J.M.; Trujillano, R.; Rives, V.; Soria, M.A.; Madeira, L.M. High temperature  $\text{CO}_2$  sorption over modified hydrotalcites. *Chem. Eng. J.* **2017**, *325*, 25–34. [[CrossRef](#)]
86. Miguel, C.V.; Trujillano, R.; Rives, V.; Vicente, M.A.; Ferreira, A.F.P.; Rodrigues, A.E.; Mendes, A.; Madeira, L.M. High temperature  $\text{CO}_2$  sorption with gallium-substituted and promoted hydrotalcites. *Sep. Purif. Technol.* **2014**, *127*, 202–211. [[CrossRef](#)]
87. Silva, J.M.; Trujillano, R.; Rives, V.; Soria, M.A.; Madeira, L.M. Dynamic behaviour of a K-doped Ga substituted and microwave aged hydrotalcite-derived mixed oxide during  $\text{CO}_2$  sorption experiments. *J. Ind. Eng. Chem.* **2019**, *72*, 491–503. [[CrossRef](#)]
88. Faria, A.C.; Trujillano, R.; Rives, V.; Miguel, C.V.; Rodrigues, A.E.; Madeira, L.M. Alkali metal (Na, Cs and K) promoted hydrotalcites for high temperature  $\text{CO}_2$  capture from flue gas in cyclic adsorption processes. *Chem. Eng. J.* **2022**, *427*, 131502. [[CrossRef](#)]
89. Martínez-Gallegos, S.; Herrero, M.; Rives, V. Preparation of composites by in situ polymerisation of PET-hydrotalcite using dodecylsulfate. *Mat. Sci. For.* **2008**, *587*, 568–571.
90. Martínez-Gallegos, S.; Herrero, M.; Labajos, F.M.; Barriga, C.; Rives, V. Dispersion of layered double hydroxides in poly(ethylene terephthalate) by in situ polymerization and mechanical grinding. *Appl. Clay Sci.* **2009**, *45*, 44–49. [[CrossRef](#)]
91. Pereira, C.M.; Herrero, M.; Labajos, F.M.; Marques, A.V. Rives Preparation and properties of new flame retardant unsaturated polyester nanocomposites based on layered double hydroxides. *Polym. Degrad. Stab.* **2009**, *94*, 939–946. [[CrossRef](#)]
92. Herrero, M.; Benito, P.; Labajos, F.M.; Rives, V.; Zhu, Y.D.; Allen, G.C.; Adams, J.M. Structural characterization and thermal properties of polyamide 6.6/Mg,Al/Adipate-LDH nanocomposites obtained by solid state polymerization. *J. Solid State Chem.* **2010**, *183*, 1645–1651. [[CrossRef](#)]
93. Rives, V.; Labajos, F.M.; Herrero, M. Effect of preparation procedures on the properties of LDH/organo nanocomposites. In *Nanocomposites: Synthesis, Characterization and Applications*; Wang, X., Ed.; Nova Sci. Pub. Inc.: New York, NY, USA, 2013; pp. 169–202.
94. Rives, V.; Labajos, F.M.; Herrero, M. Layered double hydroxides as nanofillers of composites and nanocomposite materials based on polyethylene. In *Polyethylene Based Blends, Composites and Nanocomposites*; Visakh, P.M., Martínez Morlanes, M.J., Eds.; Wiley Inc.: Hoboken, NJ, USA; Scrivener Pub.: New York, NY, USA, 2015; pp. 163–199.
95. Dietmann, K.M.; Linke, T.; Reischer, M.; Rives, V. Fluorescing Layered Double Hydroxides as Tracer Materials for Particle Injection during Subsurface Water Remediation. *ChemEngineering* **2020**, *4*, 53. [[CrossRef](#)]
96. Dietmann, K.M.; Linke, T.; Trujillano, R.; Rives, V. Effect of Chain Length and Functional Group of Organic Anions on the Retention Ability of MgAl-Layered Double Hydroxides for Chlorinated Organic Solvents. *ChemEngineering* **2019**, *3*, 89. [[CrossRef](#)]
97. Dietmann, K.M.; Linke, T.; Nogal Sánchez, M.d.; Pérez Pavón, J.L.; Rives, V. Layered Double Hydroxides with Intercalated Permanganate and Peroxydisulphate Anions for Oxidative Removal of Chlorinated Organic Solvents Contaminated Water. *Minerals* **2020**, *10*, 462. [[CrossRef](#)]

98. Alonso-de-Linaje, V.; Mangayayam, M.C.; Tobler, D.J.; Dietmann, K.M.; Espinosa, R.; Rives, V.; Dalby, K.N. Sorption of chlorinated hydrocarbons from synthetic and natural groundwater by organo-hydrotalcites: Towards their applications as remediation nanoparticles. *Chemosphere* **2019**, *236*, 124369. [[CrossRef](#)]
99. Alonso-de-Linaje, V.; Mangayayam, M.C.; Tobler, D.; Rives, V.; Espinosa, R.; Kim, K.N. Enhanced sorption of perfluorooctane sulfonate and perfluorooctanoate by hydrotalcites. *Environm. Technol. Inn.* **2021**, *21*, 101231. [[CrossRef](#)]
100. Misol, A.; Labajos, F.M.; Morato, A.; Rives, V. Synthesis of Zn, Al layered double hydroxides in the presence of amines. *Appl. Clay Sci.* **2020**, *189*, 105539. [[CrossRef](#)]
101. Misol, A.; Jiménez, A.; Morato, A.; Labajos, F.M.; Rives, V. Quantification by Powder X-ray Diffraction of Metal Oxides Segregation During Formation of Layered Double Hydroxides. *Eur. J. Eng. Technol. Res.* **2020**, *5*, 1243–1248.
102. Trujillano, R.; Nájera, C.; Rives, V. Activity in the photodegradation of 4-nitrophenol of a Zn, Al hydrotalcite-like solid and the derived alumina-supported ZnO. *Catalysts* **2020**, *10*, 702. [[CrossRef](#)]