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Functionalization of Surfaces in Layered Double Hydroxides and Hydroxide Salt Nanoparticles

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Additional information is available at the end of the chapter

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Abstract

Layered double hydroxides (LDH) and layered hydroxide salts (LHS) are widely studied as matrices to design new materials with applications in several areas of science and technology. Both LDH and LHS are composed of molecular layered units with surfaces fully covered by hydroxyl groups and positive-charge residues within the layers; therefore, anions in the interlayer space are needed. Even though these anions are described as interlayer species without a covalent interaction with the molecular layered units, the substitution of hydroxyl groups is also possible; in other words, the functionalization of the surface could occur. This chapter reviews results previously published related to the functionalization phenomenon in LDH and LHS, which is not considered in most of the scientific reports of new materials derived from these compounds. In this text, the use of copper probes to study electron paramagnetic resonance spectra, reinforced with infrared spectroscopy to confirm functionalization, is described. The occurrence of functionalization instead of a simple anion exchange provides a change of properties in the final nanosized material.

Keywords: functionalization, layered double hydroxide, layered hydroxide salt, electron paramagnetic resonance

1. LDH

1.1. Layered double hydroxides

Layered double hydroxides (LDH) form a class of ionic lamellar inorganic materials that are positively charged. These compounds are also named as anionic clays or hydrotalcite-like compounds. The structure of these compounds is formed by metal cations octahedrally coordinated by hydroxyl groups. The resulting octahedra share their edges to form infinitely large layers where hydroxyl groups cover both surfaces of each layer. The peculiar feature in LDH is that metal cations must be a combination of divalent and trivalent cations with ionic radii close to that of Mg^{2+} [1]. The trivalent cations in the layers produce a positive charge residue in the octahedra where they are located.

The interlayer domain contains charge compensation anions and solvation molecules. The size and orientation of species intercalated inside the interlayer region influence the interlayer distance and basal space of the resulting materials [2]. The basal space of LDH observed by powder X-ray diffraction is around 7–10 Å [3]. Anions may be small, e.g., CO_3^{2-} , Cl^- , SO_4^{2-} , RCO_2^- , or large such as methotrexate, 5-fluoruracil, and ibuprofen [4–6].

The chemical composition of LDH is represented by the general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_x/n \cdot z\text{H}_2\text{O}$, where M and A^{n-} correspond to metallic and anionic species, respectively. The most common M^{2+} are Mg^{2+} , Zn^{2+} , Ni^{2+} , Ca^{2+} , Co^{2+} , Cu^{2+} , and Mn^{2+} , whereas M^{3+} are Al^{3+} , Ga^{3+} , Fe^{3+} , and Mn^{3+} [7]. The x mole fraction of the trivalent cation is normally between 0.2 and 0.4 [8]. This fraction determines the electrostatic charge density in the layers, thus influencing the size of the interlayer space and a variety of physicochemical properties such as adhesion, reactivity, ion-exchange capacity, and rotation of chemical species into the interlayer space and on the surface [7]. More details related to the structure of LDH can be found in some published revisions [9, 10].

1.2. Reversible ion exchange

The LDH have a flexible interlayer space, which allows it to retain ions with different sizes, such as proteins, enzymes, deoxyribonucleotides, viruses, pesticides, drugs, and dyes. The intercalated species improve their solubility and biocompatibility as they are protected from degradation by external chemical and biological attack, thus extending half-life and function. The intercalation of this large variety of anions is reversible and this effect is used to design nanoparticles for controlled release. The releasing mechanism in LDH is carried out by ion-exchange reaction due to the presence of electrolytes or due to the partial dissolution of layers in slightly acidic conditions, thus the molecule intercalated or functionalized into LDH can be released in a controlled manner [11, 12].

1.3. Synthesis

A number of easy and low-cost synthetic techniques have been successfully employed in the preparation of LDH. The most commonly used is a simple coprecipitation method; the second is based on the classical ion-exchange process; the third is the reconstruction or memory effect

process [1, 13], although a recent analysis demonstrates that this “memory effect” is merely a direct synthesis [14].

The coprecipitation method with alkali is performed with a solution of inorganic salts. The most used salts are nitrates, chlorides, or carbonates. In some cases, an ageing step is required to increase crystallinity or the particle size [8].

The ion-exchange method is based on the exchange of the anions present in the interlayer region. In addition, it is strongly influenced by the electrostatic attraction between the layers and the new anion [8]. Nitrate ions are usually used as precursors for ion-exchange reactions because they are easily replaced [1].

The synthesis by calcination reconstruction has been widely reported. It is based on the capacity of layered hydroxides to be transformed in oxides by calcination and then converted reversibly to layered double hydroxides by hydration for 24 hours. This process can be realized in the presence of organic ions/molecules to intercalate them inside the interlayer galleries of LDH. However, the recent analysis of the growth process determined that the divalent metal oxides (with alkaline nature) react with the amphoteric aluminum oxide in water, thus this method is not an actual reconstruction [14].

Some other methods, such as salt hydrolysis [15, 16], sol-gel synthesis using ethanol and acetone solutions, and a fast nucleation process followed by a separate aging step at elevated temperatures, have also been reported [8].

1.4. Advanced applications

LDH have found a wide field of applications in the last two decades, which reflects the importance of studying these compounds. Advanced applications have been found in the biomedical field as nanovehicles for delivery of ibuprofen, enalaprilate [17], 5-fluoracil, methotrexate [18], DNA segments [19], cosmeceuticals [20], as well as nanoparticles for diagnoses through fluorescent or magnetic analyses [21–23].

2. Layered hydroxides salts

Layered hydroxide salts (LHS) form a family of inorganic crystalline compounds with a similar layered structure of that found in LDH and a similar anion-exchange ability [24, 25]. The particles of LHS can be synthesized in the nanometric scale and they have been used as a basis to produce novel materials with tunable properties [26, 27].

Although the first articles reporting the anion-exchange property in LHS appeared in the early 1970s [26], the use of these compounds to prepare new materials by exchanging the interlayer anion occurred after 1990 [28, 29]. In order to understand the anion-exchange process and the possibility of functionalization events in LHS, the structure and composition will be described in the next section.

2.1. Structure and composition

The structure of LHS, as well as that of LDH, is based on the layered organization of single hydroxides, such as Brucite, $\text{Mg}(\text{OH})_2$ [30], where a divalent cation occupies the octahedral position coordinated, in principle, by hydroxyl groups (**Figure 1a**). A single hydroxide, when synthesized in the presence of other anions, could retain them while conserving the coordination of the metal cations exclusively by hydroxyl groups. This is the case of α -nickel hydroxide, which is capable of allocating nitrate anions between two electrostatically neutral hydroxide layers (**Figure 1b**). However, by modifying synthesis parameters detailed in the bibliography [31], the nitrate anions can isomorphically replace some hydroxyl groups, thus producing an LHS structure: nickel hydroxide nitrate with composition $\text{Ni}_3(\text{OH})_4\text{NO}_3$. This structure is represented in **Figure 1c** and is the most common LHS containing chloride, nitrate sulfate or acetate (**Figure 1b**) [24, 32, 33]. The molecular formula to represent this type of LHS is $\text{M}(\text{OH})_{2-x}(\text{A}^{n-})_{x/n}$ where M is the divalent cation and A^{n-} is an anion with n^- charge. Regarding the metal cation, LHS have been prepared with Mg^{2+} , Ni^{2+} , Zn^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , and Cu^{2+} , which can be combined in the same structure [28].

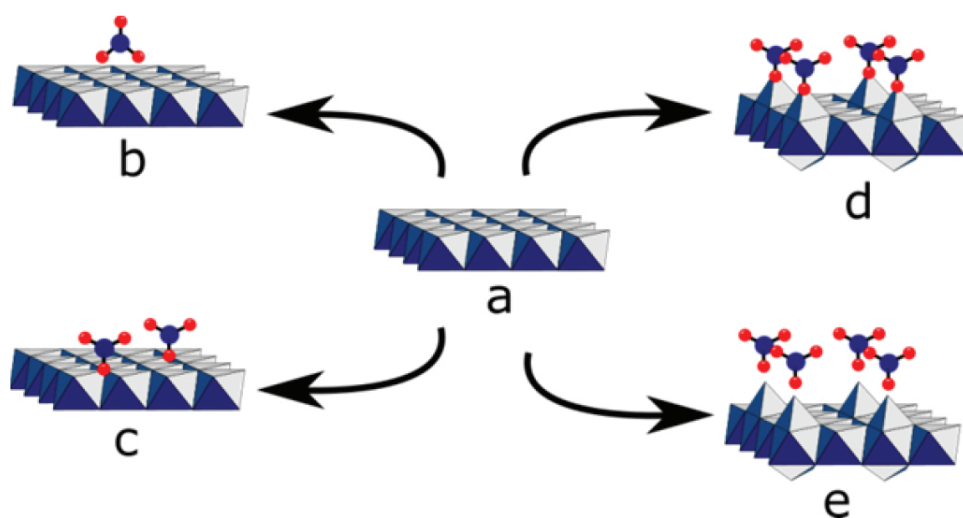


Figure 1. Single-layer representation of (a) single hydroxide, (b) single hydroxide with intercalated nitrate ions, (c) an LHS with isomorphic hydroxyl substitution by nitrate ions, (d) dentate LHS layer with functionalized tetrahedral, and (e) dentate LHS layer with loose nitrate ions.

Another structural change observed in LHS with respect to Brucite, especially those composed by zinc cations, is that 2/5 of M^{2+} is displaced from the octahedral center to the surface of the layers producing tetrahedrons and giving the aspect of dentate layers as shown in **Figure 1d** And **1e** [33]. The metal cation in the center and three hydroxyl groups in the base, shared with the octahedrons, form the tetrahedrons. The apex can be occupied either by the A^{n-} anion or by a water molecule. In the former case the A^{n-} directly coordinates the metal center (**Figure 1d**), whereas in the structure where water occupies the apex, the A^{n-} remains free in the interlayer space (**Figure 1e**) [33]. Examples of both structures are zinc hydroxychloride ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$) and zinc hydroxynitrate ($\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$), respectively [34, 35].

2.2. Synthesis

Layered hydroxide salts are synthesized by the same procedures used to prepare layered double hydroxides. The precipitation of salt solutions with sodium hydroxide is the easiest and most practical method [35, 36–38]. This method is recommended when a large amount of product is desired. For example, when a copper acetate solution reacts with sodium hydroxide, the copper hydroxide acetate is obtained [39].

Another method based on the slow decomposition of urea allows to obtain different compositions by changing the synthesis parameters [40]. For example, a mixture of cobalt nitrate with urea heated inside an oven at 80, 100, 120, and 160°C produces $\text{Co}(\text{OH})_{1.7}(\text{NO}_3)_{0.3}$, $\text{Co}(\text{OH})_{1.7}(\text{NO}_3)_{0.3} \cdot 0.35\text{H}_2\text{O}$, $\text{Co}(\text{OH})_{1.75}(\text{NO}_3)_{0.25} \cdot 0.66\text{H}_2\text{O}$, and $\text{Co}(\text{OH})_2(\text{NO}_3)_{0.3} \cdot 0.66\text{H}_2\text{O}$, respectively [40].

2.3. Surface modification with organic anions

The growing interest in studying LHS is based on the ability to exchange the interlayer A^{n-} anion either by organic or inorganic anions. The wide number of possible combinations in composition results in materials with novel properties. Nonetheless, the insertion of a new anion is not always a simple task, thus the researchers have developed some strategies to obtain new LHS. According to common definitions of functionalization [41, 42], the modification of an LHS surface with new molecules or ions produces a functionalized LHS; however, in a deeper perspective, the effective functionalization of layered units is related to the substitution of hydroxyl sites. The methods to modify the LHS are presented in this section regardless of whether they produce an effective functionalization or simply substitution of A^{n-} anions.

2.3.1. Anion exchange

This is the most applied method to modify an LHS. First, an LHS must be synthesized by the precipitation or urea method as described above, and preferably the interlayer A^{n-} anion in the starting compound should be weakly attracted by the metal cation-like acetate, chloride, or nitrate. Otherwise, anions with a large negative charge density (e.g., carbonate) are strongly retained by the layers and reduce the exchange efficiency [1].

An example of an anion exchange is the reaction of copper hydroxide acetate dispersed in ethanol, mixed with benzoic acid and stirred for 36 h. The benzoate anions substitute acetate and produce the LHS copper hydroxide benzoate [39].

2.3.2. Coprecipitation

The coprecipitation method is adequate to intercalate A^{n-} anions with large volume, for example, dyes or surfactants [43]. The layered units of the hydroxide salt are formed during the synthesis in the presence of A^{n-} anions that are captured to stabilize the stacking and form the particles. This process avoids the high activation energy needed to expand the interlayer space in the anion-exchange reactions. A representative experiment to obtain a modified LHS by coprecipitation requires an aqueous solution starting with the addition of zinc nitrate to a

vessel with water and sodium dodecylbenzenesulfonate. This solution is slowly mixed with an NaOH solution. The white suspension formed contains nanoparticles of zinc hydroxide dodecylbenzenesulfonate [43].

2.3.3. Solid state

The solid-state method was developed to reduce or avoid the use of solvents. This method requires one M^{2+} salt mixed with a reagent providing the counter ion and urea. One reaction was exemplified above with the cobalt hydroxide nitrate compounds. Another example where the A^{n-} anion is organic has been found in the reaction of magnesium nitrate, urea, and benzoic acid. The heat of this mixture at 110°C produces a magnesium hydroxide benzoate compound [44].

Although the aim of this method is also to increase the selectivity of products and reduce purification steps, the reaction periods are larger and temperatures are higher [31, 40, 44].

2.4. The nanometric dimensions of LHS

Size of LHS nanoparticles depends on the synthesis method followed. Commonly, particles obtained by precipitation or coprecipitation present nanometric dimensions. The scanning electron microscope image presented in **Figure 2** corresponds to a zinc hydroxide nitrate salt prepared by precipitation of a zinc nitrate solution with sodium hydroxide. The histogram demonstrates that the particle sizes, although with large dispersion, fall in the nanometric dimensions.

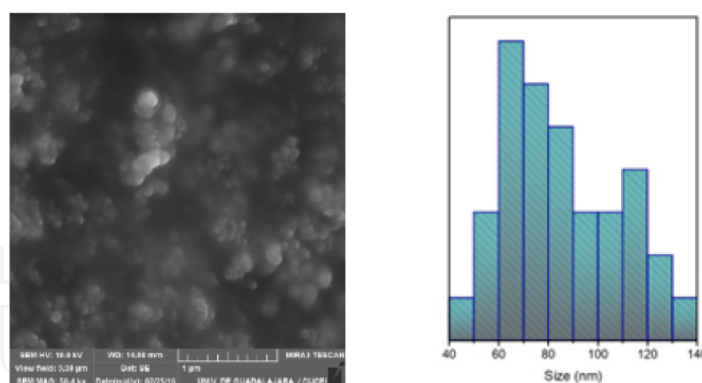


Figure 2. Scanning electron microscope image of zinc hydroxide nitrate obtained by precipitation and the histogram demonstrating that the particles presented nanometric dimensions.

3. Functionalization studies in LDH and LHS

Functionalization of materials is defined as the insertion of chemical functional groups in the surface of materials regardless of their crystalline or amorphous nature [45]. Functionalization reactions can be conducted in metals [46], ceramics [47], and synthetic or natural polymers [48,

49]. The aim of functionalization is to modify, tune, or add surface properties to a material once they play a key role in the overall performance of materials [42], especially those with nanometric sizes. For example, the functionalization of silica with sulfonic or thiol groups enables the scavenging of Cr^{3+} and Pb^{2+} cations from aqueous solution [50, 51]; gallium nitride nanoparticles become stable in aqueous suspension after functionalization with cysteine [52]; bismuth germanate ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) nanoparticles could recognize leukemia cells after functionalization with a monoclonal antibody [53]; and functionalization could also be useful to reduce toxicity of nanoparticles (like hydroxyapatite) in biomedical applications [54].

A recent review has detailed the strategies of functionalizing ceramic oxides and gave an important classification to understand them. This classification comprises three groups: physical, chemical, and biological reactions [42].

However, it is important to point out that this classification is one of the approaches to organize the description of functionalization methods. Another classification of ceramics functionalization includes surface coating and *in situ* surface modification [41].

At this point, in both classifications it is necessary to identify that the functionalization term is not limited to the insertion of a chemical functional group to a surface in a covalent manner, and the surface modification through a coating or physisorption is also contemplated [42]. In this regard, adsorbed molecules onto materials with high porosity are also named functionalized materials. Examples of typical functionalization reports are represented in **Figure 3**.

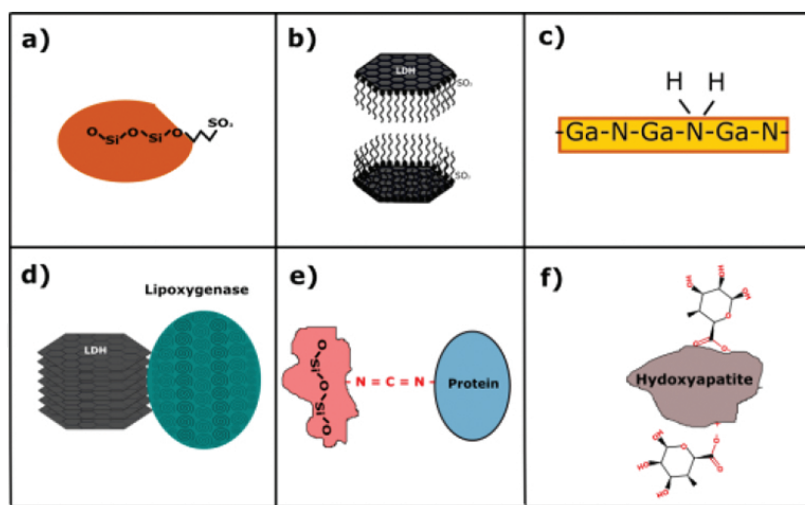


Figure 3. Representative examples of functionalization reactions. (a) Covalent functionalization of silica with propyl-sulfate [50], (b) ionic modification of an LDH with dodecylsulfate [55], (c) gallium nitride surface functionalized with amino groups [56], (d) LDH functionalized with lipoxigenase [57], (e) silica functionalized with carbodiimide and then with a protein [42], and (f) hydroxyapatite functionalized with glucuronic acid [54].

The following section strictly focuses on those functionalization reactions where the crystallographic sites of hydroxyl groups in layers of LDH and LHS are partially substituted by other anions, i.e., when the insertion of new functional groups in the surface strictly occurs.

3.1. Functionalization in layered double hydroxides and layered hydroxide salts

The covalent growth of layered units with divalent and trivalent cations involves the coordination with hydroxyl groups. Under this condition, the octahedral arrangement—where the metal cation is coordinated by six ions—satisfies the number of ligands determined by the 4th rule of Pauling [58], and the presence of additional anions to stabilize the residual positive charge located in those centers occupied by trivalent cations is strictly restricted in the first coordination sphere. Then, the anions beyond this sphere satisfy the electrostatic neutrality. The overall arrangement corresponds to layers fully covered by hydroxyl groups and A^{n-} anions loosely attached to this hydroxylated surface. Nonetheless, it is possible to find structures where anions substitute the hydroxyl sites [59].

Regarding LHS compounds, the natural functionalization—or substitution of hydroxyl groups by anions—is observed in the structures of **Figure 1c–e**. As demonstrated, these anions can be further substituted through a low-energy anion-exchange reaction [28]. Although several new materials prepared by exchange reaction have been reported, a detailed study to determine if the resulting material is functionalized or simply intercalated is not always conducted.

The following section presents a case study using Cu^{2+} cations spread in cationic sites of LDH and LHS as probes to determine if functionalization occurs by means of electron spectroscopy.

3.2. Synthesis of LDH and LHS with Cu^{2+} probes

Divalent copper cations, Cu^{2+} , are paramagnetic species with at least one unpaired electron. The magnetic coupling of this electron with a nuclear spin equal to $3/2$ results in a spectrum with four signals under an isotropic environment. In solid compounds, the anisotropic effect produces more lines, in principle, one set of four signals per orientation of the electron with respect to the applied magnetic field [60].

On the other hand, LDH and LHS are composed of metal cations with a similar radius to that of Mg^{2+} , and therefore Cu^{2+} cations can be used to prepare these structures and they serve as EPR (Electron Paramagnetic Resonance) probes if they are spread along the layers [59, 61, 62] or on other solid compounds [63].

The experiment to determine the amount of copper needed to obtain a single crystal phase along with a clear EPR signal comprised the synthesis of LDH and LHS particles with different contents of Cu^{2+} cations [62].

The synthesis of an LDH group was prepared by precipitation of a solution with nitrate salts of Zn^{2+} and Al^{3+} cations mixed with three contents of Cu^{2+} : 0.2, 1.0, and 10.0 mol% with respect to Zn^{2+} . Regarding the synthesis of the LHS, the nitrate salt solution only contained zinc cations and the same atomic percent of copper. Details of this synthesis can be found in the literature [62].

The analysis by X-ray diffraction of these compounds revealed profiles of layered structures and no second phases of copper compounds were observed in the LDH modified with 0.2 mol % of Cu^{2+} , and therefore the compound was suitable for the intercalation/functionalization

study. Another important piece of information from these diffractograms is that LDH were formed, therefore cations –including Cu^{2+} – occupied octahedral positions.

In the case of the LHS, the diffraction patterns confirmed that the structure of a zinc hydroxide salt was properly formed. This structure corresponds to that depicted in **Figure 1e**, where cationic sites occupy both octahedral and tetrahedral positions. The compound selected for the functionalization study was the LHS modified with 1.0 mol% of Cu^{2+} .

3.3. Functionalization studies by electron paramagnetic resonance spectroscopy

Once the LDH and LHS are prepared with a low amount of copper cations, the EPR spectroscopy analysis can be conducted.

The most representative EPR spectra to discuss functionalization correspond to the LDH with 0.2 mol% of Cu^{2+} and the LHS with 1.0 mol% of Cu^{2+} . The spectra plotted with black lines in **Figure 4** correspond to experimental data from the LDH and LHS. The former is composed of four lines and one intense signal of axial and parallel components of Cu^{2+} ions in Oh coordination, which is confirmed with a simulated spectrum of Cu^{2+} in octahedral coordination, fitting the experimental data. With the aid of the SimFonia software, the crucial parameters to achieve the fitting were the g factor and the spin-nucleus coupling constant A , with values of $g_{xx,yy} = 2.069$ and $A_{xx,yy} = 13 \times 10^{-4} \text{ cm}^{-1}$ for two parallel components, respectively, and $g_{zz} = 2.362$ and $A_{zz} = 139 \times 10^{-4} \text{ cm}^{-1}$ for the perpendicular components, respectively [59, 61]. Once $g_{xx} = g_{yy}$ and $g_{xx,yy} > g_{zz} > 2$, the copper cations underwent a high distortion affected by the elongation of the z -axis [60, 64]; furthermore, the $g_{xx,yy}/A_{xx,yy}$ ratio ($2.069/13 \times 10^{-4} \text{ cm}^{-1} = 172 \text{ cm}$) is close to 200 cm, and this value has been associated with such tetrahedral distortion [65, 66]; therefore, the simulated spectra correspond to copper cations in octahedral sites.

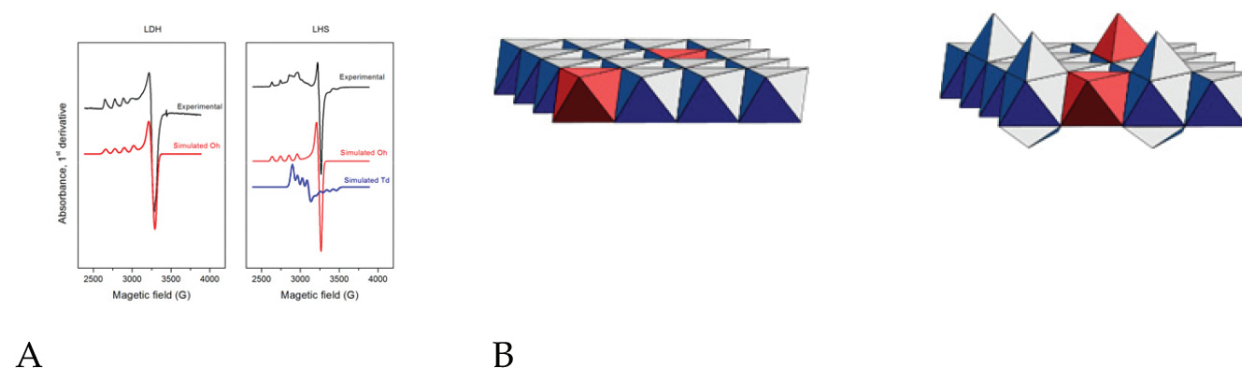


Figure 4. (A) EPR spectra of LDH modified with 0.2 mol% of Cu^{2+} and the LHS modified with 1.0 mol% of Cu^{2+} . Adapted from [62]. (B) Left: layer of LDH with octahedral units, where Cu^{2+} cations replace zinc positions (red octahedra); right: layer of LHS with octahedral and tetrahedral units, where Cu^{2+} cations replace both zinc positions (red polyhedra).

Regarding the spectra of the LHS, more absorption signals are present, and they were re-composed with the sum of two spectra: one similar to that proposed for the LDH with copper in octahedral coordination with values of $g_{xx,yy} = 2.089$, $A_{xx,yy} = 15 \times 10^{-4} \text{ cm}^{-1}$; $g_{zz} = 2.400$ and $A_{zz} = 113 \times 10^{-4} \text{ cm}^{-1}$; and a second spectrum with $g_{xx} = 2.274$, $A_{xx} = 41 \times 10^{-4} \text{ cm}^{-1}$; $g_{zz} =$

2.020 and $A_{zz} = 80 \times 10^{-4} \text{ cm}^{-1}$ associated with copper center in tetrahedral coordination [59]. These results indicate that copper cations are located in both octahedral and tetrahedral sites in the LHS as represented in **Figure 4**.

Regarding the octahedral positions, the g and A parameters, and especially the $g_{\parallel}/A_{\parallel}$ ratio, undergo a change when the crystal field of copper is modified; in other words, the substitution of hydroxyl groups from the coordination sphere by other anions corresponds to a functionalization phenomenon revealed by a change in the $g_{\parallel}/A_{\parallel}$ ratio [59, 61, 62].

The spectra in **Figure 5** belong to an LDH subjected to an exchange reaction with adipic ($\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$) and azelaic ($\text{HOOC}-(\text{CH}_2)_7-\text{COOH}$) acids. Dotted lines in the spectrum indicate that the signals after intercalation of adipic acid are in the same position, indicating that the crystal field of copper cations did not change, i.e., the hydroxyl groups were not substituted since the adipic acid only replaced nitrate ions and remained hydrated and “loose” in the interlayer space as depicted in **Figure 5B**. Conversely, the spectrum of the compound treated with azelaic acid presented shifted lines and appeared closer to each other as result of a lower spin-nucleus coupling, detected through the simulated spectrum where $A_{zz} = 123 \times 10^{-4} \text{ cm}^{-1}$ [59]. Simultaneously, the g_{zz} factor increased to 2.385. Both of these changes indicate that the crystal field was modified, and therefore the functionalization of the layers was accomplished with azelaic acid. This crystal field change of the Cu^{2+} sites is represented in **Figure 5B**.

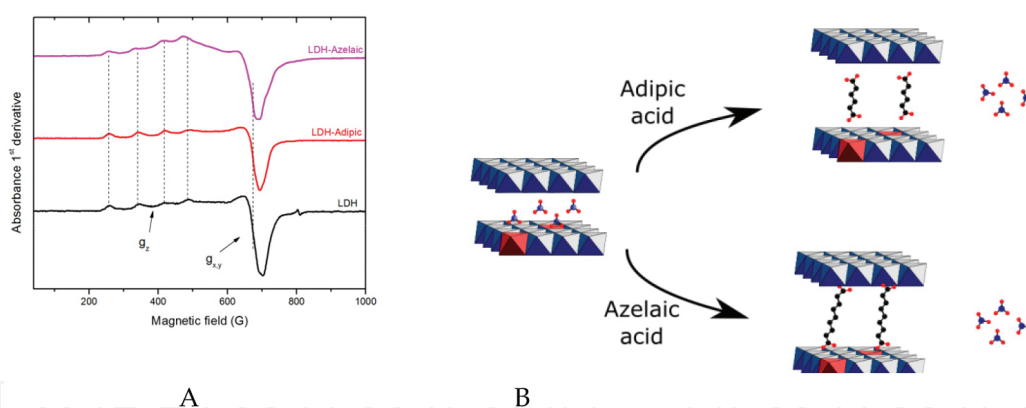


Figure 5. (A) EPR spectra of LDH modified with 0.2 mol% of Cu^{2+} and the intercalation products with adipic and azelaic acids. (B) Intercalation products of LDH with adipic acid where the exchanged anions are loosely retained between the layers and azelaic acid substituting the hydroxyl groups of the layers (functionalization).

The evidence of functionalization in the LHS was also demonstrated with the EPR spectra of the intercalation products with adipic and azelaic acids (**Figure 6A**). First, the product with adipic acid produced the same spectrum profile found in the initial LHS; in fact, similar g and A parameters were found in the simulated spectrum of copper in the octahedral and tetrahedral sites [59]. However, more information obtained from infrared and nuclear magnetic resonance indicated that the carboxylate group was probably coordinated to a metal center; in this case, only copper in octahedral position could be affected since the g and A parameters, from the octahedral simulated component, were modified slightly (**Figure 6B**).

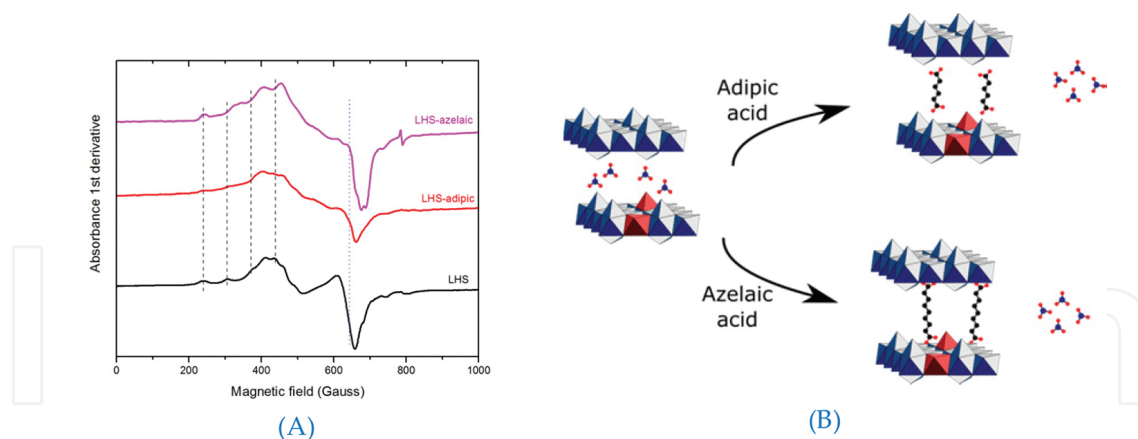


Figure 6. (A) EPR spectra of the LHS modified with 1.0 mol% of Cu^{2+} and (B) a representation of the intercalation products with adipic and azelaic acids.

The product from the reaction with azelaic acid has a clearer shift of the EPR spectrum. The simulation to fit the experimental data revealed that the coupling constant A increased for copper in the octahedral position and decreased for that in the tetrahedral position (from $A_{zz} = 80 \times 10^{-4} \text{ cm}^{-1}$ to $A_{zz} = 72 \times 10^{-4} \text{ cm}^{-1}$) [59]. This data indicates that both octahedral and tetrahedral units experience a change in the crystal field associated with functionalization of azelaic acid as presented in **Figure 6B**.

The use of EPR spectroscopy and Cu^{2+} probes demonstrated to be a useful tool to assess the functionalization of LDH and LHS layers. The information obtained is important from the point of view of basic science and can help to interpret the performance and properties of new materials based on layered hydroxide compounds.

3.4. Functionalization studies by infrared spectroscopy

Infrared spectroscopy is one of the most important techniques to analyze materials once it provides molecular information in a very short time; it is non-destructive and, in most cases, the sample does not need special treatments. Although commercial equipment is provided with detectors for the middle region of the infrared spectrum and details for the metal-oxygen bonds are not clearly observed, the information obtained from the interlayer anions, especially those related to symmetry changes, is relevant to determine if functionalization occurs, mainly in LHS.

The functionalization or effective pillaring in LDH is scarcely studied and the specific study is reported in the articles analyzed in the EPR section [59, 61, 62]. A confirmation of functionalization exclusively based on infrared spectroscopy has not been reported to the best of our knowledge. One of the deepest studies by infrared spectroscopy only determined the orientation of nitrate ions with respect to the layers [67] and the different anion-exchange ability influenced by such orientation [68]; however, the substitution of hydroxyl groups was not detected according to elemental analysis.

On the contrary, the infrared spectra on LHS, in several cases supported by X-ray diffraction, were enough techniques to determine that hydroxyl sites were substituted by other anions, resulting in the structure depicted in **Figure 1d**.

A representative example of layers exclusively formed by cations octahedrally coordinated by hydroxyl groups and functionalized with nitrate ions is found in a copper hydroxide nitrate reported by Aguirre et al. [69]. In this case, the functionalization by nitrate ions is clearly determined by infrared spectroscopy, where the nitrate ions presented two intense bands at 1426 and 1343 cm^{-1} corresponding to asymmetric and symmetric stretching, respectively, of nitrate anions coordinating some copper cations [69].

Other researchers observed the same spectral profile with two signals at 1420 and 1338 cm^{-1} for nitrate in functionalized layers, whereas free nitrate produces a single band at 1370 cm^{-1} [70]. This splitting caused by a clear functionalization phenomenon with nitrate anions is observed in **Figure 7**, where the band at 1375 cm^{-1} in nonfunctionalized layers splits and produces two signals at 1447 and 1351 cm^{-1} when nitrate is directly coordinating the metal cations in an LHS structure [62]. These examples demonstrate that infrared spectroscopy is a practical technique to determine functionalization of layers with nitrate ions.

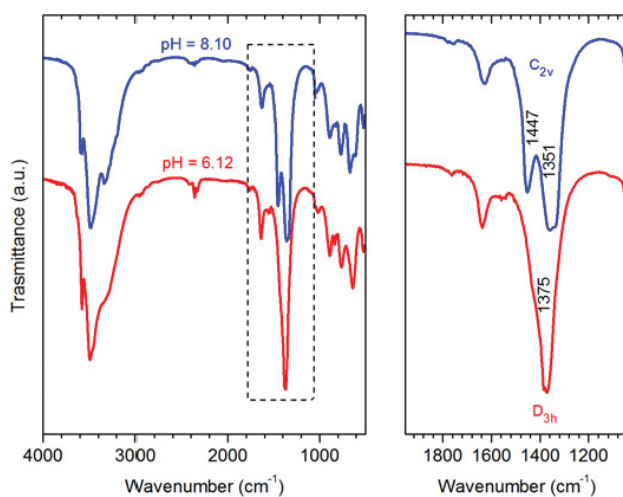


Figure 7. Infrared spectra of a zinc hydroxide nitrate salt precipitated at different pH, 6.12 and 8.10.

4. Properties of LDH and LHS dependent on functionalization

Some of the consequences of functionalization in LDH and LHS are presented in the following cases.

A physical reduction of the interlayer space is observed. Commonly, an LDH with free nitrate ions presents basal spaces between 8 and 9 Å. If nitrate ions functionalize the hydroxylated layers, the basal space decreases to 6 Å as presented in **Figure 8** [69].

The chemical reactivity clearly modified by a functionalization was observed in the LHS with composition $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The structure typically contains free nitrate ions in the interlayer space and therefore produces a single IR band of the symmetric stretching at 1375 cm^{-1} in **Figure 7**. This solid compound was added as heterogeneous catalyst to an esterification reaction with lauric acid and methanol and no activity was detected (**Figure 9**). On the contrary, the addition of the compound with the nitrate-functionalized layers leads to ester formation with yields higher than 95% [71].

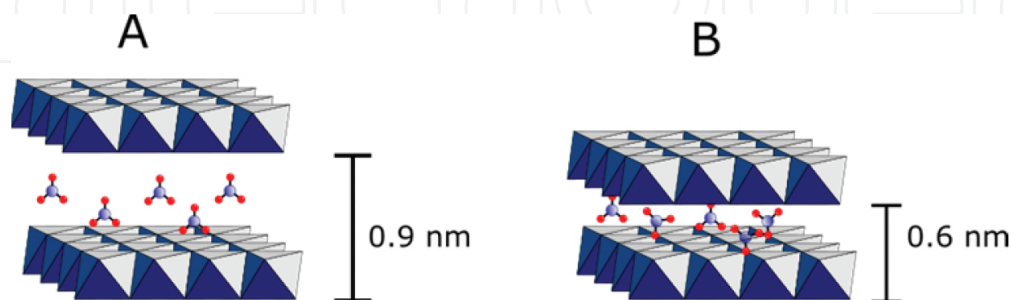


Figure 8. Basal space dependent on the interlayer anion that can be (A) “free” or (B) functionalizing the layers.

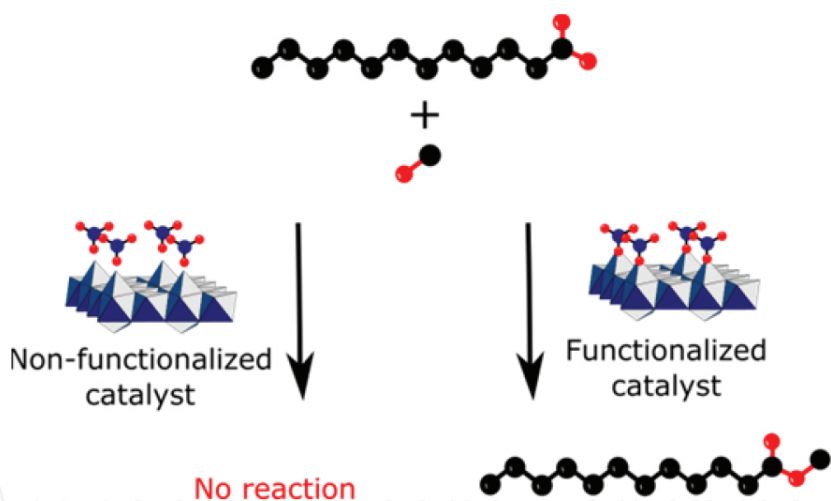


Figure 9. Methyl esterification of lauric acid is catalyzed in high yield with an LHS where nitrate ions functionalize the layers. The compound with free nitrate is not active in this reaction.

A property derived from the direct graft of nitrate anions is that nitrate functionalizing the layers in **Figure 8** has a restricted rotation degree unlike that in the LDH where nitrate is free and therefore two orientations can be adopted, one parallel and another perpendicular to the layers. Further, these two orientations influence physicochemical properties evidenced by the different anion-exchange ability [67, 68].

The functionalization of layers presented in **Figure 8B** favored a higher crystallinity degree in nickel hydroxide layers regarding better stacking. Conversely, loose intercalation of nitrate promotes rotation of layers causing a stacking disorder known as turbostraticity [31].

Another consequence observed when nitrate ions functionalize the layers is the change in thermal stability of the functionalizing anions. This effect was demonstrated with a set of LDH composed by Cu^{2+} , Mg^{2+} , Zn^{2+} , and Ni^{2+} , where the nitrate ion decomposes at a temperature dependent on the charge density of the metal cation, thus the main decomposition step occurred at 220–300, 200–320, 290–420, and 380–500°C for the LHS composed by Cu^{2+} , Zn^{2+} , Ni^{2+} , and Mg^{2+} cations, respectively [72]. This thermal stability is derived from the direct bond between the nitrate and the metal cation.

5. Conclusions

Surface functionalization of LDH and LHS can be produced by physical and chemical methods. Physical modification through anion-exchange processes is the most common phenomenon to add new properties to the layered compounds. Although this physical modification is also considered functionalization, this text discussed functionalization as a chemical reaction where hydroxyl groups were substituted by other functional groups. Based on this concept, the data demonstrated that the functionalization of hydroxylated layers in LDH or LHS is capable of modifying the physicochemical properties of those particles. Such modification of nanometric particles is relevant to adjust properties needed in specific applications.

Some of the properties modified by chemical functionalization of LDH and LHS compared to those in anion-exchanged compounds are as follows: (i) the lower interlayer space, (ii) chemical reactivity, (iii) anion-exchange capability, and (iv) thermal stability. The analyzed bibliography proves that infrared spectroscopy is a practical tool capable of confirming functionalization with nitrate ions. However, the use of EPR spectroscopy and Cu^{2+} cations as probes gives deeper information to confirm the functionalization with different anions in LDH and LHS nanoparticles. The relationship between functionalization and properties could be better understood if the functionalization phenomenon was studied in detail through these spectroscopic techniques. Therefore, a rational design of new materials with controlled properties could be achieved.

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