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Aspects regarding the preparation methods of anionic clays

DIANA PALEU, ILEANA-DENISA NISTOR*

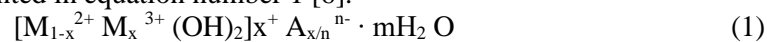
*"Vasile Alecsandrii" University of Bacău, Faculty of Engineering,
Calea Mărășești, no. 157, 600115, Bacău, Romania*

Abstract: Anionic clays, layered double hydroxides, are natural or synthetic materials that have special properties, especially regarding their retention capacity. This quality is due to their lamellar structure, formed by parallel planes, different molecules of interest could be intercalated between them. This allows the use of anionic clays in various fields such as: chemical industry, food industry, pharmaceutical and medical industry, as well as environmental protection. The paper presents important aspects regarding their preparation possibilities.

Keywords: hydrotalcites, structure, characterization, synthesis

1.1 Introduction

Hydrotalcites (HT) were first reported in 1842 by Hochstetter and synthesized in 1942 by Feitknecht. Depending on the composition and mineralogical structure, different names are used for these compounds; the most used terms being hydrotalcite (HT) and double lamellar hydroxides (LDH). A general chemical formula is represented in equation number 1 [6].



where: M^{2+} cation divalent (Mg^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} etc.)

M^{3+} cation trivalent (Al^{3+} , Fe^{3+} , Mn^{3+} , Cr^{3+} etc.)

A^{n-} the anion in the interstate region

x is the molar ratio and is noted with the ratio $M^{3+}/(M^{2+}/M^{3+})$

m- the number of water molecules [2,7,8,17].

*Correspondence address: dnistor@ub.ro

The hydrotalcite has a lamellar structure similar to that of brucite $[\text{Mg}(\text{OH})_2]$ with low white hardness and density [6].

The octahedral symmetry having Mg^{2+} in the center and the 6 peaks coordinated with OH^- groups equally divides the edges thus forming an infinity of planes. These planes are placed on top of other octahedra belonging to other planes and are assembled by hydrogen bonds. When divalent Mg^{2+} ions are substituted by trivalent ions (Al^{3+} , Fe^{3+}) with an ionic radius approximately equal to that of Mg^{2+} a positive charge is generated in the burning plane [2, 7, 8, 32, 33].

This positive charge is compensated by anions (CO_3^{2-} , OH^- , etc. which is in the region between the burning planes. Crystallization water is also placed in the interplanar free space [2, 7, 8, 32, and 33].

The main characteristics of the hydrotalcite structure are determined by the nature of the burning plane, the position of the anions and the water in the interplanar region but also by the type of arrangement of the burning planes [2, 34, 35]. Compared to the plan of the standard $\text{Mg}(\text{OH})_2$ burnt layer, the layer of hydrotalcite compounds is wrinkled (corrugated) due to the ordering of the cations (Figures 1, 2 and 3).

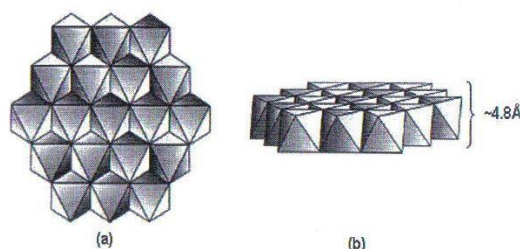


Fig. 1 Scheme of burnt type layers (a) in the plane and (b) perpendicular, the thickness of a layer being 4.8Å [34, 35]

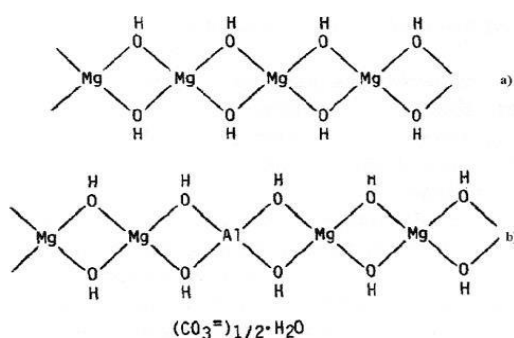


Fig. 2 Schematic of the side view of the structures: (a) Brucit $-\text{Mg}(\text{OH})_2$; (b) Hydrotalcite [36]

The hydrotalcite crystallizes in $3R$ rhombohedral symmetry, the cell parameters being a and c (where $c = 3c'$, c' being the thickness of a plane, respectively 4.8Å , and of an interplanar space).

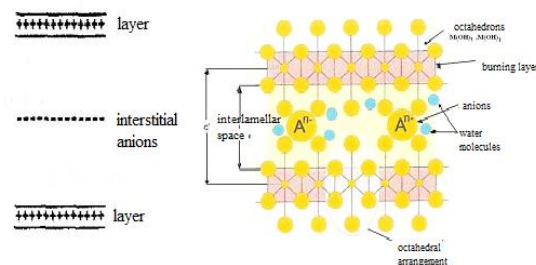


Fig. 3 Schematic representation of the structure of a hydrotalcite [32, 33]

As properties double-layered hydroxides have a variety of characteristics due to the methods of preparation and synthesis. Morphological behavior, specific surface area, particle size, porosity are important and necessary to describe the structure of hydrotalcites.

The structural shape, morphology and specific adsorption surface are determined by the conditions and methods of preparation [6, 11, 12, 13].

The stratified structure of double-lamellar hydroxides changes to oxides or a mixture of oxides under the effect of calcination at a certain temperature and these changes the morphology [6, 10, 11, 14].

The porosity of the prepared hydrotalcites changes from the microporous to the mesoporous domain, depending on the preparation conditions, and the particle sizes may be different due to the composition and crystallinity [6].

The thermal stability of hydrotalcites can be discussed and analyzed by thermogravimetry (TGA), residual mass at final temperature and differential scanning calorimetry (DSC). The thermal decomposition stages of double-layered hydroxides are influenced by several factors such as: temperature range, types of divalent or trivalent metals, nature of intercalated compounds, molar ratio between elements, heating rate and inert atmosphere N_2 or CO_2 [6].

1.2 Methods and materials

There are several options for preparing double-layered hydroxides. Each of these methods has advantages but also disadvantages in obtaining different nanocomposites.

1.2.1. Coprecipitation method

It is one of the most widely used methods for synthesizing LDH in both the laboratory and industry. The working principle of this method is to add as slowly as possible the solution containing a mixture of salts from divalent metals M^{2+} and trivalent M^{3+} in a special reactor that initially contains water (figure 4) [42].

In order for the salts to precipitate, an alkaline solution of (NaOH, Na₂CO₃, etc.) is added to the reactor which has an important role in maintaining the pH at the value specific to each type of hydrotalcite obtained.

This pH value depends on the nature of the cations derived from the divalent M²⁺ and trivalent M³⁺ metals, but also on the organic anion that will be intercalated.

The pH value set for each pair of cations should not exceed the optimum limit, as impure compounds are obtained. In order to obtain crystalline, homogeneous phases, specific to hydrotalcites, we must take into account several conditions.

- precipitation to be performed in an inert atmosphere;
- the temperature in the reactor must be between T = 338.15 K and T = 348.15 K;
- the pH of the reaction medium should be chosen correctly for each pair of cations;
- the concentration of the salt solutions to fall within the limits given by equations 2 and 3;
- the flow rate of the reactants should be as low as possible;
- the maturation of the precipitate must be within a time interval between t=12 h until t = 18 h [44.45]

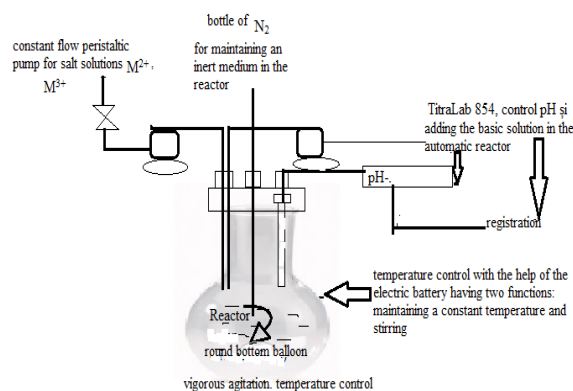


Fig. 4 LDHs block installation by co-precipitation method [46]

1.2.1.1. Co-precipitation in aqueous solutions

It is one of the simple, reliable and low-cost methods of obtaining double-layered hydroxides [6].

As a rule, the first requirement to obtain a pure double layered hydroxide is to choose the correct ratio of cations and anions, these values must be (in the final material) between 0.2 and 0.4, as follows:

$$0,2 \leq M(\text{III}) / [M(\text{II}) + M(\text{III})] \leq 0,4 \quad (2)$$

$$1/n \leq A^n / M(\text{III}) \leq 1 \quad (3)$$

In order to co-precipitate two or more cation it is necessary to achieve the supersaturation conditions. Supersaturation conditions are achieved by physical (evaporation) or chemical (pH variation) methods.

Three precipitation methods are used:

- titration with NaOH and / or NaHCO₃ (sequential precipitation or pH increase method);
- constant pH at low supersaturation, the pH is controlled by the slow addition in a single vessel of two dilute solutions (concentrations 0.5-2 mol/L), the first solution contains ions of M^(II) and M^(III) and the second solution contains the base (KOH, NaOH, NaHCO₃);
- constant pH at high supersaturation; the solution containing M^(II) and M^(III) is added very quickly in a solution containing NaHCO₃ or NaOH [6, 7, 30, 31]

Supersaturation is the thermodynamic force underlying all processes of precipitation and crystallization.

This is usually defined as the difference ("absolute supersaturation") or ratio ("saturation ratio") between the concentration and solubility of a chemical compound. Using the concept of reaction coefficient (QR) the classical expression of the chemical potential (μ) as a function of the molar fraction (x_i) and the activity coefficients (y_i) can be written as follows:

$$\mu = \mu_0 + RT \sum \log x_i y_i = \mu_0 + RT Q_R / K_S \quad (4)$$

where: K_s - solubility constant, - μ_0 chemical potential at T₀ [39]

By entering the supersaturation ratio (S) the following expressions are obtained:

$$S = Q_R / K_S \quad (5)$$

$$\mu = RT \log S \quad (6) \quad (6)$$

In the classical coprecipitation technique, the slow addition of the alkaline solution is used to achieve $Q_R > K_S$ ($S > 1$), but the consumption of cations decreases during precipitation leading to a decrease in S and Q_R over time. As a result, during the precipitation of $Q_R \rightarrow K_S$ and the properties of the crystals thus formed can change over time [38, 39].

Using a coprecipitation technique in which the addition of the two solutions (metal cation solution and alkaline solution) is performed simultaneously a better control of the supersaturation level can be obtained: the supersaturation ratio is constant over time and S can be accurately adjusted using convenient reagent.

In both cases, supersaturation governs the kinetics of the nucleus and the growth of crystals, it can also affect the mechanism of the nucleus and growth process [6,7,19,34,37].

Co-precipitation at low supersaturation, at constant pH, is the most commonly used method for the preparation of anionic clays. The most used conditions are pH = 7-10, T = 333-353K, low concentration of reagents and slow flow of the two solutions.

Maturation is performed under precipitation conditions, washing is performed with hot water and drying temperature does not exceed T = 393K [6, 12, 37, 39].

Low supersaturation conditions usually give rise to precipitates which are more crystalline than those obtained under high supersaturation conditions, because in the latter situation the nucleation rate is higher than the crystal growth rate. A large number of particles are obtained, small in size [20, 21, 36, 37].

Preparation under high supersaturation conditions generally gives rise to the least crystalline materials due to the large number of crystallization nuclei [20, 21, 39].

1.2.1.2. Co-precipitation in non-aqueous solutions

The morphology and texture, described by the particle size, crystallinity, porosity and specific surface area, depend on factors such as reaction time, temperature, concentration of reactants, post-preparative treatments and reaction solvent.

Most precipitation reactions were performed in aqueous solutions [6,9,19,38]. Malherbe and collaborators showed that an Mg Al-AA system precipitated in an organic solvent mixture and water formed crystalline double layered hydroxide particles [6,38].

The organic solvents used for this purpose were: methanol, ethanol, propanol, ethylene glycol, glycerol and acetone. With the exception of ethylene glycol and glycerol, the organic solvent did not greatly affect the specific surface area or pore distribution.

In contrast, in the case of ethylene glycol, a significant increase in the specific surface area ($136 \text{ m}^2 / \text{g}$) was observed, a value that is almost double that observed in the sample synthesized in water ($75 \text{ m}^2 / \text{g}$). This increase can be mainly attributed to the increase in pore volume [6, 7, 19, 37, and 38]. In the case of glycerol, the opposite effect was observed: a loss in the specific surface resulting from a considerable decrease in pore volume. The specific surface area observed in the case of glycerol coprecipitation is approximately $54 \text{ m}^2 / \text{g}$.

This method of preparation can be used to obtain columnar anionic clays which can be used as precursors for the preparation of transparent double layered hydroxide films [6, 16, 17, 19].

Also negatively charged vitamin C was efficiently encapsulated by the method of coprecipitation in the double lamellar hydrotalcite LDH / Ca / Al with a molar ratio of $\text{Ca}^{2+} / \text{Al}^{3+} = 3/1$ [6].

Also by this method LDH / Ca / Al was intercalated with tri-ethoxy-vinyl-silane (TEVS) to form a lasting bond and increase the sites to actively interact with polymeric resins [6, 14]. Infrared spectroscopy confirms changes in the adsorption bands in the structure. The performance and adsorption capacity is higher compared to unmodified layered double hydroxides.

Coprecipitation was selected for intercalation of carboxymethyl-modified cyclodextrin into the LDH structure [6, 31]. By this method it was possible

to control the pH of the resulting solution and establish the optimal pH equal to 10 [6].

1.2.2. Sol-gel method

This method is a colloidal way of synthesis of materials in which the intermediate stages comprise a sol and a gel [6, 16, 20, 21]. It is frequently used to obtain mixed oxides which are characterized by: molecular scale homogeneity and purity. The sol-gel method has the advantage that the structural properties of the finished solids can be controlled at the level of synthesis by simply modifying the composition of the precursors, the synthesis temperature, the maturation time and by adding or removing reactant species.

The sol is formed by hydrolysis of the metal precursor and then a gel is formed with its partial condensation [6, 30, 31]. Various compounds can be studied as metal precursors, including inorganic compounds and oxides that can affect the rate of hydrolysis and condensation and the entire physical behavior of sol-gel prepared materials. The double layered hydroxides obtained with this method show high specific surface area, high purity and homogeneity [2, 6, 13, 14]. The advantages of this method refer to a high efficiency, a low temperature and a simplified way of working [6, 12].

Chubar et al. [2, 6, 22] used this procedure to synthesize Mg-Al-CO₃ LDH with and without alcohol. Hydrotalcite prepared without alcohol reveals the reactive structure with many surface hydroxyl groups and mobile intermediate ion while the alcohol procedure results in a material with fewer hydroxyl groups [6, 11]. The hydrotalcite prepared with the sol-gel method shows a large specific surface area compared to the double layered hydroxides synthesized by the coprecipitation method [12].

Smalenskaite et al. [6, 10] used two coprecipitation methods and the sol-gel method for synthesizing double-layered hydroxides.

LDH/Mg/Al and Mg/Al/Ce/LDH samples were synthesized from solutions of the same reagents as those used by the coprecipitation method [6, 10, 55]. Nitrates of metal ions were dissolved in distilled water, then a solution of citric acid was added [55]. The mixture was stirred for 1 h at T = 353.15 K, in the second step ethylene glycol was added to the resulting mixture with continuous stirring at T = 423.15 K until complete evaporation of the solvent was observed. that the crystal structure and specific surface area is larger than the coprecipitation method [55]. Also, Smalenskaite, [10] used the sol-gel technique to intercalate the terephthalate in the structure of the hydrotalcite that influenced the change in the behavior of hydroxides [6, 55].

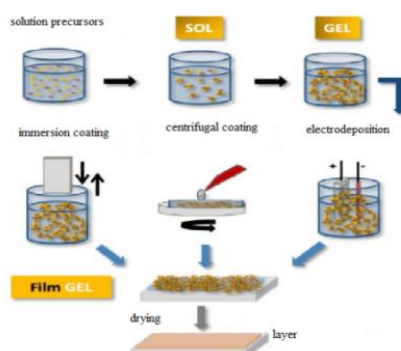


Fig. 5 Scheme for obtaining LDHs by the sol-gel method

The synthesis of hydrotalcites by the sol-gel method is used when the aim is to obtain high purity composites with applications in the field of medicines, etc. The technique of the sol-gel method consists in introducing the desired compound (organo-metallic complexes, organic or inorganic salts and organo-metallic compounds) in the structure of LDHs following:

- the precursors are either hydrolyzed in water or aqueous solutions or in organic solvents at room temperature to obtain a polymeric soil in the form of particles;
- to increase the solubility of the mixture either changes the temperature or add a suitable solvent.

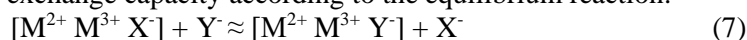
The biggest advantages that the sol-gel method has are:

- LDHs with large specific surfaces are obtained ($200\text{m}^2 / \text{g}$);
- anionic clays manifests stronger basic properties than a product obtained by another conventional method.

Lorret [47] synthesized by the sol-gel method a hydrotalcite to which he sought to modify the textural properties during synthesis. To the reaction vessel was added $\text{Al}(\text{OC}_4\text{H}_9)_3$, distilled water and HCl to a known ratio, after which the required amount of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ and Na_2CO_3 was added to this solution. The specific surface area was determined and it was observed that the particle size can be changed by decreasing the synthesis temperature or by decreasing the reaction time. Increasing the acid-salt molar ratio has the effect of changing the pore size and porosity of hydrotalcites. And if the nature of the anions and cations changes, the physico-chemical properties of the double-layered hydroxides also change [47,55].

1.2.3. Ion exchange method

LDHs have the ion exchange capacity according to the equilibrium reaction:



This method is based on two types of intercalated compounds and pillared compounds. An intercalated compound refers to the insertion of chemically and thermally unstable guest species into the inter-layer region. A pillar compound is a chemically and thermally stable mesoporous or microporous layered material interspersed between layers. Host anions are usually exchanged with guest anions in the basal space of double-layered hydroxides [6].

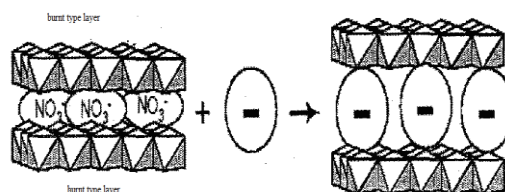
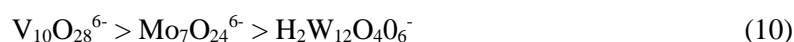
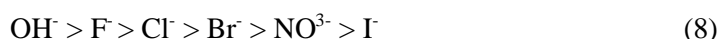


Fig. 6 Pre-pillar and post-pillar structure [16,17]

Also to limit product contamination, the process is performed in an inert atmosphere. pH has an important role in this method because the resulting material must be stable in relation to this characteristic [13]. This method is good in direct interactions between intermediate anions and cationic metals and the high solubility of cations and anions in the base solution [12].

Hydrotalcite compounds are special in that there is an accessible inter-layer space for the insertion of bulky polyvalent anions such as polyoxometalates (POMs) and phthalocyanines (Pc). Polyoxometalates are acidic in character and thus acidic properties are introduced into basic double-layered hydroxides or oxides, resulting in compounds with acidic catalytic properties (AA-POMs). Pillar compounds can also be used as oxidation catalysts when the columns are redox active anions [12, 13, 20, 21]. From the calculation of equilibrium constants [48], he established the following order of selectivity for monovalent, divalent and poly-oxometallate anions:



From a thermodynamic and practical point of view, the anion exchange in the structure of LDHs depends mainly on [1, 56]:

- electrostatic interactions between positively charged hydroxylated layers and exchange anions;
- the pH exchange.

The literature [48] has shown that the most commonly used LDHs in ion exchange are those that have NO_3^- anions in the interlamellar space because they are easily replaced. These ion exchange reactions figure 4 take place between the anion that is already in the interlamellar space of the hydrotalcite and an aqueous solution that contains in excess different species of anions [48].

Most ion exchange reactions take place in an inert nitrogen medium, using decarbonated water and less organic solvents as the solvent. These anion exchanges are performed at room temperature or up to temperature $T = 323.15$ K, this influencing the exchanges between anions [46 and 48].

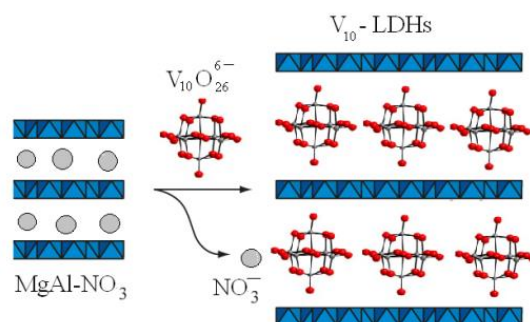


Fig. 7 Ion exchange between NO₃⁻ anions in the interlamellar space and V₁₀O₂₆⁶⁻ ions in aqueous solution [46]

1.2.4. Hydrothermal method

This method is often used in the production of nanocomposites with catalysis applications. The crystals are grown in a pressurized steel autoclave in which the composite material has been previously added.

The advantages of this method are:

- during the hydrothermal treatment the crystallinity and the chemical composition of the compound are improved;
- stability of the compound increases, and the results obtained after use are better;
- rigid structures are obtained due to the conditions of the hydrothermal treatment.

These reactors are usually thick-walled, sealed steel cylinders that must withstand high temperatures and pressures for predetermined periods of time (Figure 8). In addition, the autoclave material must be inert to the solvent. Closing is the most important element of the autoclave. To prevent corrosion of the autoclave's internal cavity, walls made of: carbon-free iron, copper, silver, gold, platinum, titanium, glass (or quartz), or Teflon is used, depending on the temperature and the solution used.

The double-layered hydroxides obtained by the methods discussed above are often poorly crystalline and with disordered metal hydroxide layers. In cases where increased crystallinity and uniformity are sought, anionic clays are often modified by post-preparative treatments. These post-preparation treatments consist of the maturation of precipitates at room temperature or, more often, at higher temperatures under reflux. Thus, larger and more perfect crystallites are formed by dissolution / reformation processes. These treatments are, in fact, steps used immediately after the actual synthesis step in which the precipitates containing AA nuclei are generated.

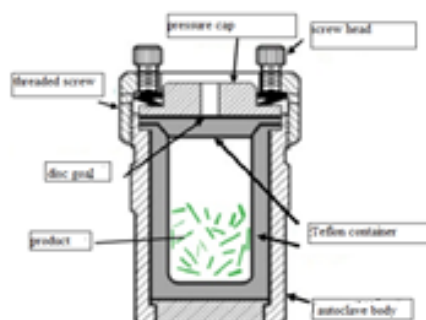


Fig. 8 Schematic representation of an autoclave used in hydrothermal treatment [46]

Hydrothermal treatments are used to process double layered hydroxides obtained by the above methods. The hydrothermal treatment favors the dissolution and recrystallization by heating the solution during the formation of the material.

1.2.5. Reconstruction method

In 1980, Miyata first obtained LDHs by the reconstruction method. This method is based on the memory effect of LDHs, on the ability of mixed oxides resulting from the controlled calcination of LDH precursors to restore the lamellar structure when they are brought into contact with the aqueous solution of an anion [42].

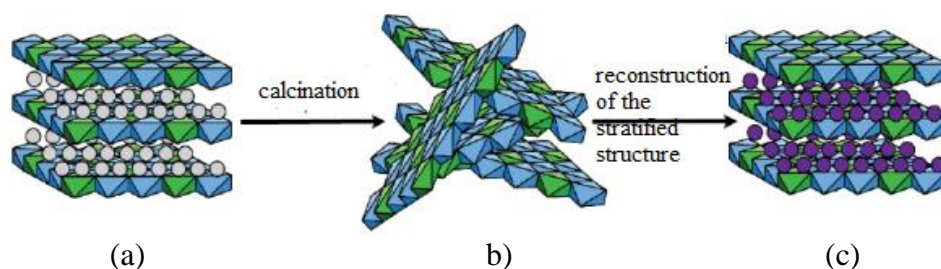


Fig. 9 The steps taken in the reconstruction process of an LDH, (a) initial LDH structure, (b) LDH structure after calcination, (c) restoration of the lamellar structure of LDH [49]

The method has been used by other researchers to obtain mixed oxides of the Mg-Al precursor [50, 51, 52, 53] in order to intercalate several oxoanionic species (CrO_4^{2-} , HVO_4^{2-} , HPO_4^{2-} , SO_4^{2-} , etc.). Figure 7 shows the structure of an LDH before being calcined (a), after calcination (b) and the reconstruction of the lamellar structure after contact with the aqueous solution of an anion (c) [49].

LDHs are stable up to about $T = 673.15 \text{ K}$. In the process of progressive calcination of LDH there are several stages: first the water molecules adsorbed on the outer surface are lost ($T = 373.15 \text{ K} - T = 383.15 \text{ K}$), then the water molecules

retained in the interlamellar space are lost. ($T = 473.15$ K), after which in the general temperature range $T = 473.15$ K - $T = 623.15$ K there is a process of dehydroxylation of the lamellae which ultimately leads to the destruction of the structure.

The calcination conditions (temperature, time) are very important in order to obtain the restoration of the lamellar structure.

The mixed oxides obtained after calcination of LDHs can be introduced into various solutions containing the intercalated anion, but the reconstruction is done in an inert medium to avoid contamination with CO_3^{2-} anions from the atmosphere [50, 51, 52, 53].

1.2.6. Urea hydrolysis method

This method consists in precipitating the precursors with the help of an in situ generated agent. It is based on the hydrolysis reaction of urea:



Urea is a very weak, water-soluble Brönsted base, the hydrolysis of which can be controlled by temperature. The urea hydrolysis method was first developed by Costantino in 1998 [54].

The method used was: a solution of 1.0 M urea, 0.1 M magnesium chloride and 0.1 M aluminum chloride was added to a flask using a Mg / Al / urea molar ratio of 4: 1: 10 below magnetic stirring at room temperature [55].

After the precipitate was cooled to room temperature, it was separated by centrifugation and then washed with decarbonated water subsequently.

In the case of this experiment, the size of the crystals formed during the synthesis and their comparison with LDH-type materials obtained by other conventional methods were followed [54, 55].

Properties of LDHs with possible applications in environmental protection and catalysis

Specialist studies have shown that double lamellar hydroxides can be used in different fields because they are characterized by:

- high ion exchange capacity;
- following the calcination operation over $T = 773.15$ K, the lamellar structure is destroyed, forming mixed oxides. In contact with a solution containing various anions, they regain their structure based on a "memory effect" that allows them to reach their original shape;
- have a large specific surface area that can vary between $100 \pm 300 \text{ m}^2 / \text{g}$;
- there are no toxic substances that affect human health;
- can be used successfully in different fields due to the typical structure of LDHs, such as: adsorbents of organic molecules (textile dyes, pesticides, drugs, etc.), as additives in the cosmetics industry, catalysis matrix;
- degree of swelling in the presence of water;
- has acid-base properties;
- they are cheap to synthesize and with a high reproducibility of the structure.

1.3. Conclusions

Among the most important applications of LDHs is the absorption of pollutants from the environment. Hydrotalcites can be used as adsorbents for metals Cu (II), Cd (II), Pb (II) or Zn (II) in aqueous medium, LDH intercalated with L-cysteine, Cys-LDH used as an adsorbent for ion removal U (VI) from aqueous solution with adsorption capacity = 211.58 mg g^{-1} , modification of LDHs with ethylene diamine tetra acetic acid (EDTA) and study of Cr (VI) ion uptake from wastewater or soil. Double-layered hydroxides are also used to remove toxic dyes from aqueous solutions such as Congo red, sunset yellow or indigo carmine [40, 41].

In medicine, double lamellar hydroxides are used as anti-inflammatory agents [16, 17, 26, 27, 28] and phosphate binding in the gastrointestinal fluid to prevent the hyperacidity [16, 27, 28].

Due to the biocompatibility, double layered hydroxides have been introduced in the process of obtaining pharmaceuticals, for example brufen [29] because hydroxides can control the efficacy of drugs in areas of action [28, 29].

Another application of double layered hydroxides relates to biomolecule transfers for certain cell types. Hydrotalcite have a favorable effect on transmembrane transfer [16, 17].

Enzymes can be immobilized because double lamellar hydroxides present a class of catalytic hybrid materials active against hydrolysis, polymerization, isomerization or redox reactions [16, 17]. Due to their anionic properties, hydroxides are of interest for the absorption of molecules that pollute the environment. Promotes the stability of interlamellar anions and prevents substitution with other anionic compounds [16, 17, 30, 31].

Their intercalation with other materials of organic or inorganic nature favors the diversity of studies and results. Therefore, the aim is to apply the best synthesis method with the most satisfactory results in the shortest possible time and with low costs, therefore based on the analysis of the literature, as a method of preparation of hydrotalcites is indicated the method of coprecipitation at low supersaturation, at constant pH. The conclusion of this study is that anionic clays can be used successfully in many industrial applications and their preparation is important.

References

- [1] Giuseppe F., *Radioactive emanations and food counteraction*, The Clay Handbook, Revised Edition, G. Fusconi, Le scienze n° 254 from 1989.
- [2] Steiner R., The Clay Handbook, Fifth Conference, Anthroposophical Journal, March-April 2006, Anthroposophical Publishing House, Milan, Dornach July 2, 1922.
- [3] <http://pronaturissimo.blogspot.com/2010/07/tipuri-de-argile-si-actiunea-lor.html>
- [4] Cunha V.R.R., Ferreira A.M. Da C., Constantino V.R, Tronto J., ValimJ. B., *Hidróxidos duplos lamelares: nanopartículas inorgânicas para armazenamento e liberação de espécies de interesse biológico e terapêutico*, Quím. Nova, **33**, 1, São Paulo, 2010.
- [5] Mishra G., Dash B., Pandey S., *Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials*, ApplClay Sci, 153 – 172 – 86, 2018.
- [6] Shadpour M., Masoud H., Chaudhery M. H., *Recent innovations in functionalized layered double hydroxides: Fabrication, characterization, and industrial applications*, Advances in Colloid and Interface Science, **283**, 2020, 102216, Elsevier B.V

- [7] Mishra G., Dash B., Pandey S., *Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials*, Appl Clay Sci, 15-172–86, 2018.
- [8] Kuthati Y., Kankala R.K., Lee C.-H., *Layered double hydroxide nanoparticles for biomedical applications: Current status and recent prospects*, Appl Clay Sci, 2015.
- [9] Peng C., Xing H., Xue Y., Wang J., Li J., Wang E., *Ratiometric sensing of alkaline phosphatase based on the catalytic activity from Mn-Fe layered double hydroxide nanosheets*, Nanoscale, **12**, 2020, p. 2022–2027.
- [10] Benício L.P.F., Silva R.A., Lopes J.A., Eulálio D., R.M.M. Santos, Aquino J.A., *Layered double hydroxides: nanomaterials for applications in agriculture*, Brasileira de Ciência do Solo, **39**, 2015, p. 1–13.
- [11] Yao W., Yu S., Wang J., Zou Y., Lu S., Ai Y., *Enhanced removal of methyl orange on calcined glycerol-modified nanocrystalline Mg/Al layered double hydroxides*, Chem Eng J, **307**, 2017, p. 476–86.
- [12] Liang R., Xu S., Yan D., Shi W., Tian R., Yan H. et al. Cd., *Te quantum dots/layered double hydroxide ultrathin films with multicolor light emission via layer-by-layer assembly*, Adv-Function-Mater, **22**, 2012, p. 4940-4948.
- [13] Purohit P.J., Wang D.Y., Wurm A., Schick C., Schönhals A., *Comparison of thermal and dielectric spectroscopy for nanocomposites based on polypropylene and layered double hydroxide-proof of interfaces*, Eur Polym J, **55**, 2014, p. 48–56.
- [14] Lyu B., Wang Y.F., Gao D.G., Ma J.Z., Li Y., *Intercalation of modified zanthoxylum bungeanum maxim seed oil/ stearate in layered double hydroxide: Toward flame retardant nanocomposites*, J Environ Manag, **238**, 2019, p. 235–242.
- [15] Ding Y., Alpay E., *Equilibria and kinetics of CO₂ adsorption on hydrotalcite adsorbent*, Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London, SW7 2BY, UK.
- [16] Zeradni A., Bettahar N., Bahmani A., Bendraoua A., Morsli Amine Synthèse, *Caractérisation et propriétés des matériaux de type : $[M_{2/3}^{II} M_{1/3}^{III} (OH)_2^{(1/3)+} A_{1/3m}^{m-} n H_2O$ avec A: CO₃²⁻, Cl⁻, NO₃⁻*, Département de Génie des matériaux, Faculté de Chimie, Année Universitaire 2015 / 2016.
- [17] Mersellem M., Bettahar N., Derriche Z., Ilikti H., Belkhadem F., *Synthèse et caractérisation des Hydroxydes Double Lamellaire (HDL) et application au transfert de biomolécules*, Faculté de chimie Département de Génie des matériaux, Année Universitaire 2013/2014
- [18] Vial S., Thèse de Doctorat, Université Blaise Pascal, U.F.R de Recherche Scientifique et Technique, Ecole Doctorale des Sciences Fondamentales, 2005.
- [19] Mostarih R., Thèse de doctorat, *Syntheses, Caracterisations et Applications D'Argiles Anioniques du type hydrotalcite a la Depollution dex eaux*, Université Blaise Pascal, Ecole Doctorale des Sciences Fondamentales, 2006.
- [20] Segal D.L., J. Non-Crystalline Solids 63, *Sol-gel processing: routes to oxide ceramics using colloidal dispersions of hydrous oxides and alkoxide intermediates*, Journal of Non-Crystalline Solids 63 (1984) 183-191 183 North-Holland, Amsterdam, Chemistry Division. Aere Harwell, Oxfordshire, OX11 0RA, England, 1984, p. 183-191.
- [21] Lopez T., Bosh P., Ramos E., Gomez R., Novaro O., Acosta D., Figueras F., *Synthesis and characterization of sol-gel hydrotalcites*, Structure and texture, Langmuir, **12**, 1996, p. 189–192.
- [22] Chubar N., Gerda V., Megantari O., Mičušík M., Omastova M., Heister K., et al., *Applications versus properties of Mg-Al layered double hydroxides provided by their syntheses methods: alkoxide and alkoxide-free sol-gel syntheses and hydrothermal precipitation*, Chem Eng J, **234**, 2013, p. 284–299.
- [23] Vaccari A., *Clays and catalysis: a promising future*, Appl. Clay Sci., Dipartimento di Chimica Industriale e dei Materiali, Università degli Studi di Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy, **14**, 4, 1999, p. 161–198.
- [24] Pasel J., Kazner P., Montanari B., Gazzano M., Vaccari A., Makowski W., Lojewski T., and Dziembaj H., R. and Papp. Appl Catal B, *Transition metal oxides supported on active carbons as low temperature catalysts for the selective catalytic reduction (SCR) of NO with NH₃*, **18**, 1998, p. 199–213.

- [25] Lòpez Nieto J. M., Dejoz A. and Vazquez M. I. Applied Catalysis A, *Preparation, characterization and catalytic properties of vanadium oxides supported on calcined Mg/Al-hydrotalcite*, **132**, 1995, p. 41–59, [https://doi.org/10.1016/0926-860X\(95\)00153-0](https://doi.org/10.1016/0926-860X(95)00153-0).
- [26] Virgile B., *Étude de la fragmentation de molécules d'intérêt biologique isolées et nano-solvatées induite par collision avec des ions multichargés et des particules neutres*, Université de CAEN / Bassenormandie, 2009.
- [27] M. del Arco, Gutierrez S., Martin C., Rives V., Rocha J., Chemistry, *Synthesis and characterization of layered double hydroxides (LDH) intercalated with non-steroidal anti-inflammatory drugs*, Journal of Solid State (NSAID), **177**, 2004, p. 3954–3962.
- [28] Ookubo A., Ooi K., Hayashi H., J. Pharm. Sci., *Hydrotalcites as Potential Adsorbents of Intestinal Phosphate*, Journal of Pharmaceutical Sciences, I, **81**, 11, 1992, p. 1139-1140.
- [29] B. Li, J. He, Evans D.G., Duan X., *Inorganic layered double hydroxides as a drug delivery system intercalation and in vitro release of fenbufen*, Applied Clay Science **27**, 2004, p. 199 – 207.
- [30] Marcio Jose dos Reis, *Effects of pH, temperature, and ionic strength on adsorption of sodium dodecylbenzenesulfonate into Mg–Al–CO₃ layered double hydroxides*, Journal of Physics and Chemistry of Solids, **65**, 2004, p. 487–492.
- [31] Shuangling C., *Studies on adsorption of phenol and 4-nitrophenol on Mg-Al mixed oxide derived from Mg-Al-layered double hydroxide*, Separation and Purification, **67**, 2009, p. 194-200.
- [32] Abraham C., *Inorganic Ion Exchangers: A Technology Ripe for Development*, Ind. Eng. Chem. Res. 1995, **34**, p. 2865-2872, Department of Chemistry, Texas A&M University, College Station, Texas 77843.
- [33] Clearfield A., *Role of Ion Exchange in Solid-state Chemistry*, Received May 18, 1987 (Revised Manuscript Received October 1, 1987), Department of Chemistry, Texas-ABM-University-College-Station-Texas-77843.
- [34] Benício L. P. F., Rejane A. S., Lopes J. A., Eulálio D., Menezes dos Santos R. M., Leonardo A., Vergütz L., Novais R. F., Marciano da Costa L., Frederico G. P. and Tronto J., *Layered double hydroxide: Nanomaterials for applications in agriculture*, Revisao de literature, 2015.
- [35] Merlen E., Gueroult P., d'Espinose de la Caillerie J.-B., Rebours B., Bobin C., Clause O., *Hydrotalcite formation at the alumina/water interface during impregnation with Ni(II) aqueous solutions at neutral pH*, Institut Francais du Pétrole, 1&4 Avenue de Bois Prdau, BP 311, F-92506 Rueil Malmaison Cedex, France, Applied Clay Science, **10**, 1995, p. 45-56.
- [36] Cavani F., Trifirb F., Vaccari A., *Hydrotalcite-type anionic clays: preparation, properties and applications*, Dipartimento di Chimica Industriale e dei Materiali Wale del Risorgimento 4, 40136 Bologna (Italy).
- [37] Malherbe F., Forano C., Besse J.P., Microporous Materials, **10**, p. 67-84, 1997
- [38] François M., Claude F., J.P. Bess, *Use of organic media to modify the surface and porosity properties of hydrotalcite-like compounds*, Laboratoire Physico-Chimie des Matériaux, CNRS URA 444, Université Blaise Pascal, 63177 At&e, Ckdex, France Received 26 September 1996; revision 11 November 1996; accepted 25 November 1996.
- [39] Popovici E., Seftel E., *Materiale nanostructurale avansate*, Prezent și viitor, vol III, Ed. Demiurg, Iași, 2007.
- [40] Asiabi H, Yamini Y, Shamsayei M, Tahmasebi E., *Highly selective and efficient removal and extraction of heavy metals by layered double hydroxides intercalated with the diphenylamine-4-sulfonate: A comparative study*, Chem Eng J, **323**, 2017, p. 212–23.
- [41] Huang D, Liu C, Zhang C, Deng R, Wang R, Xue W et al., *Cr(VI) removal from aqueous solution using biochar modified with Mg/Al-layered double hydroxide intercalated with ethylenediaminetetraacetic acid*, Biores Technol, **276**, 2019, p. 127–32.
- [42] Shigeo Miyata, *Physico-chemical properties of synthetic hydrotalcites in relation to composition*, Kyowa Chemical industry Co., Ltd., Yashimanishi-machi, Takamatsu-shi, Japan, Clays and Clay Minerals, **28**, 1, 1998, p. 50-56.
- [43] del Arco M., Malet P., Trujillano R. and Rives V., *Synthesis and Characterization of Hydrotalcites Containing Ni(II) and Fe(III) and Their Calcination Products*, Departamento de Química Inorgánica, Universidad de Salamanca, Salamanca, Spain, and Departamento de Química

- Inorgánica-Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla-C.S.I.C., Sevilla, Spain, Chem. Mater. 1999, 11, 624-633.
- [44] Miyata S., *Physico-chemical properties*, Clays and Clay Minerals, **28**, p. 50–56.
- [45] Rives V., Ulibarri M. A., *Layered double hydroxides (LDH) intercalated with metal ordination compounds and oxometalates*, Coordination Chemistry Reviews, **181**, 2010, p. 61-120.
- [46] Iuliana (Dobrea) D., Marcel Popa, *Materiale micro si nanostructurate utilizate în cataliza si protectia mediului*, Facultății de Inginerie Chimică și Protecția Mediului, Iași, 2019.
- [47] Lorret O., Morandi S., Prinetto F., Ghiotti G., Tichit D., Durand R., *Synthesis and Characterization of Pt/Mg(Al)O Catalysts Obtained From Layered Double Hydroxides by Different Routes*, Microporous Mesoporous Materials, **103**, (1–3), 2008, p. 48–56.
- [48] Shigeo Miyata, *Anion-exchange properties of hydro talc-like compounds*, Kyowa Chemical Industry Co" Ltd" 305 Yashimanishi-machi Takamatsu, Kagawa, 761-01, Japan, Clays and Clay Minerals, Vol. 31, No.4, 305-311, 1983.
- [49] Maria Amélia Nortadas Duarte de Almeida Lemos, Bogdan Samojeden, *Catalytic Pyrolysis of Biomass Katarzyna Ewa Kucharczyk Thesis to obtain the Master of Science Degree in Energy Engineering and Management*, November 2018, Tecnico Lisboa.
- [50] Kooli F., Rives V., Ulibarri M.A., *Vanadate-pillared hydrotalcite containing transition metal cations*, Materials Science Forum, 1994, p. 152–153.
- [51] Kooli F., Rives V., Ulibarri M.A., *Preparation and study of decavanadate-pillared hydrotalcite-like anionic clays containing transition metal cations in the layers. I. Samples containing nickel-aluminum prepared by anionic exchange and reconstruction*, Inorganic Chemistry. **34**, 1995, p. 5114–5121.
- [52] Kooli F., Jones W., *Direct synthesis of polyoxovanadate-pillared layered double hydroxides* *Inorganic Chemistry*, **34**, 1995, p. 6237–6238.
- [53] Kooli F., Jones W., Rives V., Ulibarri M.A., *An alternative route to polyoxometalate-exchanged layered double hydroxides: the use of ultrasound*, Journal of Materials Science Letters, **16**, 1997, p. 27–29, b.
- [54] Costantino U., Marmottini, F., Nocchetti, M., Vivani, R., *New synthetic routes to hydrotalcite-like compounds. Characterization and properties of the obtained materials*, European Journal of Inorganic Chemistry, **10**, 1998, p. 1439–1446.
- [55] Cornelia-Magda Pușcașu, Gabriela Carja, *Double lamellar hydroxides as advanced materials with specific properties and applications*, summary of the doctoral thesis, "Gheorghe Asachi" Technical University, from Iași, Doctoral School of the Faculty of Engineering Chemistry and Environmental Protection, Iași, 2015.
- [56] Bahramian A., *The effect of thermal and non-thermal routes on treatment of the Mg-Al layered double hydroxide catalyst dispersed by titania nanoparticles in products distribution arising from poly (ethylene terephthalate) degradation*, Chemical Engineering Department, Hamedan University of Technology, P.O. Box, 65155, Hamedan, Iran, Polymer Degradation and Stability, 179, 2020, 109243.
- [57] Jingfang Yu, Jean-Charles Buffet, and Dermot O'Hare*, *Aspect Ratio Control of Layered Double Hydroxide Nanosheets and Their Application for High Oxygen Barrier Coating in Flexible Food Packaging*, American Chemical Society, ACS Appl. Mater. Interfaces, 12, 2020, p. 10973–10982.
- [58] Thaís Aparecida Candida Balbino, Carlos Roberto Bellato, Alexandra Dias da Silva, José de Oliveira Marques Neto, Sukarno Olavo Ferreirab, *Preparation and evaluation of iron oxide / hydrotalcite intercalated with dodecylsulfate/ β -cyclodextrin magnetic organocomposite for phenolic compounds removal*, Department of Chemistry, Universidade Federal de Viçosa, Av. PH Hofs, s/n, 36570-900 Viçosa, Minas Gerais, Brazil, Applied Clay Science, 193, 2020, 105659.
- [59] Prakash R.a,b, Sujata Mandala, Bheeter S.R.b, *Bio-polymer modified layered double hydroxide extrudates: A novel approach towards adsorptive purification of water*, CLRI-Center for Analysis, Testing, Evaluation and Reporting Services (CATERS), CSIR- Central Leather Research Institute, Adyar, Chennai, 20, India b Department of Chemistry, St. Joseph's College, Trichy, 620002, India, Journal of Water Process Engineering, **35**, 2020, 101208.