

Journal of Material Sciences & Engineering

Dpen Access

Characteristics, Preparation Routes and Metallurgical Applications of LDHs: An Overview

Maria Richetta*

Department of Industrial Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133, Rome, Italy

Abstract

The peculiar properties of layered Double Hydroxides (LDH) have progressively drawn the attention of the scientific community. The main characteristic of LDH is the ability to capture anionic species (organic and inorganic) to build different composites. This is made possible by the sandwich structure of the LDH, similar to the brucite architecture, made up of positive charged lamellas interspersed by anions. Several distant fields, ranging from medicine to physics and engineering, exhibit interest in LDH applications. To satisfy all those requirements, energy was spent to sculpt LDHs physical and chemical properties and for designing layered double hydroxides "*ad hoc*" for different needs and employments. Notably, among the many applications, those related to metallurgical processes and products are of particular interest. This paper presents the characteristics, the main preparation routes and reviews the applications of LDH to metallurgy with some examples taken from the experimental research of the author.

Keywords: LDH; Nanomaterials; Alumina refinement; Anticorrosion film; Surface functionalization; Catalysis; VOCs remediation; Heavy metal removal

Introduction

Layered Double Hydroxides belong to the hydrotalcite family and are also known as anionic clays. They exhibit a sandwich structure, similar to the brucite architecture, made up of positive charged lamellas, containing either divalent M^{2+} or trivalent M^{3+} metal cations, interspersed by six counterbalancing OH⁻ hydroxyl groups [1,2].

When divalent (M^{2+}) cations are substituted by trivalent (M^{3+}) ones, an imbalance of charges arises. Positive hydroxide layers are therefore alternated by negative ions (A^{n-}), intercalated between lamellas, thus forming an almost continuous repetition (Figure 1). The ratio x= $M^{3+}/(M^{3+}+M^{2+})$, known as molar ratio, varies within the range (0.2 ÷ 0.4).

Several papers appeared in scientific literature regarding different fields of applications of LDHs, thanks to their peculiar morphology and growing mechanism. Foremost, by virtue of the widespread range of metal cation options, structures with different physical and



chemical properties have been realized; in addition the considerable surface/volume ratio linked to the repetitive LDHs organization can be exploited to design high-performance solids; last but not least, the power of interwoven in interlayer space different species, such as: metal ions of mixed valences, water and even more complex organic molecules, has made them attractive for top applications in the most varied fields, from engineering to medicine. Just to recall only some of the possible utilizations we can cite: surfaces design with super hydrophobic properties [1], anticorrosion coatings [2,3], flame-retardants [4], water waste treatments [5,6], biomedical applications [7,8], gas sensors [7], nanostructured-modified textiles [8]. Furthermore, the possibility of substituting transition metals cations to divalent cations made LDHs very interesting in energy conversion and harvesting [9].

Among such various applications of particular interest are those regarding metallurgy. Since '60 they have been used in the Bayer process of alumina refinement, as demonstrated by the wide number of industrial patents. Other applications regard: Volatile Organic Compounds (VOCs) remediation in exhaust fumes emitted by industrial plants, ii) anticorrosion coatings, iii) catalysis, iv) metal surface functionalization, v) heavy metal capture in liquid wastes of industrial plants.

This work briefly describes the LDH characteristics and synthesis routes, and discusses the metallurgical applications. Some experimental results obtained by the author will be also reported.

Characteristics

The basic structure of a LDH is similar to the brucite $[Mg(OH)_6]$ one, in which the Mg cation is enveloped by OH⁻ anions thus resulting

*Corresponding author: Maria Richetta, Department of Industrial Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133, Rome, Italy, Tel: +39 06 72597197/+39 3486665489; Fax: +39 06 72597158; E-mail: richetta@uniroma2.it

Received November 01, 2017; Accepted November 19, 2017; Published November 29, 2017

Citation: Richetta M (2017) Characteristics, Preparation Routes and Metallurgical Applications of LDHs: An Overview. J Material Sci Eng 6: 397. doi: 10.4172/2169-0022.1000397

Copyright: © 2017 Richetta M. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Page 2 of 11

in an nearly octahedral shape. The octahedral arrays build up a layered three-dimensional structure, in which each single sheet is positively charged. The charge is linked to the substitution of a "x" fraction of divalent cations M^{2+} with a trivalent ones M^{3+} , as shown in Figure 1 [3-7].

Within the interlamellar space an assortment of commutable anions and water molecules can be intercalated to guarantee charge balance. The general formula describing this hydrotalcite-like structure can be expressed by the following general formula:

 $[[M^{2+} 1-xM^{3+} x(OH)2]^{x+} (A)^{n-}x/n] mH_2O.$

The lattice stability imposes that the molar ratio $M^{3+}/(M^{3+}+M^{2+})$ may vary within the interval (0.2÷0.4). The electrostatic repulsion between adjacent cations and Pauling's law are responsible of the upper limiting value. The lower one is instead related to the requisite of maintaining separate layers together with a 3D configuration.

Disparate metallic anions, either divalent (Zn, Mg, Mn, Fe, Co, Ni, Cu, Ca) or trivalent (Al, Mn, Cr, Fe, Co, Ni, La), have been adopted to compound LDHs. Even more than two different metal cations have been used to obtain additional physical/chemical properties. Jung et al. [8] investigated the effects of substituting Zn^{2+} in relation to structural properties such as: lattice parameter, interlayer distance, water content, ionic conductivity.

The above reported stoichiometric formula for LDHs has to be regard as a "*rationale*" since LDHs are not stoichiometric, even from a microscope point of view. De facto metals cations are customarily presumed to be haphazardly distributed, on a hexagonal texture, within the layers. Also the lattice constant "*a*" results in a linear combination of ionic radii and molar fraction *x*. Nevertheless, some local cations order has been documented, and some authors have highlighted long-range cation ordering of organized superstructures [4,9,10]. Anyway results are still controversial.

As it was already underlined before, the LDHs interlayers' host, besides water molecules, also charged or neutral species, both organic and inorganic. These moieties are usually faintly bound to the lamellas. Therefore they can be settled during the three dimensional formation stages or subsequently substituted by anions exchange. The anions can be gather as follows:

- Halides: Cl^- , F^- , Br^- , I^- , etc.
- Non-metal oxoanions: carbonate, nitrate, sulfate, etc.
- Oxometallate anions: CrO_4^{2-} , MnO_4^{-} , VO_4^{3-} , $Cr_2O_4^{7-}$, $W_{10}O_{32}^{4-}$, etc.
- Anionic complexes of transition metals: *Fe*(CN)²⁻₆, anionic metal porphyrins, Eu complexes, etc.
- Organic anions: $-COO^-$, $-SO_4^-$, $-PO_3^-$, etc.
- Anionic biomolecules: aminoacids, enzymes, proteins, DNA, TPA, etc.
- Anionic polymers: poly(styrene sulphonate), PMMA, etc.

To realize devices capable to control conductivity, or to be applied in water splitting, Zheng et al. [11] intercalated also neutral molecules, together with anions. After intercalation they suffered dissociation into the water content of the interlayer domain.

The disordered state of the interlamellar domain is demonstrated also by structural characterization, through XRD and/or EXAFS analysis, or by some physical properties of layered double hydroxides as electrical conductivity behaviour and hydration properties. All these peculiarities have driven some authors to consider this state a "quasiliquid" one [12]. Needless to say, all these singularity are heavily tied to the significant interlayer water content. Two types of water can be recognized in LDHs [13]. First: the *crystallite water*, bounded to the interlayers and to the external surface. It is always present, also in dry conditions. Second: the *adsorbed water* that, depending on temperature, water vapour pressure and humidity, is alternately adsorbed and desorbed. It is evident that this is the most influential contribution not only to the previously described "architectural disorder" but also to one of the most significant phenomena occurring within the LDH: the anionic exchange. It is surprisingly easy to replace a large number of "old" ions with other "new" ones simply by immersing the LDH in a solution with an excess of new anions. This property is also adopted to prepare LDHs.

The fact that the ion exchange reaction has occurred is revealed by the variation in the distance between the lamellas, which is tightly linked to shape and density of the intercalated anions. This interlamellar space "d" is defined as the thickness of one hydroxide sheet plus one interlayer distance, and is normally determined by X-ray diffraction (XRD). The capability of intercalating even large and complex molecules is a direct consequence of the above-described adaptability of layered double hydroxides.

Preparation Routes

There are several procedures to synthetized LDHs. The option grounds on what types of cations form the layers, which are the intercalated anions and, particularly, which are the properties requested to the LDH, such as: crystallinity, porosity, morphology, etc. [3-7].

Two main groups distinguish the different synthesizing methods: direct and indirect.

Among the direct procedures we can enumerate: co-precipitation, salt-oxide method, sol-gel and electrochemical synthesis, *in situ* film growth. For what concerns indirect processes, it must be stressed that they consist essentially in modifications of pre-synthesized LDHs, such as: anion exchange, LDH reconstruction and delamination.

Co-precipitation

Co-precipitation was the first approach for preparing mixed double hydroxides [14], and it is still the simplest and most commonly used. In this method a low temperature chemical reaction develops inside an aqueous solutions of M^{2+} and M^{3+} salts in appropriate proportions, together with the specific anion "A" to be intercalated and in the attendance of an alkali metal base. Generally there are two conditions for co-precipitation; namely at low supersaturation (constant pH) and at high supersaturation (variable pH). During the process the pH behaviour must be kept under control, as well as the operating temperature. The alkali metal base causes the precipitation of the divalent and trivalent cations in hydroxide forms:

$$(1-x)M^{2+}A^{q-}_{3/q} + xM^{3+}A^{q-}_{3/q} + 2NaOH + nH_2O \rightarrow M^{2+}_{1-x}M^{3+}_x(OH)_2A^{q-}_{x/q}.nH_2O + 2NaA^{q-}_{1/q}$$

To enhance crystallinity and size of the material, after precipitation a hydrothermal treatment is performed [15-17], followed by an aging process (from few hours to several days). Vigorous stirring and ultrapure water are used to ensure the purity of the LDH.

According to the above, co-precipitation represent a direct procedure, which ensures a high control of growth parameters, such as pH, temperature, solution concentration, cations ratio, aging time, providing a direct procedure to synthesize Layered Double Hydroxides with well-defined composition, well-crystallized phases, and good tuning of the cation ratio.

Salt-oxide method

This approach was introduced to synthesize Zn-Cr-Cl LDHs [18], to be later extended to Zn-Al-Cl and Cu-Cr-Cl [5,6]. It consists in a solid-liquid reaction between an aqueous solution of the trivalent metal chloride and the aqueous solution of the divalent metal chloride in excess. Several attempts were done to synthesizes LDHs with composition different from Zn-Cr-Cl, Zn-Al-Cl, and Cu-Cr-Cl but without success. The reason relies on the fact that salt oxide synthesis permits a high degree of crystallinity, but does not allow varying and determining the stoichiometry as co-precipitation does.

Sol-gel method

The synthesis involves formation of a colloidal suspension (sol) followed by gel formation, as a consequence of internal crosslinking. The precursor of the sol-gel transition, are metal-based-alkoxides and/ or acetylacetonides that suffer strong hydrolysis and polymerization with HCl and HNO_3 . The sol-gel approach was introduced by Lopez et al. [19] to increase the cation ratio. It was further extended to include transition metals Ni, Cr, and CO [20-22] thanks to the demonstrated properties of homogeneity, thermal stability, quite good control of stoichiometry, high porosity [23].

Electrochemical deposition

In 1994 the first films of Ni-Al, Ni-Mn, Ni-Cr and Ni-Fe LDH were electro-deposited on the working electrode of a conventional battery containing a metal-nitrate bath [24]. The principle bases on the electrically induced reduction of nitrate ions to produce hydroxide ions on the working electrode. This implies a local enhancement of the pH and a subsequent precipitation of the LDH film. It is essentially a one-step technique that permits direct deposition with good adhesion, control of film density, morphology and thickness, advantages that the conventional methods do not provide. In those cases, in fact, first we have to recover the LDH powder, treat it, and only after these passages, deposit it onto substrate by means of physical procedures with not the same reproducibility and morphology. Recently sol-gel technique attracted much interest not only to involve other metals, but also to produce modified electrodes for applications in several different fields of electrochemical sensing [25-29].

In situ film growth

It can be consider a sort of modified version of the co-precipitation technique. It is still a one-step recipe that guarantees quite a good adhesion and morphology [30-32]. Instead of adopting dissolved metal salts, one of the two metals is provided as a substrate, which behaves either as a sacrificing element for the film growing on it, or a reacting source of one of the corresponding metal. Differently from electrochemical deposition, in this case there is only the need to submerge the metal substrate into the aqueous solution of the other metal salt and the base. Apparently it could be possible to deposit LDH films on any substrate. The only thing to do is to deposit on a surface appropriate sacrificial metal films that react in solution. Moreover, and very important, is the fact that the surface can be patterned to form a circuit with a thin layer of the sacrificial metal to support the growth of LDH. Integrated sensors and devices could take great advantage from this technique [33].

Nevertheless, it is still far to be reached a good control of the

deposited LDH morphology and composition. In a previous work of Richetta et al. [34] (Zn-Al) LDH nanostructures were grown on Al foils. A nutrient solution composed of a 1:1 ratio of zinc chloride ZnCl₂ and hexamethylenetetramine ($C_6H_{12}N_4$) at 5 mM concentration was employed for the hydrothermal growth of LDH. The same concentration of Zn(NO₃)₂ was used for samples intercalated with NO₃ anions. Hexamethylenetetramine acted as a pH regulator for the solution basicity, through the hydrolyzation and release of ammonia.

The XRD spectrum displayed in Figure 2 evidenced that (Zn, Al) LDH crystal structure is hexagonal. For all the samples (intercalated with Cl^{-} and NO_{3}^{-} anions) the lattice parameter a=3.065 Å and represents the distance between two metal cations. The lattice parameter c, namely the spacing between basal planes of hexagonal cell exhibited some differences depending on the intercalated anions ranging from 7.55 to 7.57 Å. Figure 3a and 3b shows the structures obtained by operating at 80°C with different time and different intercalated anions. The samples exhibit a similar petal-like morphology and it was observed that longer time of growth gives rise to a coarser structure.

X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) results demonstrated a correlation between the Al content and the LDH morphology. In particular, a high available content of Al is connected to a small dimension of petals, as it could favour the nucleation by increasing the number of nucleation sites.

The kinetics of petals growth has been investigated by measuring the petal thickness vs. temperature and time of treatment. Under the assumption that the diffusion of Al atoms controls the speed of LDH growth process, the present author calculated an activation energy Q=0.73 eV. Such value is quite lower than the self-diffusion energy of Al (Qsd=1.31 eV [35]) thus it seems that the petal growth strongly depends on the specific microstructural features of aluminium



Figure 2: XRD spectrum of (Zn-AI) intercalated with Cl⁻ anions.



Figure 3: SEM micrographs of (Zn-Al) LDHs grown on an aluminium substrate with Cl⁻ (a) and NO₃ (b) intercalated anions.

substrate. On these grounds the calculated Q value has been compared with pipe diffusion activation energy (Qp=0.85 eV [36]), i.e. the diffusion along dislocations, and grain boundaries diffusion activation energy (Qgb=0.55 eV [37]). Since Qgb Q Qp the value of 0.73 eV is an apparent activation energy because it does not depend on a single physical phenomenon but on the diffusion along both types of defects, i.e. grain boundaries and dislocations. In other words the growth is substantially controlled by the lattice defects present in the Al substrate. Similar conclusion were drawn by Forticaux et al. [38] who pointed out that the commonly observed nanoflower morphology could be the result of uncontrolled overgrowth from discrete dislocation-driven nanoplates and/or partial detachment of spiral layers that are tied by the dislocation core and suggested that the growth of nanostructures of LDHs are likely to be dislocation-driven. Of course, the controlled crystal growth can lead great benefits to the preparation of LDHs with well-defined nanostructures and potentially improved properties. Further work is underway to assess the achieved results and control LDH growth kinetics by changing the microstructure of the aluminum substrate through mechanical and heat treatments.

Anion-exchange

When it is not possible to produce the desired anion to be intercalated within the LDH by co-precipitation, the desired ion, by ion exchange, replace the anion present in a previously prepared LDH. The reaction is possible thanks to the peculiarities of LDHs. This indirect method has been widely applied to synthesize new LDH phases by anionic exchange reactions, described by:

The reaction equilibrium constant favours the income of ions with higher charge density in such a way that it permits to define a comparative list of ion selectivity [5,6], which for monovalent ions reads: OH^- , F^- , Cl^- , Br^- , NO_3^- , I^- . In other words we have the reaction is carried out by stirring a water suspension of a LDH precursor or of a pre-synthesized LDH.

Reconstruction by rehydration after thermal treatment

When we take LDHs at temperature within the range 500-800°C, it calcinated and transforms into a mixture of metal oxides. If they are rehydrated with an aqueous solution containing anions, they transform into new LDHs, as was demonstrated by Miyata [39] with Mg-Al-CO₃. Also organic anions have been recently intercalated by this procedure [40].

Delamination/restacking method

The delamination process consists in a complete separation of the brucite-like sheets of a layered double hydroxide, which leads to a stable colloidal solution of monodispersed lamellas. Gradually drying this colloidal compound, well-ordered LDHs can be retrieved, with the potentiality of intercalating changed anionic species. Delamination can be achieved by several different mechanisms, in particular if we use organically modified LDHs [3,41]. To give some examples, organic intercalated anions like acetate, formate, or lactate abet delamination in water [42]. Alternatively, in formamide it is possible to delaminate nitrate-based [43] or amino-acid intercalated [44]. A subsequent drying process permits to recover well-ordered LDHs and LDHpolymer complexes [42].

Metallurgical Applications

The number of LDHs applications is very high and makes impossible a comprehensive description, therefore the attention will be focused on the most relevant ones: i) Bayer process, ii) volatile organic compounds (VOCs) remediation in exhaust fumes of industrial plants, iii) heavy metal capture in liquid wastes of industrial plants, iv) anticorrosion coatings.

Bayer process

Aluminium is extracted from bauxite and an intermediate step is the production of alumina from bauxite through the Bayer process. Aluminium production stands at 90% on alumina stockpiles. The Bayer process is the fundamental and most economical method for obtaining aluminium oxide from bauxite.

Alumina extraction and processing derive by a series of operations, mostly independent one with respect to the other, that takes place in different plants. To describe how LDHs are employed in Bayer process, which is quite complex, it is worth to summarise its main steps.

a) Extraction: To form what is generally called "pregnant liquor", i.e. a supersaturated solution of sodium aluminate, bauxite (gibbsite, böhmite, diaspore) is stepped into a hot caustic soda (NaOH) solution to dissolve the aluminium bearing minerals. The chemical reactions are:

$$Al(OH)_3 + Na^+ + OH^- \rightarrow Al(OH)_4^- + Na^+$$

 $AlO(OH) + Na^{+} + H_2O \rightarrow Al(OH)_4^{-} + Na^{+}$

where the first one refers to gibbsite, and the second one to böhmite and diaspora.

Depending on the bauxite ore the suitable caustic concentration, temperature, and pressure of the digester are chosen. Several flash tanks at atmospheric pressure and at about 106°C cool down the slurry, together with steam flashing.

b) Clarification/settling: Sedimentation is the first stage of clarification. During this stage the solids (bauxite residue) is separated from the pregnant liquor (sodium aluminate in solution). To assist the sedimentation you need to adjoin some chemical additives. Residue of bauxite sinks in the settling tanks. These residues are then removed and transferred into washing tanks to go through several washing stages. Along this line the caustic soda is recovered to be reused in the digestion process. The pregnant liquor is further taken out of the bauxite residue by means of security filters. Therefore the final product is not polluted by impurities.

c) **Precipitation:** The pregnant liquor is progressively cooled down. During this stage crystallization process starts, forming small crystals of aluminium trihydroxite Al(OH)₃ that grow and agglomarate in larger structures.

d) Evaporation: A chain of heat exchangers heats the spent liquor, which is successively cooled in flash tanks. Inside the heaters a condensate is formed and rehashed, for example to wash bauxite residue or as boiler feed water.

e) Classification: It consists in classifying into size range the precipitated gibbsite crystals. Normally cyclones, or gravity classification tanks carry it out. Coarse crystals, after being separated from the spent liquor by vacuum filtration, are doomed to calcination, while the fine crystals, after being purified from organic impurities, return to precipitation step to be agglomerated.

f) Calcination: Calciners roast at temperature up to 1100°C the filtered cakes. This step is necessary to drive off free moisture and chemically connected water. Therefore alumina solids are achieved.

Calcination is described by the following reaction:

 $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

Alumina is the product of this last stage.

The liquid part of the slurry is highly alkaline and requires neutralization to render it environmentally benign. A common practice is neutralization using Mg reach seawater. This treatment results in the forming of LDH hydrotalcite [45].

 $Mg_{6}Al_{2}(OH)_{16}CO_{3}.4H_{2}O.$

LDHs can be used for removing several species (both organic and inorganic) in the Bayer process and several methods have been patented. The removal mechanism couples intercalation of small anions with adsorption of larger organic molecules on the external surfaces [46-50]. Two LDHs, hydrotalcite and hydrocalumite, have received particular attention for removing impurity in the liquors. Hydrotalcite has been adopted to remove the organic humate present in Bayer liquor. The outcome of adding Mg compounds to contaminated Bayer liquors is a precipitate containing Mg/Al hydroxides [50]. The precipitate consists in an impure hydrotalcite, derived by the reaction of the Mg salt with the aluminate anion. It seems that is the surface adsorption rather then intercalation of anions that reduce the humate concentration in the Bayer liquor, because the large humate molecules do not fit between the hydrotalcite layers.

Nigro and O'Neill [48] have patented a method to remove coloured impurities, such as ferrate. They used calcined hydrotalcite in the temperature range 450-650°C with their re-hydration in Bayer liquor.

Reduction of oxalate in spent liquor was observed by Perrotta and Williams [51] following the formation of hydrocalumite at 60°C.

An alumina producing process was patented by O'Hare, et al. [52]. During this process bauxite was treated with an alkali to form a mixture of a solution of alumina trihydrate and aluminated-ions. The solution was treated before or after the precipitation phases, with a layered double hydroxide to remove impurities by intercalation into the LDH layers made of [LiAl,(OH),].

In the Bayer process, the main purpose is to extract as much bauxite as possible. Many investigators proposed novel processes to get back the alumina from liquor [48-51]. Most of those procedures relies on the following steps: i) form an Al-bearing LDH (Al-LDH) by operating on the first liquor with a metal hydroxide (being the metal different from aluminium), and recovering a treated stream of first liquor that carries an aluminate concentration lower than the first one; ii) separate the Al-LDH from the first liquor; iii) sand back the first liquor treated stream to an initial location inside the alumina refinery. The separate Al-LDH can be stored, sold or reprocessed within the same plant to extract its alumina content. It is sometimes contacted with a solution containing carbonate ions to give rise to both slurry containing an insoluble salt of metal other than aluminium and to obtain a second liquor containing aluminate ions released by the Al-LDH. Several different types of Al-LDH can be employed. Among them: hydrotalcite, hydrocalcite, Li/Al and Mg/Al LDHs, just to give some examples. A model is represented by the process studied by Rosenberg [53].

VOCs remediation in exhaust fumes of industrial plants

One of the main drawbacks of some industrial activities is the trace of Volatile Organic Compounds (VOCs) that represent a serious environmental problem. This is the case of various solvents, required in a number of technological processes. Some of those solvents escape into the atmosphere and contribute to air pollution.

Types of common VOCs that need treatment when present in an air stream are: (i) aliphatic carbon; (ii) aromatic hydrocarbons; (iii) chlorinated hydrocarbons; (iv) alcohols, ethers, and phenols; (v) ketones and aldehydes. In Table 1 vapour treatment technologies to the above contaminants are reported.

A well effective technology for VOCs control is oxidation, either thermal or catalytic. Oxidation units can destroy nearly 75% of VOCs and toxic emissions. Heating a VOC to an adequately high temperature, in presence of oxygen, will convert the VOC to an harmless end product. During thermal oxidation, the air polluted by VOC is captured by a ventilation system, preheated and combusted at high temperature to form carbon dioxide and water. In addition to combustion temperature, also residence times are parameters that influence VOC reduction efficiency [54].

Catalytic oxidation, similar to the thermal one, combines a conventional heat exchanger with a catalyst. It employs a bed of active materials (catalyst) that facilitates the overall combustion reaction. A catalyst inside the combustion unit lowers the activation energy for combustion, which occurs at lower temperature (320-540°C) avoiding formation of NOx by-products [55]. These processes have been demonstrated to be very up-and-coming to get rid of VOCs at low concentration. As a result, fuel costs for catalytic oxidation are lower. Typical catalyst materials include platinum, palladium, and metal oxides such as chrome-alumina, cobalt-oxide, copper-oxide, and manganese-oxide. Catalytic materials may be inserted into the combustion unit in either a monolithic or beaded configuration.

The control of the micro kinetics, consisting of micro pore diffusion, chemisorption, surface reaction, and desorption, is the task of the catalyst developer. The efficiency of catalytic oxidation process is highly affected by the catalyst material and its physic-chemical properties. In many catalytic oxidation procedures noble and transition metals are applied. Catalysts made with noble metals degrade VOCs easily. However, they are not suitable for large-scale applications due to high cost and rapid deactivation, determined by poisoning of sulphur and chlorine.

For these reasons a great effort has been made to find new metallic oxide catalysts capable of having the same or even better performance

VOC	Treatment					
	Thermal Oxidation	Catalytic Oxidation	Adsorption	Condensation	Biofiltration	Membrane Filtration
Aliphatic carbon	Х	X	Х	Х	Х	X
Aromatic carbon	Х	X	Х	Х	Х	Х
Chlorinated hydrocarbon	Х	Sometimes applicable	Х	Х	Sometimes applicable	Х
Alcohols/Ethers/Phenols	Х	Х	Х	Х	Х	Х
Ketones/Aldeides	Х	Х	Х	Х	Х	Х

 Table 1: Technologies used for treating vapour contaminants.

than those based on noble metals [56-58]. The LDHs shows very promising potential for generation of well-dispersed, active, and stable mixed oxides. The wide range of possible cations and anions that can be incorporated in the structure gives rise to a large number of catalytic materials [59,60]. Mixed oxides have been shown to be very active and selective in the decomposition of NOx [61] or in total oxidation of VOCs [62-64]. In different redox reaction (e.g.: selective oxidation of hydrocarbons or the total oxidation of VOCs [65]) mixed oxides, obtained after the calcination phase, have been able to act as catalysts [59,62], or as catalyst support [63-65].

Thanks to their activity and robust stability for VOCs combustion, LDHs can be catalyst or catalyst precursor. The activity of a catalyst or its physic-chemical characteristics is deeply depending on synthesis routes, calcination temperature, precursors and promoters. Nanosized structures show higher activity because of higher specific surface area and also superficial chemisorbed oxygen. Therefore, research is addressing new synthesis methods that lead to the synthesis of new thermally stable systems with even smaller crystallite dimensions (~10 nm).

Heave metal capture in liquid waste

The presence of various environmental pollutants in water has raised worldwide concerns. Toxic contaminants include organic and inorganic compounds such as phenolic compounds, pesticides, dyes, oxyanions, heavy metals, which are originating from the wastewaters of different industries such as steel, electroplating, plastics, battery manufacturing, mining etc. [66]. Heavy metal, principally, but also the other by-products, are not biodegradable. They use to gather in living structures, inducing severe risks to the human beings and to the environment [67,68]. Also in this case LDHs represent a suitable solution for contaminants uptake, since they posses: a) large surface area; b) anion exchange capacity; flexible interlayer region, accessible to polar molecules and anions. Three different mechanisms are responsible of the pollutants removal from aqueous media. Namely: anion exchange, surface adsorption, and memory effect. The charge balance between layer charge density and intercalated anions influences the anion exchange, while, for what concerns surface adsorption the involved mechanism is the adhesion of pollutants to the LDH surface. The memory effect is one of their most attractive features as an adsorbent. When LDHs are thermally decomposed around 500°C, they can be calcined and can lose the layer structure, forming highly active composite metal oxides with high thermal stability, large surface area, basic properties, small crystal size, and high stability against sintering even under extreme conditions [69]. Rehydration or sorption of different anions permits the reconstruction of these calcined products.

Several papers appeared during the past few years discussing the potentiality of LDH for contaminants uptake. Those pollutants include: oxyanions [70-75], monoatomic anions [76-78] cations [79-81], organics [82-84], and gas [85,86]. For example, Kovanda et al. [87] demonstrated the capabilities of Co:Mn:Al LDH (calcined at 500°C) in the total oxidation of ethanol (Figure 4).

Thus far, the most investigated oxyanions are arsenites, arsenates, chromates, phosphates, selenites, selenates, borates, nitrates, perrhenates, pertechnetates, iodates, molybdates and vanadate. The ionic radius of these oxyanions falls in the range of 0.19-0.26 nm. In the case in which the interlayer region is sufficiently large to fit the oxyanions for exchange process, the ion exchange would reach its maximum. The steps following adsorption are desorption of the adsorbed anion and regeneration of the adsorbent LDH. This is the most difficult and expensive part of an adsorption technology. It may



account for 70% of the total operating and maintenance cost for an adsorption system. A successful desorption/regeneration process should restore the adsorbent similar to its initial properties for effective reuse. Adsorbates can be recovered either for reuse or for proper disposal, depending on their market demand.

Various alkaline, salt and mixed solutions have been successfully used to desorb oxyanion-loaded LDHs. Uncalcined carbonate-LDHs adsorbs more than 85% of As(III) and Cr(VI) [88,89]. The desorption of As(V) and Se(IV) was dependent on the anion species and their concentrations in the desorbing solutions [90].

A number of studies also showed that oxyanion-loaded LDHs could be regenerated [91-96]. The adsorption capacity of the LDHs is gradually reduced after a few cycles of regeneration. Moreover, some research works appeared on the possible recovery of adsorbates, such as As(V), PO_4^{3-} and Cr(VI) from spent LDHs [75,96,97]. Gillman [96] reported that the minute amount of As in the As- loaded LDHs could be easily recovered by saturating As-loaded LDHs with phosphate, while Kuzawa et al. [95] proposed a scheme whereby the desorbed PO_4^{3-} in the spent desorption solution could be recovered as calcium phosphate precipitate by addition of CaCl₂, and the remaining spent desorption solution could also be reused after supplementing additional NaOH (Figure 5) [98,99].

LDH based novel nanocomposites originated by the hybridization of LDH with other materials, such as carbon nanotubes, graphene and carbon nanofibers [100]. The relevant importance of nanocomposites is determined by their high surface area and enhanced adsorption capacity with respect to their parental LDHs. The hybrids capacities derive from the mixed qualities of both parental materials and hence have better adsorption properties. Synthesis route and applications of these nanocomposites are described in detail [101,102].

Compared to LDH alone as an adsorbent, LDH-containing hybrids exhibit enhanced adsorption tendency of toxic pollutants due to their improvement in surface area [100-103], higher anion exchange tendency [104,105], better stability [106], increase in chelating and binding

Page 6 of 11

Citation: Richetta M (2017) Characteristics, Preparation Routes and Metallurgical Applications of LDHs: An Overview. J Material Sci Eng 6: 397. doi: 10.4172/2169-0022.1000397



sites [107], excellent selectivity for different metal ions [108-110], low toxicity and ease in separation and reusability when hybridized with magnetic particles [111-113]. As a result of these superior properties, they are up-and-coming adsorbents for wastewater treatment.

Anticorrosion coatings

Many technological applications demand materials with welldefined surface properties. Recently, surface functionalization of metallic materials has become a very active research area. Surface functionalization aims at improving specific responses of the material when interacting with its environment. Advances in surface engineering, nanomaterials and nanotechnology allow material manipulation down to the molecular scale. Functional coatings have been widely studied for various applications, including that requiring corrosion protection. In this last case, coatings must behave as a physical barrier against the attack of aggressive species toward the metallic interface. Moreover, if the protective barrier is disrupted, coating might inhibit the corrosion process. Therefore, corrosion protection needs anticorrosion pigments or corrosion inhibitors to protect the metal underneath.

Depending on the final application of the coated material, the thickness of the coating and the number of layers can range from few microns up to several hundreds of micrometres. During the past, effective systems relied on the use of chromate-rich surface treatments and/or primers and pigments based on chromates. However, nowadays the use of hexavalent chromium in almost all sectors is forbidden.

Many alternatives have been explored so far. In particular, two main strategies have been pursued: i) encapsulation/loading of functional active species in bearers; ii) handling of the coating matrix composition to incorporate functional groups of bulk and/or surface. LDHs have been able to store inorganic corrosion inhibitors, and to release them by ion exchange mechanisms [114-116]. Recently, attention has been given to LDH composition, ability to store different functional species and impact on the barrier properties of hybrid and organic coatings. For example, different ions (vanadates, organic inhibitors) were intercalated in LDH [117-119]. Localised impedance spectroscopy revealed the inhibiting effect of LDH loaded with mercaptobenzothiazole and added to epoxy coatings applied on AA2024. The corrosion inhibition efficiency was tested in artificial defects formed in the coated AA204. Snihirova et al. [119] demonstrated that LDH containers provide effective early-stage corrosion inhibition. LDHs evidenced an interesting property, i.e. they act as chloride ion trappers [119-121]. LDHs modified with nitrates are sensitive to the concentration of chlorides [121-123] and, based on this, nitrates can be released from the LDHs. This process is governed by an ion-exchange equilibrium mechanism, and allows the entrapment of chloride ions. Tedim et al. [120] highlights the capability of nitrate-containing LDH to trap chloride ions, which are diffusing through a coating, a process that can contribute to increase corrosion.

It is expected that LDH deliver the inhibitor into the corroding areas when the matrix is damaged. LDH dispersions in polymeric matrices may also result in better mechanical properties and stress dissipation ability. Moreover they do not damage the organic matrices barrier properties as proved in recent studies [123,124]. LDHs loaded with effective corrosion inhibitors seem to be a powerful option to design new smart organic coatings and present scale-up potential. For better compatibility with the organic matrices the key parameters to observe include surface functionalization of the LDH, its concentration and effective dispersion in the coating formulation as well as long-term stability.

Electrochemical and corrosion tests, integrated by physocochemical cgaracterization, demonstrate inhibiting efficiency of various healing systems. However it is difficult to predict the healing efficiency and the response time of carriers embedded in coatings. Very few articles are published on this issue. Recently, Javierre et al. proposed some mathematical/analytical models, correlating the healing kinetics with the coating composition. The authors conclude that the healing process depends on: thickness of the layers present in the coating; elastic modulus of the coating; dimensions of the initial damaged area [125,126].

If necessary LDHs can be deposited with micrometric precision to form desired patterns and protect specific parts of a surface, as shown in the example of Figure 6 [127].

A very important application is to magnesium alloys. They have excesllent mechanical properties thus are expected to be applied in automobile, aerospace and electronics industry; however they are vulnerable to the aggression by chlorine ions in a neutral or acidic environment due to their lower potentials. Corrosion of magnesium alloys is a critical issue for their industrial applications on a large

J Material Sci Eng, an open access journal

ISSN: 2169-0022

Page 7 of 11

Page 8 of 11



scale. Zeng et al. [125] prepared nano-sized ZnAl-LDHs coating by co-precipitation and hydrothermal method on AZ_{31} Mg alloy, and in order to prolong the service life of the ZnAl-LDH coating, a a polylactic acid (PLA) coating was sealed on the top layer of the coating using a vacuum freeze-drying method.

The ZnAl-LDH coating was synthesized by the combination of the co-precipitation and the hydrothermal process on AZ_{31} Mg alloy. It exhibits two layers, namely a compact inner layer and porous outer layer. A thick PLA coating was sealed on the porous outer layer of the LDH coating with a strong adhesion and the PLA coating can delay the penetration of aggressive ions to provide a longer protection effectively. The system provides a very good corrosion protection owing to the barrier function, ion exchange and self-healing ability.

The reported examination remarks late approaches introducing sharp anti-corrosion functionalities in protective coatings, by guest reservoirs carriers of corrosion inhibitors. LDHs, used as chloride trappers and corrosion inhibitor exchangers, provide effective corrosion inhibition, while contributing for good barrier effects. To enhance other coating properties, such as wear or abrasion resistance as reported elsewhere [127], addition of nanoparticles may contribute. This is undoubtedly an interesting area to explore in order to reach more efficient self-healing functionalities. Furthermore, the size and geometry of the defects to be healed, the number of defects and the area or volume to be protected as well the possibility of occurrence of multiple damaging events are still open questions for which very few answers exist.

Conclusions

A lot of papers are published today focusing different aspects of LDHs synthesis and/or applications in several and different fields. The present paper provided an overview of the characteristics and the main preparation routes of LDHs. Moreover, it reviews their applications to metallurgical processes and products. Since '60 they have been used in the Bayer process of alumina refinement, as demonstrated by the wide number of industrial patents. Other more recent applications regard:

i) Remediation of volatile organic compounds (VOCs) in exhaust fumes,

- ii) Heavy metal capture in liquid wastes of industrial plants,
- iii) Anticorrosion coatings.

Some examples were taken from the experimental research of the author. Moreover, when LDHs are grown on a metallic substrate, it is important the knowledge of the substrate microstructural characteristics. On the basis of previous results of the author and coworkers the paper shows how dislocation density and grain size of the aluminium substrate may affect the LDHs growth rate. Therefore, in some preparation routes metallurgy becomes of fundamental importance to control the process of LDHs growth and the final characteristics.

Finally, it is noteworthy to observe that the high frequency with which innovative applications appear is stimulated by the high versatility and low cost of LDHs and suggests that these nanomaterials could play an increasing role in metallurgy in the near future.

References

- Chen H, Zhang F, Fu S, Duan X (2006) In situ microstructure control of oriented layered double hydroxide monolayer films with curved hexagonal crystals as superhydrophobic materials. Advanced Materials 18: 3089-3093.
- Shao M, Zhang R, Li Z, Wei M, Evans DG, et al. (2015) Layered double hydroxides toward electrochemical energy storage and conversion: design, synthesis and applications. Chemical Communications 51: 15880-15893.
- Bergaya F, Lagaly G (2006) General introduction: clays, clay minerals, and clay science. Developments in clay science 1: 1-18.
- 4. Ferrell R (2007) Handbook of Clay Science. Clays and Clay minerals 55: 116-117.
- De Roy A, Forano C, El Malki K, Besse JP (1992) Anionic clays: trends in pillaring chemistry. In Expanded Clays and other microporous solids (pp: 108-169). Springer US.
- De Roy A, Forano C, Besse JP (2001) Layered double hydroxides: synthesis and post-synthesis modification. Layered Double Hydroxides: Present and Future pp: 1-39.
- Kai Y, Wu G, Jin W (2016) Recent Advances in the Synthesis of Layered, Double-Hydroxide-Based Materials and Their Applications in Hydrogen and Oxygen Evolution. Energy Technology 4: 354-368.
- Jung H, Ohashi H, Anilkumar GM, Zhang P, Yamaguchi T (2013) Zn²⁺ substitution effects in layered double hydroxide (Mg_(1-x) Zn_x)₂AI: textural properties, water content and ionic conductivity. Journal of Materials Chemistry A 1: 13348-13356.
- Long X, Wang Z, Xiao S, An Y, Yang S (2016) Transition metal based layered double hydroxides tailored for energy conversion and storage. Materials today 19: 213-226.
- Marappa S, Kamath PV (2015) Structure of the Carbonate-Intercalated Layered Double Hydroxides: A Reappraisal. Industrial & Engineering Chemistry Research 54: 11075-11079.
- Zheng S, Lu J, Yan D, Qin Y, Li H, et al. (2015) An Inexpensive Co-Intercalated Layered Double Hydroxide Composite with Electron Donor-Acceptor Character for Photoelectrochemical Water Splitting. Scientific Reports 5:12170.
- Lal M, Howe AT (1980) High proton conductivity in pressed pellets of zinc-chromium hydroxide. Journal of the Chemical Society, Chemical Communications 0: 737-738.
- Yun SK, Pinnavaia TJ (1995) Water content and particle texture of synthetic hydrotalcite-like layered double hydroxides. Chemistry of Materials 7: 348-354.
- Feitknecht W (1942) Über die Bildung von Doppelhydroxyden zwischen zweiund dreiwertigen Metallen. Helv. Chim. Acta 25: 555-569.

Citation: Richetta M (2017) Characteristics, Preparation Routes and Metallurgical Applications of LDHs: An Overview. J Material Sci Eng 6: 397. doi: 10.4172/2169-0022.1000397

- Reichle WT (1986) Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). Solid State Ionics 22: 135-141.
- Reichle WT (1985) Catalytic reactions by thermally activated, synthetic, anionic clay minerals. Journal of Catalysis 94: 547-557.
- 17. Miyata S (1983) Anion-Exchange Properties of Hydrotalcite-Like Compounds. Clays and Clay Minerals 31: 305-311.
- Boehm HP, Steinle J, Vieweger C (1977) Zn₂Cr(OH)_eX.2H₂O, new layer compounds capable of anion exchange and intracrystalline swelling. Angew Chem. 89: 265-266.
- Lopez T, Bosch P, Ramos E, Gomez R, Novaro O, et al. (1996) Synthesis and Characterization of Sol- Gel Hydrotalcites. Structure and Texture. Langmuir 12: 189-192.
- Tadanaga K, Miyata A, Ando D, Yamaguchi N, Tatsumisago M (2012) Preparation of Co-Al and Ni-Al layered double hydroxide thin films by a sol-gel process with hot water treatment. Journal of sol-gel science and technology 62: 111-116.
- 21. Chubar N, Gerda V, Megantari O, Mičušík M, Omastova M, et al. (2013) Applications versus properties of Mg-Al layered double hydroxides provided by their syntheses methods: Alkoxide and alkoxide-free sol-gel syntheses and hydrothermal precipitation. Chemical engineering journal 234: 284-299.
- 22. Jitianu M, Zaharescu M, Bălăsoiu M, Jitianu A (2003) The sol-gel route in synthesis of Cr (III)-containing clays. Comparison between Mg-Cr and Ni-Cr anionic clays. Journal of sol-gel science and technology 26: 217-221.
- Prinetto F, Ghiotti G, Graffin P, Tichit D (2000) Synthesis and characterization of sol-gel Mg/Al and Ni/Al layered double hydroxides and comparison with coprecipitated samples. Microporous and Mesoporous Materials 39: 229-247.
- Indira L, Kamath PV (1994) Electrogeneration of base by cathodic reduction of anions: novel one-step route to unary and layered double hydroxides (LDHs). Journal of Materials Chemistry 4: 1487-1490.
- Yarger MS, Steinmiller EMP, Choi KS (2008) Electrochemical synthesis of Zn– Al layered double hydroxide (LDH) films. Inorganic chemistry 47: 5859-5865.
- 26. Li Y, Zhang L, Xiang X, Yan D, Li F (2014) Engineering of ZnCo-layered double hydroxide nanowalls toward high-efficiency electrochemical water oxidation. Journal of Materials Chemistry A 2: 13250-13258.
- Scavetta E, Ballarin B, Gazzano M, Tonelli D (2009) Electrochemical behaviour of thin films of Co/Al layered double hydroxide prepared by electrodeposition. Electrochimica Acta 54: 1027-1033.
- Liu X, Ma R, Bando Y, Sasaki T (2012) A general strategy to layered transitionmetal hydroxide nanocones: tuning the composition for high electrochemical performance. Advanced Materials 24: 2148-2153.
- Fang J, Li M, Li Q, Zhang W, Shou Q, et al. (2012) Microwave-assisted synthesis of CoAl-layered double hydroxide/graphene oxide composite and its application in supercapacitors. Electrochimica Acta 85: 248-255.
- Liu J, Huang X, Li Y, Sulieman KM, He X, et al. (2006) Facile and largescale production of ZnO/Zn- Al layered double hydroxide hierarchical heterostructures. The Journal of Physical Chemistry B 110: 21865-21872.
- Guo X, Xu S, Zhao L, Lu W, Zhang F, et al. (2009) One-step hydrothermal crystallization of a layered double hydroxide/alumina bilayer film on aluminum and its corrosion resistance properties. Langmuir 25: 9894-9897.
- Guo X, Zhang F, Evans DG, Duan X (2010) Layered double hydroxide films: synthesis, properties and applications. Chemical Communications 46: 5197-5210.
- 33. Scarpellini D, Leonardi C, Mattoccia A, Di Giamberardino L, Medaglia PG, et al. (2015) Solution-Grown Zn/Al layered double hydroxide nanoplatelets onto Al thin films: fine control of position and lateral thickness. Journal of Nanomaterials.
- 34. Richetta M, Digiamberardino L, Mattoccia A, Medaglia PG, Montanari R, et al. (2016) Surface spectroscopy and structural analysis of nanostructured multifunctional (Zn, Al) layered double hydroxides. Surface and Interface Analysis 48: 514-518.
- 35. Robinson SL, Sherby OD (1970) Activation energy for lattice self-diffusion in Aluminium. Phisica Status Solidi (a) 1: K119-K122. s
- No ML, Esnouf C, San Juan J, Fantozzi G (1985) Dislocation motion in pure aluminium at 0.5 Tf: analysis from internal friction measurements. J. de Phys. 46: 347-350.

 Levenson LL (1989) Grain boundary diffusion activation energy derived from surface roughness measurements of aluminium thin films. Applied Physics Letters 55: 2617-2619.

Page 9 of 11

- Forticaux A, Dang L, Liang H, Jin S (2015) Controlled Synthesis of Layered Double HydroxideNanoplates Driven by Screw Dislocations. Nano Lett. 15: 3403-3409
- 39. Miyata S (1983) Anionic exchange properties of hydrotaicitelike compounds. Clays Clay Miner 31: 305-311.
- 40. Sato T, Okawaki A (1991) Intercalation of benzenecarboxylate ions into the interlayer of hydrotalcite. Solid State Ionics 45: 43-48.
- 41. O'Leary S, O'Hare D, Seeley G (2002) Delamination of layered double hydroxides in polar monomers: new LDH-acrylate nanocomposites. Chemical Communications 0: 1506-1507.
- Wang Q, O'Hare D (2012) Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets. Chemical reviews 112: 4124-4155.
- 43. Wu Q, Sjåstad AO, Vistad ØB, Knudsen KD, Roots J, et al. (2007) Characterization of exfoliated layered double hydroxide (LDH, Mg/AI= 3) nanosheets at high concentrations in formamide. Journal of Materials Chemistry 17: 965-971.
- Hibino T (2004) Delamination of layered double hydroxides containing amino acids. Chemistry of materials 16: 5482-5488.
- Johnston M, Clark MW, McMahon P, Ward N (2010) Alkalinity conversion of bauxite refinery residues by neutralization. Journal of Hazardous Materials 182: 710-715.
- 46. Misra S (1987) Adsorbent and substrate products and method of producing the same. US Patent 4656156 A.
- 47. Misra C (1990) Synthetic hydrotalcite. US Patent 4904457.
- Nigro WA, O'Neil GA (1991) Method for reducing the amount of colorants in a caustic liquor. US Patent 5068095 A.
- Phillips RB, Fitzgerald NM, McCormick BL (1997) Method for improving the brightness of aluminium hydroxide. US Patent 5624646.
- Schepers B, Bayer G, Urmann E, Schanz K (1977) Method for removing harmful organic compounds from aluminate liquors of the Bayer process. US Patent 4046855 A.
- Perrotta AJ, Williams F (1995) Hydrocalumite formation in Bayer liquor and its promotional effect on oxalate precipitation. Light Metals pp: 77-87.
- O'Hare DM, Fogg AM, Parkinson GM (2006) Process for regenerating a layered double hydroxide. US Patent 7,084,085 B2.
- Rosenberg SP (2010) Alumina recovery using aluminum containing layered double hydroxide. US Patent US7666373 B2.
- 54. Douglas GB (2010) Treatment or remediation of natural or waste-water. US Patent CA 2755868 A1.
- 55. Salari D, Niaei A, Hosseini SA, Aleshzadeh R, Afshary H (2010) Remediation of various naturally oxygenated volatile organic compounds (O-VOCs) by Mnand Cr-supported γ-Al2O3 nanocatalysts. Turk. J. Chem. 35: 1-10
- Decker SP, Klabunde JS, Khaleel A, Klabunde KJ (2002) Catalyzed destructive adsorption of environmental toxins with nanocrystalline metal oxides. Fluorochloro-bromocarbons, sulfur, and organophosophorus compounds. Environ. Sci. Technol. 36: 762-768.
- Lomnicki S, Dellinger B (2003) Development of supported iron oxide catalyst for destruction of PCDD/F. Environ. Sci. Technol. 37: 4254-4260.
- Ma XD, Zheng MH, Liu WB, Qian Y, Zhang B, et al. (2005) Dechlorination of hexachlorobenzene using ultrafine Ca-Fe composite oxides. J. Hazard. Mater. 127: 156-162.
- Gennequin C, Siffert S, Cousin R, Aboukaïs A (2009) Co-Mg-Al Hydrotalcite Precursors for Catalytic Total Oxidationof Volatile Organic Compounds. Top. Catal. 52: 482-491.
- Debecker DP, Gaigneaux EM, Busca G (2009) Exploring, tuning, and exploiting the basicity of hydrotalcites for applications in heterogeneous catalysis. Chemistry 15: 3920-3935.
- 61. Chang KS, Song H, Park YS, Woo JW (2004) Analysis of N2O decomposition

over fixed bed mixed metal oxide catalysts made from hydrotalcite-type precursors. Appl. Catal A 273: 223-231.

- 62. Tanasoi S, Mitran G, Tanchoux N, Cacciaguerra T, Fajula F, et al. (2011) Transition metal-containing mixed oxides catalysts derived from LDH precursors for short-chain hydrocarbons oxidation. Appl. Catal. A 395: 78-86.
- Genty E, Cousin R, Capelle S, Siffert S (2013) Influence of Gold on Hydrotalcitelike Compound Catalysts for Toluene and CO Total Oxidation. Catalysts 3: 966-977.
- 64. Carpentier J, Lamonier JF, Siffert S, Zhilinskaya EA, Aboukaïs A (2002) Characterisation of Mg/Al hydrotalcite with interlayer palladium complex for catalytic oxidation of toluene. Appl. Catal. A 234: 91-101.
- 65. Kovanda F, Rojka T, Dobešová J, Machovič V, Bezdička P, et al. (2006) Mixed oxides obtained from Co and Mn containing layered double hydroxides: Preparation, characterization, and catalytic properties. J. Solid State Chem. 179: 812-823.
- 66. Fu F, Wang Q (2010) Removal of heavy metal ions from wastewaters: a review. J. Environ. Manag. 92: 407-418.
- Nordberg GF, Fowler BA, Nordberg M, Friberg LT (2007) Introduction-general considerations and international perspectives.
- Sajid M, Ilyas M, Basheer C, Tariq M, Daud M, et al. (2015) Impact of nanoparticles on human and environment: review of toxicity factors, exposures, control strategies, and future prospects. Environ. Sci. Pollut. Res. 22: 4122-4143.
- 69. Li F, Duan X (2005) Applications of layered double hydroxides. Struct. Bond. 119: 193-223.
- Kang MJ, Chun KS, Rhee SW, Do Y (1999) Comparison of sorption behavior of I- and TcO-4 on Mg/Al layered double hydroxide. Radiochim. Acta 85: 57-63.
- 71. Toraishi T, Nagasaki S, Tanaka S (2002) Adsorption behavior of IO_3^- by CO_2^{3-} and NO-3-hydrotalcite. Appl. Clay Sci. 22: 17-23.
- Zhang M, Reardon EJ (2003) Removal of B, Cr, Mo, and Se from wastewater by incorporation into hydrocalumite and ettringite. Environ. Sci. Technol. 37: 2947-2952.
- Wang SL, Hseu RJ, Chang RR, Chiang PN, Chen JH, et al. (2006) Adsorption and thermal desorption of Cr(VI) on Li/Al layered double hydroxide. Colloids Surf. A 277: 8-14.
- 74. Yang L, Dadwhal M, Shahrivari Z, Ostwal M, Liu PKT, et al. (2006) Adsorption of arsenic on layered double hydroxides: effect of the particle size. Ind. Eng. Chem. Res. 45: 4742-4751.
- 75. Ay AN, Zümreoglu-Karan B, Temel A (2007) Boron removal by hydrotalcitelike, carbonate-free Mg-Al-NO3-LDH and a ratio- nale on the mechanism. Micropor. Mesopor. Mater. 98: 1-5.
- Liu M, Yang JJ, Wu GQ, Wang LY (2006) Performance and mechanism of Mg, Al layered double hydroxides and layered double oxides for sulfide anion (S2-) removal. Chin. J. Inorg. Chem. 22: 1771-1777.
- 77. Lv L, He J, Wei M, Evans DG, Duan X (2006) Factors influencing the removal of fluoride from aqueous solution by calcined Mg-Al-CO3 layered double hydroxides. J. Hazard. Mater. 133: 119-128.
- Paredes SP, Fetter G, Bosch P, Bulbulian S (2006) Iodine sorption by microwave irradiated hydrotalcites. J. Nucl. Mater. 359: 155-161.
- Lehmann M, Zouboulis AI, Matis KA (1999) Removal of metal ions from dilute aqueous solutions: a comparative study of inorganic sorbent materials. Chemosphere 39: 881-892.
- Seida Y, Nakano Y (2001) Removal of phosphate in dissolu- tion-coagulation process of layered double hydroxide. J. Chem. Eng. Jpn. 34: 906-911.
- Lazaridis NK (2003) Sorption removal of anions and cations in single batch systems by uncalcined and calcined Mg-Al-CO₃ hydrotalcite. Water Air Soil Pollut. 146: 127-139.
- Zhu MX, Li YP, Xie M, Xin HZ (2005) Sorption of an anionic dye by uncalcined and calcined layered double hydroxides: a case study. J. Hazard. Mater. 120: 163-171.
- Bruna F, Pavlovic I, Barriga C, Cornejo J, Ulibarri MA (2006) Adsorption of pesticides Carbetamide and Metamitron on organohydrotalcite. Appl. Clay Sci. 33: 116-124.

- 84. Li YJ, Yang M, Zhang XJ, Wu T, Cao N, et al. (2006) Adsorption removal of thiocyanate from aqueous solution by calcined hydrotalcite. J. Environ. Sci. 18: 23-28.
- Cantu M, Lopez-Salinas E, Valente JS (2005) Sox removal by calcined MgAlFe hydrotalcite-like materials: effect of the chemical composition and the cerium incorporation method. Environ. Sci. Technol. 39: 9715-9720.
- Ritter JA, Reynolds SP, Ebner AD (2005) Dynamic adsorption and desorption of carbon dioxide in potassium-promoted hydrotalcite. In Proceedings of the AIChE Annual Meeting, Cincinnati, OH, USA pp: 1702.
- Kovanda F, Kovacsova E, Kolousek D (1999) Removal of anions from solution by calcined hydrotalcite and regeneration of used sorbent in repeated calcination-rehydration-anion exchange processes. Collect. Czech. Chem. C 64: 1517-1528.
- Manju GN, Gigi MC, Anirudhan TS (1999) Hydrotalcite as adsorbent for the removal of chromium (VI) from aqueous media: equilibrium studies. Indian J. Chem. Tech. 6: 134-141.
- Marchi AJ, Apesteguia CR (1998) Impregnation-induced memory effect of thermally activated layered double hydroxides. Appl. Clay Sci. 13: 35-48.
- Yang L, Shahrivari Z, Liu PKT, Sahimi M, Tsotsis TT (2005) Removal of trace levels of arsenic and selenium from aqueous solutions by calcined and uncalcined layered double hydroxides (LDH). Ind. Eng. Chem. Res. 44: 6804-6815.
- Shin HS, Kim MJ, Nam SY, Moon HC (1996) Phosphorus removal by hydrotalcite-like compounds (HTLcs). Water Sci. Technol. 34: 161-168.
- Lazaridis NK, Pandi TA, Matis KA (2004) Chromium (VI) removal from aqueous solutions by Mg-Al-CO3 hydrotalcite: sorption-desorption kinetic and equilibrium studies. Ind. Eng. Chem. Res. 43: 2209-2215.
- Bhaumik A, Samanta S, Mal NK (2005) Efficient removal of arsenic from polluted ground water by using a layered double hydroxide exchanger. Indian J. Chem. A 44: 1406-1409.
- Peng S, Yang Y, Chen T, Jiang S, Xu H (2005) Adsorption of arsenate anion by Mg-Al anionic clay. J. Chin. Ceram. Soc. 33: 1023-1027.
- 95. Kuzawa K, Jung YJ, Kiso Y, Yamada T, Nagai M, et al. (2006) Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent. Chemosphere 62: 45-52.
- Gillman GP (2006) A simple technology for arsenic removal from drinking water using hydrotalcite. Sci. Total Environ. 366: 926-931.
- Goh KH, Lim TT, Dong Z (2008) Application of layered double hydroxides for removal of oxyanions: a review. Water Res. 42: 1343-1368.
- Nalawade P, Aware B, Kadam VJ, Hirlekar RR (2009) Layered double hydroxides: a review. Journal of Scientific & Industrial Research 68: 267-272.
- Zhao MQ, Zhang Q, Huang JQ, Wei F (2012) Hierarchical nanocomposites derived from nanocarbons and layered double hydroxides - properties, synthesis, and applications. Adv. Funct. Mater. 22: 675-694.
- 100. Cao Y, Li G, Li X (2016) Graphene/layered double hydroxide nanocomposite: properties, synthesis, and applications. Chem. Eng. J. 292: 207-223.
- 101.Daud M, Kamal MS, Shehzad F, Al-Harthi MA (2016) Graphene/layered double hydroxides nanocomposites: a review of recent progress in synthesis and applications. Carbon 104: 241-252.
- 102. Kameda T, Takeuchi H, Yoshioka T (2011) NiAl layered double hydroxides modified with citrate, malate, and tartrate: preparation by coprecipitation and uptake of Cu2 from aqueous solution. J. Phys. Chem. Solids 72: 846-851.
- 103. Yanming S, Dongbin L, Shifeng L, Lihui F, Shuai C, Haque MA (2017) Removal of lead from aqueous solution on glutamate intercalated layered double hydroxide. Arab. J. Chem 10: S2295-S2301.
- 104. Yasin Y, Ahmad FBH, Ghaffari-Moghaddam, M, Khajeh, M (2014) Application of a hybrid artificial neural network-genetic algorithm approach to optimize the lead ions removal from aqueous solutions using intercalated tartrate-Mg-Al layered double hydroxides. Environ. Nanotechnol. Monit. Manag. 2: 2-7.
- 105. González MA, Pavlovic I, Rojas-Delgado R, Barriga C (2014) Removal of Cu²⁺, Pb²⁺ and Cd²⁺ by layered double hydroxide-humate hybrid. Sorbate and sorbent comparative studies. Chem. Eng. J. 254: 605-611.
- 106. Pavlovic I, Pérez MR, Barriga C, Ulibarri MA (2009) Adsorption of Cu2+, Cd2+ and Pb2+ ions by layered double hydroxides intercalated with the chelating

agents diethylenetriaminepentaacetate and meso-2,3-dimercaptosuccinate. Appl. Clay Sci. 43: 125-129.

- 107.Xu Y, Dai Y, Zhou J, Xu ZP, Qian G, et al. (2011) Removal efficiency of arsenate and phosphate from aqueous solution using layered double hydroxide materials: intercalation vs. precipitation. J. Mater. Chem. 20: 4684-4691.
- 108. Bi B, Xu L, Xu B, Liu X (2011) Heteropoly blue-intercalated layered double hydroxides for cationic dye removal from aqueous media. Appl. Clay Sci. 54: 242-247.
- 109. Zhang X, Ji L, Wang J, Li R, Liu Q, et al. (2012) Removal of uranium (VI) from aqueous solutions by magnetic Mg-Al layered double hydroxide intercalated with citrate: kinetic and thermodynamic investigation. Colloids Surf. A Physicochem. Eng. Asp. 414: 220-227.
- 110. Ma S, Chen Q, Li H, Wang P, Islam SM, et al. (2014) Highly selective and efficient heavy metal capture with polysulfide intercalated layered double hydroxides. J. Mater. Chem. A 2: 10280-10289.
- Shan RR, Yan LG, Yang K, Hao YF, Du B (2015) Adsorption of Cd(II) by Mg-AI- CO3- and magnetic Fe3O4/Mg-AI-CO3-layered double hydroxides: kinetic, isothermal, thermodynamic and mechanistic studies. J. Hazard. Mater. 299: 42-49.
- 112. Reddy DHK, Yun YS (2016) Spinel ferrite magnetic adsorbents: alternative future materials for water purification, Coord. Chem. Rev. 315: 90-111.
- 113. Zheludkevich ML, Serra R, Montemor MF, Yasakau KA, Salvado IMM, et al. (2005) Nanostructured sol-gel coatings doped with cerium nitrate as pretreatments for AA2024-T3: Corrosion protection performance. Electrochim. Acta 51: 208 -217.
- 114. Zheludkevich ML, Serra R, Montemor MF, Ferreira MGS (2005) Oxide nanoparticle reservoirs for storage and prolonged release of the corrosion inhibitors. Electrochem. Commun. 7: 836-840.
- Buchheit RG, Mamidipally SB, Schmutz P, Guan H (2005) Active Corrosion Protection in Ce-Modified Hydrotalcite Conversion Coatings. Corrosion 58: 3-14.
- 116. Poznyak SK, Tedim J, Rodrigues LM, Salak AN, Zheludkevich ML, et al. (2009) Novel Inorganic Host Layered Double Hydroxides Intercalated with Guest Organic Inhibitors for Anticorrosion Applications. ACS Appl. Mater. Interfaces 1: 2353-2362.

- 117. Zheludkevich ML, Poznyak SK, Rodrigues LM, Raps D, Hack T, et al. (2010) Active protection coatings with layered double hydroxide nanocontainers of corrosion inhibitor. Corrosion Science 52: 602-611.
- Zheludkevich ML, Tedim J, Ferreira MGS (2012) "Smart" coatings for active corrosion protection based on multi-functional micro and nanocontainers. Electrochim. Acta 82: 314-323.
- 119. Snihirova D, Liphardt L, Grundmeier G, Montemor MF (2013) Electrochemical study of the corrosion inhibition ability of "smart" coatings applied on AA2024. J. Solid State Electrochem. 17: 2183-2192.
- 120. Tedim J, Kuznetsova A, Salak AN, Montemor MF, Snihirova D, et al. (2012) Zn-Al layered double hydroxides as chloride nanotraps in active protective coatings. Corros. Sci. 55: 1-4.
- 121.Javierre E, García SJ, Mol JMC, Vermolen FJ, Vuik C, et al. (2012) Tailoring the release of encapsulated corrosion inhibitors from damaged coatings: Controlled release kinetics by overlapping diffusion fronts. Prog. Org. Coat. 75: 20-26.
- 122.Zhang H, Zhang H, Zhou LY, Eger C, Zhang Z (2013) Abrasive wear of transparent polymer coatings: considered in terms of morphology and surface modification of nanoparticles. Compos. Sci. Technol. 88 : 151-157.
- 123. Roussi E, Tsetsekou A, Skarmoutsou A, Charitidis CA, Karantonis A (2013) Anticorrosion and nanomechanical performance of hybrid organo-silicate coatings integrating corrosion inhibitors. Surf. Coat. Technol. 232 : 131-141.
- 124. Montemor MF, Snihirova DV, Taryba MG, Lamaka SV, Kartsonakis IA, et al. (2012) Evaluation of self-healing ability in protective coatings modified with combinations of layered double hydroxides and cerium molibdate nanocontainers filled with corrosion inhibitors. Electrochim. Acta 60: 31-40.
- 125.Zeng RC, Li XT, Liu ZG, Zhang F, Li SQ, et al. (2015) Corrosion resistance of Zn-Al layered double hydroxide/ poly (lactic acid) composite coating on magnesium alloy AZ31, Front. Mater. Sci. 9: 355-365.
- 126. Mattoccia P, Bernardone E, Digiamberardino L, Gaudio P, Malizia A, et al. (2015) Studio morfologico di nanostrutture di Layered Double Hydroxides (LDH) depositate su film sottili di alluminio. La Metallurgia Italiana 9: 15-21.
- 127.Kartsonakis IA, Athanasopoulou E, Snihirova D, Martins B, Koklioti MA, et al. (2014) Multifunctional epoxy coatings combining a mixture of traps and inhibitor loaded nanocontainers for corrosion protection of AA2024-T3. Corros. Sci. 85: 147-159.

Page 11 of 11