https://doi.org/10.52676/1729-7885-2022-4-17-29
УДК 541.73:547.458.81

THE SYNTHESIS METHODS AND APPLICATIONS OF LAYERED DOUBLE HYDROXIDES – A BRIEF REVIEW

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Layered double hydroxides (LDHs) which are one type of layered material are promising materials due to some of their interesting properties, such as ease of synthesis, unique structure, uniform distribution of different metal cations in the brucite layer, surface hydroxyl groups, flexible tunability, intercalated anions with interlayer spaces, swelling properties, and high chemical and thermal stability, ability to intercalate different type of anions, and also high biocompatibility. This review article is focused on more information about synthesis methods of layered double hydroxides, and their applications in many fields. The most common synthesis methods for layered double hydroxides are co-precipitation, urea hydrolysis, hydrothermal synthesis, sol-gel, reconstruction, etc. are discussed. LDHs shows excellent performance as a multifunctional material for its promising applications in the fields of catalysts, water treatment, flame retardants, polymer additivies, adsorbents, nuclear industry, environmental protection, photocatalysts, and material science.

Keywords: *layered double hydroxide, co-precipitation, hydrothermal synthesis, sol-gel method, sonochemical synthesis.*

1. INTRODUCTION

Layered double hydroxides (LDHs) are a family of natural and synthetic materials having a general formula of $[M(II)_{1-x}M(III)_X(OH)_2](A^{n-}_{x/n})\cdot nH_2O$. M (II) and M (III) are divalent and trivalent metals, respectively, and $A^{n-}$is the anion between the layers. Where divalent metals can be Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, etc. Trivalent metals can be Al^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, Mn^{3+}, etc. Many anions can be used, including Cl^-, NO_3^-, CO_3^{2-}, and many organic anions. LDHs are also known as hydrotalcite-like compounds or anionic clays [1–5]. LDHs often find application in pharmaceuticals, as polymer additives, adsorbents, supercapacitors, and in catalysis. This is due to having variable layer charge density, reactive interlayer space, ion exchange capabilities, a wide range of chemical compositions, and rheological properties [6]. LDH materials can be synthesized using different techniques, of which the most common are used methods such as co-precipitation, hydrothermal synthesis, urea hydrolysis, sol-gel, mechanochemical, sonochemical, ion exchange, and reconstruction methods [7]. Layered double hydroxides have prominent properties for example unique structure, mixed metal hydroxide layers, exterior hydroxyl groups, ease of synthesis, electrochemical activity, non-toxicity, flexible anions and cations tunability, biocompatibility, remarkable chemical and thermal stability, high surface, superb anion exchangeability, the sustainable transmission of intercalated anions [8–10]. Because of these properties, pure layered double hydroxides embedded with functional materials and layered double hydroxide nanocomposites, particularly carbon-based graphene becoming popular materials for wide applications [11]. In this review paper, we could get more information about different synthesis methods of LDHs and applications in many fields.

2. SYNTHESIS METHODS OF LDHS

2.1. Co-precipitation method

Co-precipitation method is commonly used procedure for preparing LDHs because it produces large amount of material and is easy to handle at laboratory level. It has been used extensively for the one-pot direct synthesis of LDHs containing a variety of layer cations and interlayer anions [12].

The synthesis of LDHs with co-precipitation method can be applied at both constant and variable pH. This method offers great freedom in choosing the interlayer anions. LDHs with a great variety of both metal ions and interlayer anions can be synthesized with this technique [12]. To assure precipitation of the metal ions, it is necessary to control the pH in the solution such that the reaction takes place under supersaturated conditions. Layered double hydroxides are prepared at low and high supersaturation conditions.

Precipitation at low supersaturation

Precipitation at low supersaturation requires slow addition of divalent and trivalent metals salt in the chosen ratio into aqueous solution containing desired anion, and pH is maintained at selected value. A second solution of an alkali is added into the mixture salts solution simultaneously at such a rate as to maintain the pH at a selected value leading to facilitate homogeneous precipitation of the two metallic salts [13]. The anion that is to be introduced should have a high affinity for the LDH layers and be present in excess, otherwise the counter-anions of the metal salts may be incorporated by competing reactions. Consequently, metal nitrate and chloride salts are commonly used because of the low selectivity of LDHs toward these anions. Furthermore, LDHs have a high affinity for carbonate anions and hence, unless this is the target anion, reactions are generally carried out under nitrogen in order to avoid absorption of atmospheric carbon dioxide which would generate carbonate ions in situ [14]. One advantage of this method is that in many cases it allows careful control of the charge density (M^{2+}/M^{3+} ratio) of the hydroxide layers of the resulting LDH by means of precise control of the solution pH. The second advantage is that low supersaturation conditions usually give rise to precipitates with higher crystallinity than those obtained under high supersaturation conditions, because in the former situation the rate of crystal growth is higher than the rate of nucleation [14, 15].

Precipitation at high supersaturation

High supersaturation of LDHs precipitation was performed by the instantaneous addition of mixed M^{2+}/M^{3+} salt solution into an alkali solution containing desired interlayer anion. Preparations under conditions of high supersaturation generally give rise to less crystalline materials, because of the high number of crystallization nuclei. Because this method leads to a continuous change in the pH of solution, the formation of impurity $M(OH)_2$ and/or $M(OH)_3$ phases, and consequently an LDH product with an undesired M^{2+}/M^{3+} ratio, often results [16]. Thermal treatment performed following co-precipitation may help increase the crystallinity of amorphous or badly crystallized materials. Hence the synthesis of LDHs at high supersaturation method is less common than low supersaturation for the preparation of LDHs materials [17].

In general, this is achieved by holding the pH equal to or higher than the pH necessary for precipitation of the most soluble metal hydroxide [18]. The concentration of base solution during precipitation and the nature of base solution can also affect the hydrotalcite formation. Depending on the precipitation conditions, well-crystallized hydrotalcite or amorphous materials can be obtained [19]. These conditions are pH of the reaction, medium, concentration of the base solution, nature of the base solution, aging time and aging temperature, total cation concentration, and M^{2+}/M^{3+} molar ratios.

The variation of the compositional gradient in the co-precipitated LDH is narrower as the precipitation conditions are constant. This is achieved by careful control of solution pH. Table 1 lists pH values for precipitation of hydroxides of the most common LDHs [20].

Table 1. Preparation of Layered Double Hydroxides: pH values of precipitation of some M(III) and M(II) hydroxides

Cation	pH at 10^{-2} M	pH at 10^{-4} M	pH at which hydroxide re-dissolves	Reference
Al^{3+}	3.9	8.0	9.0–12.0	[9]
Cr^{3+}	5.0	9.5	12.5	[16]
Cu^{2+}	5.0	6.5		[7]
Zn^{2+}	6.5	8.0	14	[15]
Ni^{2+}	7.0	8.5		[5]
Fe^{2+}	7.5	9.0		[10]
Co^{2+}	7.5	9.0		[11]

An advantage of this method is that it allows good control of the cation composition in the brucite-like layers. The effect of pH is considered in this review since LDH for different metal salts can be formed at different. Another advantage of this method offers an LDH product with better crystallinity than the similar method of high supersaturation. This is because the rate of crystal growth is higher than the rate of nucleation in low supersaturation conditions [21]. This method is often done by the slow addition of metal nitrate solutions to a solution of hydroxide and carbonate. The crystallite size distribution is wider when there is no additional aging step reported by Valim [22]. Pinnavia and co-workers compared the aging step with the level of crystallinity of hydrotalcite and found there was an enhancement in crystallinity [23] with increased aging time. There was no correlation, however, between base catalytic activity and improved crystallinity. Zhao et al. [24] synthesized MgAl-LDHs with the different Mg:Al molar ratios by co-precipitation method. The precipitation was done at 100°C. After precipitation, the slurry was aged at 100°C for 2, 6, or 13 h. XRD patterns of the MgAl-LDH with the Mg:Al molar ratio of 3 exhibited the characteristic reflections of the hydrotalcite phase. The peaks became narrower with the increase of aging time indicating that the crystallite size increased. The average crystallite size is estimated by using the Scherrer equation [25, 26]:

$$D = \frac{\alpha\lambda}{\beta\cos\theta} \qquad (1)$$

Where, D is the crystallite size, R is the Scherrer constant (R = 0.89), λ is the wavelength of the incident radiation (λ=0.1542 nm), and β is the FWHM value for the peak at the Bragg diffraction angle θ. The crystallite size increases with the aging time (Table 2).

Table 2. Crystallite size depending on aging time and aging temperature [19]

Sample	Aging time, h	Aging temperature, ℃	D, nm
Mg_3Al-LDH	2	100	23.6
	6		28.6
	13		31.9
Mg_2Al-LDH	6	40	11.8
		60	15.1
		100	31.0

A large variety of LDH systems have been reported successfully synthesized with the co-precipitation method, both di-metallic and multi-metallic systems are reported, including LDHs such as NiMn-CO_3, MgAl-CO_3, NiAl-CO_3, CoMnAl-CO_3, CoMnMgAl-CO_3 and NiCrAl-CO_3 [27].

2.2. Urea hydrolysis method

The urea hydrolysis method is frequently used for synthesis of highly crystalline LDHs to use a urea solution, which gradually hydrolyses to release hydroxide ions and allows an extremely fine control over precipitation. Urea was used as an agent for precipitation from “homogeneous” solution very attractive, and it has long been used in gravimetric analysis to precipitate several metal ions as hydroxides or as insoluble salts when in the presence of a suitable anion [23]. Urea hydrolysis rate can be controlled by the reaction temperature. Hydrolysis of urea proceeds in two steps, the formation of ammonium cyanate (NH_4CNO) as the rate determining step, and the fast hydrolysis of the cyanate to ammonium carbonate [28].

$$\mathrm{CO(NH_2)_2} \rightarrow \mathrm{NH_4CNO} \qquad (2)$$

$$\mathrm{NH_4CNO} + 2\mathrm{H_2O} \rightarrow 2\mathrm{NH_4^+} + \mathrm{CO_3^{2-}} \qquad (3)$$

Hydrolysis rate of urea can be adjusted by controlling the applied temperature during reaction. The hydrolysis of ammonium carbonate gives pH of about 9 which is suitable for precipitating a wide variety of metal hydroxides. Since the working pH for the co precipitation of LDHs is in the range of 9–11, urea is a good candidate for the synthesis of LDHs. On the other hand, the urea method is an ideal way for the preparation of LDHs since during hydrolysis ammonia liberates the hydroxide and carbonate anions which are the main components of LDHs [29]. The compounds prepared using this method display homogeneous sizes and platelet-like primary particles with well-defined hexagonal shapes, crystallinity and specific surface area are observed to increase by using urea, which may be very interesting from the viewpoint of nanotechnology since LDHs offer nano-size two-dimensional spaces for the creation of functional materials [28]. The degree of crystallinity of LDHs depends on the synthesis temperature and decomposition rate. At low temperatures, large particles are formed due to the slow nucleation and slow decomposition rates of the urea [24]. The urea hydrolysis method is uniquely used in the synthesis of LDHs with a high charge density [25].

The hydrolysis of urea can easily be controlled by controlling the temperature [26]. The rate constant increases by about 200 times when the temperature is increased from 60 to 100 °C [27]. Oxidation states of the metal cations can be controlled by the addition of oxidizing agents such as ammonium persulfate [28]. Typically, the pH of the solution is controlled to be in the area of pH = 6-10, which is where precipitation of most LDHs will occur. The urea method favors the growth of larger particles than the earlier mentioned co-precipitation method. The urea method consequently yields products with much higher crystallinity [32]. A disadvantage is that the formation of LDHs with the urea method will nearly just give carbonate as the interlayer anion because of its high affinity for carbonate. However, the relatively gradual way in which the pH increases with urea hydrolysis is not always advantageous. For example, most divalent cation nitrates will precipitate as hydroxides quite readily using urea but trivalent cations, except aluminum, will not. A. Inayat et al. [30] have recently reported a direct synthesis of ZnAl-LDHs with nitrate as the interlayer anion using the urea hydrolysis method. This is achieved by careful control of the pH of the solution and by adding an excess of nitrate, the intercalation of the interlayer anion can be manipulated to other interlayer anions such as nitrate, as well.

Costantino et al. [31] prepared M(II)/Al-carbonate LDHs (M(II) = Mg, Zn, and Ni) by this method. The effects of varying the temperature, total metal cation concentration, molar fraction Al/Al+M(II), and molar fraction urea/M(II)+Al in solution on the composition and the crystallinity of the samples were investigated. The optimum conditions to prepare LDHs with a good crystallinity in a relatively short time using a simple procedure were suggested to involve dissolving solid urea in a 0.5 M solution of the chosen metal chlorides to give a urea/metal ion molar ratio of 3.3. The clear solution was maintained at 100◦C for 36 h. The urea method is not suitable for the preparation of Mg/Al-LDHs with low charge density but allows the preparation of compounds with high charge density not easily obtainable using other procedures [32]. Adachi-Pagano et al. [33] prepared mono-disperse sub-micron-sized Mg/Al-LDHs by the urea hydrolysis method, and the results were compared to the constant pH co-precipitation method. The compounds prepared using the urea method displayed platelet-like primary particles with a hexagonal shape.

2.3. Hydrothermal method

The hydrothermal method is usually used when organic guest species with low affinity for LDHs are required to be intercalated into the interlayers, and when the ion exchange and co-precipitation techniques are ineffective in this case. Hence hydrothermal synthesis has proven efficient because this method ensures no competing anion in the interlayer other than the intended by making insoluble hydroxides as inorganic source. The key features of this method is utilized to control particle size and its distribution [13]. Hydrothermal approach is usually carried out to improve crystallinity and is studied for Mg-Al-LDHs. It is found that increase in LDH crystal size results in improved crystallinity of hydrothermally treated samples. One advantage of hydrothermal method, when compared with other co-precipitation ones, is to avoid undesirable waste discard which may be harmful to the environment for instance NO_3^-, OH^-, Cl^-, etc. [15].

The method follows two synthesis routes. The first route is where the materials are prepared at temperatures above 373 K in a pressured autoclave. Here, the LDHs are synthesized from MgO and Al_2O_3 precursors or mixtures formed through the decomposition of the precursor nitrate compounds [34, 35]. In the other synthesis route, LDHs are prepared at low temperatures and are also subjected to a process of aging. During the aging process, the LDH precipitate is refluxed at a specific temperature for 18 h.

Hydrothermal synthesis is effective in such cases because insoluble hydroxides, for example, magnesium and aluminum hydroxides can be used as the inorganic sources ensuring that the desired anions occupy the interlayer space since no other competing anions are present [36, 37]. Hydrothermal synthesis has been used to control the particle size and its distribution when soluble magnesium and aluminum salts were used together with an alkali solution to prepare Mg/Al-carbonate LDHs [38, 39], but is particularly useful when LDH-like materials are prepared using powders as starting materials. Single crystals of a layered compound with the formula $3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O$ were synthesized by a hydrothermal process using $Ca(OH)_2$, $Al(OH)_3$, and $CaCO_3$ as starting materials, with a molar ratio of 3.5:2:0.5 [40]. It was found that the hydrothermal temperature influenced the crystal structure of the resulting material. An ordered structure was obtained at 120◦C, and a disordered one at 100◦C. Both disordered and ordered structures have identical main layers $[Ca_4Al_2(OH)_{12}]^{2+}$, but they have different arrangements of water molecules and carbonate groups forming the interlayer region of composition.

2.4. Ion-exchange method

Ion-exchange method is also a commonly used method for the synthesis of LDHs composites and has been effectively useful for the intercalation of a number of different types of anions. The anion exchange method is useful when the co-precipitation method is inapplicable, in particular when the chosen divalent or trivalent metal cations or the anions involved are unstable in the alkaline solution, or when there is a strong possibility of interaction between the guest species and the metal ion [38]. It is also known as the first LDHs are prepared by co-precipitation method with host anions, most commonly NO_3^-, CO_3^{2-}, and Cl^- as the exchange is easier than multi charged anions. In the later stages, anions present in the interlayer region are exchanged with the preferred anions by stirring the LDH precursor in a solution containing an excess of the anion to be intercalated. To avoid carbonate intercalation the whole process of anion-exchange should be carried out under inert atmosphere [13, 15]. Owing to the fact that the process is reversible, LDHs can be incorporated into polymers after intercalation to improve the chemical and physical properties of the materials, that is, the thermal stability and optical and magnetic properties, and also to change the surface properties of the host from hydrophobic to hydrophilic [15]. The host–guest exchange generally depends on the electrostatic forces between positively charged LDH layers and the exchanging anions. Target anions can be intercalated in two possible ways, as described in the equations [38]:

$$LDH\cdot A^{m-} + X^{n-} \rightarrow LDH\cdot (X^{n-})_{m/n} + A^{m-} \quad (4)$$

There exists weak electrostatic interaction with layers, and hence these anions can be easily replaced by anions with higher electrostatic interaction with layers [39]. Figure 1 shows the schematic representation of ion-exchange method. There are several factors which determine the extent of ion-exchange in any given case:

Affinity for incoming anion

The exchange efficiency varies depending on the ability of the exchanged anions to stabilize the lamellae and/or to their proportion with respect to the LDHs precursor anion. Generally, the exchange ability of incoming anions increases with increasing charge and decreasing ionic radius. The order of intercalation is as follows: $CO_3^{2-} > HPO_4^{2-} > SO_4^{2-}$ for divalent anions and $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ for monovalent anions. The co-intercalation of a second anion was found to have no effect on the order of ion exchange preference. Because nitrate is exchanged most easily, nitrate pillared LDHs are usually used as the precursors for ion exchange [40].

Exchange medium

The appropriate solvent will favor the anion-exchange process. The interlayer space of LDHs can be expanded to some extent in a suitable solvent medium, which favors the ion exchange process. For example, in aqueous medium favors the exchange by inorganic anions, whilst an organic solvent favors exchange by organic anions [39].

pH value

The working pH should be 4.0 or above 4.0. A low pH value therefore favors liberation of the original anion as the conjugate acid and incorporation of a less basic anion from solution and the hydroxyl layers will break [40].

Chemical composition of the layers

The chemical composition of the LDH sheets influences the charge density of the sheets and the hydration state, thereby affecting the ion exchange process. Some other factors such as temperature also have an impact on the ion exchange process. Anion-exchange process will be more favorable at high temperatures. However, that too high a temperature might have an adverse effect on the structural integrity of the LDHs. Moreover, this method depends on the chemical composition of the brucite type layers [41].

The ion-exchange method is especially useful when the co-precipitation method is inapplicable such as when, for example, the divalent or trivalent metal cations or the anions involved are unstable in an alkaline solution, or the direct reaction between metal ions and guest anions is more favorable. In this method, the guests are exchanged with the anions present in the interlayer regions of preformed LDHs, as shown in figure 1 to produce specific anion pillared LDHs. In thermodynamic terms, ion exchange in LDHs depends mainly on the electrostatic interactions between the positively-charged host sheets and the exchanging anions and, to a lesser extent, on the free energy involved in the changes of hydration [42–44].

This method was first proposed by Bish [45], who demonstrated the anion exchange of carbonate by chloride, nitrate, bromide, and sulfate. Several factors determine the extent of ion exchange [41] such as affinity

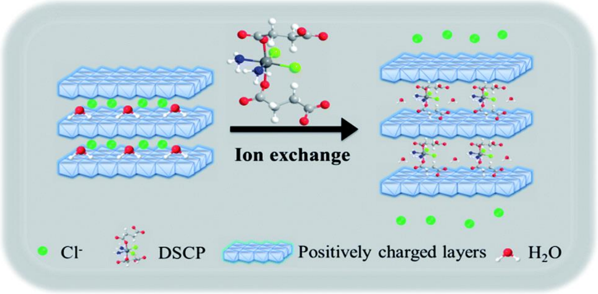

Figure 1. Schematic illustration of loading cisplatin prodrug DSCP to LDH through ion exchange [44]

for incoming anion, exchange medium, pH value, and chemical composition of the layers

2.5. Synthesis of LDHs by sol-gel method

In this method, is initially the formation of a sol by hydrolysis and partial condensation of a metallic precursor is then followed by the gel formation. Metallic alkoxides, acetates, or acetylacetonates, as well as many inorganic salts can be used as metallic precursors. The properties of the obtained solid LDHs depend on the hydrolysis and condensation rates of the metallic precursors and can be tuned by controlling different reaction parameters such as pH, nature and concentration of the metallic precursors, solvent and the temperature of synthesis [44].

The sol-gel method has several advantages over traditional methods:

(1) low temperature processing and consolidation is possible

(2) smaller particle size and morphological control in powder synthesis

(3) the homogeneity and structural properties of the resulting solids are controllable at the synthesis level by simply varying the composition of the precursors, temperature, aging time, and removal/addition of reactant species. The material prepared by sol–gel method has well controlled pore sizes, high specific surface area and high purity [45]. However, currently, it is the less exploited method.

The sol-gel method forms LDHs with a larger surface area than those formed by the co-precipitation method [43]. However, properties such as basicity as well as the divalent and trivalent metal ion molar ratios of LDHs synthesized with the sol-gel method are still not understood [48–50]. The sol-gel method is a low-cost, simple preparation method and efficient wet-chemical method of high-purity metal oxide materials from LDH precursors through hydrolysis and condensation processes [51]. LDHs are prepared by the sol-gel process, the mechanism shows the formation of sol during hydrolysis and the partial condensation of a metallic solution which is the first step, and the second step is followed by gel formation. Hence, metallic alkoxides, acetates, acetyl acetates, and inorganic salts are used as metallic precursors. The interesting properties of the resulting solid LDHs depend on certain defined parameters, such as hydrolysis and slow condensation of metallic precursors, that are finely tuned by regulating different reaction parameters adopted such as pH, the concentration of the metallic precursors, solvent, and temperature. The materials synthesized by the sol-gel method show pore sizes that are well controlled and have a high specific surface area as reported by Yang et al. [52].

2.6. Reconstruction method

Reconstruction method is based on “memory effect” of some LDH. This method involves calcination of LDHs. Calcination is a process of heating to high temperatures in inert atmosphere to remove the interlayer water, anions, and breakdown partially the hydroxyls from lamellae and convert interlamellar anion into volatile, forming a double oxyhydroxide. After calcined, a solution containing the anion of interest is added, regenerating the LDHs by hydrolysis and the new intercalated anion. In general, during regeneration process, pH is raised, so it must be corrected to avoid hydroxyl from occupying the interlayer space [49, 50]. This is the method of choice when large anions should be intercalated into LDH or when the chosen anions are not favored for intercalation by ion exchange method. The incorporation of competing anions is also limited, even if particular care should be paid to the pH value that when raises too much can favor the OH^- insertion [52].

This is the most necessary and interesting method which has the advantages of the “memory effect” of LDHs. In detail, these materials, once heated at elevated temperatures of about 650°C in inert conditions, result in the formation of a mixture of metal oxides that are easy to regenerate the hydroxide layers when exposed to water. These are highly applicable in base-catalyzed reactions such as Aldol, Michael, and Wittig reactions [53]. The prepared LDH-CO_3 are thermally decomposed to a mixture of oxides which is easily dispersed in the desired anion solution under inert conditions in deionized water to avoid CO_3^{2-} contamination. This is the common method used when larger anions have to be intercalated in LDHs [54]. The incorporation of competing anions is also restricted, depending on parameters such as pH value which increases leading to favor the OH^- formation. Various examples have been reported in the literature, such as pesticides, vitamins, and antibiotics [55, 56].

2.7. Sonochemical method

In a sonochemical method, LDHs are prepared by the co-precipitation method followed by sonochemical treatment. In the first step, the co-precipitation method is performed in the latter as explained fully above. In the second step after successful completion of mixing, the resultant solution is subjected to ultrasound irradiation at a given time and temperature. The solid precipitate is filtered, washed thoroughly with deionized water, and put in an oven overnight for further drying. This sonochemical method is best described as a synthetic and

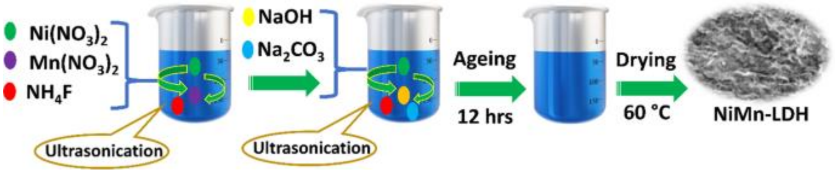

Figure 2. One-step sonochemical synthesis of NiMn-LDH for supercapacitors [60]

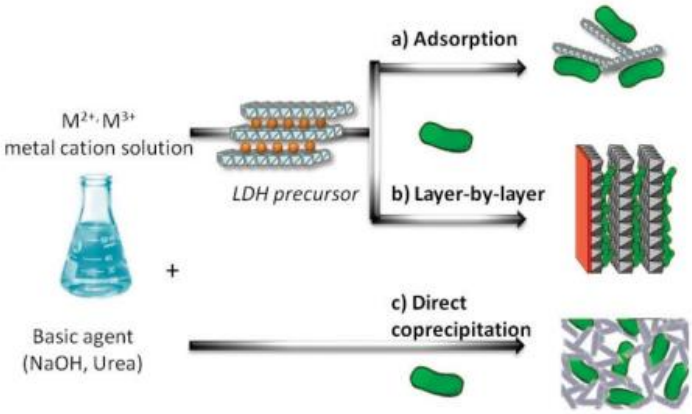

Figure 3. Schematic representation of (a) adsorption method, (b) layer-by-layer deposition and (c) direct co-precipitation method of layered double hydroxide (LDH) [62]

high-intensity ultrasonic/three-fold acoustic cavitation phenomenon that assists in improving the crystallinity of LDH phases [57, 58]. When the solution mixture is subjected to ultrasonic irradiation, rapid movement of the fluid leads to a three-fold acoustic cavitation phenomenon (Figure 2) in which microbubbles undergo nucleation formation, growth, and implosive collapse [59]. The formation of microbubbles produced a distinctive hot spot due to the compressional heating induced by collapsing of the bubble and therefore yields the bubble with extremely high temperature, pressure, and cooling rates [60].

2.8. Adsorption and Layer-by-Layer method

In this case, adsorption (Figure 3, a) can be referred to as the adhesion of divalent and trivalent ions from a liquid or dissolved solid to surface of the LDH adsorbent. This creates a film of the adsorbate over the surface in many processes like chemical, physical, biological and natural systems and widely used in various industrial applications [61]. The adsorption process may occur through weak van der Waals forces (physisorption) or covalent bonding (chemisorption) and also may occur due to electrostatic attraction between the adsorbate and surface of the adsorbent. It is a surface phenomenon most widely adopted in wastewater treatment for removal of various organic contaminants from aqueous solution.

Layer-by-layer (LBL) assembly (Figure 3, b) is a universal method for coating substrates with polymers, colloids, biomolecules, and even cells. This presents superior control and versatility when compared to other thin film deposition techniques in certain research and industrial applications. The LBL technique is known to support electrostatic interactions between positively charged layers and negatively-charged molecules and leads to nanostructured thin films [63]. This LBL deposition technique has three types of methods known as (I) the dipping layer-by-layer deposition technique (dipping-LBL); (II) spray layer-by-layer deposition method (spray-LBL) and (III) spin layer-by-layer deposition method (spin-LBL) method. Dipping-LBL is executed by chronologically adsorbing opposite charged materials onto a substrate via enthalpic and entropic driving forces [64]. In this method, the time depends on both the diffusion and adsorption of molecules, solutions or suspensions. Spray-LBL is a deposition technique where divalent and trivalent solutions are sprayed onto a vertical substrate, and the layer is formed after completion of drying in an oven overnight [58]. In spin-LBL method, the solutions or suspensions are deposited on a substrate attached to a spin coater, and the rotation speed generates a high centrifugal force. Thus, high rotational speed with high airflow rate at the surface leads to fast drying times of the liquid which in turn quickly and easily produce very uniform layers or thin films. In both spray-LBL and spin-LBL methods, the total time does not depend on the diffusion of molecular species.

3. APPLICATIONS OF LDHS

Layered double hydroxides known as anionic clays or hydrotalcite materials have attracted increasing attention in recent years. These materials are of interest as catalysts and catalyst precursors and supports [61], as ceramics precursors, as hosts for photoactivation and photocatalysis [63], as anion exchangers [64], as traps for anionic pollutants including some kinds of nuclear waste [65], as flame retardants [66], and additives for polymers [67]. Additionally, much work has been done in preparing noble metal-containing catalysts by the calcination of LDHs carrying the metal in question. For example, Mg-Al LDHs have been prepared with intercalated hexacyanoruthenate (II) anions. Layered double hydroxides have anion exchange capacity, and the ability to capture organic and inorganic anions make makes them unique as inorganic materials. Our review deals with the current and potential applications of these materials, including in catalysis, ion exchanges, pharmaceutics, water treatment, nanomedicine, flame retardants, photochemistry, polymer additives, and electrochemistry. LDHs are 2D materials with great potential [68]. Their structural and morphological characteristics can foresee future even wider employment [69].

3.1. Catalysts

The LDHs structure is well-known as an effective solid catalyst. Zhang et al. used the Cu^{2+}-based LDH powder as a catalyst for wet oxidation [70] and reported that the array of active Cu^{2+} centers on the surface of CuZnAl-LDH is ordered net shaped, which is influenced by the effect of the ordered cross trap. The advantages of novel LDH films can overcome the problems of the use of powdery catalysts on an industrial scale, such as high-pressure drop and difficult catalyst separation. Lv et al. reported that the activated MgAl-LDH film was promising to be used as a precursor to synthesize monolithic catalyst for the aldol condensation of acetone and other base-catalyzed reactions [71]. Velu and co-workers. reported that Mg/Al mixed oxides derived by calcination of LDHs catalyzed the diastereoselective synthesis of nitroalkanes from aldehydes, these facile hydrogenation reactions, which occur with retention of configuration, allow the formation of pharmacologically important derivatives [72, 73]. Recently, the Mg/Zn/Al/Fe mixed oxides obtained from an LDH precursor gave ethylbenzene conversion as high as 53.8% and a styrene selectivity of 96.7% at 773 K in the dehydrogenation of ethylbenzene reported by Gao [74]. The high catalytic activity and stability of the Mg/Zn/Al/Fe catalyst were attributed to the presence of a large number of strong acid sites and a moderate number of base sites on the catalyst. Higher content of iron oxide species favors the redox cycle and also enhances the dehydrogenation activity [75].

MgAl-LDHs has been studied by Choudary et al. [75] as support for metals, e.g. nanopalladium (0). These catalysts were prepared by ion-exchange with $PdCl_4^{2-}$ followed by reduction. Choudary et al. found that using this material in ionic liquids the catalysts has higher activity and selectivity than the homogeneous $PdCl_2$ system in the Heck olefination of electron-poor and electron-rich chloroarenes. In addition, these catalysts showed higher activity in the C-C coupling reactions of chloroarenes than other heterogeneous catalysts with nanopalladium (0) on supports as alumina or silica [75]. Additionally, LDH supported rhodium(0) catalyst was effectively used in the Heck, Suzuki and Stille cross-coupling of haloarenes. Catalyst could be easily removed and reused in several cycles [77].

3.2. Water Treatment

Wastewater often contains oxyanions such as $F^–$, $Cl^–$, $Br^–$, $PO_4^{3–}$, which are harmful to both humans and wildlife. Enhanced ability to remove oxyanions is of importance in environment protection. Structured LDHs is one new type of promising material due to their ability to capture organic and inorganic anions which can be used in water treatment. Calcined LDH powder is also an important type of material used in water treatment since LDH can afford mixed metal oxides and has a special property called the memory effect. The main advantages of LDHs over conventional anionic exchange resins include their higher anion exchange capacity for certain oxyanions and their good thermal stability. Furthermore, LDHs can be fully regenerated in a short time for reuse. Lv et al. used MgAl-NO_3-LDH powder [71] and calcined powder [76] to remove $F^–$, $Cl^–$, $Br^–$, and $I^–$, and concluded that the rate constant for exchange of nitrate anions by halide decreases in the order of $F^– > Cl^– > Br^– > I^–$, following pseudo-second-order kinetic models. The novel and well-dispersed nanocrystals of LDH on the paper substrate without aggregation were considered to provide a large specific surface area as well as good accessibility, underlying the superior adsorption performances of the film sample [77].

3.3. Flame retardants

The LDHs is also commercially promising as an additive in flame retardants. Many flame retardants are considered harmful, having been linked to liver, thyroid, reproductive, and neurological effects. Currently, halogen-free alternatives are one active research area. LDHs have been widely investigated as additives in this context. Compared to other flame retardants [78], LDH is a new type of material due to high smoke suppression, nontoxicity, or low toxicity. LDH is currently explored as a second-generation flame retardant with enhanced properties by either modification of the layers or intercalation of different anions. Lin et al. found that a borate-pillared MgAl-LDH with ethylene vinyl acetate (EVA) as the polymer component was a promising flame retardant [79]. By tuning the composition of the layers, the flame retardancy of LDHs was steered. For example, ternary ZnMgAl-LDH showed better flame retarding properties than binary MgAl-LDH [79].

LDHs as stabilizing agents for PVC and other polymers Chlorine-containing polymers such as poly(vinyl chloride) PVC undergo an autocatalytic dehydrochlorination reaction under the influence of elevated temperatures or UV radiation. Since the HCl originating from the de-hydrochlorination of the PVC chains is believed to sustain this autocatalytic process, stabilizers that irreversibly bond HCl can thus inhibit the degradation. Heavy metal compounds such as cadmium stearate or lead stearate are currently used for this purpose; alternatives are required however in the light of environmental concerns associated with the use of heavy metals. LDHs have been employed to good effect and, indeed, the largest current commercial application of LDH materials is in the polymer industry, mainly to stabilize PVC [80].

3.4. LDHs as additives in functional polymer materials

Chlorine-containing polymers such as polyvinylchloride (PVC) undergo an autocatalytic dehydrochlorination reaction under the influence of elevated temperature and UV radiation. Since the HCl originating from the dehydrochlorination of the PVC chains is believed to sustain this autocatalytic process, stabilizers that irreversibly bond HCl can thus inhibit the degradation. Heavy metal compounds such as cadmium stearate or lead stearate are currently used for this purpose. However, alternatives are required due to environmental problems associated with the use of heavy metals. Indeed, the largest current application of LDH materials is in the polymer industry, mainly to stabilize PVC [80, 81]. Recently, Duan et al. [82] found that MgAl-LDHs with Mg/Al = 2 have the optimum stabilizing effect on PVC because of their higher layer charge density and consequent stronger driving force for the uptake of Cl^- into the interlayer galleries. However, this LDH contains the highest quantity of interlayer CO_3^{2-} ions but the lowest overall HCl absorption capacity, suggesting that it is the reaction of HCl and CO_3^{2-} ions that are most important in stabilizing the PVC against thermal degradation. Flame retardant materials may be formulated to be more resistant to ignition or to have slower rates of flame spread in a major fire. LDHs have also found useful applications as flame retardants in PVC and other polymers as well leading to reduced quantities of smoke during combustion [83]. The most significant flame retardant effects, observed using a mass loss calorimeter, indicated that the EVA polymer filled with 50 wt.% of LDHs has the slowest heat release rate and the lowest evolved gas temperature.

3.5. Adsorbent and anion-exchange

Fast growing industrial sector has loaded environment with pollutants and toxicants which can cause adverse effects to human health and the surroundings. Recently, environmental pollution is one of the most serious problems in the world due to its deep effect on the future of human beings. Then the investigation for resolving the problem of the environmental pollution in the world began to draw major public attention. Heavy metal ions and organic dye molecules have high toxicity and poor biodegradability for plants and animals at higher concentrations [62]. In recent years, LDHs have been aroused increasing interest as adsorbents by virtue of their properties, which make them attractive materials for adsorbing heavy metal ions and organic dyes. Their abundance in nature, low cost, and good adsorptive properties, a result of their negatively charged layers and high large surface per unit of mass, large porosity, high anion-exchange capacities and flexible interlayer space, etc. i.e. it satisfies all the requisite properties of adsorption of heavy metal ions and organic dye molecules. [62, 69]. The anion- exchange capacity of LDHs is affected by the nature of the interlayer anions initially present and the layer charge density. When the layer charge density is very high the exchange reaction may become difficult. LDHs greater affinities for multivalent anions compared with monovalent anions [62]. Adsorption is a surface phenomenon, used for the accumulation of contaminants between two phases such as solid-liquid interface or solid-gas interface. Normally, adsorption mechanism occurs due to intermolecular forces of attraction between adsorbent and adsorbate. When a solution having adsorbate encounters the adsorbent, surface forces at the interface concentrate the solutes on the surface of the adsorbent [84–87]. LDHs can take up anion species from solution by three different mechanisms: surface adsorption, interlayer anion-exchange and reconstruction of a calcined LDH precursor by the “memory effect” [62]. Removal of dyes from wastewater is of significant consideration because dyes being colored pollutant cause environmental hazards. Up until now, many researches have been reported to synthesize pure LDHs materials or LDHs-based on composites due to their have high anion exchange and adsorption ability which allows them to be an alternative adsorbent or ion exchanger, make these materials favorable to remove contaminants from aqueous systems [44, 45] Moreover, LDHs have been successfully applied in the removal of toxic metals and organic dyes in aqueous solution. Heavy metal cations and radioactive metals were eliminated by using chelate ligands intercalated LDH because of flexible interlamellar region and specific pH. The adsorption characteristics of metal cations were separately studied and concluded that metal cations were separated due to high bond energy and high sensitivity of OH of LDHs. Various uncalcined and calcined of LDHs have been used to investigate the adsorption of heavy metal cations [88]. ZnAl-LDHs have been widely reported to be able to adsorb a wide range anionic and cationic dyes from aqueous solution such as methyl orange (MO), congo red (CR) and methylene blue (MB). Adsorption efficiencies of calcined and uncalcined LDHs were compared and found that better removal efficiency is exhibited by calcined LDHs [45, 47]

3.6. Effect of LDH on the photocatalytic activity

Several biological dyes are mainly using in various industries like leather, cosmetics, paper and textile industries. The wastes generated from those industries, particularly textile industries includes a huge amount of toxic substances and dyes which are adding throughout the colouring procedure. They are hard to eliminate from various water treatment processes and be able to disposed through rivers and sewers easily. They might also endure degradation to produce extremely carcinogenic and toxic substances [89]. That's why there is an urgent need to develop an economic and efficient treatment method which are adept of deals through huge amount of polluted waters including significant amount of organic dyes. So many techniques were described for the elimination of toxic dyes from polluted water, comprising sedimentation, flocculation, coagulation, adsorption, photodegradation, etc. [90]. The because of the opportunity, by means of solar light that is free of cost besides renewable energy source. Layered double hydroxides (LDHs) have been concentrated as of late, all things considered, as environmental-friendly materials that can be utilized as photo catalysts or photocatalyst supports. The researchers found that was one of the first to report the high photocatalytic activity of the ZnCr-LDHs, which energized future research in LDH materials as photocatalysts, considering that the utilization of LDHs as photocatalysts has for the most part been ignored up till then [91]. LDH found an expanding interest for the most recent couple of centuries and generally connected to the area of photocatalysis on account of their constancy, simplicity of planning and reduced cost. Besides, LDH can be synthesised with an assortment of trivalent and divalent cations and in this way, semiconductor constituents can be acquired by picking a appropriate chemical configuration. These were utilized for the photodegradation of various molecules, for example, phenolic mixes, pesticides, anionic dyes and cationic dyes [92].

3.7. Applications in nuclear industry

L. Aimoz et al. [93] analyzed the applicability of MgAl-I, ZnAl-I and ZnAl-IO3 as potential matrices to store ^{129}I. Theiss et al. [94] studied the iodine and iodide adsorption capacity of previously calcined ZnAl-LDH and its thermal decomposition and suggested that iodine species may form non-removable anions by thermal decomposition of the LDH structure when these anions are intercalated into the LDH structure. Bastianini et al. [95] studied the ZnAl-I and ZnAl-I_3 LDHs obtained via intercalation of molecular iodine from nonaqueous solution and described a mechanism of iodine diffusion into the interlayer space to combine with iodide. One of the factors that can significantly affect the iodine retention capacity of LDHs is the presence of carbonate in the interlayer space, an anion with higher affinity than iodide or iodate [96]. Therefore, several studies [97, 98] investigate diverse intercalation methods involving dissolution and recoprecipitation procedures to obtain MgAl-LDHs avoiding any presence of carbonate in the material. Prasanna et al. showed that iodide-containing MgZnAl-LDHs lost the intercalated iodide by leaching even at neutral pH, since hydroxide ion (coming from the aqueous medium) can displace the former [99].

MgAl-LDH has been used by Kulyukhin et al. [100] as adsorbent materials for ^{137}Cs and ^{90}Sr with poor results; however, a material based on MgNd-LDH may be used for ^{90}Sr recovering. LDHs applications in adsorption and ion exchange processes are also important; there is a considerable interest in the use of LDHs to remove negatively charged species. LDHs can take up anion species from solution by three different mechanisms: surface adsorption, interlayer anion-exchange and reconstruction of a calcined LDH precursor by the memory effect [101]. Both uncalcined and calcined LDHs have also been used as sorbents for decontamination of radioactive wastewater, Toraishi et al. [102] reported the adsorption behavior of IO_3^- anions from radioactive wastewater by LDHs, concluding that IO_3^- is weakly adsorbed on the external surface of carbonate−LDH, whereas IO_3^- is exchanged for interlayer NO_3^- in nitrate−LDH.

4. CONCLUSIONS

This review article has demonstrated the wide variety of methods that are available for the synthesis of LDHs and their applications in many fields. The method of choice will depend on the purpose for which the LDH is to be used. If accurate structural information is required, then pure phases with high crystallinity are necessary. LDHs with layered structure are exciting materials for their attractive properties. LDH materials can be successfully synthesized by co-precipitation, urea hydrolysis, hydrothermal, sonochemical methods and etc. depending on formation conditions. Sodium carbonate and sodium hydroxide, ammonia, or urea can be used as precipitating agents. The most general base solution for the layered double hydroxide synthesis is the mixture of Na_2CO_3 and NaOH. We have described some data in our review applications of layered double hydroxides in different fields. LDHs represent one of the most technologically promising materials as a consequence of their low cost, relative ease of preparation, and the large number of preparation variables that may be adopted. Many applications of LDHs, such as in energy storage, catalysis, and adsorption fields, are based on its surface area and electrical conductivity. At present, even though a great deal of work of academic and commercial interest on LDH materials has been carried out, still more remains to be done to exploit completely their potential applications. In the future, we believe work on applications of these layered compounds will continue to expand rapidly.

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ҚАТТЫ ҚОС ГИДРОКСИДТЕРДІҢ СИНТЕЗІ ӘДІСТЕРІ ЖӘНЕ ҚОЛДАНЫЛУЫ – ҚЫСҚА ШОЛУ

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Қабатты материалдың бір түрі болып табылатын қабатты қос гидроксидтер (LDHs) синтезделу жеңілдігі, бірегей құрылымы, бруцит қабатында әртүрлі металл катиондарының біркелкі таралуы, беттік гидроксил топтары, икемді реттелу сияқты кейбір қызықты қасиеттеріне байланысты перспективалы материалдар болып табылады, қабат аралық кеңістіктері бар интеркалирленген аниондар, ісіну қасиеттері және жоғары химиялық және термиялық тұрақтылығы, әртүрлі типтегі аниондарды интеркалациялау қабілеті, сонымен қатар жоғары биоүйлесімділік. Бұл шолу мақаласы қабатталған қос гидроксидтердің синтез әдістері және олардың көптеген салаларда қолданылуы туралы қосымша ақпаратқа бағытталған. Қабатты қосарланған гидроксидтерді синтездеудің ең көп тараған әдістері бірігіп тұндыру, мочевина гидролизі, гидротермиялық синтез, золь-гель, реконструкция және т.б. LDHs катализаторлар, суды тазарту, жалынға қарсы заттар, полимерлі қоспалар, адсорбенттер, атом өнеркәсібі, қоршаған ортаны қорғау, фотокатализаторлар және материалтану салаларында перспективалы қолдану үшін көп функционалды материал ретінде тамаша өнімділікті көрсетеді.

Түйін сөздер: *қабатты қос гидроксид, қоса тұндыру, гидротермиялық синтез, золь-гель әдісі, сонохимиялық синтез.*

МЕТОДЫ СИНТЕЗА И ПРИМЕНЕНИЕ СЛОИСТЫХ ДВОЙНЫХ ГИДРОКСИДОВ – КРАТКИЙ ОБЗОР

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Слоистые двойные гидроксиды (СДГ), которые представляют собой один из типов слоистых материалов, являются перспективными материалами благодаря некоторым интересным свойствам, таким как простота синтеза, уникальная структура, равномерное распределение катионов различных металлов в бруситовом слое, поверхностные гидроксильные группы, гибкая перестраиваемость, интеркалированные анионы с межслоевыми пространствами, свойствами набухания, высокой химической и термической стабильностью, способностью интеркалировать различные типы анионов, а также высокой биосовместимостью. Эта обзорная статья посвящена информации о методах синтеза слоистых двойных гидроксидов и их применении во многих областях. Обсуждаются наиболее распространенные методы синтеза слоистых двойных гидроксидов: со-осаждение, гидролиз мочевины, гидротермальный синтез, золь-гель, реконструкция и др. СДГ демонстрирует отличные характеристики в качестве многофункционального материала для его перспективных применений в области катализаторов, водоподготовки, антипиренов, полимерных добавок, адсорбентов, атомной промышленности, защиты окружающей среды, фотокатализаторов и материаловедения.

Ключевые слова: *слоистый двойной гидроксид, со-осаждение, гидротермальный синтез, золь-гель метод, сонохимический синтез.*