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SYNTHESIS, MODIFICATION AND CHARACTERIZATION OF LAYERED HYDROXIDES AND MAGNETITE AND THEIR NANOHYBRIDS WITH D-GLUCONATE AND GALLATE ANIONS

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Formation of organic-inorganic nanohybrid material of D-gluconate in the lamellae of zinc-aluminum-layered double hydroxide was accomplished by both spontaneous self-assembly (direct method) and ion-exchange methods. PXRD together with CHNS and FTIR analyses showed that the hybridization of D-gluconate with pure phase and good crystallinity was successfully accomplished using both direct and indirect methods. This work showed that a food additive, such as D-gluconate can be hybridized into an inorganic host for the formation of a new nanohybrid compound which can be used to regulate the release of acidity in the food industry.

A new organo-mineral nanohybrid material, in which the organic moiety was hybridized into the inorganic interlamellae, was prepared using gallate anion (GA), an anti-carcinogenic, anti-mutagenic, and anti-microbial agent as a guest, and Zn-Al-layered double hydroxide, as

an inorganic layered host using the ion-exchange technique. The release of the anion from the interlamellae of the nanohybrid was found to be of controlled manner, governed by the first order kinetic and it was also concentration-dependent.

Zinc hydroxide nitrate, a brucite-like layered material, was synthesized using pH controlled method. Poly (vinyl alcohol) and poly (ethylene glycol) were used at various percentages as size decreasing agents during the synthesis of zinc layered hydroxide. SEM images, PXRD, TGA and surface area analyses showed the decrease of size and thickness of the resultant zinc layered hydroxides. When zinc layered hydroxides were heat-treated at 500 $^{\circ}$C, the sizes of obtained nano zinc oxides were depended on the size of the parent material, zinc layered hydroxide nitrate.

The memory effect of calcined zinc layered hydroxide nitrate, with gallate anion solutions, was studied. The brucite-like material, zinc layered hydroxide nitrate was heat-treated at 150-800 ºC. XRD analysis showed the growth of the calcined materials, nano sized zinc oxides in both thickness and diameter occurring simultaneously with increasing calcination temperature. The rehydration behavior of the calcined material was investigated by placing the material in a solution containing gallate anions. The best result for brucite-like phase reconstruction was obtained for a sample heated at 500 ºC and treated with 0.1 M anion. XRD analysis showed the formation of a layered structure material after rehydration process.

Brucite-like materials, undoped and doped zinc layered hydroxide nitrate with (2 % molar in mother liquor) Fe^{3+}, Co^{2+} and Ni^{2+} were synthesized. Their organic-inorganic nanohybrid materials with gallate anion as a guest, and the undoped and doped zinc hydroxide materials,

as inorganic layered hosts, were prepared by the ion-exchange method. The nanohybrid materials were heat-treated at various temperatures, 400-700 ℃. XRD, TGA/DTG and FTIR results showed that incorporation of the doping agents within the zinc layered hydroxide has enhanced thermal stability of the nanohybrid materials in the thermal decomposition pathway. FESEM images have illustrated porous carbon materials obtained from the heating of the nanohybrids at 600 and 700 ℃ after the acid washing process.

Magnetite nanoparticles with narrow size distribution was prepared by using poly (vinyl pyrrolidone) as a stabilizing agent during the synthesis. Immobilization of gallate anion (GA), onto the surface of magnetite nanoparticles was accomplished by adsorption technique that was found to be efficient for the hybridization process in the formation of the core-shell nanohybrid. FTIR and CHNS results indicated that the GA was actually adsorbed onto the surface of the magnetite nanoparticles. Also, size analysis showed successive size increases of the particles after the adsorption process. The release of the anion from the surface of the nanohybrid was found to be controllable by the selection of the release media.

This study showed that the formation of organic-inorganic nanohybrid materials of D-gluconate and gallate anions as organic guests and zinc-aluminum-layered double hydroxide, zinc layered hydroxide nitrate and also magnetite nanoparticles as hosts can be successfully accomplished.

CHAPTER I

INTRODUCTION

Nanotechnology

Professor Norio Taniguchi (1974) introduced the concept of nanotechnology, which entailed processing, separation, consolidation, and deformation of materials with structural features in between atoms as well as bulk materials. Dr. K. Eric Drexler subsequently wrote several books which included *Nanosystems: Molecular Machinery, Manufacturing and Computation* [1] which gave more in-depth knowledge on the technological significance of nano-scale phenomena and devices.

Nanotechnology, a field of applied science and technology, covers a broad range of topics. It deals with the design, construction and utilization of functional structures with at least one characteristic dimension measured in nanometer, as well as the fabrication of extremely small devices. It is multidisciplinary in nature, encompassing colloidal science, device physics, and supramolecular chemistry. There is still much speculation with regards to what new science and technology applications would emerge from these lines of research. This resides on the fact that when structural features are intermediate in extent between isolated atoms and bulk macroscopic materials, within a range of 10^{-9} m to 10^{-7} m (1-100 nm), they do display physical attributes substantially different from those displayed by either atoms or bulk materials, which would naturally result in new technological opportunities and challenges [2-5].

Nanomaterials

Nanotechnology is particularly unique in the sense that there is a substantial increase in the ratio value of surface area to volume as apparent in many nanoscale materials. This opens new areas in surface-based science research, such as catalysis. Many physical phenomena will become more pronounced as the size of the system decreases. Among others, these include statistical mechanical effects and quantum mechanical effects. For instance, the "quantum size effect" is greatly altered when electronic properties of solids are affected with large reductions in particle size. In addition, a number of physical properties are changed, when compared to the corresponding macroscopic systems [2-5].

Nanoparticles

Nanoparticles (or nanopowders) are regarded as microscopic particles. The size of a particle is measured in nanometer (nm) with at least one dimension <100nm. These particles are important to science and technology, as they are essentially a bridge between bulk materials and atomic or molecular structures. The physical properties of a bulk material are constant regardless of its size, but at the nano-scale this is not necessarily so (Figures 1.1 and 1.2). In fact, the properties of a material start changing as its size approaches the nanoscale and as the percentage of atoms at its surfaces becomes significant. For bulk materials larger than one micrometer, the surface atom percentage is minuscule relative to the total number of atoms. Nanoparticles exhibit three-dimension confinement-quantum confinement in semiconductor particles, surface

plasmon resonance in some metal particles and superparamagnetism in magnetic materials.
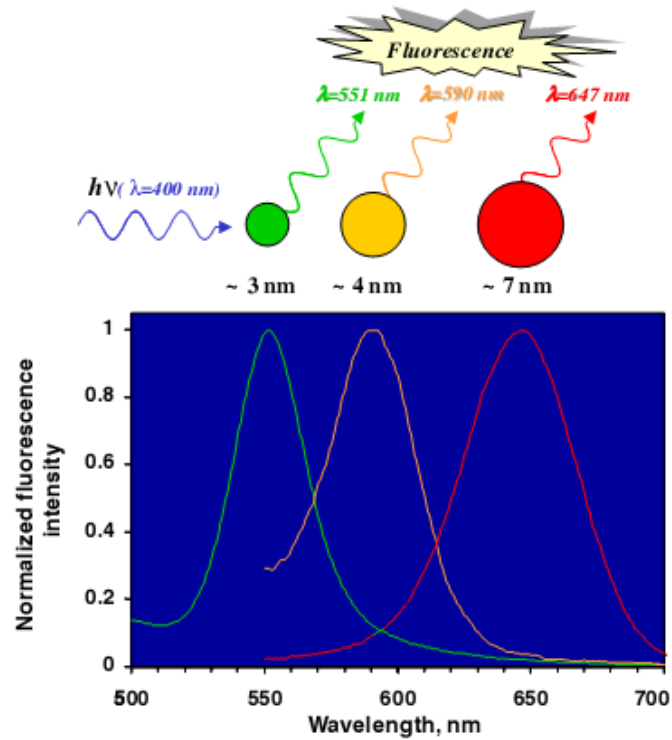

Figure 1.1: Size-Tunable Fluorescence Spectra of CdSe Quantum Dots [6].
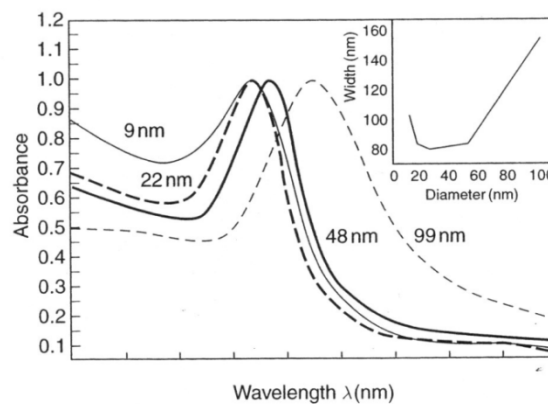

Figure 1.2: Size Dependence of the Optical Absorption Wavelength for Gold Nanoparticles and (inset) the Corresponding Value of the Full Width at Half Maximum (FWHM) of the Absorption Peak [5].

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The interesting and sometimes unexpected nature of nanoparticles is partly due to the surface aspects of the material dominating the properties instead of the bulk properties [2, 4, 5].

Nanocomposites

Nanocomposites are composite materials in which nanoparticles are embedded in a host phase. This is part of the growing field of nanotechnology. The nanomaterials tend to intensify the electrical and thermal conductivities as well as the mechanical strength of the original material. Supported nanoparticles of metals or metal oxides are widely used as heterogeneous catalysts. The percentage by weight of the nanomaterials introduced is maintained very low (0.5% - 5%) due to the incredibly high surface area to volume ratio of the particles. A high dispersion of the active components maximizes the contact area of the catalyst with reactant and support. The hardness of ceramics can be considerably enhanced by dispersing nanoparticles or nanocrystalline fibers as a second phase [2, 3].

A two dimensional layered structure consisting of thin crystalline inorganic layers with a thickness of molecular scale in nanometer range can be used as an ideal host for layered nanocomposite or organic-inorganic nanohybrid materials. One example for this type of structure is layered double hydroxide (LDH). A variety of anionic species can be inserted as guests into the interlayer spaces of the LDH, resulting in an expansion of the interlayer distance to a nanometer sized dimension to form a new nanohybrid material [7].

Objectives of the Study

The objectives of this study are to:

a) Study the effect of synthesis method on the resulting properties of nanohybrid (zinc-aluminum-layered double hydroxide-D-gluconate)

b) Synthesize and characterize of zinc-aluminum-gallate nanohybrid and its controlled released study

c) Study the effect of poly vinyl alcohol (PVA) and poly ethylene glycol (PEG) onto the size of zinc layered hydroxide and its calcined products

d) Synthesize and characterize of zinc-layered-gallate nanohybrid, ZLG using the "structural memory effect"

e) Study the decomposition pathways of undoped and doped ZLGs with Fe^{3+}, Co^{2+} and Ni^{2+} and characterize the resulting materials heated at various temperatures

f) Prepare magnetite nanoparticles, coating of the nanoparticles with gallate anion and study of its controlled release property

CHAPTER II

LITRATURE REVIEW

Layered Double Hydroxides (LDHs)

History

Layered double hydroxides (LDHs) were initially approached from two different directions - mineralogy and inorganic chemistry. Hydrotalcite, a soft solid mineral easily crushed into a white powder, was discovered in Sweden around 1842. It was a hydroxycarbonate magnesium/aluminum layered material that occurred in nature in foliated, distorted plates and/or fibrous shapes [8].

Pyroaurite, another mixed hydroxycarbonate, isostructural with hydrotalcite of magnesium and iron, was described by Flink (1910) [8]. It was called pyroaurite because of a likeness to gold when heated. In 1930 [8], it was reported that Mg^{2+} precipitated at lower pH in $Al(OH)_3$ to form $Mg(OH)_2$. This phenomenon was attributed to the formation of an adsorption complex. Feitknecht (1942) [8] published papers on the formation of these materials by addition of alkali to solutions containing M(II) and M(III) ions, but incorrectly labeled them as double layer materials, in which M^{2+}-rich layers were alternated with those of M^{3+}-rich layers (Figure 2.1) [9]. He described the

materials having double layered structure as *"layered double hydroxides"*, perhaps a felicitous misinterpretation of the term.

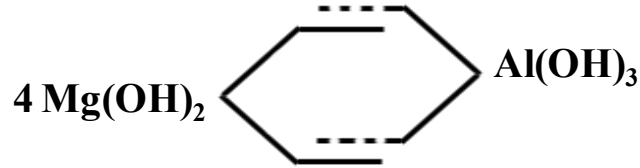$$4\,Mg(OH)_2 \quad\diagup\!\!\!\diagdown\quad Al(OH)_3$$

Figure 2.1: Structure of LDH Based on Feitknecht 's Hypothesis [9].

Allmann, 1968 [8] and Taylor, 1969 [8] by means of single crystal XRD showed that all the cations were located in the same layer, and the anions together with water molecules in the interlayer region. This had refuted Feitknecht's hypothesis. The terms hydrotalcite (HT) compounds or anionic clays were not generally accepted, considering that HT referred strictly to a specific mineral and that HT compounds did not fulfill some clay properties, for example the very small particle size [8, 9]. The determination of the precision structure, distances between atoms, and angles between atoms and the arrangement of anions on the surface of LDHs was made possible in 1998, when atomic force microscopy, AFM and scanning tunneling microscopy, STM have been used [10, 11]. Synthesis of LDHs under steady-state conditions was done in 2005 [12].

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Structure

Basic Structure

The structure of LDH is similar to brucite, $Mg(OH)_2$. In a brucite layer, Mg^{2+} cations occupy the octahedral vacancies formed by six hydroxides. These octahedra share edges to form infinite layers in two dimensions. These sheets are stacked on top of another held together by hydrogen bonds (Figure 2.2) [8].

The octahedrons are a little modified, with the distance between OH^- neighbors on the same side of the layer at 3.14 Å apart (lattice parameter, *a*, the length AB in Figure 2.2. However, the distance between OH^- neighbors on the opposite side of the sheet is only 2.70 Å (CD in Figure 2.2). The bond length of Mg–O is ca.2.07 Å while the stacked layer thickness is 4.78 Å [8, 9, 13].
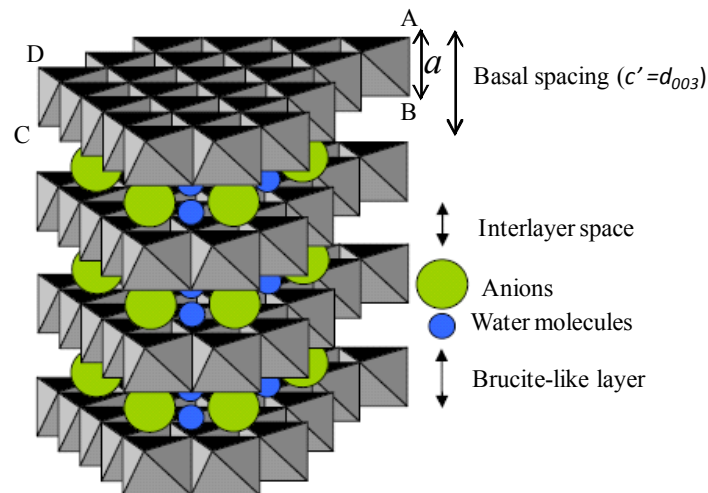

Figure 2.2: Schematic Representation of a Hydrotalcite-Like Material [14].

Partial replacement of Mg^{2+} ions by trivalent cations having slightly different radii such as Fe^{3+} for pyroaurite and Al^{3+} for hydrotalcite gives the brucite-like layers a positive charge, which in hydrotalcite is balanced by carbonate anions, located in the interlayer region (gallery) between two brucite-like layers (Figure 2.3) [8, 9].

The interlamellae also contain water molecules with hydrogen bonded to hydroxide group within the layers and/or bonded to the interlayer anions. The electrostatic interactions and hydrogen bonds between the layers and the contents of the gallery hold the layers together, forming the three-dimensional structure [8], as shown in Figure 2.2. Thus the main features of hydrotalcite-like (HTl) structures are determined by the nature of the brucite-like sheet (M(II) and M(III) cations used); the positions of anions and water molecules in the interlamellae space and the type of stacking of the brucite-like sheets [9].
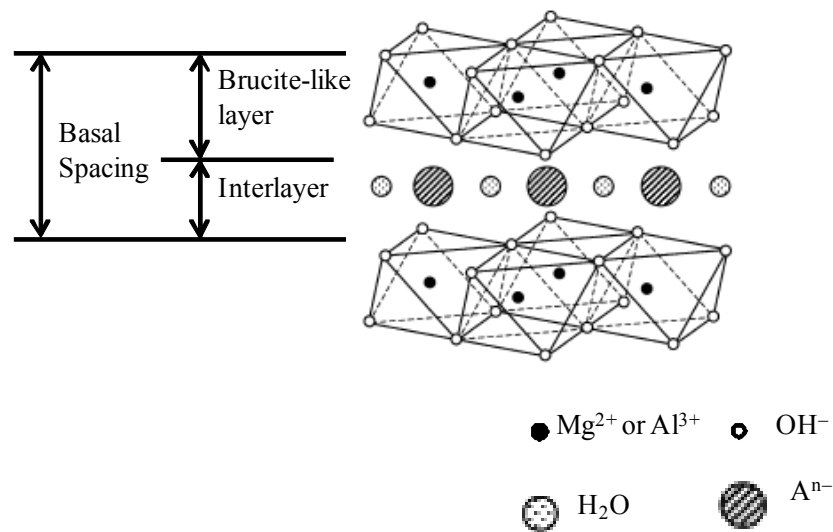

Figure 2.3: Structure of Mg-Al-LDH [15].

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LDHs have two kinds of crystal lattices - rhombohedral (3R) or hexagonal (2H). The lattice parameters for hydrotalcite [$Mg_6Al_2(OH)_{16}(CO_3).4H_2O$] with 3R stacking sequence, are $a = 3.05$ Å and $c = 3d_{003} = 22.81$ Å, where d_{003} is the basal spacing, 7.60 Å [8, 9]. The thickness of the brucite-like layer is 4.80 Å and the spacing occupied by the anion (gallery height) is *ca*. 2.80 Å [8].

Within the Hydroxide Layers

LDHs can be formed from various combinations of divalent and trivalent cations. Divalent cations among others, include Mg^{2+} [16-18], Ni^{2+} [19, 20], Co^{2+} [21], Zn^{2+} [22-25], Fe^{2+} [26], Mn^{2+} [27], Cu^{2+} [28], Ti^{2+} [21], Cd^{2+} [29], Pd^{2+} [30], and Ca^{2+} [31, 32] while the trivalent cations include Al^{3+} [16, 17, 22], Ga^{3+} [33], Fe^{3+} [20], Cr^{3+} [19], Co^{3+} [34], V^{3+} [35], In^{3+} [36], Y^{3+} [37] and Sc^{3+} [38]. For trivalent cations, the only requirement is that their radii differ slightly from those of Mg^{2+} and Al^{3+} [8, 9].

Sometimes combinations of three different cations have been used such as Zn/Cd/Cr [29] and Pt/Zn/Al [39] systems. Some tetravalent cations, such as Zr^{4+} [40, 41] and Sn^{4+} [42] have been introduced into the brucite-like layers to replace part of the trivalent cations in LDH compounds. Also, monovalent cations such as Li together with Al have been used to obtain LDH compounds [43].

LDHs ($[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}.nH_2O$) are reported to synthesize for values of x from 0.1 to 0.5 [8, 9, 13] but high value of x has caused the electrostatic repulsion between positive charges of M^{3+} cations, which should ideally be kept apart and not adjacent to each other as in the brucite-like layer. Then again the x value should not be more than 1/3. Otherwise, the formation of $M^{3+}(OH)_3$ can occur. Low x value will lead to a high concentration of M^{2+} and increase the possibility of $M^{2+}(OH)_2$ formation. Thus many experimental results have indicated that it was usual to obtain pure LDHs for $x = 0.2\text{-}0.33$ [8, 9, 13].

The value of cell parameter, a for hydrotalcite-like compounds, HTlcs containing Mg and Al linearly decreases with increasing x [9]. It is believed that as x increases a stronger interaction between the central cations and the coordinated OH^{-} anions occurs [44, 45]. However, it is also reported to have obtained HTlcs of up to 0.67 [46] with higher values of x. Also, in very low carbonate concentration, Miyata has reported an increase in the parameter a for values of x below 0.2 [9]. But under such condition, brucite and hydromagnesite were also obtained. It also produced multi-cation LDHs, such as Cu/Zn/Co/Al/Cr and Cu/Zn/Co/Cr-LDHs [47-49]. However, the ratio of divalent to trivalent cations should be kept within a range of 2-5.

Anions between the Layers

There is practically no limitation to the nature of the anions, which can compensate for the positive charges of the hydrotalcite-like sheet, and the choice is much more versatile.

The only problem lies in the preparation of pure or well crystallized materials. For example, when preparing HTlcs containing anions apart from carbonate, it is very difficult to avoid contamination from the CO_2 present in the aqueous solution. Previous works have been accomplished to synthesize a variety of LDHs with various anions between the layers. Some anions were used are:

i) Inorganic anions: F^-, Cl^-, Br^-, I^-, $(ClO_4)^-$, $(NO_3)^-$, $(ClO_3)^-$, $(IO_3)^-$, OH^-, $(CO_3)^{2-}$, $(SO_4)^{2-}$, $(S_2O_3)^{2-}$, $(WO_4)^{2-}$, $(CrO_4)^{2-}$, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[SiO(OH)_3]^-$ [9], $(PO_3)^-$, $(PO_4)^{3-}$, $(HPO_4)^{2-}$, $(H_2PO_4)^-$, $(P_2O_7)^{2-}$, [50-52] $(AsO_3)^-$ [53], borate and tetraburate [54], $(TcO_4)^-$, $(ReO_4)^-$ [8], $(MnO_4)^-$ [8], $(MoO_4)^-$ (208h) [55], $(HVO_4)^{2-}$, $(VO_4)^{3-}$ [8] and C_{60} anion [56], etc.

ii) Heteropolyacids: $(PMo_{12}O_{40})^{3-}$, $(PW_{12}O_{40})^{3-}$ [9], and Iso- and hetropolyoxometalates (POMs): $(Mo_7O_{24})^{6-}$ [55, 57, 58], $(W_7O_{24})^{6-}$ [57], $(PW_6Mo_6O_{40})^{3-}$ [8], $(PW_{12}O_{40})^{3-}$ [8], and $(PV_3W_6O_{40})^{6-}$ [59], $Au(Cl)_4^-$ [60].

iii) Organic acids: carboxylates [61-64], dicarboxylates [64, 65], acrylates [66], benezenecarboxilates [65, 67, 68], alkylsulfonates [64, 65], cholorocinnamates [8], glycolate [69], glycerolate [8], glyphosate [70], β-cyclodextrin [71], adipic, oxalic, succinic, malonic, sebacic, acyl and arylsulphonates, chlorocinnamic acid, cinnamic

acid [72] and metallorganic complexes: [Ru(4,7-diphenyl-l,10-phenanthrolinedisulphonate)$_3$]$^{4-}$ [9], EDTA [73, 74] and organic dyes [18, 75].

iv) Biochemical anions: various amino acids [62, 76], penicillin [77], biopolymer [78], DNA [76, 79], CMP, AMP, GMP, ATP, ADP and related species [8].

Orientation of the Anion

Anions with different structures, dimensions and charges can be located between the hydrotalcite-like layers. The thickness of the interlayer and thus basal spacing, d_{003} is affected by the size and the orientation of anions and also the strength of the bonds between the anions in the gallery with the brucite-like layers [8, 9, 64]. Anions are oriented in the interlayer in such a manner to enable maximization of their interactions with the surroundings. For example, in the case of planar carbonate group, carbonate anions are usually placed in parallel to the hydrotalcite-like layer due to the formation of stronger hydrogen bonds between three oxygen atoms of carbonate anions and the brucite-like layers [8]. This orientation decreases the gallery height and causes to maximize the electrostatic interaction between carbonate group and the positively charged layers. However, the anion orientation changes with other parameter such as x. For example the CO_3^{2-} orientation changes from flat lying (D_{3h}) to tilted (C_{2v}) in the interlayer, when the trivalent cation content increases in $Ni_{1-x}Al_x$-LDH [80]. The nitrate group, positioned in flat-lying model at low values of X, changes to an alternating upper-lower gallery surface model at high X values [81]. The orientations of organic

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anions are more complicated and are affected by anionic concentration and reaction temperature [8].

Water in LDHs (n)

Water molecules normally are localized in the interlayer sites available, not occupied by the anions [82]. Such site is provided by each OH group in brucite-like layers. The water molecules form hydrogen bonds with the hydroxide layer OH and/or with the intercalated anions. Usually, the amount of water is determined by thermogravimetric measurements of weight loss [9]. However, it is possible to calculate the maximum amount of H_2O based on the number of sites present in the interlayer, assuming a closely packed configuration of oxygen atoms, and subtracting the sites occupied by the anions [9]. The following formulas are used:

a) according to Miyata equation [9], $n = 1 - N\,x/c$;   Eq. 2.1

where : N = number of sites occupied by the anions;

c = anionic charge;

$x = M(III)/((M(II)+M(III))$

for $(CO_3)^{2-}$ $n = 1 - 3\,x/2$

for example, in $NiMgAl-CO_3-LDH$, when $x = 0.29$, the calculated n is 0.565, which is in good agreement with 0.530 ± 0.020 obtained from five samples [9].

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b) according to Taylor equation, $n= 1 - 3x/2 + d$ where $d= 0.125$; [9]   Eq. 2.2

c) according to Mascolo et al. equation, for Mg-Al-HT. $n= 0.81-x$ [9]   Eq. 2.3

An increase in x causes a decrease in the calculated amount of water. The maximum amount of water in the hydrotalcite, HT based on Miyata's formula, will be $n = 0.625$, thus giving $Mg_6Al_2(OH)_{16}CO_3.5H_2O$, but the natural hydrotalcite has four molecules of water. The latter value was reported in papers and direct measurement of the water amount was not made. Direct measurements of synthetic products usually give values lower than 4. Using the inelastic neutron scattering investigation, it was revealed that the water molecules could rotate freely and move around hydroxide oxygen sites in the interlayer but not fixed in one position [83]. Also Raman spectroscopy showed three types of structured water: (a) water interacted to the interlayer carbonate anion by formation of hydrogen bonds, (b) water interacted to the hydrotalcite hydroxyl surface by formation of hydrogen bonds, and (c) interlamellae water [84]. Depending on the strength of the interaction, the water is moved within a temperature range of 120-250 °C [85]. It is reported that the temperature at which interlayer water is lost is shifted towards the lower end as x decreases [9]. Also, the relative humidity (RH) of the media affects the basal spacing. The gallery height increases with increasing RH [8].

The basal spacing often decreases in the dehydrated LDHs but water can be reabsorbed while cooling in humid media [9]. Moreover, the water can be physically adsorbed on

the surface of LDHs and their intercalated products. Heating to 100 °C can remove the weakly adsorbed water [9].

Preparation Methods

Direct Method

In this method, LDHs can be produced in the following methods: [8, 9]

a) Dropwise additions of alkaline solution into a solution containing mixed cations (increasing pH method).

b) Dropwise additions of the mixed cations into an alkaline solution at high super-saturation.

c) Keep pH constant at low supersaturation by slow additions in a container of two diluted streams - mixed cations solution and alkaline solution.

To produce a LDH with a desired anion (nanohybrids), the anion is used together with an alkaline or mixed cations solution. It has been demonstrated that LDH materials were formed preferably from a mixture of individual metal hydroxides [86]. In the case of aluminum as a trivalent cation; they were formed through an aluminum hydroxide intermediate. Variation of this method includes titration at constant or varied pH resulting in buffered precipitation. In this method, the anion to be incorporated in the

LDH should not form insoluble salts with the constituent cations, too readily. The plots of pH versus reactant volume have been done (Figure 2.4) [87]. Two types of pH curves were observed. One, observed with Cr^{3+}-containing LDH, consists of a single plateau at a pH lower than that necessary to precipitate $Cr(OH)_3$ or $M(II)(OH)_2$. This is an indication of a direct formation of the LDH from solution. The other more common pH curve exhibits two plateaus occurring during LDH formation for almost all materials containing Al as M^{3+}.
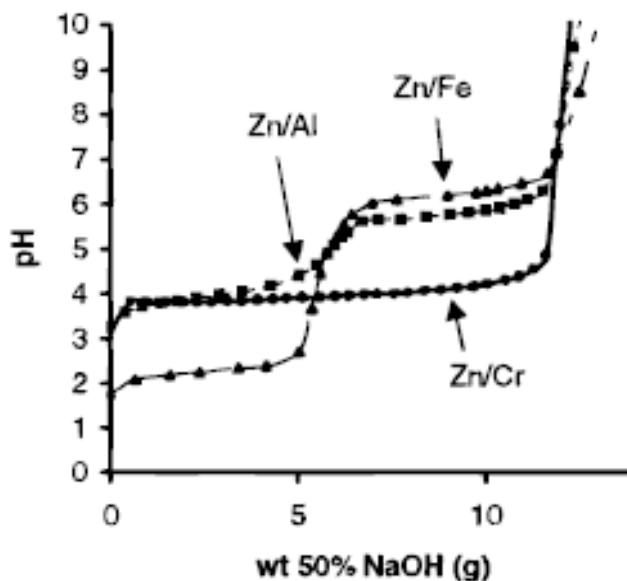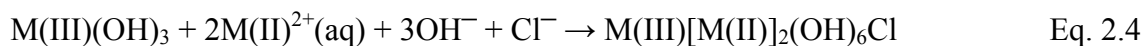

Figure 2.4: Titration Curves of Zn(II)/M(III) Solutions: ■, Zn/Al; ▲, Zn/Fe; ●, Zn/Cr [87].

Braterman et al. observed that $Al(OH)_3$ was formed first at pH ~ 4, with LDH resulting from the conversion of this initial precipitate to the final product [87].

$$M(III)(OH)_3 + 2M(II)^{2+}(aq) + 3OH^- + Cl^- \rightarrow M(III)[M(II)]_2(OH)_6Cl \qquad \text{Eq. 2.4}$$

k_{spLDH} was calculated for the prepared materials and equilibrium constant for their LDHs [87, 88].

Direct Method in Nonaqueous Solutions

LDHs are prepared by the co-precipitation method in various solutions of alcohols to form mixed alkoxide/inorganic anion-intercalated LDH materials [89]. When this compound is dispersed into an aqueous solution overnight, hydrolysis of the alkoxide anion and the formation of a transparent LDH suspension occurs.

Indirect (Ion-Exchange) Method

The interlamellae anions in LDHs are exchangeable and the order of affinity to exchange [8, 9] is:

$$CO_3^{2-} > HPO_4^{2-} > HAsO_4^{2-} > CrO_4^{2-} > SO_4^{2-} > MoO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^-$$
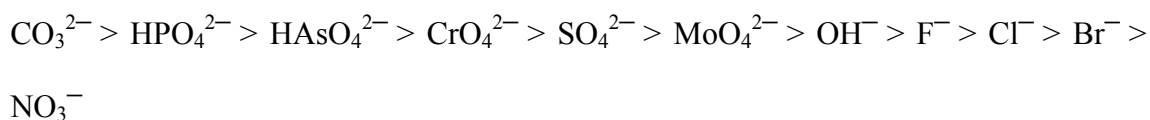
This means that a weakly held anion can be replaced by another anion with higher affinity. Ion-exchange is done by stirring the LDH containing the anions in a solution with excess of the exchange anions. Sometimes ion-exchange is not complete because the affinity of the guest anions is not strong enough [90]. LDH nitrate and chloride are

often used as starting materials in this procedure. Although various organic and inorganic anions of different sizes, shapes and charges have successfully been intercalated into interlamellae of LDHs, it is difficult to use this method for the most weakly held anions, such as iodide and perchlorate.

Ion-exchange can be accomplished in the presence of glycerol or polyols. Glycerol causes the expansion of the distance between the hydroxide layers thus promoting the uptake of guest anions into the interlamellae of LDHs [64].

Preparation from Oxides and Hydroxides

This reaction involves the hydration of metal oxides and/or metal hydroxides in the presence of an anion [91].

Preparation using Memory Effect Technique

This technique involves heating a LDH containing a thermally labile anion. The resulting oxide is then rehydrated in the presence of the desired replacement anion to form a new LDH. Two important factors in this method are the choice of starting material and the temperature of calcinations. Excessive heating would result in the formation of spinel, which is resistant to rehydration [33, 92, 93].

Preparation by Oxidation of Transition Metals

Introducing air or oxygen during the aging stage of an oxidizable metal hydroxide can also be adapted to synthesize metal compositions of LDHs. This method was used to produce $Co^{II}Co^{III}$-, $Mg^{II}Co^{II}Co^{III}$-, and $Co^{II}Co^{III}Al^{III}$-LDHs [85, 94, 95]. Mg-Mn-LDH was also prepared by oxidizing Mn^{2+} into Mn^{3+} in the solid state condition [96].

Preparation by Hydrothermal Treatments at High Temperature

In this method, the synthesis of LDH is started from a mechanical mixture of two metal oxides, or from mixtures derived through decomposition of their nitrates. The mixtures are then treated in an autoclave at high temperatures and pressure.

Preparation by Sol-Gel Technique

This process is a wet-chemical technique, involving the formation of a colloidal suspension (sol) that produces an integrated network gel due to internal cross-linking. Good homogeneity, high surface and high porosity are the characteristics of the material prepared by this technique. LDH is formed from the hydrolysis and polymerization of a solution of a typical precursor, metal alkoxide. The alkoxide is first dissolved in an organic solvent and refluxed. Water is then slowly added, causing the hydrolysis and polycondensation reaction to form cross-linkage [97].

Preparation of LDHs in an Emulsion Solution

In this method, the LDH is prepared in a water-in-oil emulsion solution containing octane and water [98]. The resulting LDH shows high surface area and a narrow distribution of mesopores. The oil-water interface in emulsion plays a significant role in the inhibited and oriented growth of LDH particles.

Aging

LDHs obtained in various methods do not have high crystallinity and good ordered metal hydroxide layers. Aging, a post preparative treatment, causes increase in uniformity and modifies the crystallinity of LDHs and its nanohybrids. This is carried out at or often above ambient temperature [9].

Physicochemical Characterization Methods

Many techniques are used to characterize and analyze the LDHs and their nanohybrids. The most commonly used techniques are: