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RESEARCH ARTICLE

Facile Synthesis of Nanosized Magnesium-Aluminium Layered Double Hydroxides

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Abstract

We report facile methods of preparing nanosized hydrotalcite-like compounds, the layered double hydroxides (LDH), with ordinary chemistry laboratory settings to educate the young scientists from high schools to undergraduate university level fostering their research interest in preparing these nanomaterials of practical importance. Coprecipitation and urea hydrolysis methods have been recommended as facile routes of preparing the magnesium-aluminum layered double hydroxides (Mg-Al LDH). The LDH thus prepared were characterized by Fourier transform infrared (FTIR) spectroscopic and powder X-ray diffraction (XRD) techniques. The observed weakening of some FTIR peaks and XRD planes shifting concerning standard JCPDS 89-5434 data implied the slight structural variation of the compounds and the presence of some impurities. The average grain diameter of LDH particles was found in the range of 20 to 60 nm.

Keywords: Hydrotalcite, layered double hydroxides (LDH), FTIR spectroscopy, X-ray diffraction

Introduction

Layered double hydroxides (LDH) are 2-dimensional, hydrotalcite $[Mg_6Al_2(OH)_{16}CO_3.4H_2O]$-like basic inorganic compounds. They are represented by the general formula.

$$[M^{2+}_{(1-x)}\ M^{3+}_{x}\ (OH)_2]^{x+}\ (A^{n-}_{x/n}).mH_2O,$$

where,

M^{2+}= divalent metal cation
M^{3+} = trivalent metal cation
x = an integer = $M^{3+} / (M^{2+} + M^{3+})$ = molar fraction
A^{n-} = organic or inorganic charge compensating anion in inter-lamellar region
m = number of water molecules present per formula weight of compound [1-4].

The general structural scheme of LDH is presented in Figure 1[5].

According to the general formula and the structural scheme shown in Figure 1, these compounds involve positively charged hydroxylated layers $[M^{2+}_{(1-x)} M^{3+}_{x}(OH)_2]^{x+}$ separated by interlayered anionic species $[(A^{n-}_{x/n}).mH_2O]$ and water molecules [6,7].

Double hydroxides of transition metals of the first row (divalent cations) in periodic table [M(II)] and that of Fe, Al, Cr, Ga, etc. (trivalent cations) [M(III)] compose hydroxylated layers of these compounds.

The tetravalent cations such as Mn^{4+}, $Sn^{4+,}$ etc. can also be incorporated between the layers [5,6]. Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, etc., and Al^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}, $Co^{3+,}$ etc. are M(II)] and [M(III)] cations generally present in basic layers of these compounds. Meanwhile, CO_3^{2-}, SO_4^{2-}, Cl^-, NO_3^-, OH^- etc. are charge compensating anions present in the interlayer space between two successive layers [2,3,5,8]. 'x' is the number of moles of M (III) per formula weight of the compound which is equal to the molar fraction i.e. ratio of the molar concentration of M(II) to the sum of that of M(II) and M(III). It determines the charge density of the hydroxide layers of these compounds. The value of 'x' lies in the range $0.2 \leq x \leq 0.4$ according to the stoichiometry of the compounds. Ionic radii of M(II) and M(III) cations, in the range of that of Mg^{2+} are taken as the best be accommodated in their octahedral sites. On the other hand, too small and too large

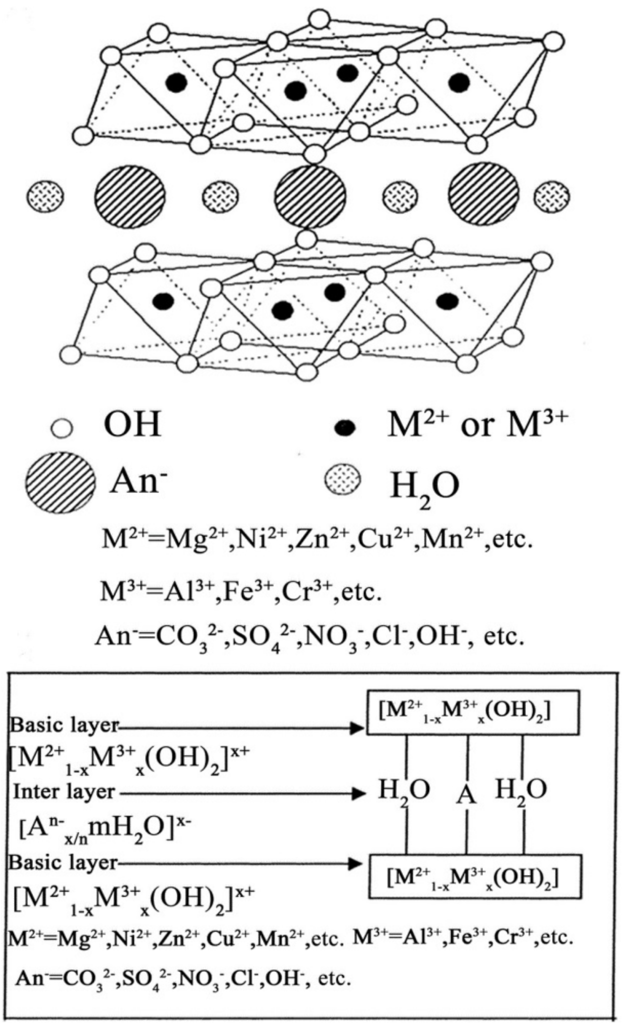

***Figure 1**: Schematic structure of LDH showing double hydroxide layers (basic layers), metal cations [M(II) and M(III)]as layer-species, and anions (A^{n-}) and H_2O as interlayer species [5].*

cations such as $Be^{2+}$and Cd^{2+}respectively produce another type of compound instead of LDH [8,9].

The structure of LDH resembles that of brucite [$Mg(OH)_2$] in which Mg atoms are coordinated with -OH groups in regular octahedral linked to one another through their vertices. The basic hydroxylated layers acquire positive charge because M(II) cations in the lattice are substituted by M(III) cations and the resultant charge is balanced by anions present between these layers. These positively charged layers make them basic [10]. They are porous compounds and exhibit some extraordinary physicochemical properties such as delamination (into positively charged cationic nano-sheets), ion (inorganic and organic) exchange property, extraordinarily high thermal stability, high surface area, and ease of surface modification, etc. These particular properties and unique chemistry make them applicable in various fields in their pristine and modified forms as illustrated in Figure 2 [3,11-15].

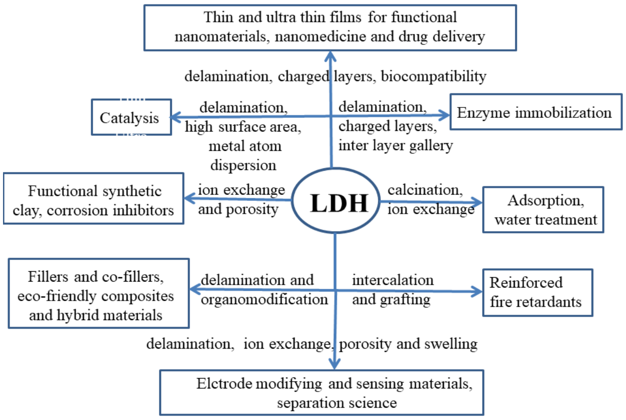

***Figure 2**: Schematic chart illustrating properties and modifications based applications of LDH (adapted from references [3,11,13,15-21,24-33]*

To name the most important applications of the LDH, their delaminated nano-sheets are promising materials for sensing [13,18,29,31-33] and catalytic purposes [19], wastewater treatment (such as removal of As(V) and Cr(VI), phosphates and nitrates) [15,16,21,26], as fire-retardant [12,24,25,30], corrosion inhibitors supercapacitors, as biomaterials, drug delivery hosts, etc. [7,27,30]. Based on their porosity and ion exchange property, LDH is emerging as synthetic clay, an alternative to varieties of natural clay [9].

These important materials can be prepared by different wet chemical methods such as coprecipitation, urea hydrolysis, ion exchange, hydrothermal, sol-gel, electro-synthesis, etc. It should be noted that these versatile and yet highly valuable nanomaterials with their unique properties can easily be prepared in an ordinary chemistry laboratory using easily accessible chemicals as starting materials. In this work, we employ coprecipitation and urea hydrolysis methods as facile synthetic routes of preparing nano-LDH.

Materials and Methods

Materials

Magnesium nitrate hexahydrate [$Mg(NO_3)_2.6H_2O$], aluminum nitrate nonahydrate [$Al(NO_3)_3.9H_2O$], sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and urea (NH_2CONH_2) of analytical grade were purchased from Merck Limited, India. Distilled water was used to prepare the corresponding chemical solutions. $Mg(NO_3)_2.6H_2O]$ and $Al(NO_3)_3.9H_2O]$ were used as starting materials for the preparation of Mg-Al LDH in both methods.

Preparation of Mg-Al LDH

Coprecipitation and urea hydrolysis methods adopted in this experiment are presented in Figure 3. 500 mL mixture salt solution was prepared by mixing 250 mL of 0.1M solution of $Mg(NO_3)_2.6H_2O$ and 250 mL of 0.05M solution of $Al(NO_3)_3.9H_2O$. Similarly, 500 mL of a caustic mixture solution was prepared by mixing 250 mL of 0.8M Na_2CO_3 solution and 250 mL of 1.6M solution of NaOH. The caustic mixture solution was added to 500 mL mixture salt solutions in a dropwise manner with continuous and vigorous stirring pH~9 of the reaction mixture was maintained because precipitation of all LDH occurs at a pH range of 8.5-9.0. As the caustic mixture solution was added to the mixture salt solution, a white precipitate of hydrotalcite was formed and the stirring was continued overnight for complete precipitation. The precipitate was washed with 0.8M Na_2CO_3 solution followed by distilled water until neutrality, filtered, and dried at 80 °C in an oven overnight to obtain the solid flakes of Mg-Al LDH.

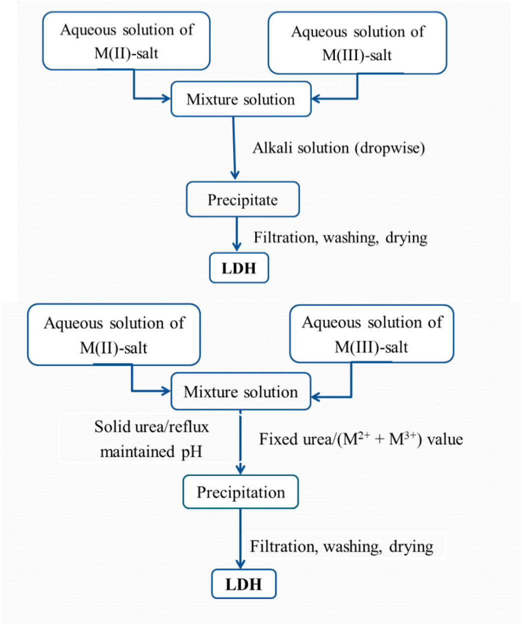

Figure 3: *Schemes showing the procedures to prepare nano-LDH by coprecipitation (top) and urea hydrolysis (bottom) methods*

Similarly, optimized conditions of molar fraction, temperature, pH value, and reflux-time as reported in Costantino's method were maintained for the preparation of materials by urea hydrolysis method [8]. 150 mL of 0.1M $[Mg(NO_3)_2.6H_2O]$ solution and 150 mL of 0.05M $[Al(NO_3)_3.9H_2O]$ were prepared in such a way that molar fraction $(Al^{3+}/Al^{3+}+Mg^{2+})$ value would be 0.33. These two salt solutions were mixed at a pH value of ~9. The solubility of $Mg(OH)_2$ will be higher than that of $Al(OH)_3$ at this pH value due to which all Al^{3+} ions will be coprecipitated with Mg^{2+} maintaining 2:1 stoichiometry of Mg and Al-ions present in each sheet of LDH. Solid urea was added to the solution mixture with continuous stirring until the molar fraction $[urea/\ (Al^{3+}/Al^{3+}+Mg^{2+})]$ became 3.3. A clear solution was obtained after the dissolution of urea which was refluxed for 36 hours at 100°C. The white precipitate of LDH obtained was filtered out, washed with distilled water, and dried at 60°C in an oven.

Characterization techniques

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded using SHIMADZU spectrophotometer (IR tracer 100) in the wavenumber range of 400-4000 cm^{-1}.

X-ray diffraction (XRD)

The crystalline phase and structure of the samples were determined by X-ray diffractometer (Bruker D2 Phaser) with a monochromatic CuKα radiation source (λ = 0.15418 nm) at 2θ values ranging from 20° to 80°. The acceleration voltage of 30 kV and emission current of 10 mA were used.

Results and Discussion

FTIR spectra of LDH prepared by coprecipitation and urea hydrolysis methods are presented in Figure 4. The peaks that appeared at different wavenumber range in the spectra are due to metal-oxygen bonds, CO^{3--}, NO_3^- and OH^-. However, bands shifting (from actual wave number value) and bands weakening are found to occur. The peaks located below700 cm^{-1} (i.e. 454, 560, 698, and 712 cm^{-1}) signify O-M-O and M-O-M vibration and stretching bands of magnesium and aluminum (where M = Metal) [36,37]. Similarly, the peaks centered at 830, 972, 1180 and 2350 cm^{-1} are due to free CO^{3--} ions present in the materials which might have been formed by the reaction of atmospheric CO_2 during the material synthesis and/or CO^{3--}derived from Na_2CO_3 used [37,38]. The prominent band appearing at 1032 cm^{-1} is because of the stretching vibration of the C-O bond present in CO_3^{--} ions [38]. Similarly, peaks centered at 1366 and 1508 cm^{-1} (more intense in the urea hydrolysis method) corresponds to the vibrational mode of interlayer CO_3^{--} ions as well as NO_3^-[36,38,39]. Characteristic peaks centered around 1600 $cm^{-1}$are due to bending vibration of-OH from interlayer H_2O molecules [36-38]. Weak and broad bands located between 3000 and 3100 cm^{-1} are due to the H-bonds formed by the interaction of CO_3^{--} ions and water molecules present in interlayer space [37]. Weak bands at 3695 cm^{-1} correspond to stretching vibration of -OH derived from metal hydroxides layers, interlayered H_2O molecules as well as water adsorbed during synthesis [36,38]. The spectra of the samples prepared from both synthetic routes resemble each other that confirms the formation of similar materials from both of the methods employed.

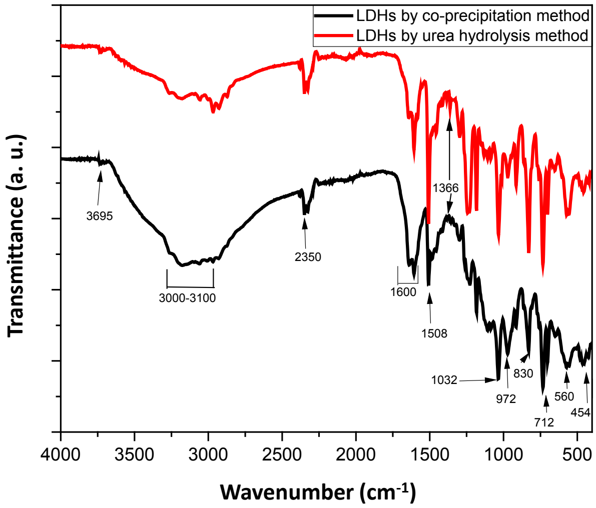

Figure 4: *FTIR spectra of LDH prepared by different methods; the spectra are shifted along Y axis for the sake of better comparison*

Figure 5 presents the XRD pattern of Mg-Al LDH prepared by the urea hydrolysis method. It shows changes in crystallinity pattern with a little shifting of standard peaks according to JCPDS file number 89-5434 [23,35,36]. Shifting of standard peaks to appear at 2θ values of 32°, 69° and 72° to 35°, 71° and 73° respectively and the appearance of some additional peaks at 29°, 40°, 56°, 61°, 62°, 67°, 71°, 73°, and 75° may be attributed to structural modification along with the adhered impurities of unwashed CO_3^{--} and NO_3^- ions present in the materials, moisture absorbed during storage, etc. [40].

The average particle size of LDH was calculated using the Debye-Scherrer formula given in equation (1).

$$D = K\lambda/\beta Cos\theta \qquad (1)$$

where K is shape factor (0.9), λ is the wavelength of X-ray for Cu target (0.1541 nm), β is FWHM (full width at half maxima) in radians, θ is the Bragg's angle. The average particle size of LDH prepared was calculated to be 59.39 nm whereby the value of β (roughly validated by Gaussian fitting of highest intensity peak at 2θ = 35°) was 0.44°. Similarly, the peak corresponding to 2θ value at 11.67° is another characteristic peak of Mg-Al LDHs [35,36] which could not be measured by X-Ray diffractometer (Range: 20° to 80°) used in this experiment.

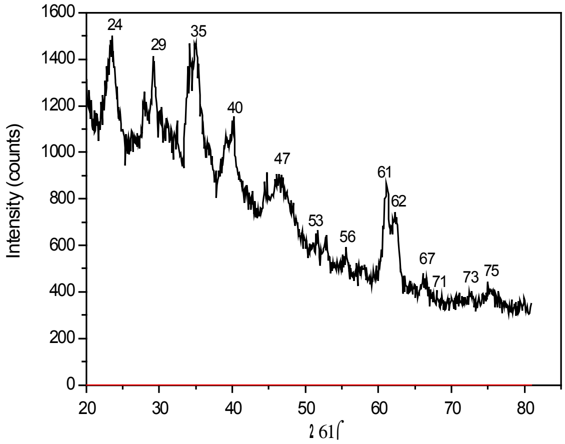

Figure 5: *XRD pattern of LDH prepared by urea hydrolysis method; the figures presented at the peaks are 2θ values of the corresponding peaks*

Conclusion

Mg-Al layered double hydroxides were successfully prepared by coprecipitation and urea hydrolysis methods using nitrate salts of magnesium and aluminum as starting materials. It has been demonstrated that nano-LDH can be prepared easily in an ordinary chemistry laboratory, even in high schools. FTIR spectra confirm the structure of $Mg(OH)_2$ and $Al(OH)_3$ with CO_3^{--} and NO_3^- ions and H_2O molecules as interlayer species. These results are further supported by XRD patterns of the materials whereby the peaks appearing at 2θ values of 35°, 71°, and 73° of corresponding to the Mg-Al hydrotalcites. The average grain diameter of the particles is in the range of 20 to 60 nm. Some impurities such as free CO_3^{2-} ions, and moisture have been detected.

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