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Synthesis and Characterization of Co-Al-LDH

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Abstract: ***Present work involves the preparation of Co-Al-LDH through Precipitation method and its characterization. Co-Al-LDH Layered double hydroxides (LDHs) are typical two-dimensional nanomaterial layered solids and are very interesting because of their multiple applications as catalysts, ion exchangers, sorbents, etc. Co–Al LDHs with divalent Co^{+3} ion and trivalent Al^{+3} ion, are one of the most commonly studied LDHs because of their excellent electrochemical properties and low cost. The main aim of the present work is to examine the effect of Co–Al layered double hydroxide (LDH) concentration on the structural, thermal and rheological properties of poly(methyl methacrylate) (PMMA) nanocomposites. PMMA/Co–Al LDH nanocomposites were prepared and analyzed by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and thermo gravimetric analysis (TGA).***

Keywords: Co-Al-LDH, nanomaterial, Precipitation method, X-ray diffraction

1. Introduction

Layered double hydroxides comprise a category of inorganic materials with highly tunable composition and structures. These materials have shown exciting properties such as high surface area, two dimensional structures, positive charge on the surface, resistant to changes upon heating that is high thermal stability, and excellent anion exchange capabilities. The structure of these materials is based on positively charged metal hydroxide layers, which require the presence of interlayer anions to maintain overall charge neutrality. The most important class of LDHs can be represented by the general formula $[M^{+2}_{1-x}M^{+3}_{x}(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$. The layers have a brucite like structure, in which the isomorphic substitution of some divalent cations by trivalent ones gives rise to the positive residual charge. Co-Al-LDH on calcinations gives mixed CoO and Al_2O_3.These oxides can act as catalysts towards various organic transformations. Co-Al-LDH can also act as precursor for the preparation of nanocomposites. LDHs also known as hydrotalcite-like compounds (HTLCs) or anionic clays are layered compounds that consist of positively charged metal hydroxide sheets with intercalated anions and water molecules in the interlayer region .

The general formula of LDHs is $[M^{II}_{(1-x)} M^{III}x (OH)_{2]}A^{n-}_{x/n}.mH_2O$[30], where

- M^{II} is a divalent metal such as Ca^{+2}, Mg^{+2}, Ni^{+2}, Zn^{+2}, Mn^{+2}, Fe^{+2}, Cu^{+2} or Co^{+2}
- M^{III} is a trivalent metal such as Al^{+3}, Mn^{+3}, Fe^{+3}, Cr^{+3} or Co^{+3}
- A^{n-} is anion with a valency n
- X, defined as $[M^{III}]/([M^{III}]+[M^{II}])$, is usually between 0.25 and 0.33 [27-29]

LDHs have excellent adsorbing properties because of three major reasons

1) Large interlayer spaces(high porosity)
2) Huge number of exchangeable anions in between the positively charged layers
3) Water resistant structures

The above mentioned properties of LDHs enable these materials to have certain distinguished applications in various fields such as catalysis, Water and air purification and nuclear waste treatment. Recent research has indicated that LDHs can be used as potential drug carriers and controlled drug delivery system.

Reagents and solutions

$Co(NO_3)_2\cdot6H_2O$, $Al(NO_3)_3\cdot9H_2O$, NH_3 solution, acetone and p-nitrophenol were used as received. The solvent used for the preparation of solutions was double distilled water. 250.0 mL of aqueous solution containing 145.52g $Co(NO_3)_2\cdot6H_2O$ and 93.7825g $Al(NO_3)_2\cdot9H_2O$ was prepared in double distilled water. The aqueous NH_3 solution (250.0 mL) was also prepared in double distilled water.

Synthesis of Co-Al LDH: $Co_2Al(OH)_6(NO_3)\cdot2H_2O$

$Co_2Al(OH)_6(NO_3)\cdot2H_2O$, was prepared according to method described by Olanrewaju et al. About 145.52 g of $Co(NO_3)_2\cdot6H_2O$ and 93.7825 g of $Al(NO_3)_3\cdot9H_2O$ were dissolved in 250mL of boiled and cooled distilled water. The above solution was added drop wise, under vigorous stirring, to 250 mL of aqueous ammonia solution. After the addition the precipitate was allowed to stand at 60°C for next two hours. Then it is kept for aging at 60°C in hot air oven for an overnight. The material obtained was washed five times with boiled and cooled distilled water and finally with acetone and dried at 60ºC in an air oven to constant weight.

2. Results and Discussions

Characterization of Co-Al-Nitrate LDH using IR spectroscopy

IR spectrum of prepared Co-Al-LDH was recorded. Fig.1 shows the IR spectrum of Co-Al-LDH. A strong and broad absorption at 3510.4 cm^{-1} is attributed to the stretching vibration of the hydroxyl groups of the brucite-like-sheets (along each layer) and water in the interlayer space. The O─H bending vibration of interlayer water molecules is observed at 1633.6 cm^{-1} [52]. The presence of interacted nitrate ions in interlayer region can be confirmed by the presence of a sharp peak at 1384 cm^{-1}. The peaks at lower wave numbers indicate the Metal-Oxygen stretching

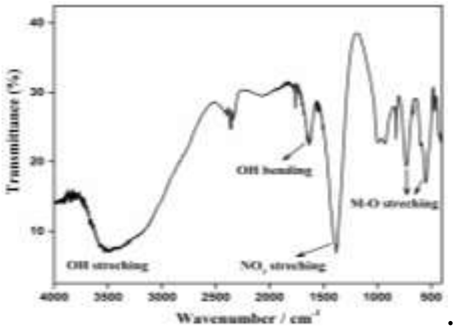

Figure 1: IR spectrum of Co-Al-LDH.

Characterization of Co-Al-Nitrate LDH using PXRD

The prepared LDH, Co-Al-Nitrate was characterized using X-Ray diffraction technique. The resulted PXRD pattern of Co-Al-Nitrate is shown in Fig.2. PXRD pattern indicates crystalline nature for Co-Al-Nitrate LDH. The peaks in the left side of PXRD pattern relates to the interlayer region of LDH while peaks on right are a characteristic of individual layers. The basal or d-spacing of the prepared Co-Al-Nitrate LDH was calculated using Bragg's equation and found to be ~9.01 Å .

$$2\theta = 9.8°, \theta = 4.9°, \lambda = 0.154 \text{ nm} \ \& \ n=1$$

$$n\lambda = 2d\sin\theta, d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 0.154}{2 \times \sin(4.9)} = 0.901 \text{ nm} = 9.01 \text{ Å}$$

This basal spacing also suggests that the nitrate ion is in a tilted orientation in the interlayer region, with its plane almost perpendicular to the hydroxide sheets [53].This interlayer distance has been reported by a number of groups [52, 53] and it is the most common interlayer spacing obtained for a nitrate intercalated Co-Al LDH. PXRD pattern of Co-Al-Nitrate is also compared with International Centre for Diffraction Data (ICDD) database and found to be matching with typical hydrotalcite-type LDH structure (JCPDS 38-0487).

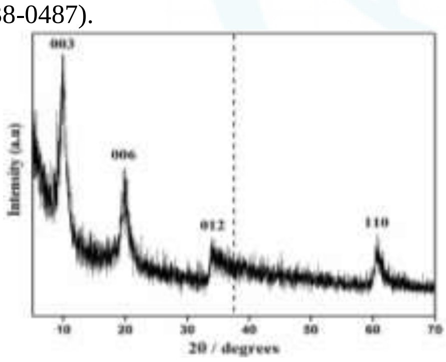

Figure 2: PXRD pattern of Co-Al-Nitrate.

Structure of Co-Al-Nitrate LDH

Based on the observations from IR spectrum and PXRD pattern structure of Co-Al-Nitrate LDH can be proposed. The layered structure of Co-Al-Nitrate LDH is closely related to that of hydrotalcite, $Co(OH)_2$. In a hydrotalcite layer, each Co^{2+}ion is octahedrally surrounded by six OH^- ions, and the different octahedra share edges to form an infinite two-dimensional layer. Partial isomorphous substitution of Co^{2+} ions by Al^{3+} gives the hydrotalcite-like layers a positive charge and the resulting negative charge deficiency is relatively delocalized with respect to the inter-lamellar plane. In Co-Al-Nitrate LDH the positive charge is balanced by nitrate anions, which are located in the interlayer region between the two hydrotalcite-like layers. This gallery space also contains water molecules, hydrogen bonded to layer OH and/or 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 as shown in Fig.3.

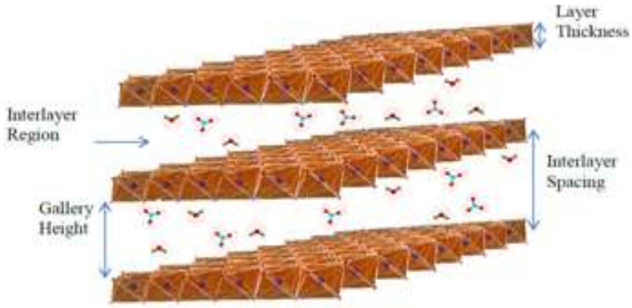

Figure 3: Co-Al-Nitrate LDH

Thermogravimetric analysis of Co-Al-Nitrate LDH

The thremogravimetric analysis (TGA) of Co-Al-NO_3 LDH was carried out under nitrogen atmosphere in the temperature range 50 − 900°C and traces obtained are shown in Fig.4. Three stages of weight loss are observed in Fig.4. The first range occurring in 60 − 200°C indicates the loss of interlayer water and weakly adsorbed water molecules. The second weight loss in the range 240 − 370°C is attributed to the removal of nitrate ions as thermal decomposition of hydrotalcite-like layers through the removal of OH groups as water molecules which leads to the destruction of layers and formation of mixed oxides of CoO and Al_2O_3

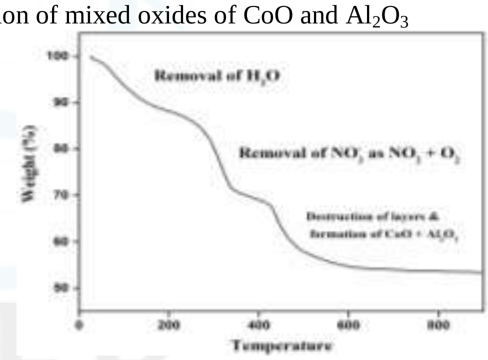

Figure 4: TGA traces for Co-Al-NO_3 LDH

3. Conclusions

Precipitation method is the most suitable way to prepare Co-Al-Nitrate LDH. The prepared Co-Al-Nitrate LDH was found to be crystalline. The prepared Co-Al-Nitrate LDH was having hydrotalcite like layers. Interlayer region of Co-Al-Nitrate LDH contains nitrate ions and water molecules. Basal spacing from PXRD and IR absorptions confirms the presence of nitrate ions in interlayer region. PXRD pattern indicates crystalline nature for Co-Al-Nitrate LDH.

Co-Al-LDH on calcinations gives mixed CoO and Al_2O_3. These oxides can act as catalysts towards various organic transformations. Co-Al-LDH can also act as precursor for the preparation of nanocomposites. Co-Al-LDH acts as photo catalyst for the conversion of CO_2 to methanol. Co-Al-LDH was also employed in the preparation of nanocomposites which acts as anticancer nanodelivery systems. Co-Al-LDH polymer nanocomposites were utilized for flame retardant materials.

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