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Research Article

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Synthesis and characterization of hydrotalcites

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ABSTRACT

A new synthesis of hydrotalcite like materials having a composition $[M+xA1^{3+}]$ $(OH)_2Ax.mH_20$, where M^{2+} is magnesium, nickel or cobalt and A^{-} is a monocarboxylic anion, is described. The synthesis involves reacting a source of the divalent cation with a monocarboxylic acid in aqueous slurry at 110^{0} C for 24 hours. The reactive source of magnesium is either magnesium oxide or hydroxide and the reactive source for nickel and cobalt are the respective hydroxides. This synthesis method results in the formation of hydrotalcite with a unique sheet-like morphology with the sheets having breadth to thickness ratio in excess of 100, in contrast to the previously known hexagonal hydrotalcites which have a breadth to thickness ratio between 5 and 10. The phrase 'sheet-like' in this work describes the macroscopic morphology of the hydrotalcite crystallites. A key finding was that the presence of monocarboxylic acid was necessary for the formation of sheet morphology. It was also demonstrated that sheet and hexagonal morphologies readily interconvert via a common mixed oxide precursor.

Key words: Hydrotalcite, Synthesis, Layered double hydroxide, Characterization

INTRODUCTION

Layered double hydroxide (LDHs) is a class of materials with a great number of applications due to their structural, chemical. Electronic, optical and magnetic properties. These compounds can be used as catalysts and catalyst support, polymer stabilizer, anion exchangers, in medical application, and in modified electrode.

The structure of the LDHs can be described considering the $ZnCl_2$ brucite structure, in which the cations are in the center of an octahedron, of which sharing chloride groups result in the planner structure. When part of the divalent cations is isomorphously replaced by trivalent cations, positively charged layers are formed. In order to neutralize the positive charge, anions must be intercalated between the layers, resulting in a hydrotalcite- like structure. The preparation of LDHs contain different M^{2+} , M^{3+} and anion combination enable variations in the visual spacing, producing compounds with properties that combine the features of the lamellar structure with those of the anions. Nitrate–nitrogen (NO₃–N) concentration in surface and groundwater has increased in many locations in the world. In recent times, the extensive use of chemical fertilizers and improper treatment of wastewater from the industrial sites and urban sites has led to several environmental problems. Rural areas characterized by heavy agricultural activities contributing to the NO₃–N contamination is livestock. The other problem is the over application of nitrogen based fertilizers. This is the largest source and the primary concern of NO₃–N contamination in groundwater. Several nitrogenous compounds, including ammonia, nitrite and nitrate have been frequently present in drinking water and various types of agricultural, domestic and industrial waste water [1,2]. US Environmental Protection Agency (EPA)

has set the maximum contamination level at 10 mg/L of NO_3 -N [3,4]. Deleterious effects of nitrate on health are well known. Elevated nitrate concentrations in drinking water sources present a potential risk to public health. It can stimulate eutrophication, which causes water pollution due to heavy algal growth. Acute poisoning occurs within 30 min to 4 hour after ingestion of plants or water high in nitrates. Thus, the problem occurs very quickly and often the cattle are observed to be normal one day and dead the next day. A very early sign is salivation followed by frequent urination. Soon after, the cattle exhibit difficult breathing increased respiratory rate, and dark brown or "chocolate" colored blood and mucous membranes. The animals then become weak, reluctant to move, and have convulsions before they die. If pregnant cattle receive a dose that is not quite deadly, they may abort soon after recovering. Nitrate contaminated water supplies have also been linked to outbreaks of infectious diseases in humans [2]. Excess nitrate in drinking water may cause methaemoglobinaemia also called a blue baby disease, in newborn infants [5]. The literature survey revealed that nitrate ion also causes diabetes [6] and is a precursor of carcinogen.

Background ions concentrations in surface waters are usually below 5 ppm, and higher concentrations are often observed in groundwater. Recent surveys revealed that the nitrate levels have been increased in drinking water supplies in the European community, the United States, Canada, India, etc. Nitrate is considered to be relatively non-toxic to adults, concentrations greater than 50 ppm can be fatal to infants under six months of age. Increased nitrate concentrations in groundwater have caused the shutdown of wells and rendered aquifers unusable as a water source. Surface waters also have experienced seasonal nitrate violations. As a result, there is renewed interest in the removal of nitrates from raw water. Unfortunately the policy of countermeasures, especially concerning agriculture and environment to limit pollution by nitrates, is efficient only in the long term. So, technical solutions become obligatory. A survey of the literature yielded an abundance of information on the technical treatment to remove nitrate from water, including ion exchange [7] biological denitrification [8–10], chemical denitrification[11–13], catalytic denitrification [14,15], reverse osmosis [16] and electro dialysis[17]. Current technologies for removal of nitrate, like ion exchange, reverse osmosis are not selective to nitrate, generate secondary brine wastes and require frequent media regeneration.

Owing to above difficulties, hydrotalcite like compounds (HTlc) was thought to prove a potential adsorbent for the removal of nitrate. Hydrotalcite-like compounds constitute an important class of inorganic materials with desirable properties to remove anionic pollutants from water [18–22]. Hydrotalcites, also known as layered double hydroxides (LDHs) or ionic clays are based upon the brucite [Mg(OH)₂] structure in which some of the divalent cations are replaced by trivalent cations (e.g., Al, Fe, Cr etc.) resulting in a charge layer. This layer charge is counterbalanced by anions such as carbonate, nitrate, sulfate or chloride in the interlayer spaces. In LDHs a broad range of compositions is possible of the type [$M^{2+}1-xM^{3+}x$ (OH) ₂] [An–] $x/n \cdot yH_2O$, where M^{2+} and M^{3+} are the divalent and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33. Anis an exchangeable interlayer anion. The degree of anionic exchange in the LDHs depends on the structural characteristics, e.g. the nature of the interplay anion and crystallinity. Exchange conditions like pH and carbonate contamination of the environment are also important limitations. Due to the high affinity of LDHs toward the carbonate ion, materials with intercalated carbonate ions have relatively smaller exchange capacities unless being calcined. High pH conditions must be applied to maintain the stability of LDH, however, OH–intercalation is competitive in this case.

Although studies have examined the synthesis of various LDHs and the way in which they interact with various anions, the synthesis of Hydrotalcite and its application towards removal of nitrate has not been examined previously. So, the present research was aimed to synthesize, characterize and to study the removal efficiency of nitrate by anions. The effect of various parameters on the effectiveness of treating nitrate contaminated water with hydrotalcite was known. Therefore, in this study, hydrotalcite was added to nitrate solutions and the effect of different variables (calcinations temperature, dose, time, pH, initial nitrate concentration, the effect of other anions etc.) on the removal of nitrate from solution by hydrotalcite was examined.

The most common approach to synthesis of HT-like materials is by co-precipitation of the aqueous solution of the two cations, with a base [5-8]. The co-precipitation is carried out at room temperature and a pH of 8-10, with an optional post-co-precipitation heating of the slurry to improve the crystalline of the final product. The HT-like materials synthesized by the above method have well-defined hexagonal crystal morphology [9, 10]. Although the thickness of these crystallites and in essence the aspect ratio has not directly been reported, this value can be inferred based on the knowledge of the surface area and the crystallographic density using the approach described in this work. Reichle et al[9,10] has reported that HT crystallized at 65 and 200^oC has a breadth of 0.1 and 0.5 mm from

TEM and surface area of 120 and 13.9 m 2 g^{-1} , respectively. The crystallographic density is estimated to be 2.0cm 3. This translates into thicknesses of 0.008 and 0.07 m and aspect ratios of 12 and 7, respectively.

EXPERIMENTAL SECTION

Reagents and chemicals

Zinc chloride, aluminum chloride, sodium chloride and sodium hydroxide used in the present study were of analytical grade and were obtained from Merck. 1000 mg/L stock solution of nitrate was prepared by dissolving 1.6305 gm. of KNO₃in 1 L decarbonated distilled water. The required concentration of nitrate solution was obtained by serial dilution of 1000 mg/L nitrate solution. The measuring cylinder, volumetric flask and conical flask and other glassware used to be from Borosil.

Synthesis of Hydrotalcite

The M^{2+} -Al HTs with M^{2+}/M^{3+} mole ratio 1: 3 were synthesized by the co-precipitation method. An aqueous solution of 200 ml containing an appropriate amount of salt was prepared. The metal chloride solution was slowly added into 200 ml of aqueous NaOH (2.25 M) and Na₂CO₃ (0.45 M) until the pH was around 8-9 under vigorous stirring at room temperature. Then the thick slurry was heated for 30 minutesat80°C for aging. Afterward, the slurry was filtered and washed several times in order to remove the alkali metals and the chloride ions with deionized water until the effluent solution was neutral. Finally, the filter cake was dried at 110°C for 24 hours and grind in a mortar. The modified HTs were prepared by Co precipitation using the method described above.

Analysis methods

The sample solution was filtered by 0.45 lm membrane before analysis. Nitrate and nitrite concentrations in the solution were measured using a Philips X'Pert spectrophotometer. The Zeta - potential was measured using a Malvern Zetasizer 2000. The scanning electron microscopy (SEM) images and electron dispersive X-ray analysis were obtained using a Philips X'Pert microscope. XRD-ray diffraction pattern of the samples was obtained using a Philips X'pert- diffractometer with Cu Ka radiation (40 KV). FT-IR spectra inthe range 4000–400 cm⁻¹ of samples as KBr pellets were recorded with a Shimadzu IR Affinity⁻¹, Fourier transform infrared spectrometer.

1. Synthesis of Mn-Al-ClLDHs Hydrotalcites

The M^{2+} Mn-Al HTs with M^{2+}/M^{3+} mol ratio 1: 3 were synthesized by the co-precipitation method. An aqueous solution of 200 mL containing an appropriate amount of MnCl₂.6H₂O and AlCl₃.6H₂O were prepared. The metal Chloride solution was slowly added into 200 mL of aqueous NaOH (2.25 M) and Na₂CO₃ (0.45 M) until the pH was around 8-9 under vigorous stirring at room temperature. Then the thick slurry was heated for 1 Hrs. at 80^oC for aging. Afterward, the slurry was filtered and washed several times in order to remove the alkali metals and the chloride ions with deionized water until the effluent solution was neutral. Finally, the filter cake was dried at 110 ^oC for 24 h and grind in a mortar. The modified HTs were prepared by co precipitation using the method described above.

Characterization Techniques

X-diffraction

Powder XRD of calcined HTlc was obtained and the graph is presented in figure 1. The difractogram was analyzed with PhilipsX'Pert High Score software to search for different phases. The results obtained from the analysis indicated that there were not any starting materials present in the HTlc but some of the HTlc formed was converted to oxides of Mn and Al due to calcination. The figure shows sharp and symmetric peaks which gives clear indication that the samples are well crystalline and peak corresponding to the planes are characteristic of clay minerals (HTlc)having layered structure.



Morphology of the catalysts by SEM micrography

Scanning electron micrograph of Mn–Al–Cl HTlc sample was obtained and is presented in figure-2. The structural morphology of the HTlc can be clearly observed from the figure. Chemical analysis of HTlc was carried out in order to calculate the molar ratios of M(II):M(III)present in the HTlc. During the synthesis, M(II):M(III)ratio was taken as 3:1. The M(II):M(III) ratios obtained were almost equal to 3:1. So, chemical analysis of HTlc Ascertain the synthesis with required M(II):M(III)ratios. The SEM image (figure-2) of the sample shows aggregates of small secondary particles of about 0.6 mm india meter.



Figure -2 : SEM Images of Mn-Al-CILDHs Hydrotalcite

Thermogravimetric and differential thermal analysis

TGA and DSC analyses of HTlc were carried out and results are presented in figure-3. One endothermic peaks were found from the DSC analysis of Mn–Al–Cl HTlc. First endothermic process was up to the temperature of 230° C and the corresponding weight loss from TGA analysis was found to be 21.14%. This weight loss was probably due to the physically adsorbed water on the HTlc.



FTIR study of Mg–Al–Cl HTlc and HTlc recovered after adsorption were carried out in order to know the presence of different groups, structures and adsorption of nitrate onto HTlc. FTIR spectrum of Mg–Al–Cl is presented in figure. An intense broad band at 3437cm–1 may be due to superimposition of deformational vibrations of physically adsorbed water [23], vibrations of structural OH– groups [24] and characteristic violent vibration of HO-OH in hydrotalcite [25].

The peak at 2362cm-1 is apparently due to CO_2 background of the measurement system [25,26]. The infrared spectra of the Mn and Al-hydrotalcites in the region between 400 and 4000 cm⁻¹. Band component analysis of the hydroxyl-stretching region between 538 -3437 cm⁻¹ reveals the presence of four bands. In general the band observed around 538- 3437 cm⁻¹ is interpreted as the CO_2^{-3} -H₂O bridging mode of carbonate and water in the interlayer. There seems to be a very small influence by the hydroxide layer composition as indicated by a shift in the band position from 3437 cm⁻¹ for the Mn-hydrotalcite to 3437 cm⁻¹ for the Mn-hydrotalcite and to 1616cm⁻¹ for the Al-hydrotalcite. A peak at 1383cm-1 is associated with the antisymmetric stretching mode of nitrate [27,28]which ascertains the adsorption of nitrate onto Mn–Al–Cl HTlc. A broad band at 538.14 cm⁻¹ is most probably due to the superposition of the characteristic bands of HTlc.



Figure -5:FTIR Spectrum of Mn-Al-ClLDHs Hydrotalcite

2. Synthesis of Cr-Al-ClLDHs Hydrotalcites

The M^{2+} Cr-Al HTs with M^{2+}/M^{3+} mol ratio 1: 3 were synthesized by the co-precipitation method. An aqueous solution of 200 mL containing an appropriate amount of CrCl_{2.}6H₂O and AlCl_{3.}6H₂O were prepared. The metal Chloride solution was slowly added into 200 mL of aqueous NaOH (2.25 M) and Na₂CO₃ (0.45 M) until the pH was around 8-9 under vigorous stirring at room temperature. Then the thick slurry was heated for 1 Hrs. at 80^oC for aging. Afterward, the slurry was filtered and washed several times in order to remove the alkali metals and the chloride ions with deionized water until the effluent solution was neutral. Finally, the filter cake was dried at 110 ^oC for 24 h and ground in a mortar. The modified HTs were prepared by co-precipitation using the method described above.



Characterization Techniques X-diffraction

X-ray powder diffraction data for Cr-Al HT-like materials with different monocarboxylic anions are shown in figure-6. The patterns are characteristic of the natural HT material, but with expanded d-spacing due to the larger size of the intercalated anions. HT-like materials prepared using our synthesis show a diffraction pattern with strong 00l lines and weak, ill-defined peak lines. This is probably due to the unique morphology of the crystals. In all the

cases, the reflections corresponding to magnesium oxide were absent indicating a complete conversion to the HTlike phase.The X-ray diffraction patterns of the HLC and its heated products are shown in figure-6. The diffraction pattern of the HLC shows the characteristic diffraction peaks of hydrotalcite (card JCPDS 22-0700) and small diffraction peaks corresponding to the brucite-type phase (card JCPDS 7-239). This result confirms that this solid has a double layered structure with a low degree of crystallization. On the other hand, the XRD pattern corresponding to HLC heated to150°C exhibits strong peaks corresponding to the hydrotalcite type material and weak signals of the brucite-type phase. Finally, the diffraction pattern of the HLC heated to 350°C shows the presence of the periclase (card JCPDS 4-0829) and hydrotalcite phases. Thus, the as-obtained product contains a hydrotalcite phase mixed with small amount of brucite phase.

Morphology of the catalysts by SEM micrography

The HT-like sheets were characterized by their aspect ratio, i.e., breadth to thickness. Scanning electron microscopy was used to measure the breadth of the sheets. The sheets produced by our synthesis have a irregular, ill-defined shape and display an open 'lettuce head' type appearance under a scanning electron microscope. Some of the smaller sheets did roll up into a spherical shape despite freeze drying. A typical SEM image isshown in figure-6, where a smaller sheet can be seenoverlaying on top of a larger sheet. Similar sheet topography was also seen for the other HT-like materials. For the purposes of the current work, the longest planar dimension was defined as the breadth of a particular sheet crystal. An average breadth was calculated by measuring the breadth of 20 such sheet crystallites. The average breadth of the sheets ranged from 10 to 30 gm. This is in sharp contrast to hexagonal crystallites which have a width of approximately 0.5 gm at similar synthesis temperatures.



Figure-7 : SEM Micrograph of Cr-Al-CILDHs Hydrotalcite

Thermogravimetric and differential thermal analysis

The TG/DTA profile of the cerium-containing Cr/Al HTlc samples is presented in figure. All the samples display strong endothermic peaks: the first one below 200° C and the second one between 420 and 450°C. The weight loss in the TG curve corresponding to the first endothermic peak in the DTA profile is due to the elimination of loosely bound water and interlayer water molecules, and the second loss is ascribed to the removal of hydroxyl groups in the metal hydroxide layers and CO₂ resulting from the decomposition of CO₂⁻³ present in the interlayer space as charge-balancing anion [29–32]. The water content in the samples has been calculated from the first weight loss in the TG curve. The sample containing exhibited a net weight loss of 44–46% of the initial weight up to 950°C, with the second weight loss always higher than the first [31,33].



The FT-IR spectra of the Cr/Al HTlcs are presented in Fig. In the HLC spectrum the band at 3377.38 cm^{-1} can be attributed to a high energy stretching vibration of the hydroxyl groups of brucite. The broad absorption band centered at 1680 cm^{-1} is due to the stretching vibration of the hydroxyl groups from water and residual ethanol. The medium intensity band at802.39 cm⁻¹ corresponds to the hydroxyl bending mode of adsorbed water.



3. Synthesis of Pb₆-Al₂-CO₃ LDHs Hydrotalcite

The M^{2+} Pb-Al HTs with M^{2+}/M^{3+} mol ratio 1: 3 were synthesized by the co-precipitation method. An aqueous solution of 200 mL containing an appropriate amount of PbCO_{3.}9H₂O and Al₂(CO₃).16H₂O were prepared. The metal Chloride solution was slowly added into 200 mL of aqueous NaOH (2.25 M) and Na₂CO₃ (0.45 M) until the pH was around 8-9 under vigorous stirring at room temperature. Then the thick slurry was heated for 1 Hrs. at 80^oC for aging. Afterward, the slurry was filtered and washed several times in order to remove the alkali metals and the chloride ions with deionized water until the effluent solution was neutral. Finally, the filter cake was dried at 110 °C for 24 h and ground in a mortar. The modified HTs were prepared by co precipitation using the method described above.





Characterization Techniques X-Diffraction

Powder X-ray diffraction (PXRD) patterns of the samples were recorded with a PAN analytical XRD-PW3050/60 Xpert diffractometer under the conditions: 40 kV, 30 mA,CuKa (λ = 0.15406 nm)Patterns were collected in the range 10 to 80° 20 with a step size of 0.02° and a rate of 30s per step. Samples were crushed into a powdered form. The X-ray diffraction patterns of the synthesized hydrotalcite and the standard reference pattern are shown in figure-11. The XRD patterns obtained for the synthesized products exhibit the same characteristic lines as the hydrotalcite reference pattern, therefore confirming the formation of hydrotalcite. The d(003) spacing values obtained for the synthesized hydrotalcite are 7.84, 7.97, and 8.01 Å. The d(003) spacing value represents the distance between hydrotalcite layers, and therefore changes in this value indicate the effect of anions on the hydrotalcite structure. The

presence of molybdate anions resulted in an increase in the basal spacing, compared to Syn-HT-CO₃, suggesting that molybdateanions are larger in size. The hydrotalcite peaks are broad due to the lack ofhydrothermal treatment, and indicates that the synthesized minerals are of poorcrystallinity. The XRD patterns indicate sodium chloride (NaCl) formed as an impurity in Syn-HT-Mo. Additional washing of the hydrotalcite would remove the presence of NaCl from the surface of the hydrotalcite.

Morphology of the catalysts by SEM micrography

An SEM image of Mg–M–LDH is shown in figure-12. After drying the precipitates obtained by co-precipitation, the structure was clearly observed. The SEM images clearly showed a card-like structure probably derived from the layered HT structures, suggesting that micropores must exist in the samples. The former pore sizes are related to the layered structure, while the latter is due to the "card house" structure consisting of many small plates [34]. In addition, the systems show a compact and smooth structure with some areas with a granular surface.

Figure presents SEM micrographs of the calcined HT. Observations at the SEM showed that the particles are formed by almost homogeneous spherical aggregates of hexagonal platelets. Evident differences are noticed on the SEM micrographs between the precursors and calcined HT. In all cases, the micrographs show the disappearance of card house structure and formation of particles aggregates of MgO phase.



Figure-12: SEM image of Pb-Al-CO₃ hydrotalcite

Thermogravimetric and differential thermal analysis

According to TGA and DTA-analysis, as prepared materials decompose in two stages, as a result of dehydration and dehydroxylation. The process is accompanied by two endothermic effects in figure-13. The first stage is observed in the 50–200°Crange for samples A and in the 100–200°C range for samples B. Since parameter c for samples A is rather small, mass loss is most probably corresponds to release of weakly bounded adsorbed water, whereas interlayer water is partly released from samples B. The second stage of decomposition is observed in the200–400°C range with the peak temperature increasing for thePb0.33/Al0.33/Pb0.33 sample. It is mainly associated with dehydroxylation of hydroxide layers and decomposition of interlayer anions [35,36]. Mass loss is decreased with increased Mn content for samples A and B indicating the decreased amount of OH groups. However, any calculation based on weight loss leads to uncertainty in determination of the content of interlayer molecular water, hydroxide and anion groups because of overlapping of dehydration, dehydroxylation, decarbonization, etc., processes. Interestingly, that the heating of pure Co(OH)₂ is accompanied by exothermic effect due to the following redox reactions.





Infrared spectroscopy

Infrared spectra were obtained using a Shimadzu FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000-525cm⁻¹range were obtained by the co-addition of 128 scans with a resolution of 4 cm⁻¹ and a mirror velocity of 0.6329 cm/s.

FT-IR spectroscopy can also give useful information about the structure of the compounds and interlamellar anions. The FT-IR spectra of Pb-Al-LDH (Pb/Al) samples are shown in figure. These spectra show similar absorption bands for all samples, and the main features arise from the interlayer anion and from the water molecules. The

obvious bands assigned to OH- stretching vibrations (about 3284.77 cm⁻¹), H-bonded stretching vibration (near 3093.82 cm⁻¹), and bending modes of interlayer water (2100.48 cm⁻¹) are present, respectively [37, 38]. The strong peak at 1066.64 cm⁻¹ can be assigned to the stretching mode of carbonate species[39].



4. Synthesis of Ce-Ni-ClLDHs Hydrotalcite

The M^{2+} Ni-Ce HTs with M^{2+}/M^{3+} mol ratio 1: 3 were synthesized by the co-precipitation method. An aqueous solution of 200 mL containing an appropriate amount of NiCl_{2.9}H₂O and CeCl_{3.16}H₂O were prepared. The metal Chloride solution was slowly added into 200 mL of aqueous NaOH (2.25 M) and Na₂CO₃ (0.45 M) until the pH was around 8-9 under vigorous stirring at room temperature. Then the thick slurry was heated for 1 Hrs. at 80°C for aging. Afterward, the slurry was filtered and washed several times in order to remove the alkali metals and the chloride ions with deionized water until the effluent solution was neutral. Finally, the filter cake was dried at 110°C for 24 h and ground in a mortar. The modified HTs were prepared by co precipitation using the method described above.

X-ray diffraction

The XRD patterns of the synthesized hydrotalcites together with the reference patterns are shown in figure-16. In the synthesis of hydrotalcites, it is not unexpected to have traces of impurities present either of the starting materials, by-products of the reaction or as synthesized impurities. In the case of the Ni–Ce hydrotalcite the pattern matched that of the standard reference pattern together with the additional pattern of NiCl. It should be remembered that the XRD. The X-ray beam voltage was40 kV and beam current was 55 mA. Debye-Scherrer equation ($t = 0.89\lambda/\beta \cos \theta$, where *t* is crystallite size, β is FWHM and θ is diffraction angle) was employed for calculation of crystallite size after taking into consideration of instrumental line broadening.

Morphology of the catalysts by SEM micrography

The scanning electron microscope showed that the particles are formed by almost spherical aggregates of fibers. In order to investigate the morphology for the LDHs and LDOs, the LDHs and LDOs with different Ni/Ce molar ratios 0.25, 4.0 and 6.0 were observed with SEM. Thin flat crystals indicating the layered structure were observed for all the LDH samples. The plate-plate overlapping of crystallites gave rise to interfaces that could accommodate extrinsic surface water, as well as other adsorbents. All the particles of the LDH Ni/Ce 4.0 showed well-developed fiber like plates with narrow size distribution(2–4 lm) and the samples could be seen to be made up of individual

fiber particles in line with the typical morphology for hydrotalcite-like materials. This was in agreement with the XRD and FT-IR results mentioned above. The morphology and particle size of the calcined material LDO with Ni/Ce 4.0 was basically similar to those of the LDH precursor, where the hexagonally lamellar morphology was integrally preserved after calcination at 500°C. It was interesting to note that the calcination process did not alter the morphology and the size of the LDH Ni/Ce 4.0 particles, similar to the result reported by Lei et al. [40]. The SEM images of the samples prepared under different conditions are shown in Fig. From the SEM images, it can be seen that, at lower temperature and less aged time, the LDHs show small patches with some amorphous conglomeration (the metallic oxide impurities, which have been proved by the XRD). The patches grow with the increase of time and temperature. Finally, when reaction temperature rises to 160 or 180°C and the reaction time is prolonged to 48 hour, large and thin sheets become prevalent. At these temperatures, prolong the reaction time, only to cause decrease in particle size and amorphous form or impure in phase. When temperature reaches 200°C, more amorphous impurities appear and the size of sheets seems not to enlarge any more.



Figure-16:PXRD of Ce-Ni-Cl hydrotalcite

Thermogravimetric and differential thermal analysis (TGA)

Thermal decomposition of the hydrotalcite was carried out in a TA high-resolution thermo gravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm $3 min^{-1}$). The samples were heated in an open platinum crucible at a rate of 2.0 K min⁻¹ up to 500°C. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases were analyzed. Thermal analysis is a technique for the measurement of the thermal stability of hydrotalcite. In this work we report the stability and thermal decomposition of Ce³⁺and Ni ²⁺ based LDH's with carbonatein the interlayer. Representative differential thermo gravimetric analysis curves (DTG) Ce-Ni-Cl.xH₂O hydrotalcite and their mass spectrometric analysis curves of water and carbon dioxide are shown in Figs .The results of the integral of the DTG curves as determined by the band component analysis of the DTG curves are reported in figure. Each peak in the DTG curve represents a mass loss step and the total mass loss step is 27.63%. The DTG curves are divided into mass loss steps according to the band component analysis. These steps correspond to the maxima in the DTG curves. The mass loss steps are further categorized according to the actual temperature of the mass loss.



Figure-17:SEM image of Ce-Ni-Cl hydrotalcite



Figure-18:TGA Graph of Ce-Ni-Cl hydrotalcite



Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on the Shimadzu FT-IR, IR Affinity-1 in the range of 3635.34–1535.34 cm⁻¹. The advantage of DRIFT technique is that any special treatment of the samples before measurement is required High temperature experiments are faster and easier than in transmission technique, especially in the case of the samples not transparent enough for IR radiation.



5. Synthesis of Ni-Al-PO₄ LDHs Hydrotalcites

The M^{2+} Ni-Al HTs with M^{2+}/M^{3+} mol ratio 1: 3 were synthesized by the co-precipitation method. An aqueous solution of 200 mL containing an appropriate amount of NiPO_{4.9}H₂O and Al₂(PO₄).16H₂O were prepared. The metal Chloride solution was slowly added into 200 mL of aqueous NaOH (2.25 M) and Na₂CO₃ (0.45 M) until the pH was around 8-9 under vigorous stirring at room temperature. Then the thick slurry was heated for 1 Hrs. at 80^oC for aging. Afterward, the slurry was filtered and washed several times in order to remove the alkali metals and the chloride ions with deionized water until the effluent solution was neutral. Finally, the filter cake was dried at 110 ^oC for 24 h and ground in a mortar. The modified HTs were prepared by co precipitation using the method described above.

Characterization techniques of Hydrotalcite.

X-Ray Diffraction

The nature of the resulting material was checked byX-ray powder diffraction (XRD). The XRD analyses were carried out on a PAN analytical PW 1050/25vertical goniometer equipped with a graphite diffracted beam monochromator. The d-values and intensity measurements were improved by application of an in-house developed computer aided divergence slit system enabling constant sampling area irradiation(20 mm long) at any angle of incidence. The goniometer radius was enlarged from 173 to 204 mm. The radiation applied was Co K α from a long one focus co tube operating at 35 kV and 40 mA. The samples were measured at 50% relative humidity insteps can mode with steps of 0.028° 2 θ and a counting time of 2 sec.





Morphology of the catalysts by SEM micrography

SEM of the material shows high crystallinity and lamellar structure. The particles of HT exhibit the hexagonal shape. However, big needle shape particles are also visible and it is found in Ni and Al catalysts. It can be seen that the solids do not present a lamellar structure after without calcination. New aggregates are formed on the support surface due to the introduction of the metal. Its crystal size varies from about 100 to $200\mu m$. Metals are uniformly distributed in the support.

Thermogravimetric and differential thermal analysis

Differential thermal and thermogravimetric analysis(DTA/TGA) of the hydrotalcite was obtained using a Seteram DTA/TGA instrument operating at 0.5° C/min from ambient temperature up to 1000° C under a nitrogen atmosphere. TGA/DTA plot of a characteristic Ni/Al hydrotalcite. The results of the various weight losses. The Mg-hydrotalcite shows a weight loss of approximately9.0% up to 80° C due to physically adsorbed or interlayer water. In the region between 80° C and 230° C, 9.1 wt % is lost due to decarbonisation with an endothermic maximum in the DTA at 222°C. The dehydroxylation basically takes place between 230° C and 420° C with a weight loss of approximately 30.41%. This weight loss is accompanied by an endothermic maximum in the DTA at 400°C. Above 400°C, still a minor weight loss is observed of approximately 5%.



Figure-22: SEM image of Ni-Al-PO₄ hydrotalcite



Figure-23: TGA graph of Ni-Al-PO₄ hydrotalcite



Figure-24:DSC graph of Ni-Al-PO₄ hydrotalcite

The infrared spectra of the Ni-, and Al-hydrotalcites in the region between 400-4000 cm⁻¹. Band component analysis of the hydroxyl-stretching region between 558.24 and 3393.81 cm⁻¹ reveals the presence of four bands. In general the band observed around 2950- 3050 cm⁻¹ is interpreted as the CO_2^{-3} -H₂O bridging mode of carbonate and water in the interlayer. There seems to be a very small influence by the hydroxide layer composition as indicated by a shift in the band position from 1355.96 cm⁻¹ for the Ni-hydrotalcite to 3393.81 cm⁻¹ for the Al-hydrotalcite.



Figure-25: FT-IR spectra of Ni-Al-PO₄ hydrotalcite

RESULTS AND DISCUSSION

In this chapter hydrotalcite having different cation has been synthesized by reflux and co-precipitation method and hydrotalcite having different ratio has also been synthesized and characterized them with different technique i.e

XRD, TG-DSC, SEM, TEM, FTIR and concluded that hydrotalcite is crystalline in structure but there are some amorphous.

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