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A GREEN SYNTHESIS AND CHARACTERIZATION OF Zn-Al-CO₃ AND Ni-AL-CO₃ HYDROTALCITE CATALYSTS BY USING GRINDING METHODS

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ABSTRACT

The study of different types of synthesis of hydrotalcites were studied. In the current research, hydrotalcites like Zn-Al-CO₃ and Ni-Al-CO₃ were synthesized using the grinding method. The reaction conditions were optimized and the best results and yields were obtained at room temperature keeping the pH constant in 30 minutes. The effect of different molar ratios of hydrotalcites were also investigated and were further characterized using XRD, FTIR, and TGA. The results exhibited that the hydrotalcites were synthesized as the synthesized samples were found to be identical to the reported hydrotalcites materials. The confirmation was done on the basis of X-ray diffractogram and FTIR. Generally, the results exhibited the effect of molar ratio on the structure and material properties of hydrotalcites synthesized.

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INTRODUCTION

The search for alternative cleaner, safer, and environmentally friendly technologies is one of the priorities in chemistry. With this objective, the reduction of wastes together with the use of renewable feedstocks, environmentally friendly reagents and catalysts are important parameters to achieve more sustainable processes (Horvath, 2007). In addition to those, catalysis can improve sustainability of chemical processes by means of process intensification. Therefore, catalysis plays prominent role in chemistry. The majority of actual industrial chemical processes, involving the manufacturing of commodity-, petro-, pharmaceutical, and fine chemicals, clean fuels, etc. as well as the pollution abatement technologies, have a common catalytic origin. It is well recognized that ~90% of industrial processes involve at least one catalytic step. Among various solid base catalysts studied in literature, hydrotalcites-like (HT-like) compounds, are receiving an increasing attention in recent years for their diverse applications like catalysts, supporters, ion-exchangers, additives and precursors for multicomponent reactions. To briefly introduce, hydrotalcite (HT) are minerals belonging to the family of anionic clays, are layered materials with Mg(OH)₂ structure wherein partial substitution of Mg²⁺ by Al³⁺ occurs and the excess positive charge density is compensated by anions which occupy between the sheets

along with water molecules (Geuens 2014). It is also known in the chemistry of hydrotalcites that, changing the nature of the cations in the layers, M²⁺/M³⁺ ratio, nature of the compensating anions or activation/synthesis methodology can modify the acid-base and redox properties of these materials and in turn on their catalytic behavior (Feofilova 2010 and Joshi 2007). These materials hydrotalcites are double layered lamellar anionic clays with a general formula (Mg₆Al₂(CO₃)(OH)₁₆·4(H₂O)). The formula as outlined above was first described (Allman 1968; Allman 1970; Taylor 1969 and Taylor 1973). In this formula, M²⁺ (M = Mg, Ca, Fe, Co, Cu, Ni, or Zn) and M³⁺ (M = Al, Cr, Ga, Mn or Fe) are di- and trivalent cations, respectively, the value of x is equal to the molar ratio of M²⁺/(M²⁺ + M³⁺) and is generally in the range 0.2–0.33; Aⁿ⁻ is an anion to balance the charge. As a result, a large class of iso-structural materials with versatile physical and chemical properties can be obtained by changing the nature of the metal cations, the molar ratios of M²⁺/M³⁺, as well as the types of interlayer anions. The first hydrotalcites were synthesized in the early 1940s (Feitknecht 1942). Nowadays, it has been recognized that co-precipitation is one of the most reliable and reproducible techniques for the preparation of hydrotalcites. But grinding method is also most important technique synthesis of hydrotalcites. It allows homogeneous precursors to be used as starting materials, where bivalent or trivalent more elements are primary mixed together. For grinding method it is necessary to work under conditions of supersaturation, mostly achieved by variation in pH

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Hydrotalcites, including layer double hydroxide like compounds, have received considerable attention due to their potential applications in catalysis, electrochemistry, polymerisation, photochemistry, magnetisation, biomedical science and environmental applications (Cavani 1991; Rives 2001; Li 2005; Evans 2006 and Mandal 2008). To date, various synthetic protocols including the coprecipitation method, classical ion exchange method, reconstruction method, salt oxide method, sol-gel method, topochemical synthesis, SNAS (separate nucleation and aging steps), electro-synthesis, urea hydrolysis, combustion synthesis, and hydrothermal and microwave treatments have been employed for the preparation of hydrotalcites (He 2005). Fig 1. The structure of HTs. In this current work, zinc-aluminium and Nickel-aluminium-layered double hydroxides intercalated with carbonate was synthesized by using grinding method. The synthesized hydrotalcites were characterised by powder XRD, FTIR, and TGA. The effects of factor affecting of depend upon nature and structure of hydrotalcite were studied.

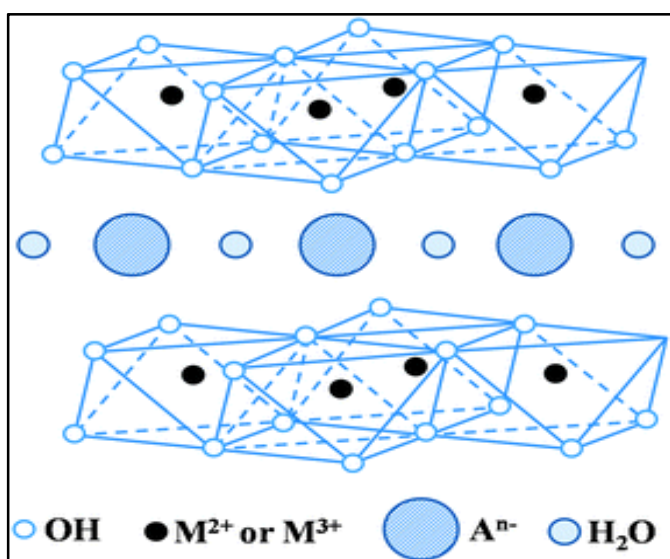


Figure 1. Structure of hydrotalcite

EXPERIMENTAL SECTION

Reagents and chemicals: Zinc chloride (ZnCl₂), Aluminum nitrate Al(NO₃)₃, Nickel Nitrate (NiSO₄) sodium hydroxide (NaOH) and Sodium Carbonate (Na₂CO₃) analytical grade chemicals were purchased from Rankem, for the synthesis of Zn-Al, Ni-Al, hydrotalcites. During the whole process of synthesis only deionized water was used for avoiding impurities during the synthesis process. The measuring cylinder, volumetric flask and conical flask and other glassware used were of Borosil.

Characterization techniques: Synthesis of different hydrotalcites were characterized by various X-Rd (x-ray Diffraction), FTIR (Fourier Transform Infra-Red), TGA (Thermo-gravimetric analysis). X-RD was performed on a Rikaguminiflex 600 diffracto-meter. FTIR was performed on a Perkin Elmer 4000-400cm⁻¹ using by identification of functional group in the compound. TGA graph was analyzed form TW60 Shimadzu anal. Ltd.

Synthesis of different hydrotalcites by using grinding method: The Zn-Al-X, Ni-Al-X, (X= CO₃²⁻) hydrotalcites with different ratios were synthesized using the grinding

method. In this method, first the oxides were taken and suspended in 2 ml distilled water further accurate amount of measured hydroxides were added while maintaining the pH at 8. To increase the pH some sodium bicarbonates were added to enhance the pH from 8 to 10. For next 5 minutes the mixture was taken and grinded homogeneously in mortar and pestle. Further, it was washed with distilled water several times for removing the impurities and was dried at 100⁰C overnight and calcined at 723 k for another 1.5 hours.

RESULTS

Characterization of Zn-Al-CO₃ hydrotalcite

A) X-RD: The P-XRD pattern showed symmetric and sharp peaks with high intensity at low 2θ angle of typical layered structure, whereas asymmetric and broad peaks at high 2θ angle. This XRD patterns gave information of good crystallinity of synthesized hydrotalcites. There intense reflections at 2θ values of 12.20°, 23.04°, 32.53°, 34.42⁰, 40.15°, 46.64° and 68.75°, respectively synthesized Zn/Al hydrotalcites molar ratio of 3:1 were observed. The sharp and symmetrical diffraction peaks with a low and stable baseline indicate the well crystallized layered structure of the Zn-Al-LDH. The XRD patterns of Zn-Al-hydrotalcites with various molar ratios are similar. This hydrotalcites can be successfully synthesized with three various ratios of Zn/Al (1; 1, 2; 1, 3; 1). Figure 2.

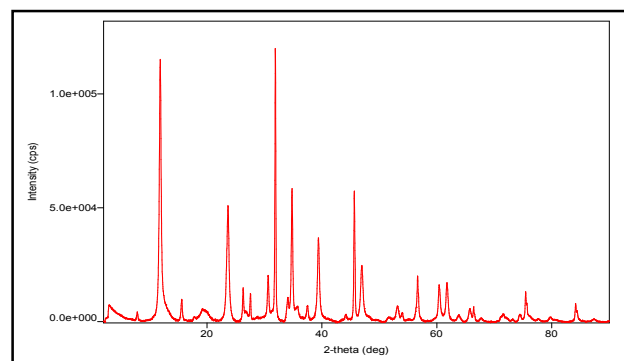


Figure 2. X-RD of Zn-Al-CO₃hydrotalcite

B) FTIR: The hydrotalcite synthesized with a ratio of 3:1 of Zn-Al-CO₃ depicts a band at 3454 cm⁻¹ which can be ascribed to νOH vibration bands. The peaks obtained at 1365 cm⁻¹ is ascribed to the bending water molecules mode and antisymmetric stretching of the intercalating carbonates. The bands observed at 563 cm⁻¹ depicts the vibration modes between M-O and O-M-O. Figure 3.

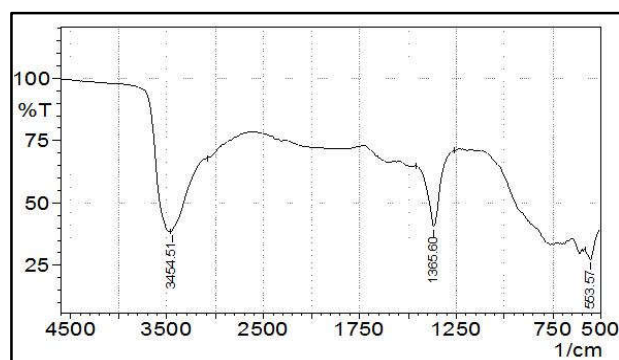


Figure 3. FTIR of Zn-Al-CO₃hydrotalcite

C) TGA: The TGA results of Zn-Al-CO₃ exhibits a total loss of -23.037 % mainly in three regions. The loss of weight started from 196°C depicting total loss of. This weight loss is because of the water loss in interlayer region. The second weight loss seen in the area between is because of the removal of remaining water molecules present in the interlayer region. The third and the final weight loss is due to the interlayer carbonate anion decomposition including the OH de-hydroxylation in brucites like sheets. Figure 4.

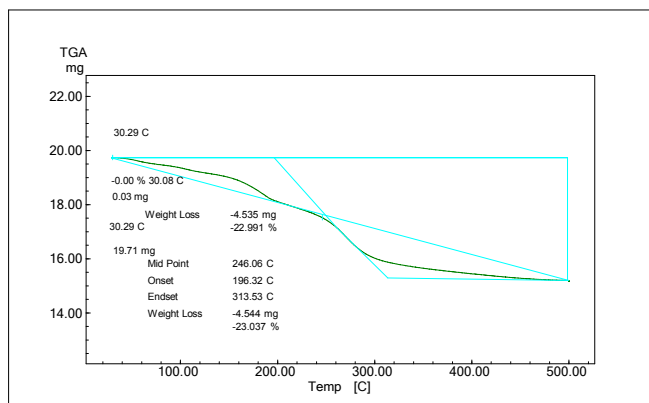


Figure 4. TGA of Zn-Al-CO₃hydroxalcite

present in the interlayer region. The third and the final weight loss is due to the interlayer carbonate anion decomposition including the OH de-hydroxylation in brucite like sheets. Figure 7.

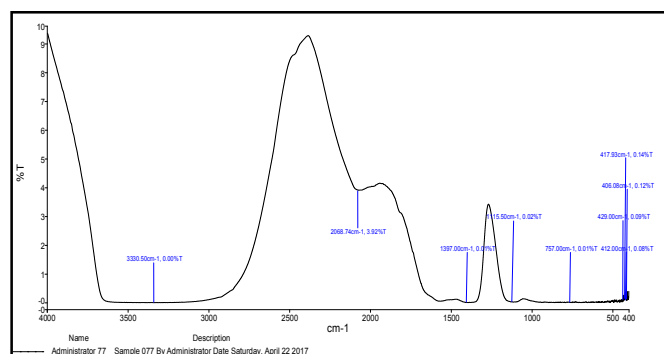


Figure 6. FTIR of Ni-Al-CO₃hydroxalcite

Characterization of Ni-Al-CO₃hydroxalcites

A) XRD: The spectra of Ni-Al-CO₃ hydroxalcites depicts diffraction peaks at 11.1, 23, 35, 40, 46, 61, and 67 indexed at 003, 006, 012, 015, 018, 110, 113 and 116 planes exhibit excellent purity and crystallinity. The height calculated of the gallery was found to be 3.5 with a value of 1.26 which is in good agreement with the values which are already reported. Figure 5.

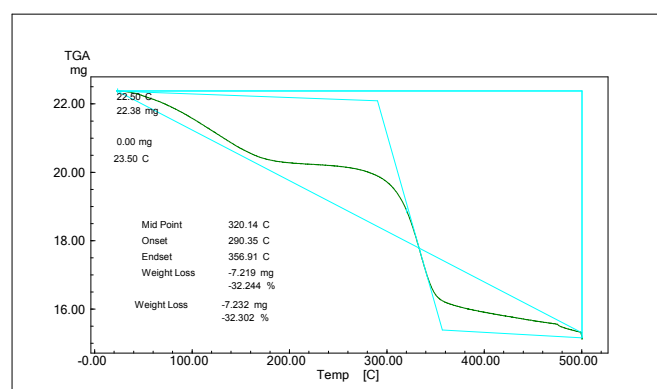


Figure 7. TGA of Ni-Al-CO₃hydroxalcite

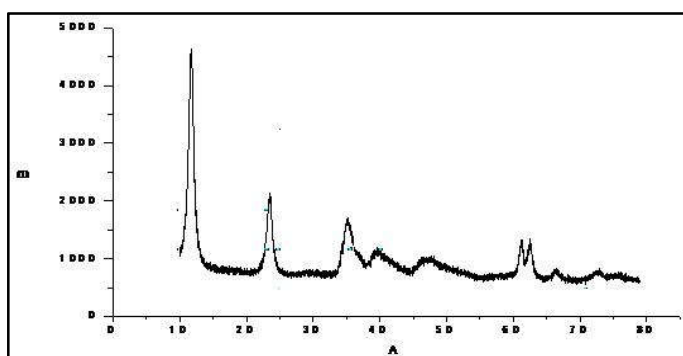


Figure 5. X-RD of Ni-Al-CO₃hydroxalcite

B) FTIR: IR spectra shows that Ni⁺ and Al-hydroxalcites was analyzed in the regions between 4000 to 400 cm⁻¹. IR spectra exhibiting a peak at 3350.50 cm⁻¹ depicts the peak of hydroxyl group (OH) stretching vibration. The weak band is observed at 757 cm⁻¹ which is ascribed to carbonate anion or the strong and sharp band of carbonates were observed at 1397 cm⁻¹. Figure 6.

C) TGA: The TGA results of Ni-Al-CO₃ exhibits a total loss of 32% mainly in three regions. The loss of weight started from 290°C depicting total loss of. This weight loss is because of the water loss in interlayer region. The second weight loss seen in the area between is because of the removal of remaining water molecules

Table 1. Yields and various metal ratios of Zn-Al-X Hydroxalcites

S. No.	Ratio Al : Zn	Chemical (I) Al(NO ₃) ₃	Chemical (II) ZnCl ₂	Grinding Method
1.	1:2	2.6	1.7	3.156g
2.	1:3	2.6	3.4	4.687g
3.	1:4	2.6	5.1	5.924g

Table 2. Yields and various metal ratios of Ni-Al-X Hydroxalcite

S. No.	Ratio Al : Ni	Chemical (I) Al(NO ₃) ₃	Chemical (II) AlNO ₃ (g)	Grinding Method
1.	1:2	1.9	2.6	2.894g
2.	1:3	3.8	2.6	4.056g
3.	1:4	5.7	2.6	5.218g

DISCUSSION

Factor affecting the structure of hydroxalcites: These properties of hydroxalcites are influenced by various parameters such as the nature of the trivalent and bivalent cations and their various ratio, nature of the anions, the concentration of alkali solution and metal salt solution, the rate of addition of alkali and metal solution, the reaction pH, the aging temperature and time, and drying temperature of the obtained precipitate. The specific surface area, morphology and particle size distribution of the hydroxalcites also depend on the synthesis method (Schutz; 1987).

Comparison with different method of synthesized same hydroxalcites: These types of hydroxalcites were synthesized by many other researchers as reported in previous work using

various methods of synthesis. The synthesis of Zn-Al hydrotalcites was performed by Zhao *et al.* using the co-precipitation method keeping the stirring constant thus keeping the obtained slurry aged for 15 hours at 60°C for 5 hours. The product thus obtained was dried overnight at 80°C (Zhao; 2003). The slurry obtained after drying was calcined at 500°C for 5 hours (Gennequin; 2014). Another researcher Gennequin *et al.* reported the synthesis of Zn-Al hydrotalcites using the co-precipitation method with a metal ratio of 3. The precipitate obtained was aged at 60°C for 1 hour drying it for 1 day further washing, filtering it, then drying it for 2 days or 48 hours at 60°C and calcining it at 400°C. Doping of copper was done via memory effect. The solution of copper was agitated for 1 hour at RT then transferred it to rotator evaporator at 60°C for 24 hours and then calcinations was done for another 12 hours at 500°C.

The synthesis of Zn-Al was reported by Tian *et al.* via co-precipitation method. There was homogeneous mixture of Zn, Al and buffer solution under constant stirring. The slurry prepared was aged for 20 hours at 353 K and further dried for 12 hours at same temperature, then calcinations was done between 413-773K temperatures for another 2 hours. The synthesis of Ni-Al-NO₃ hydrotalcites was reported via co-precipitation method by Touhra *et al.* The pH was maintained at 12. The buffer solutions were added drop wise along with vigorous stirring. The precipitated was then washed, filtered, dried for 15 hours at 80°C. These precipitates were further subjected for drying overnight at 90°C in oven along with calcining it for 6 hours at 800°C. The benefit of our work over the reported ones is that they were synthesized using the co-precipitation method and our hydrotalcites were synthesized using the grinding method. In the co-precipitation method the time consumed for the complete synthesis was about 16 to 18 hours followed by calcinations at higher temperatures for 5 to 8 hours. These hydrotalcites were prepared at temperatures between 60 to 80°C. The hydrotalcites prepared by our method was much more simpler than the aforementioned method as it just took 5 minutes of grinding with further drying and calcinations for 2-3 hours at compared lower temperatures with reduced amount of time. So, the main advantage of our work was that the yields obtained in our work were higher than the co-precipitation method with reduced time, temperature and energy. The recyclability of our catalyst was also good.

Conclusion

The product prepared in this current research was synthesized in reduced time and further subjected to drying and calcinations. The time of the reaction was reduced from 3 to 15 hours to lower temperature as compared with other literatures. The main profit of this work is that the catalyst prepared exhibited higher activity of the catalyst, the work up of the reaction was easy with good recyclability decreasing the cost of production of the catalyst.

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