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Synthesis and Structural Analysis of Double Layered Ni-Mg-Al Hydrotalcite Like Catalyst

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Abstract

Hydrotalcites are double layered lamellar clays. It has high surface area and different types of active sites can be fused on its surface this make hydrotalcites an ideal structure for hetero generous catalytic reactions. In this article synthesis of Ni-Mg-Al hydrotalcite by coprecipitation is discussed alongwith its characterization. The hydrotalcite formation is verified by powder XRD. FTIR and BET characterization is carried out to understand the structural characteristics of the material and its possible use as a catalyst. High surface area with large porosity and a consistent atomic percentages was measured during these analysis.

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1. Introduction

Several organic production methods of fine chemicals use homogeneous catalysts like minerals, organic acids and bases. Such homogeneous catalysts are difficult to recover, cause waste disposal problems and can corrode the pipes too by salt formations [1]. A greener solution to these problems is by using solid; acid or basic catalysts for heterogeneous catalytic reactions. Furthermore, a polar solvent can completely be removed by their use and such catalysts can also be used under rigorous high temperature and pressure conditions [2].

Layered double hydroxides [LDH], generally named as Hydrotalcites [HTs] is a lamellar clay and is an ideal material for solid catalyst, catalyst precursor and catalyst support [3, 4]. Their layered structure provides high surface area with the freedom to compensate various dimetallic (M^{II}) and trimetallic (M^{III}) ions on its surface [5]. HTs consists of brucite-like positively charged layers, with an anionic layer sandwiched between them compensating the positive charge, along with the water molecules trapped inside these layers [6, 7]. This layered structure of HTs provides high surface area, thermal stability and maximum concentration of active sites on the catalyst surface. HTs existed in the form of both bivalent and trivalent cationic layers, most commonly occurring HT compound is: $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ [8]. A variety of highly active catalysts can be made by replacing Mg and Al

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cations by M^{II} and M^{III} catalytically active species respectively in the octahedral sheets during synthesis [9, 10]. It is worth mentioning that both the layered structure (as synthesized) and mixed metallic oxides (obtained after calcinations) is catalytically active in nature [11]. In this work, Nickel is used as an active site, fused within the octahedral layer of Mg-Al hydrotalcites. Its synthesis by co-precipitation method and characterization is presented in this article.

2. Experimental

2.1. Materials

Magnesium Nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), Aluminum Nitrate ($Al(NO_3)_3 \cdot 9H_2O$), Nickel Nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), and Sodium Carbonate (Na_2CO_3) were purchased from Sigma Aldrich® Ltd., for the synthesis of Ni-Mg-Al HTs. Deionized water was used during the synthesis.

2.2. Synthesis of Mg-Ni-Al Hydrotalcite

0.25 M solutions of $Mg(NO_3)_2$ and 0.5 M solutions of $Al(NO_3)_3$ and of $Ni(NO_3)_2$ are prepared. 1 M solution of Na_2CO_3 was used as a precipitating agent. A mixture of known quantities of Mg, Al, and Ni nitrate solution was added drop wise to a vigorously stirred 1 M solution of Na_2CO_3 in a glass reactor. Temperature was kept constant at 70°C and pH is kept constant at 10pH by drop wise addition of NaOH solution. Precipitates formed were washed by deionized water followed by filtration. Vacuum filtration of solution was carried out 5 times until the precipitates are free from sodium ions. Precipitates thus produced were then dried in air drier for 18hrs at 80°C and are further calcined at 700°C for 18hrs. Catalysts of three different concentrations were synthesized by repeating the same method. Their concentrations are given in Table 1.

Table1. Percentage concentration of synthesized Samples

Catalyst	%age Concentration		
	Mg	Ni	Al
MNA-121	25	50	25
MNA-211	50	25	25
MNA-535	12.5	75	12.5

2.3. Characterization

Elemental analysis and topographical images of MNA HTs were taken by Zeiss Supra 55-VP Field-Emission Scanning Electron Microscope (FESEM). Powder X-Ray Diffraction (XRD) patterns of hydrotalcites were recorded in the 2θ range from 2° to 80° with a 0.02 per second step increase on D8 Advance Bruker X-Ray Diffractometer. FTIR spectra is recorded in the range of 400-4400 cm^{-1} on Shimdazu 8400S-FTIR. N_2 physisorption at -150°C is used to characterize the BET surface area, pore volume, and pore dia using ASAP 2020 surface area analyzer.

3. Results and Discussion

3.1. Elemental Analysis

EDX analysis of the synthesized HTs was carried out to determine their chemical composition. The analysis revealed that Ni/Mg/Al ratio is in close proximity to the pre-calculated ratios. Measured atomic percentages of HTs compared with calculated values are shown in Table 2. This result confirmed effectiveness of the co-precipitation technique for the synthesis of HTs.

Table2. Measured and calculated Atomic Percentages

Catalyst	Ni:Mg:Al Atomic %age	
	Measured by EDX	Calculated
MNA-121	28:43:28	25:50:25
MNA-211	46:33:21	50:25:25
MNA-535	17:68:15	13:75:12

3.2. X-Ray Diffraction (XRD)

Pattern of XRD analysis of as synthesized HTs is shown in Figure 1. Sharp peaks for (003), (006), (009) planes and broader peak for (015) plane is observed. Peaks are matched with the available library cards and matching confirmed the layered HT structure. The calculated a value is 0.307nm which is the lattice parameter and is related to the cation composition and the cell parameter c value is equal to 2.34nm and is related to the interlayer distance [12].

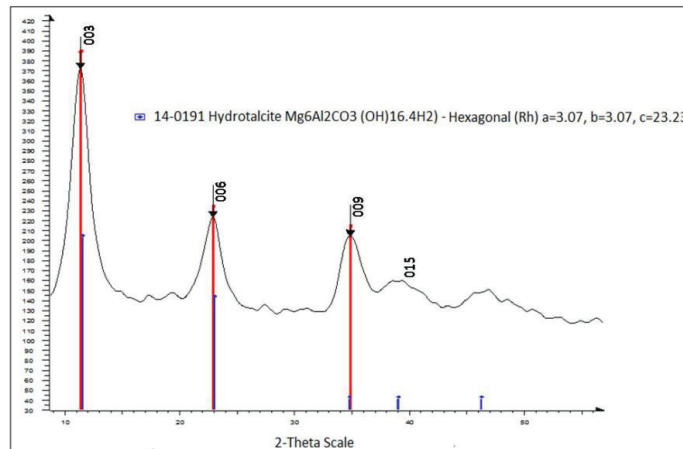


Fig 1: XRD pattern of synthesized HTs

3.3. FESEM Analysis

Topographical images of three samples are shown in figure (2). Large particle size could be seen in MNA-535 compound due to the high concentration of Ni active site which is subsequently reduced with Ni concentration [13] and MNA-211 having the least particle size. Though all the samples remain highly porous in nature but porosity reduce with increase in Nickel concentration, as more and more surface is occupied with active sites. This leads to the conclusion that Nickel concentration increases the overall stability of the catalyst but causes a significant reduction in the overall surface area of the catalyst which has a direct relation with catalytic activity of any substance. On further investigating by elemental mapping it was found that all materials have equal highly dispersed structures, which implies to good catalytic activity.

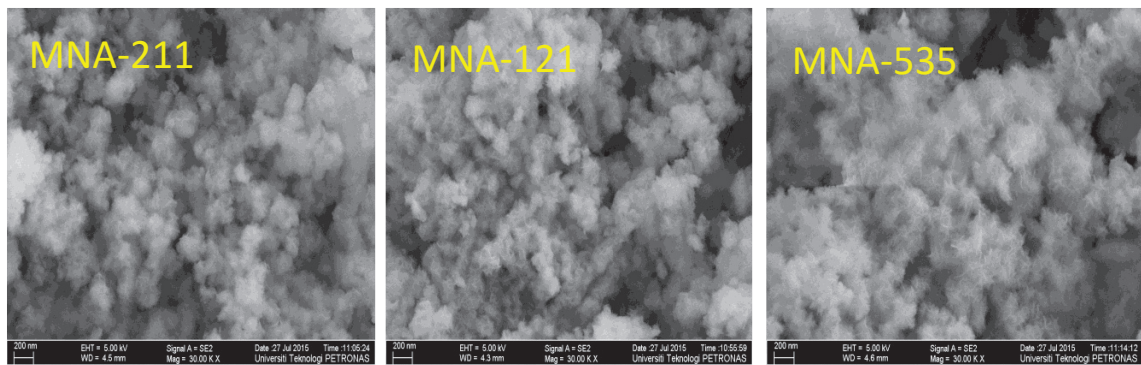


Fig 2: FESEM analysis of HTlcs

3.4. Fourier Transform Infra-Red Spectroscopy (FTIR)

FTIR spectra of Mg-Ni-Al HTs is shown in figure 3. All the three synthesized materials had shown similar behavior under IR spectra, however bonding strategy of HTs can be guessed from it. A broad band observed around 3500 cm^{-1} is assigned to the O-H stretching vibration confirming the presence of hydroxyl group in the hydroxide layer [14]. The shoulder around 2800 cm^{-1} has been associated to the bridging mode of hydroxyl interactions with carbonate ions at the interlayers of the HT structure [15]. Broader peaks below 1000 cm^{-1} correspond to the Mg-OH or Al-OH bond stretching.

Main anionic adsorption bands are observed between $1800\text{--}1000\text{ cm}^{-1}$. Disordered nature of interlayers or lowering of carbonate symmetry is associated with the shoulder around 1400 cm^{-1} . In literature this lowering of symmetry is attributed to the activation of 1050 cm^{-1} band. Serna et al.[16] had hypothesized this 1050 cm^{-1} band as an indication of perturbation of carbonate ions in the interlayer which causes weakening of covalent bond with outer layers thus making the material more catalytically active as weak structural bonding of catalyst increase overall catalytic activity of the material.

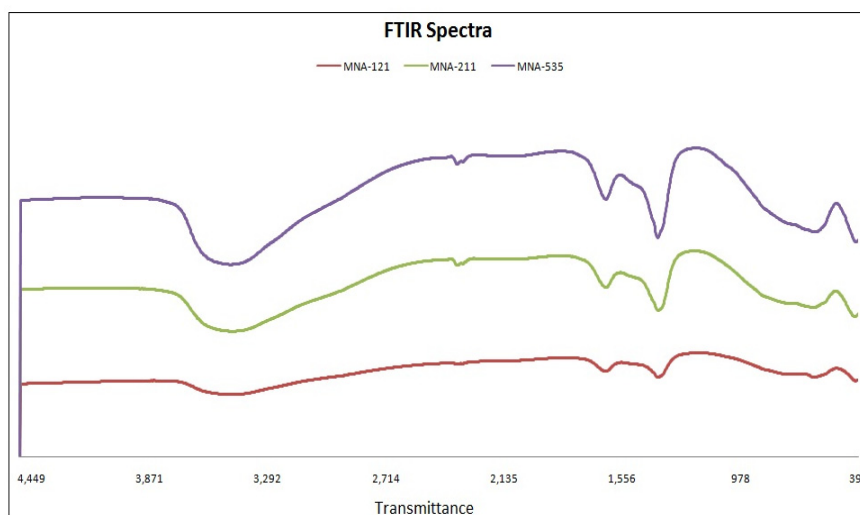


Fig 3: FTIR Spectra

3.5. Thermal Gravimetric Analysis (TGA)

Thermal behavior of HTs can be subdivided into two sections

- i. Steady endothermic loss of weight at lower temperatures due to the loss of water from interlayer region.
- ii. Abrupt endothermic loss of weight at high temperature due to the loss of hydroxyl group from brucite like layer of the material called transition step.

The first change is temporary and regenerative; however, the second is permanent and disrupts the double layered structure of HTs and are then generally categorized as HTlc. This change is achieved at the calcinations step of catalyst synthesis. Though due to the memory effect property of HTlc layers are still loosely overlapped with each other and random stacking of brucite like layers is observed. In this study different transition temperatures are observed for three materials as shown in figure 4. MNA-535 decomposed at a relatively lower temperature; this could be explained due to the presence of high Nickel concentration weakening the interlayer bonding structure of Mg-Al HTs. This further implies that MNA-535 catalyst could easily be activated at lesser temperatures proving high chemical reactivity compared to others. After thermal decomposition of double layered structure HTlc are stable over a longer temperature range making them ideal as a catalyst support, however it is imperative to mention after longer run and high temperature, sintering or delocalization of active sites occur thus decreasing the catalytic activity of catalyst. Memory effect property of HTlc plays a vital role in regeneration of catalyst, after reducing HTlc regain their layered structure and could be reused.

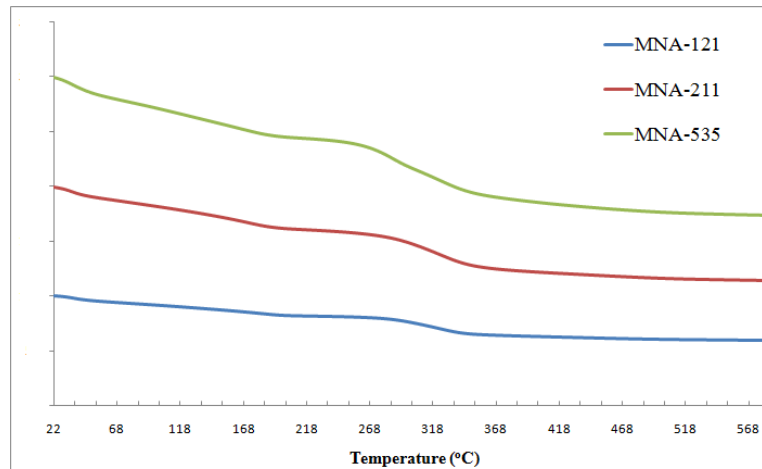


Fig 4: TG Analysis of HTlcs

3.6. N_2 Physisorption

N_2 adsorption/desorption isotherms of synthesized Mg-Ni-Al HTs is shown in figure 5. H-3 type hysteresis at high relative pressure is displayed for all the samples; which is a characteristic of plate-like particles. Adsorption/desorption plots make an enclosure around high relative pressure of $P/P^0=0.7$, depicting the structure to be highly mesoporous in nature [17]. Such isotherms are typical for materials having large open pores, allowing easy diffusion of reactants through the materials. On comparing the amount sorbed per gm of solid MNA-211 having the least active sites has the highest physisorption proving to have highest porosity whereas MNA-535 has the least porosity.

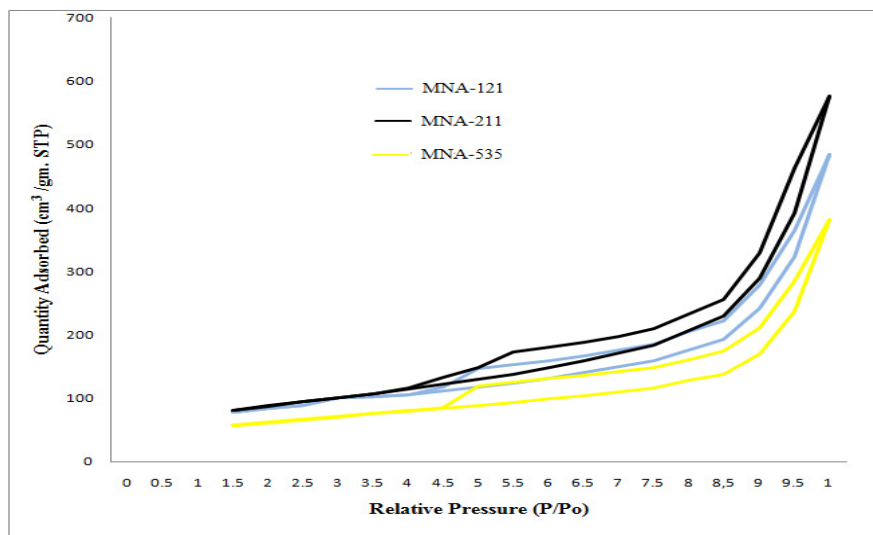


Fig 5: Adsorption/ desorption isotherms of HTlc

High surface area was found during N_2 physisorption BET analysis of the samples, details of which are shown in Table 3. It is observed high Nickel concentration has resulted into a decrease in overall surface area of the catalyst it is because of the larger ionic radii of the Ni^{2+} ion occupying larger space compared to the Mg^{2+} ion on the surface. Pore volume has also been decreased with the increase of active Nickel sites.

Table3. Texture properties of Hydrotalcite Samples

Sample	S_{BET} (m^2/gm)	V_p (cm^3/gm)	r_p (\AA)
MNA-211	313.9	0.804	102.46
MNA-121	295.25	0.668	90.59
MNA-535	225.27	0.575	93.16

Pore Size Distribution (PSD) is another important factor in analyzing the performance of a catalyst. Synthesized HTlcs have PSD in the range of 25-45 \AA . This attributes to the highly dispersed large open pores on the surface, ideal for any catalyst. Among the synthesized materials MNA-535 has the highest PSD in the range of 40 \AA , whereas the other two materials have PSD in the range of 30 \AA as shown in Figure (6). High PSD of MNA-535 is because of high Mg^{2+} concentration in the brucite layer of HTlc.

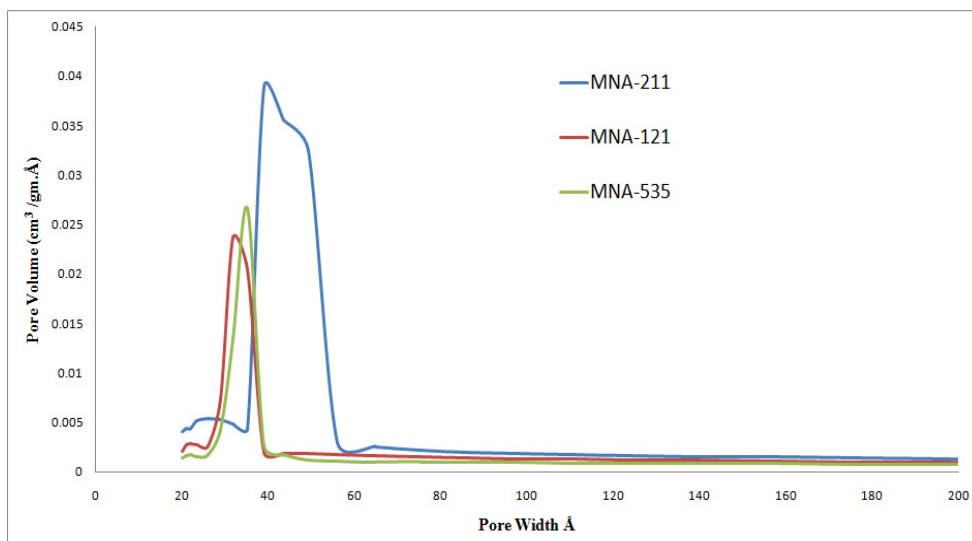


Fig 6: PSD of HTlc

4. Conclusion

Three different samples of Ni-Mg-Al hydrotalcites were successfully synthesized using coprecipitation technique at constant pH. Their percentage concentration was confirmed by EDX analysis. XRD spectra shows high crystalline double layered structure of synthesized material. Material having high Nickel content were proven to be more reactive in nature but a reduction in the overall surface area of the catalyst was also found during BET analysis.

Acknowledgement

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