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Synthesis and Structural Analysis of Mg/Al-NO_3 Hydrotalcite

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Abstract-A fine-quality of hydrotalcite based heterogeneous catalyst is synthesized by co-precipitation technique, and the physical and chemical properties of the catalyst were characterized by XRD, EDX, SEM, FTIR and TGA. XRD diffractro meter identified the sharp peak (104) is highly crystalline materials hexagonal lattice with an R3m rhombohedral symmetry with the lattice constants, a & c were 2.98 and 9.12Å respectively. EDX is identified the Mg, Al, NO3- components present in sample and SEM identified the clear morphologies. FTIR spectroscopy identified frequency peaks of NO3- anions was observed at 1384.7 cm-1, Mg-O at 469cm-1 and Al-O at 704-637cm-1. TGA shows the endothermic and exothermic curves. This catalyst is then used simultaneously to catalyze the transesterification of biodiesel from waste cooking oil. Thus, the heterogeneous catalyst had highly active for transesterification. In addition, the catalyst had excellent stability and thereby having potential use of heterogeneous catalyst for biodiesel production from waste cooking oil.

Keywords: Mg/Al-NO3 Hydrotalcite, XRD, FTIR, TGA, SEM Technique

I. INTRODUCTION

Now-a-days, Hydrotalcite based catalysts are having more attention compared with homogeneous catalysts due to their basicity nature & surface area and their potential industrial applications as CO2 adsorbents, ion exchangers, fire retardants, base catalysts, and precursors of well-mixed oxides for various catalytic applications (Climent et al., 2010; Hutson and Attwood, 2008; Manzi-Nshuti et al., 2008; Montanari et al., 2010; Nyambo et al., 2008; Oliveira et al., 2008; Reijers et al., 2006; Takagaki et al., 2010; Wang et al., 2010a, 2010b; Wang et al., 2011a, 2011b and Qiang Wang et al., 2012). The structure of Hydrotalcite resembles that of brucite, Mg (OH)2, where the magnesium cations are octahedrally coordinated by hydroxyl ions, resulting in stacks of edge-shared layers of the octahedral. In the Hydrotalcite structure, part of the Mg2+ ions are replaced by Al3+ ions forming positively charged layers. Charge-balancing anions (usually SO42−) and water molecules are situated in the inter layers between the stacked brucite like cation layers. Calcinations at high temperature decomposes the Hydrotalcite into interactive, high surface area and well-dispersed mixed Mg–Al oxides which present basic sites that are associated with structural hydroxyl groups as well as strong Lewis basic sites associated with O2− Mn+ acid–base pairs (Xie, W et al., 2006; Zeng, H et al., 2008; Yang, Q.Z et al., 2003 and A. Obadiah et al., 2012). The change of the Mg/Al ratio in Mg–Al Hydrotalcite leads to the variation of the basic property that is induced by the redistribution of acid base sites, change of structure and transformation of the cations (Mg2+ or Al3+) environment (Diez VK et al., 2003). Surface basic sites of calcined Hydrotalcite consists of low (OH- groups), medium (O- in Mg-O pairs), and strong (O2- anions with unsaturated coordination) basic sites (Cantrell DG et al., 2005; Diez VK et al., 2003; Di Cosimo JI et al., 1998). The relative abundance of low and medium strength basic sites increased with increasing Al content. By calcining Hydrotalcite materials at high temperature, the interlayer water is lost first, followed by dehydroxylation and decomposition of interlayer carbonate to CO2, which generate a porous structure and specific surface area ranging from 150 to 300m2/g (McKenzie AL et al., 1992).

This calcined Mg-Al-NO3 Hydrotalcite show a change of chemical structure, elements present in the composition, nature of morphology present in the composition and highlights the possibilities of peaks formed in FTIR and also shows the strong thermal stabilities and high basicities. These effects could combine to make the catalyst quite competitive as a heterogeneous basic catalyst to various application purposes.

II. MATERIALS & METHODS

The materials sources were: Al(NO3)3.9H2O of 99.8 % purity, Mg(NO3)2.6H2O of 99.8 % purity, Na2CO3 of 98 % purity and NaOH pellets of 97% purity which were purchased from Nice Chemicals, Kerala. The following methods are used to identify and characterize the heterogeneous catalyst: X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material; Energy Dispersive X-Ray Analysis (EDX) is an x-ray technique used to identify the elemental composition of materials; SEM describes morphological phenomena of the sample; FTIR

Technique is used to identify the functional groups which may be present in the catalyst and TGA analysis can describe thermal effects with respect to the weight changes & also identify reaction may be exothermic or endothermic one.

III. PROPOSED METHODOLOGY

Al(NO3)3.9H20 (0.01mol) and Mg(NO3)2.6H2O (0.05 mol) were dissolved in de-ionized water (70 ml). A second de-ionized water solution (100 ml) of Na2CO3 (0.1 mol) and NaOH (0.35 mol) was prepared. The first solution was slowly added to the second. The resulting mixture was heated at 65°C under autogeneous pressure for 18 h. After the heating period, the slurry was cooled to room temperature, washed with de-ionized water up to pH≈9 and dried at 110°C for 18 h. Hydrotalcite catalyst is activated by calcinations at a rate of 2ºC/min until 500°C and maintained for 2 h in a flow of air. Later on, samples were cooled in dry nitrogen atmosphere and stored. The prepared Hydrotalcite were analyzed by using XRD, EDX, SEM, FTIR and TGA techniques.

IV. EXPERIMENTAL RESULTS

XRD Technique

Figure 3.1 shows XRD pattern of Mg/Al-NO3 Hydrotalcite. In the XRD analysis the prominent 2θ peaks obtained were at 29.24, 32.24, 38.92, 42.84 and 62.23. On comparison (JCPDS card no #:36-1474, 79-0612, 71-1241) the formation of Mg-Al Hydrotalcite was understood and some other peaks were due to intermediate compounds. The basal spacing was calculated to be 0.303nm. The sharp peak (104) indicates the formation of highly crystalline materials. Indexing of the diffraction peaks was done using a standard JCPDS file.

The reflections were indexed in a hexagonal lattice with an R3m rhombohedral symmetry. The parameter of Hydrotalcite corresponding to the cation-cation distance within the brucite-like layer can be calculated as follows: a = 2 × d (222). On the other hand, the c parameter is related to the thickness of the brucite-like layer and the interlayer distance and can be obtained from the equation c = 3 × d (104) (Radha et al 2004 and Yang et al 2009).

The values of the unit cell parameters, assuming rhombohedral symmetry, with the c parameter corresponding to three times the thickness of the expanded brucite like layer, are presented in Table 3.1. The a and c parameters decreased with increasing aluminum content, which can be explained by the substitution of larger Mg2+ ions by smaller Al3+ ions (Anbarasan et al 2005, Diez et al 2003, Rao et al 1998).

Table 1 XRD calculation of interlayer distance of Mg/Al-NO3 HT

Mg/Al-NO_3 HT	2θ (211)	d211(Å)	d , c and Basal spacing
d(104)	29.36	3.04	c = 9.12
d(222)	62.23	1.49	a = 2.98
d(104) crystal basal space	-	-	0.303 nm

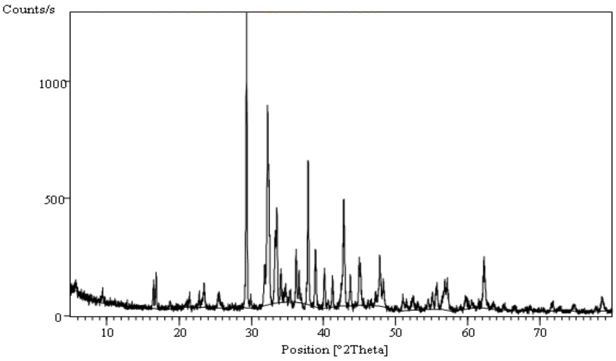


Figure 1 XRD pattern of Mg/Al-NO3 Hydrotalcite

Using Scherrer formula, one can find the size of the crystal or particle size.

$$\tau = \frac{K\lambda}{\beta cos\theta}$$

Where K is the shape factor, λ is the X-ray wavelength, typically 1.54 Å, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle; τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than 0.1 μm, which precludes those observed in most metallographic and ceramographic microstructures. Using the Scherrer formula the crystal size was found to be within 4.66 nm to 21.2 nm (Rao et al 1998, Anbarasan et al 2005).

EDX Technique

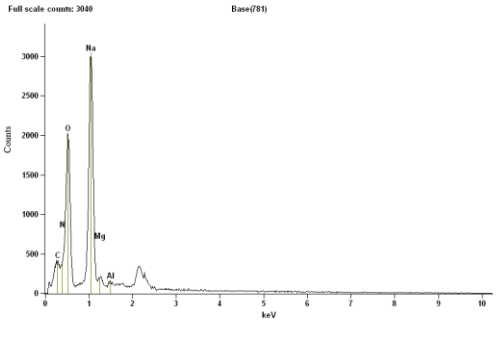


Figure 2 EDX Diagram of Mg/Al-NO3 Hydrotalcite

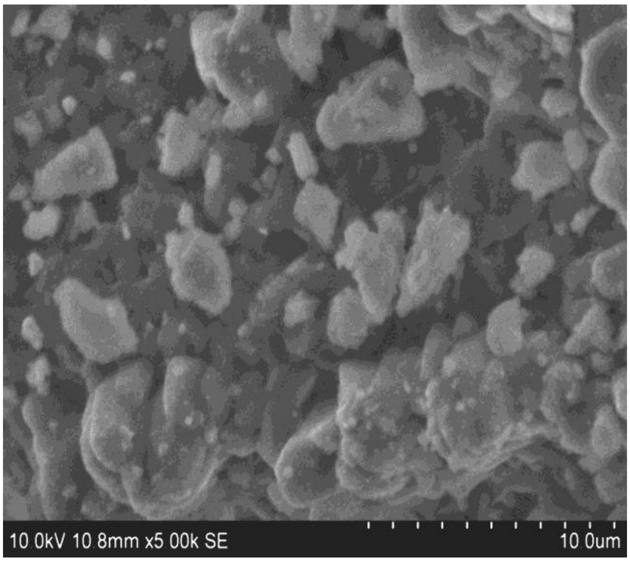
Table 2 EDX Quantitative results of Mg/Al-NO3 Hydrotalcite

Element	Net Counts	Weight %	Atom %
C	2625	18.54	25.53
N	1072	6.52	7.69
O	20758	41.07	42.45
Na	31544	33.37	24.01
Mg	96	0.08	0.05
Al	500	0.43	0.26
Total	-	100.00	100.00

Figure 3.2 shows the EDX quantitative results of base peak (781) for Mg/Al-NO3 Hydrotalcite and this figure clearly indentified peaks formed with respect to total scale counts versus kilo voltage of energy dispersion. Table 3.2 shows detailed net counts increases with respect to the atom weight (%). In that, Mg, Al elements were composed in 1:5 molar ratios with nitrogen, oxygen elements were formed in 7:1 ratios and remaining nearly 24.01% sodium present and also obtained 25.03% of oxygen combined carbon. It might be that, Sodium is not properly washed with DI water catalyst at the time of catalyst preparation procedure. Anyway, it is a base compound and gives the positive effect to the biodiesel production.

SEM Analysis

The Hydrotalcite formation was confirmed by SEM analysis. Figure 3.3 shows that it indicates two kinds of materials obtained. White fine powder indicates the MgO particles and grey colour fine powder indicates the Al2O3. So, both of the Mg/Al-NO3 HT catalysts are conformed and particles are indentified in 5µm and 10µm. 10µm image indicates particles well mixed position and 5µm image indicates well closure position of the particles.



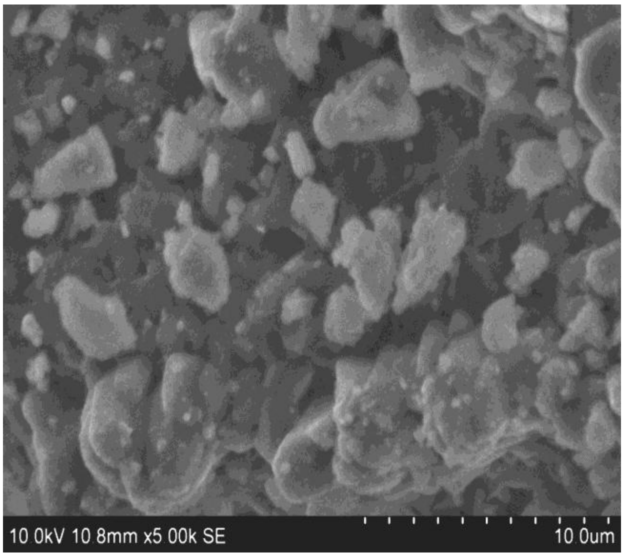


Figure 3 SEM Image of Mg/Al-NO3 Hydrotalcite

FTIR Technique

Figure 3.4 shows the FTIR spectrum of Mg/Al-NO3 Hydrotalcite. The spectrum was characterized with asymmetric and symmetric stretching vibrations of carboxyl group at 2990.5 cm-1, along with the O-H stretching of the hydroxyl group and deformation vibration of H2O at 3452.9 cm-1. The spectrum is skewed on the right hand side and the net small peak at 2990.5 cm-1 is due to the hydrogen bonding of H2O and interlayer of NO3- anions at 1636.4 cm-1 and in this lower frequency, the samples can be attributed to the bending mode of the interlayer water. The main absorption band of the NO3- anions was observed at 1384.7 cm-1. In the low energy ranges of the spectra 704-637 cm-1, peaks around 469cm-1 are attributed to the presence of Al-O and Mg-O bond. (Obadiah et al 2012).

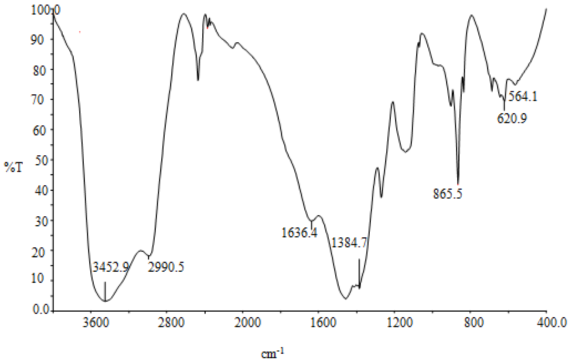


Figure 4 FTIR Spectrum of Mg/Al-NO3 Hydrotalcite

TGA Analysis

TGA curve weight losses change with respect to temperature as shown in Figure 3.5. In that, TGA curve evaluates weight changes with respect to the temperature. First region up to 228.59ºC there is endothermic peak which relates to the dehydration of the sample upto 2.637% weight loss. The second region 377.66ºC corresponds to weight loss due to the dehydroxylation and de-carbonation reactions, resulted in mass loss of 1.877% and remaining is 90.26% % is a solid materials content upto 980ºC. The weight loss corresponds to the decomposition of interlayer anion present in the brucite layer and the dehydroxylation of vicinal OH groups in the hydrotalcite (Kim et al 2004, Yang et al 2007 and Obadiah et al 2012).

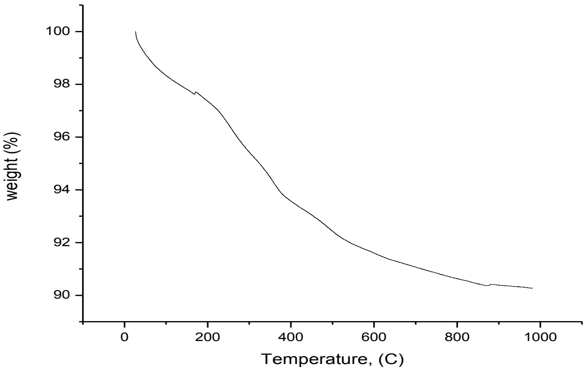


Figure 5 TGA Curve of Mg/Al-NO3 Hydrotalcite

V. CONCLUSION

The high quality of Mg/Al-NO3 synthesized by co-precipitation technique with the addition of buffer solution in the presence of nitrogen atmosphere and calcined at 500ºC. This heterogeneous catalysts formation was confirmed by physical and chemical techniques. The physical techniques: XRD technique shows the highly crystalline sharp rhombohedral symmetry peak obtained at (104) with the lattice constants, a & c were 2.98 and 9.12Å respectively. EDX unique technique identified chemical compounds such that 1:5 molar ratios Mg, Al elements Nitrogen, oxygen elements formed in 7:1 ratios. SEM identified the clear morphologies with two different variations. FTIR spectroscopy identified frequency peaks of NO3- ions at 1384.7 cm-1, Mg-O at 469cm-1 and Al-O at 704-637cm-1. TGA shows the endothermic and exothermic peaks with various temperature ranges.

REFERENCES

[1] Climent, M.J., Corma, A., Frutos, P.D., Iborra, S., Noy, M., Velty, A., Concepcion, P., “Chemicals from biomass: synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts. The role of acid–base pairs”, J. Catal. 269, 140-149, 2010.

[2] Hutson, N.D., Attwood, B.C., “High temperature adsorption of CO2 on various hydrotalcite-like compounds”, Adsorption 14, 781-789, 2008.

[3] Manzi-Nshuti, C., Wang, D., Hossenlopp, J.M., Wilkie, C.A., “Aluminum-containing layered double hydroxides: the thermal, mechanical, and fire properties of (nano) composites of poly (methyl methacrylate)”, J. Mater. Chem. 18, 3091-3102, 2008.

[4] Montanari, T., Sisani, M., Nocchetti, M., Vivani, R., Concepcion Herrera Delgado, M.,Ramis, G., Busca, G., Costantino, U., “Zinc-aluminum hydrotalcites as precursors of basic catalysts: preparation, characterization and study of the activation of methanol”, Catal. Today 152, 104-109, 2010.

[5] Nyambo, C., Songtipya, P., Manias, E., Jimenez-Gasco, M.M., Wilkie, C.A., “Effect of Mg/Al-layered double hydroxide exchanged with linear alkyl carboxylates on fire-retardancy of PMMA and PS”, J. Mater. Chem. 18, 4827-4838, 2008.

[6] Oliveira, E.L.G., Grande, C.A., Rodrigues, A.E., “CO2 sorption on hydrotalcite and alkali-modified (K and Cs) hydrotalcites at high temperatures”, Sep. Purif. Technol.62, 137-147, 2008.

[7] Reijers, H. Th. J., Valster-Schiermeier, S.E.A., Cobden, P.D., van den Brink, R.W., “Hydrotalcite as CO2 sorbent for sorption-enhanced steam reforming of methane”, Ind. Eng. Chem. Res. 45, 2522-2530, 2006.

[8] Takagaki, A., Iwatani, K., Nishimura, S., Ebitani, K., “Synthesis of glycerol carbonate from glycerol and dialkyl carbonates using hydrotalcite as a reusable heterogeneous base catalyst”, Green Chem. 12, 578-581, 2010.

[9] Wang, J., Li, D., Yu, X., Zhang, M., Jing, X., “Fabrication of layered double hydroxide spheres through urea hydrolysis and mechanisms involved in the formation”, Colloid Polym. Sci. 288, 1411-1418, 2010a.

[10] Wang, Q., Tay, H.H., Ng, D.J.W., Chen, L., Liu, Y., Chang, J., Zhong, Z., Luo, J., Borgna, A., “The effect of trivalent cations on the performance of Mg–M–CO3 layered double hydroxides for high-temperature CO2 capture”, Chem. Sus. Chem. 3, 965-973, 2010b.

[11] Wang, Q., Luo, J., Zhong, Z., Borgna, A., “CO2 capture by solid adsorbents and their applications: current status and new trends”, Energy Environ. Sci. 4, 42-55, 2011a.

[12] Wang, Q., Wu, Z., Tay, H.H., Chen, L., Liu, Y., Chang, J., Zhong, Z., Luo, J., Borgna, A., “High temperature adsorption of CO2 on Mg–Al hydrotalcite: effect of the charge compensating anions and the synthesis pH. Catal. Today 164, 198-203, 2011b.

[13] Qiang Wang, Hui Huang Tay, Zhanhu Guo, Luwei Chen, Yan Liu, Jie Chang, Ziyi Zhong, Jizhong Luo , Armando Borgna, “Morphology and composition controllable synthesis of Mg–Al–CO3 hydrotalcites by tuning the synthesis pH and the CO2 capture capacity”, Applied Clay Science Vo55 18-26, 2012.

[14] Xie, W., Peng, H. and Chen, L., “Calcined Mg-Al Hydrotalcite as solid base catalysts for methanolysis of soybean oil”, J. Mol. Catal. A: Chem., Vol. 246, 24-32, 2006.

[15] Zeng, H., Feng, Z., Deng, X. and Li, Y., “Activation of Mg-Al Hydrotalcite catalysts for transesterification of rape oil”, Fuel, Vol.87, 3071-3086, 2008.

[16] Yang, Q.Z., Zhang, C.G., Sun, D.J. and Jin, Z.L., “Studies on synthesis and properties of Mg-Al-nitrites layered double hydroxides,” Chin. Chem. Lett. Vol.14, 79-92, 2003.

[17] A. Obadiah, r. Kannan, p. Ravichandran, a. Ramasubbu,s. Vasanth kumar, "Nano hydrotalcite as a novel catalyst for Biodiesel conversion", Digest Journal of Nanomaterials and Biostructures Vol. 7, No. 1, 321-327, 2012.

[18] Diez, V.K., Apesteguia, C.R. and Di Cosimo, J.I., "Effect of the chemical composition on the catalytic performance of MgyAlOx catalysts for alcohol elimination reactions", J. of Catal., Vol. 215, 220-233, 2003.

[19] Cantrell, D.G., Gillie, L.J., Lee, A.F. and Wilson, K., "Structure-reactivity correlations in Mg-Al Hydrotalcite catalysts for biodiesel synthesis", Appl. Catal. A: Gen., Vol.287, 183-190, 2005.

[20] Di Cosimo, J.I., Diez, V.K., Xu, M., Iglesia, E. and Apesteguia, C.R., "Structure and Surface and Catalytic Properties of Mg-Al Basic Oxides", J. of Catal., Vol.178, 499-510, 1998.

[21] McKenzie AL, Fishel CT, Davis RJ, "Investigation of the Surface structure and properties of calcined hydrotalcites", J. Catal. 138:547, 1992.

[22] Radha, A.V. and Vishnu Kamath, P., "Oxidative Leaching of Chromium from layered double hydroxides: mechanistic studies", Bull. Mater. Sci., Vol. 27, No. 4, 355-360, 2004.

[23] Yang, Z., Choi, K. M., Jiang, N. and Park, S. E., "Microwave synthesis of Hydrotalcite by urea hydrolysis", Bull. Kor. Chem. Soc., Vol. 28, 2029-2033, 2007.

[24] Rao, K.K., Gravelle, M., Valente, J.S. and Figueras, F.C., "Activation of Mg-Al Hydrotalcite Catalysts for Aldol Condensation Reactions" J. of Catal., Vol. 173, No. 1, 115-121,1998

[25] Anbarasan, R., Lee, W. D. and Im S. S., "Adsorption and intercalation of anionic surfactants onto layered double hydroxide-XRD study", Bull. Mater. Sci., Vol. 28, No. 2, 145-149, 2005.

[26] Kim, H.J., Kang, B.S., Kim, M.J., Park, Y.M., Kim, D.K. and Lee, J.S., "Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst", Catal. Today, Vol.93-95, 315-320, 2004.