

Synthesis, Characterization and Application of Zn-Al Layer Double Hydroxide

Hemaprokha Saikia¹, Karishma Talukdar²

¹Assistant Professor, Department of Chemistry, Bodoland University, Kokrajhar 783370, Assam, India

²Research Fellow, IASST, Paschim Baragaon, Guwahati, Assam 781035, India

Abstract: Layer Double Hydroxide are drawing much attention as solid catalysts in recent years and have applications in various organic transformations as they possess a variety of basic sites which could be obtained by exchange of metal ions or by intercalation of suitable anions into their interlayer space. Al based complexes have widespread catalytic applications in many organic reactions. **Method:** Ternary LDH multifunctional catalyst containing Zn, and Al was prepared by co-precipitation and hydrothermal treatment. The catalyst was characterized by elemental analysis, Powder XRD, FT-IR, BET, SEM and TEM. The products of the reactions were characterized by ¹H NMR and GC-MS.

Keywords: ZnAl-LDH, condensation, transfer hydrogenation, hydroxide, condensation

1. Introduction

Layered double metal hydroxides or synthetic anionic clays having hydrotalcite like structure are receiving increasing interest in recent years owing to their potential applications in various technologies. LDH were discovered in the mid-19th century. Hydrotalcite was discovered in 1842 in Sweden but the first exact formula, $[Mg_6Al_2(OH)_{16}]CO_3 \cdot 4H_2O$ was not held until 1915 by Manasse. Interest in LDH chemistry increased in 1942 with a series of papers by Feitknecht on what he called double sheet structure [1,2].

The structure of LDHs consists of positively charged mixed metal hydroxide layers separated by charge-balancing anions and water molecule. A broad range of compositions of the type $[M_2^{2+}M_3^{3+}X(OH)_2](Am^-)_x/m \cdot nH_2O$ ($M_2^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}$ etc, $M_3^{3+} = Al^{3+}, Cr^{3+}, Ga^{3+}$ etc) are possible, wherein the M_2^{2+} and M_3^{3+} metal ions occupy octahedral positions in the hydroxide layers. The value of x is typically between 0.17 and 0.33, even though there is no strict limitation to this value. The interlayer anions Am^- are exchangeable, giving rise to rich intercalation chemistry. The guest species may be organic or inorganic, simple or complex [3]. Layered double hydroxides (LDH) with brucite like structure was modified with various anionic surfactants containing sulfonate, carboxyl, phosphonate and sulfate end group through ion-exchange method. XRD reports indicated that the sulfonate group containing surfactants led to an adsorption process whereas the sulfate, carboxyl and phosphonate group containing surfactant led to an intercalation process [4].

Intercalation of a desired anionic guest is achieved by direct synthesis, ion-exchange, or by reconstruction of the layered structure when contacting the material calcined at 300-500°C with solutions of anions. LDHs use as catalysts and catalyst supports, adsorbents, anion scavengers, anion exchangers, polymer stabilizers, and antacids [3]. Inorganic or Organic anions can be introduced between hydroxide layer by ion exchange or precipitation. The incorporation of the vinyl polymers, poly(acrylic acid), poly(vinylsulfonate), and PSS between $M_2Al(OH)_6$ (M = Mg, Ca, Co) and Zn_3M

(OH)₈ (M = Al, Cr) layers by a templated reaction to form nanocomposites. The resulting materials contain organic layers with thicknesses of 14.8 to 16.8, which correspond to the incorporation of polymer bilayers between the LDH sheets [5]. Novel biohybrids of LDH and Biomolecules are designed and organised artificially on nanometer scale to provide opportunities for reservoir and delivery carriers of functional biomolecules in gene therapy and drug delivery [6-7]. LDHs can act as a chemical flask jacket protecting host from degradation. LDHs materials being unstable, in acidic conditions, do not survive for long in stomach [8]. However, given a suitable enteric coating, slow release of drugs into small intestine could be realized leading to effective delivery of fragile genetic materials into cells [5]. Naturally occurring LDHs can be found in two polymorphic forms- Rhombohedral and Hexagonal. Most naturally occurring crystals are of Rhombohedral symmetry, however crystals containing both symmetry types have been discovered [9-10]. LDHs intercalated with carboxylate anions have been studied in recent years because these materials have interesting properties and potential applications [11]. The intercalation of terephthalate and benzoate has attracted particular attention because these anions can be arranged in different orientations in the inter layer domain under different conditions [12]. Jones and coworkers have demonstrated by experimental measurements and computer simulations that the orientation of terephthalate is strongly dependent upon the charge density on the layers and the inter layer water content of the LDH [11-13]. Zn-Al LDHs containing terephthalate, 1,2-benzene dicarboxylate, 1,3-benzene dicarboxylate and benzoate were reported recently and the results showed that terephthalate was preferentially intercalated from mixed pairs of organic acids [13-14]. Thus it may be possible to use LDHs for the chemical separation of these anions from solution. In the present work, Zn-Al LDHs intercalated by terephthalate (TPH) and biphenyl 1,4'-dicarboxylate (BPH) have been synthesized directly by co-precipitation from aqueous solution. The materials were characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), FTIR and FT Raman spectroscopy, and MAS NMR spectroscopy [3,15].

Volume 8 Issue 11, November 2019

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

2. Experimental

2.1 Catalyst Preparation

A co-precipitation method was used in the preparation of the Zn Al LDH. Dissolving 2M Zn (NO₃)₂ and 1M Al(NO₃)₂ in presence of 2M NaOH / 2M Na₂CO₃ at basic condition (PH=9), get a slurry mass/mixture. The mixture is then stirred continuously [16]. The resulting mixture is centrifuged for 10 minutes at 15000 Rpm. It is repeated for 6-10 times. It is then separated into two parts-resultant precipitation and resultant solution. The solution is discarded [17-18]. The precipitate is then dried at 50-60°C in an air oven. The precipitate is Zn Al LDH which is used as catalyst. The catalyst preparation is supported by FTIR, DRs, SA, PXRD, SEM.

2.2 Characterization of Zn-Al LDH

PXRD study- The PXRD of ZnAl LDH shows the characteristics reflections from the planes of 003, 006, 009, 012, 015, 018, 300, 303 as shown in the fig1. and the reflections are also given in table 1 and values are also given in table 1.

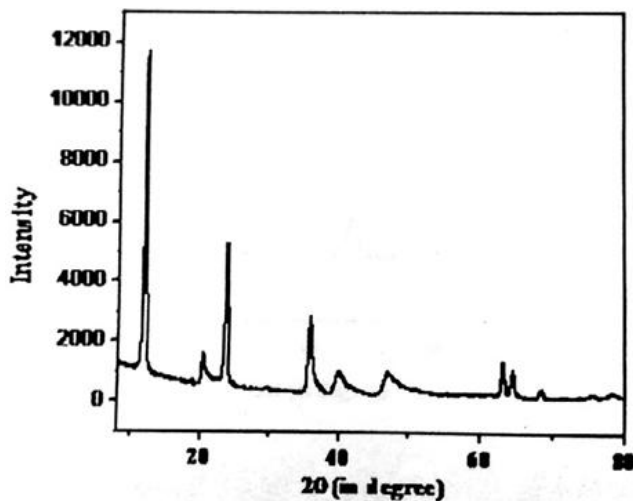


Figure 1: PXRD of Zn-Al LDH

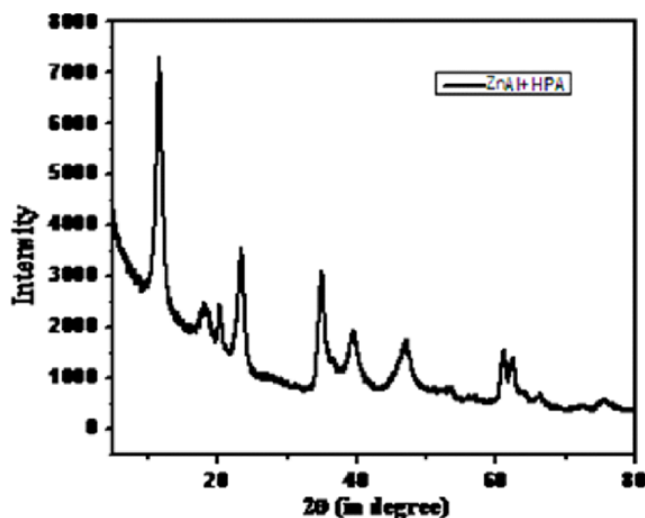


Figure 2: PXRD of heteropolyacids intercalated ZnAl LDH

Table 1: PXRD of Zn-Al LDH

ZnAl LDH	hkl	HPA intercalated Zn Al LDH	2θ	d-spacing
11.96	7.83	003	10.84	8.21
23.79	3.73	006	22.88	4.11
35.90	3.10	009	34.76	3.95
39.93	2.11	012	39.93	2.11
63.12	1.51	300	63.12	1.51
64.88	1.47	303	64.88	1.47

From the above table it has shown that, the d spacing of Zn Al LDH intercalated increases and thus the catalytic activity increases as a result we obtained maximum yield [19-20].

A. Surface Area (SA)

The Surface area of neat LDH is 31.54 m²/g and heteropolyacids intercalated ZnAl LDH is 76.06 m²/g. The images of SA of Zn-Al LDH and Intercalation of poly acids are shown below (fig 2 and fig 3) [17-18] . SA increases considerably with the intercalation of poly acids.

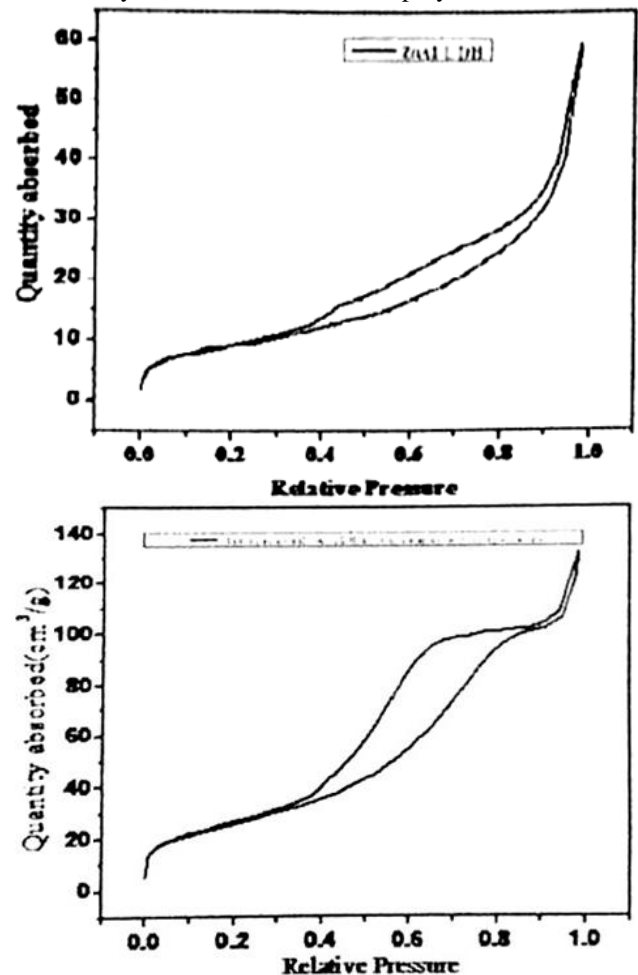


Figure 3: SA of heteropolyacids intercalated ZnAl LDH

B. Scanning Electron Microscope (SEM):

The SEM images show the layered structure of ZnAl LDH and EDX shows the presence of Zn, Al and O as shown in fig 4.

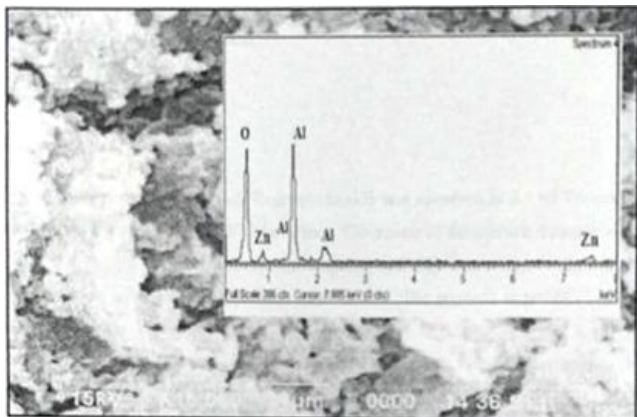


Figure 4: SEM and EDX of Zn- Al LDH

3. Friedel-Craft Acylation reaction

3.1 Benzoylation of anthracene:

Procedure:

1.25g of Anthracene and 1.75g of Benzoyl chloride was dissolved and stirred with 0.1 g of catalyst at 50°C for 1 hour [18-21]. The colour of the solution changes to dark green. The catalyst was removed by centrifugation and then evaporated to dryness. The green coloured solid was recrystallised from alcohol [22]. The products m.p=148°C and IR-Spectra shows the $\nu_{\text{C=O}}$ at 1684 cm^{-1} . The percentage of H=5.05% (4.9) and C=87.93% (89.96) [17-18] The solid product was recrystallised and identified as 9-Benzoylanthracene from NMR. [Proton NMR (300 MHz, CDCl_3), ppm 8.437 (6H, doublet), 8.145 (3H, triplet), 7.651(5H, triplet). The isolated product yield was about 76%

REACTION-

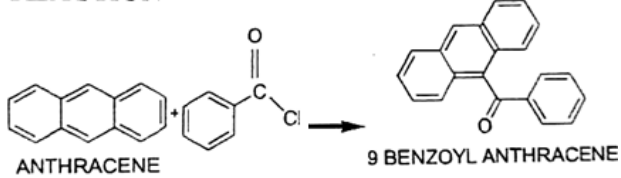


Figure 5: Benzoylation of anthracene

3.2 Benzoylation of benzene

Procedure:

1.32g of Benzene and 1.78 g of benzoyl chloride was dissolved and stirred with 0.05 g of catalyst at 50°C for 1 hour [23,24]. The colour of the solution changes to dark green. The catalyst was removed by centrifugation and then evaporated to dryness. The brown coloured solid was recrystallized from alcohol. The Products m.p. 48 °C, $\nu_{\text{C=O}}$ = 1650 cm^{-1} , C= 86.23% (86.35%) H=5.46% (5.57%) conforms the product as Benzophenone [24]. The solid product was recrystallised and identified as benzophenone from NMR.[Proton NMR (300 MHz, CDCl_3), ppm 8.152 (4H, doublet) 8.127 (2H, triplet) 7.725 (4H, triplet)]. The isolated product yield

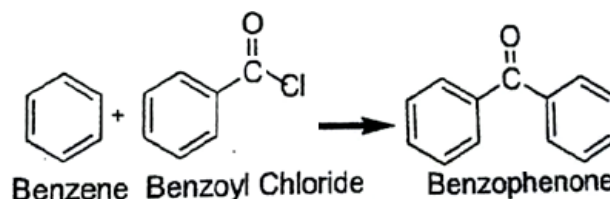


Figure 6: Benzoylation of benzene

3.3 Characterization of the compound

A. 9-Benzoyl anthracene- FT-IR spectra:

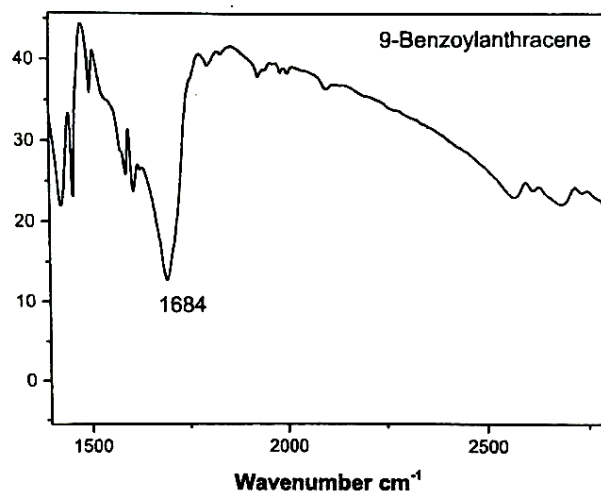


Figure 7: FT-IR Spectrum of 9-Benzoyl anthracene

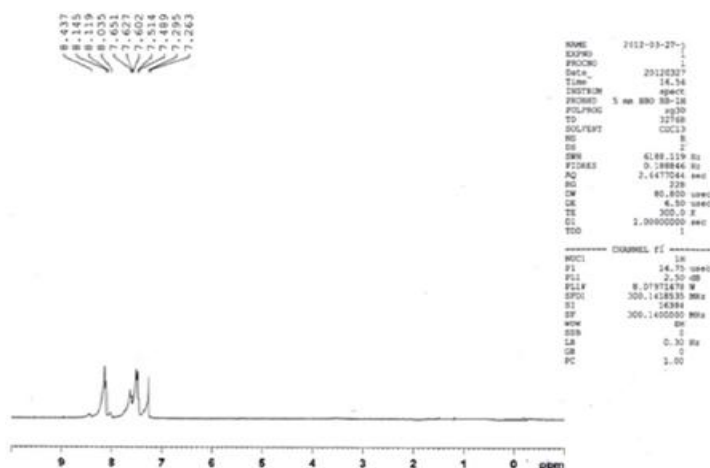


Figure 8: NMR spectrum of 9- Benzoyl anthracene

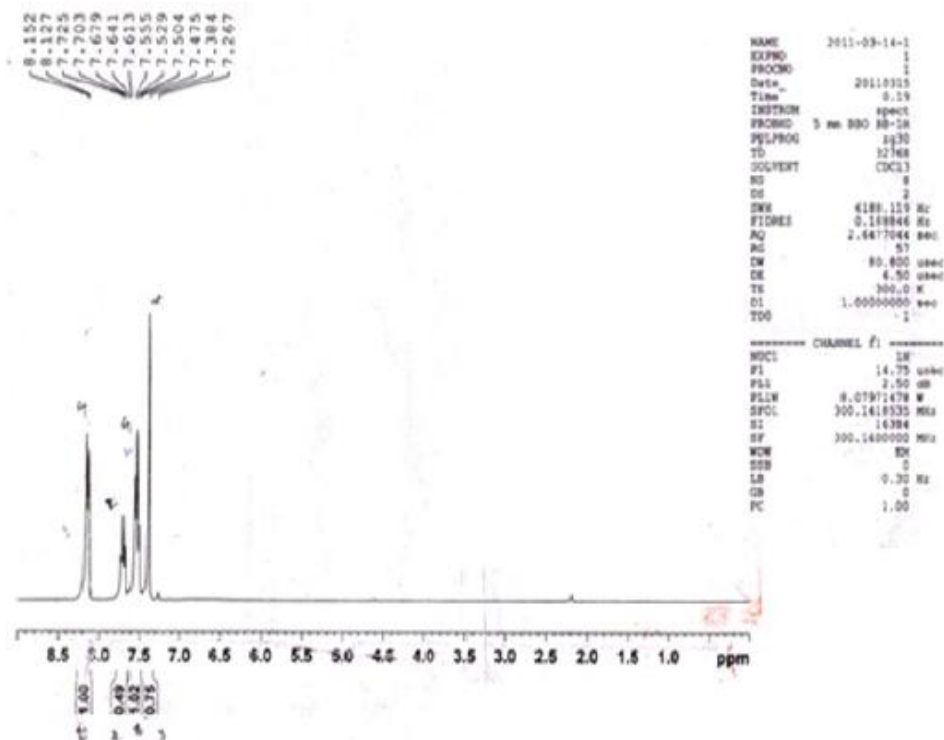


Figure 9: ^1H NMR spectrum of benzoylation of benzene using Zn-Al LDH as catalyst

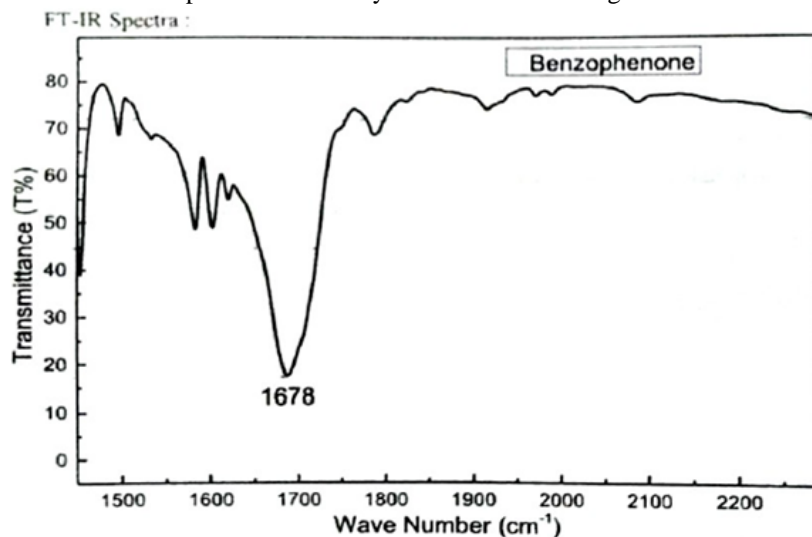


Figure 10: FT-IR Spectrum of Benzophenone

4. Conclusion

In the above project report, we have summarized synthesis of ZnAl LDH and heteropoly acids intercalated ZnAl LDH. The ZnAl LDH as well as heteropolyacids intercalated ZnAl LDH act a better catalytic activity for benzoylation of benzene and benzoylation of anthracene which was due to Lewis acids sites.

5. Funding

None

6. Conflict of Interest

The authors declare no conflict of interest, financial or otherwise.

7. Acknowledgements

The authors are thankful to IIT Guwahati, USIC Gauhati University, IASST Guwahati and National Aerospace Laboratory, Bangalore, India for facilities of the instruments.

8. Supplementary Material

Supplementary material is available on the publisher's web site along with the published article.

References

- [1] Kuang, Ye.; Zhao, Lina.; Zhang, Shuai.; Zhang, Fazhi.; Dong, Mingdong.; Xu, Sailong. Morphologies, Preparations and Applications of Layered Double Hydroxide Micro-/Nanostructures, **2010**, 3, 5220.

- [2] Cavani, F.; Trifiro, F.; Vaccari, A. *Catal Today*, **1991**, *11*, 173.
- [3] Gago, Sandra.; Martyn, Pillinger.; Santos, Teresa M.; Gomcalves, Isabel S. Zn-Al Layered double Hydroxide Pillared by different dicarboxylate anions, **2004**, *48*, 155
- [4] Anbarasan, R.; Lee, W D.; Im, S S. Adsorption and intercalation of anionic surfactants onto layered double hydroxides XRD study, **2005**, *28*, 145.
- [5] Oriakhi, Christopher O.; Farr Isaac, V.; Lerner, Michael M. Thermal Characterization Of Poly(Styrene Sulfonate)/Layer Double Hydroxide Nanocomposites, **1997**, *45*, 194.
- [6] Choudary, B.M.; Kantam, M.L.; Kavita, B.; Reddy, C.V.; Rao, K.K.; Figueras, F. Aldol condensations catalysed by novel Mg-Al-O-t-Bu hydrotalcite. *Tetrahedron Lett.*, **1998**, *39*, 3555-3558.
- [7] Choudary, B.M.; Sridhar, C.; Kantam, M.L.; Venkanna, G.T.; Sreedhar, B. Design and evolution of copper apatite catalysts for Narylation of heterocycles with chloro- and fluoro- arenes. *J. Am. Chem. Soc.*, **2005**, *127*, 9948-9949.
- [8] Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. Epoxidation of, -unsaturated ketones using hydrogen peroxide in the presence of basic hydrotalcite catalysts. *J. Org. Chem.*, **2000**, *65*, 6897-6903
- [9] Kuang, Y.; Zhao, L.; Zhang, S.; Zhang, F.; Dong, M.; Xu, S. Morphologies, preparations and applications of layered double hydroxide micro-/ nanostructures. *Materials*, **2010**, *3*, 5220-5235.
- [10] Rives, V.; Ulibarri, M.A. Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. *Coord. Chem. Rev.*, **1999**, *181*, 61-120.
- [11] King, A.G.; Keswani, S.T. Colloid mills: Theory and experiment. *J. Am. Ceram. Soc.*, **1994**, *77*, 769-777.
- [12] Choudary, B.M.; Chowdari, N.S.; Madhi, S.; Kantam, M.L. A trifunctional catalyst for one-pot synthesis of chiral diols via heck coupling-N-oxidation asymmetric dihydroxylation: Application for the synthesis of diltiazem and Taxol side chain. *J. Org. Chem.*, **2003**, *68*, 1736-1746.
- [13] Gunawan, P.; Xu, R. Direct assembly of anisotropic layered doublehydroxide (LDH) nanocrystals on spherical template for fabrication of drug-LDH hollow nanospheres. *Chem. Mater.*, **2009**, *21*, 781-783.
- [14] Zhang, L.H.; Li, F.; Evans, D.G.; Duan, X. Cu-Zn-(Mn)-(Fe)-Al layered double hydroxides and their mixed metal oxides: Physicochemical and catalytic properties in wet hydrogen peroxide oxidation of phenol. *Ind. Eng. Chem. Res.*, **2010**, *49*, 5959-5968.
- [15] Coronado, E.; Marti-Gastaldo, C.; Navarro-Moratalla, E.; Ribera, A. Confined growth of cyanide-based magnets in two dimensions. *Inorg. Chem.*, **2010**, *49*, 1313-1315.
- [16] Jaubertie, C.; Holgado, M.J.; San Roman, M.S.; Rives, V. Structural characterization and delamination of lactate-intercalated Zn, Allayered double hydroxides. *Chem. Mater.*, **2006**, *18*, 3114-3121.
- [17] Motokura, K.; Nishimura, D.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. A ruthenium-grafted hydrotalcite as a multifunctional catalyst for direct - alkylation of nitriles with primary alcohols. *J. Am. Chem. Soc.*, **2004**, *126*, 5662-5663.
- [18] Fürstner, A. Olefin metathesis and beyond. *Angew. Chem.*, **2000**, *39*, 3012- 3043.
- [19] Cornils, B. Industrial aqueous biphasic catalysis: Status and directions. *Org. Proc. Res. Dev.*, **1998**, *2*, 121-127.
- [20] Kaneda, K.; Yamashita, T.; Matsushita, T.; Ebitani, K. Heterogeneous oxidation of allylic and benzylic alcohols catalyzed by Ru- Al-Mg hydrotalcites in the presence of molecular oxygen. *J. Org. Chem.*, **1998**, *63*, 1750-1751.
- [21] Deshmukh P.H.; Bechert S. Alkene metathesis: The search for better catalysts. *Dalton Trans.*, **2007**, *24*, 2479-2491.
- [22] Gonzalez, S.D.; Nolan, S.P. Stereoelectronic parameters associated with N-heterocyclic carbene (NHC) ligands: A quest for understanding. *Coord. Chem. Rev.*, **2007**, *251*, 874-883.
- [23] Lam, F.L.; Kwong, F.Y.; Chan, A.S.C. Chiral phosphorous ligands with interesting properties and practical applications. *Topics Organomet. Chem.* **2011**, Springer, Berlin, Heidelberg.
- [24] Corma, A.; Garcia, H. Lewis acids as catalysts in oxidation reactions: from homogeneous to heterogeneous systems. *Chem. Rev.*, **2002**, *102*, 3837-3892.