

# STRUCTURE CHARACTERIZATION AND APPLICATION OF NI HYDROTALCITE AS ENVIRONMENTALLY FRIENDLY CATALYSTS FOR REDUCTIVE AMINATION OF BENZALDEHYDE

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## ABSTRACT

*Ni/hydrotalcite catalysts with ratios 2:1, 2.5 and 3:1 exhibit catalytic activity for reductive amination of benzaldehyde to amine. Ni HTLC is prepared by co-precipitation method, which is characterized by XRD, IR and TPR instruments. Carbonate present in the brucite layer of hydrotalcite and calcined hydrotalcite produce mixed oxides, exhibits catalytic activity for variety of organic transformations ex: selective aldol, nitro aldol, wittig, knoevenegal oxidation, reduction reactions. Hydrotalcites have wide applications as catalysts, for biodegradable poly(L-lactide)/layered double hydroxide nano-composites, and nano-sized silver–anionic clay matrix as nano-structured assemblies with antimicrobial activity. The author investigated application of Ni HTLC catalyst for reductive amination of benzaldehyde as representative compound with NaBH<sub>4</sub> as reducing agent to form Ni-boride insitu is generated resulting in the formation of aromatic amines with 100% conversion in methanol at room temperature. Highlighting special reference to Raney nickel catalyst, the handling of present catalyst does not require any special precautions and it can be used directly by charging into the reactor.*

**KEYWORDS:** Hydrotalcite, HTLC, structure, application, Ni-boride, NaBH<sub>4</sub>, benzaldehyde.

## I. INTRODUCTION

Heterogeneous catalysts have many advantages easy means of catalyst recovery, economic, recycling, zero emission of pollutants, and longer life time. The first formula of hydrotalcite was presented by Professor Mannase, at the University of Florence [1]. Hydrotalcites are classified as Cationic or Smectite type in which the layered structures are arranged in sheets as brucite type Mg(OH)<sub>2</sub> and Al(OH)<sub>2</sub> octahedral separated by charge balancing anions, water and these occupy the interlayer spaces. The sheets then stack (in the crystallographic c direction) to give a characteristic layered material. In many samples of hydrotalcite, few of the M<sup>2+</sup> species are substituted by M<sup>3+</sup> species, which results into the layers carrying the residual positive charge. Crystals of hydrotalcite which mostly consists of micron sized stacks of hexagonal platelets morphologically. However, fibrous and extended sheet-like morphologies is reported depending upon the conditions of synthesis [2-3]. Thermal calcinations of these materials results in the formation of non-stoichiometric mixed metal-oxides with characteristic properties, which are extremely active catalysts for many important transformations.

## II. HYDROTALCITE TYPE CLAYS

Research efforts are being made to develop catalysts based on simple inorganic oxides, mixed oxides, supported oxides, zeolites and clay minerals for environmentally safe processes. Because of their benign nature and special structural features a lot of renewed interests have emerged in using clays as catalysts and support. Generally, clays are classified into two broad groups. Cationic and anionic clays, and the cationic clays has infinite sheets of tetrahedra or octahedra of silica and alumina and also contains hydrates of magnesium, iron and other metals. The excess negative charge of the silicate sheets are compensated by alkali or alkaline cations [2]. On the other hand anionic clays are

composed of positively charged sheets of di – and trivalent metal hydroxides. The sheets share octahedral edges and contain interstitial anions to compensate the positively charged sheets [3]. Hydrotalcite (HTLC) belongs to the large class of anionic clays. Hydrotalcite has  $Mg^{2+}$ ,  $Al^{3+}$  and  $CO_3^{2-}$  ions as its constituents.

### III. STRUCTURE OF ANIONIC CLAYS

The structure of the sheet containing  $Mg^{2+}$  and  $Al^{3+}$  is similar to that of magnesium hydroxide and they are often referred to as ‘brucite like layers’. The unit cell of the hydrotalcite contains either three layers of metal hydroxide and interlayer anions with rhombohedral symmetry or two layers of metal hydroxide and interlayer anions with hexagonal symmetry. The overall composition of the HTLC can be expressed with a general formula [2].



Scheme 1: General formula of hydrotalcite

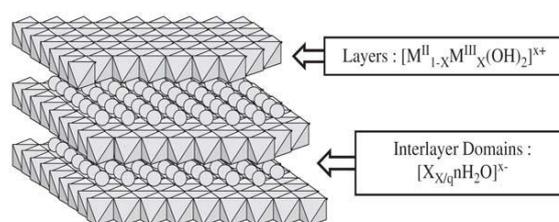


Figure 1: Structure of LDH

Where  $M^{2+}$  and  $M^{3+}$  represent divalent and trivalent metal cations,  $A^{n-}$  is the interlayer anion and  $z$  represents the varied state of hydration of the layered double hydroxide (LDH). During the past decade strong impetus was given to modify hydrotalcites for the synthesis of fine chemicals, exploring both basic and redox properties.

Both cationic and anionic clays, with sensitizers anchored onto their interlayer by ionic linkage, are found to be useful ‘micro-reactors’ to achieve triplet state reactivity of myrcene which have applications in photochemical reactions. Mixed oxides are used for  $SO_x$  burning HTLC  $CeO_2$  [2]. The combination of these two oxides may establish new acid–base properties. Therefore, use of Mg–Al mixed-metal oxide as a support can introduce wide range of properties. The Mg–Al mixed-metal oxide materials have been employed as supports in many reactions, such as Ru/MgO– $Al_2O_3$  in ammonia synthesis [3], Ni/MgO– $Al_2O_3$  in ethanol steam reforming [4], Ni/Mo/ $Al_2O_3$ –MgO, and CoMo/ $Al_2O_3$ –MgO in thiophene hydrodesulfurization. Ru-HTLC is used for double bond isomerization perfumery industry and nitrate reduction is done with Pd catalysts supported mixed oxide and resin [5].

Major applications of hydrotalcite for fine chemicals synthesis in the area of petro chemicals, pharmaceuticals, steam reforming, methanol, higher alcohol synthesis selective oxidation of alcohols to aldehydes [5], reduction of aldehydes to alcohols [6], epoxide ring opening [7], epoxidation [8], Aldol condensation [9], cyanoethylation [10], michael reaction [11], and transesterification [12]. Pinnavaia et al [13] reported excellent results on intercalation of polyoxometallates as anion pillars and exploited them in selective oxidation reactions [14]. Choudary et al [15] reported oxidative bromination of bisphenol-A excellent activity for osmate intercalated hydrotalcite for asymmetric dihydroxylation of various aliphatic and aromatic olefins [16] using NMO (N-methylmorpholine N-oxide) as co-oxidant.

The maximum amount of water present in the interlayer can be calculated on the basis of sites present in the close packed configuration of oxygen atoms [17]. Intercalation of metallophthalocyanine tetrasulfonate in the intergallery of Mg–Al HTLC which is synthesized by different routes. In general hydrotalcite catalysts are prepared by co-precipitation method depending upon the composition of the

M<sup>2+</sup> and M<sup>3+</sup> [18-19]. Choudary et al [5] reported excellent catalytic activity of Ni-Al HTLC with varied composition of (Ni-Al 2:1, 2.5:1, 3:1) were prepared by co precipitation method by employing NaOH/Na<sub>2</sub>CO<sub>3</sub> [5-6]. Fig1 represents conventional process for expoxidation of cyclohexene. Cyclohexene have been a target molecule for cyclohexene oxide as single product fig 2. Hydrotalcite catalysts is well known for conversion of cyclohexene to cyclohexene oxide in single step [1,5-8].

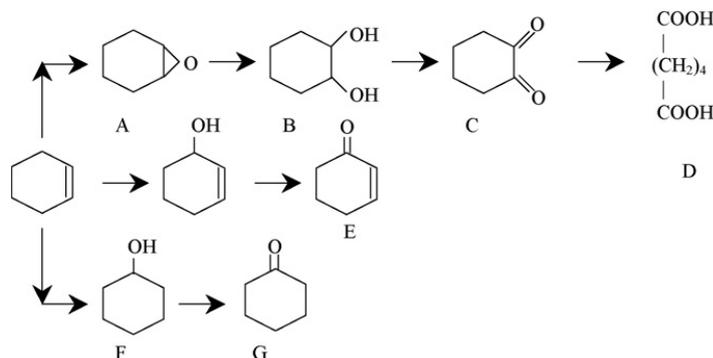


Fig 2 representation of conventional process for expoxidation of cyclohexene to cyclohexene oxide [1,5-8].

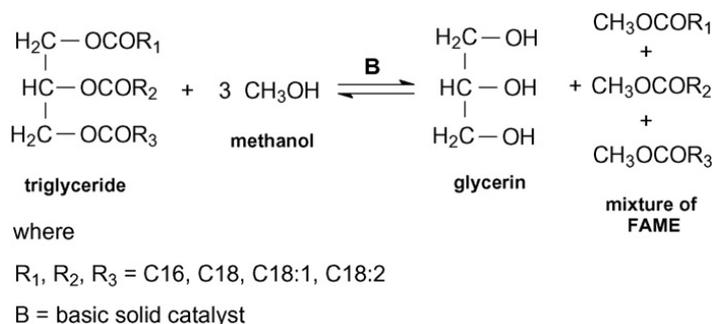


Fig 3: Soybean oil is transesterified to esters with Mg Al and ZnAl hydrotalcite solid base catalyst [1,12].

Since few years scientists working this area have paid special emphasis in the area of inorganic layered double hydroxides which are acting as hosts for biologically active molecules, as drug delivery agents, adsorbents and many more compounds have gained a growing interest in academy and industry due its important properties. Costantino et al [20-27,29,35,37] have developed Mg(Zn)Al HTLC catalysts as reservoir of species that is released upon a chemical signal, i.e. by ion exchange reactions, in particular environments. In addition the inorganic sheets can offer a photo-protection towards intercalated photo-degradable species. And the bio-compatible Mg-Al HTLC has been used as a host for many molecular anions of biological interest as amino acids, anti-inflammatory (NSAID), antibiotic and UV-filters. Ion exchange procedures have been used to obtain the intercalation compounds of Mg-Al HTLC with ibuprofen, diclofenac, indomethacin, ketoprofen and tiaprofenic acid and to study their release in solutions simulating biological fluid Among large number of enzymes used for biosensor production, urease takes a large part in enzyme sensor development due to the large demand of urea determination. Urea is one of the compounds monitored in blood as an indicator of renal function and efficiency. Moreover, urea is widely distributed in nature and its analysis is of considerable interest in agro-food chemistry and environmental monitoring. A common approach to develop urea biosensing systems is entrapment of urease enzyme into an appropriate matrix as for glucose biosensors. As pointed in section 4.1.2, clay minerals and LDHs are suitable materials for this purpose (Figure 2). [28-29].

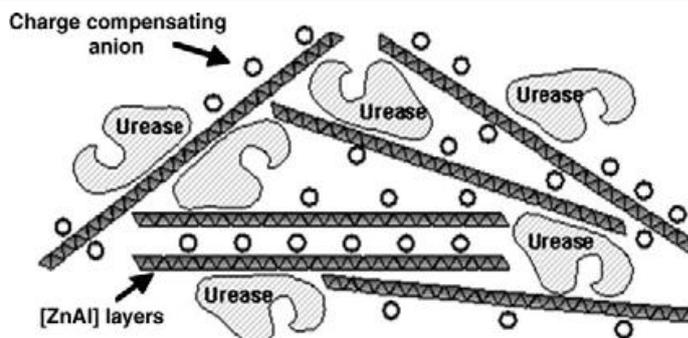


Fig 4: Ideal representation of the structure of hybrid bioinorganic [ZnAl-Urease] [29b].

Nano-composites constituted of polyethylene and organically modified Zn-Al HTLC and polymer/LDH nano-composites have become a new promising class of materials due to their exceptional thermal and mechanical properties. Only few investigations focused on the polymer/layered double hydroxide (LDH) nano-composites due to their strong electrostatic interaction between highly charged hydroxide layers and the intercalated anions to hinder the exfoliation of the LDH layers [30]. Ce-promoted Ni/Mg-Al catalysts were synthesized by means of doping of Ni-Mg-Al mixed oxides derived from hydrotalcites is used for methane reforming [9]. Ni HTLC catalysts have demonstrated special application in oil palm trees [5,7,15,16] and bacterial strain on the products of dissimulators iron reduction, [31] reduction of nitrate in water, synthesis of biodegradable poly(L-lactide)/layered double hydroxide (LDH) nanocomposites [31-35] arginine mediated-synthesis of highly efficient catalysts for transfer hydrogenations of ketones [35-36]. Ca-Al (LDHS) used as a hardening accelerator in concrete, [26] and catalysts for transesterification of tributyltin with methanol, [26] microwave-hydrothermal treatment on the properties of layered double hydroxides and related materials, nanosized silver-anionic clay matrix as nano-structured ensembles with antimicrobial activity [37].

- i. **Results and discussion** Reductive amination of benzaldehyde to amines with calcined Ni-Al HTLC in  $\text{NaBH}_4$  is discussed. Ni-Al HTLC 2:1, 2.5:1, and 3:1 is the active catalysts for the above transformation. Ni-Al 2:1 HTLC proved to be the best active catalysts for the above reaction and evaluated substituted benzaldehydes to amines listed in table 1 from S.No1 to 6. And wide range of applications of hydrotalcites have been briefed in this section.
- ii. **Experimental Section:** Preparation of Ni-Al 2:1, 2.5:1 and 3:1 are prepared by co-precipitation method [5-6].
- iii. **Characterization of Ni hydrotalcite catalysts:** Ni-Al 2:1, 2.5:1 and 3:1 HTLC characterized by XRD to confirm the crystalline structure of Ni hydrotalcite. And from IR studies it confirms that OH stretching frequency in Ni-Al HTLC catalysts is broad. From TPR results the author analysed the presence of nickel oxide in association with oxide of aluminium is the active species for reductive amination of aldehyde to amine [5-6,11].

#### IV. RESULTS AND DISCUSSION

The transformation of amines from aldehydes and ketones is an important area in organic synthesis because of their utility as intermediates for the synthesis of pharmaceuticals and agrochemicals products. Frequently it's used on an industrial scale in preference of alcohol amination when the aldehydes or ketone is cheap (acetone and lower aldehydes manufactured by oxo synthesis) [38-41]. Direct methodology of reductive amination is involved using aldehyde and amine in presence of catalysts [40]. Raney Nickel is the preferred catalysts of choice and the main limitations are special precautions in handling the catalysts during charging into the reactor, elevated temperatures, high  $\text{H}_2$  pressure are main necessities in many industrial processes. Supported Ni, Cu and Co, copper chromite, supported noble metals, or base and noble metal sulfide catalysts were suggested [27]. Sulfides of base metals and supported noble metals are used under mild conditions for the preparation of secondary and tertiary amines, but these lead to the generation of toxic wastes and byproducts [28]. Author designed Ni HTLC catalytic system for reductive amination of benzaldehyde to amines in

100% conversion and single product selectively in methanol at room temperature in 10 mins by using versatile catalytic system of 2:1 Ni-Al HTLC and NaBH<sub>4</sub> *in situ* generation of Ni-boride species, which resulted in choosing 2:1 Ni-Al HTLC catalyst exhibiting highly active. In view of the above encouraging results the author further evaluated catalytic aptitude of Ni-HTLC 2.5:1 and 3:1 catalysts exhibited less activity which is due to excess of nickel present [5,6,48-50]. In view of above positive results for benzaldehyde reductive amination the author examined substituted benzaldehydes ex: toulaldehyde, 4-bromobenzaldehyde, 4-hydroxybenzaldehyde resulted in respective amine products. With 2:1 Ni-Al HTLC the conv 100% of reaction in 10 mins, 2.5:1 Ni-Al HTLC conv 93% 12 mins and 3:1 Ni-Al HTLC conv 90% 15 mins. All reactions with 2:1 Ni-Al HTLC had 100% selectivity. Thus, the order of reactivity of Ni catalyst is 2% Ni-Al > 2.5:1 Ni-Al > 3:1 Ni-Al. Identifying that 2:1 Ni-Al HTLC as the ideal catalyst of choice under optimum conditions, all the reactions were studied in duplicate and the results were reproducible. The reaction was completed in 15 mins compared for Ni HTLC 3:1 to 2:1 Ni-Al HTLC catalyst which took 10 mins thus owing to the demonstration of nickel in association with oxide of aluminium is the active species for the reductive amination of aromatic aldehydes to amines as single product. In order to check the activity of the catalysts, blank reactions without NaBH<sub>4</sub> were conducted in similar conditions with 2% Ni-Al HTLC and with bulk NiO and in both the cases only starting material was recovered [5-6]. This confirms that nickel boride in Ni HTLC catalysts is effective system for selective reductive amination of aromatic aldehydes the standard substrate being benzaldehyde to N-Phenylaniline at room temperature. During the course of our studies on *in situ* generated nickel boride in Ni HTLC system, it was observed that the aromatic ring of aromatic aldehydes was intact under similar conditions; unlike with Raney Ni as catalyst, the reaction could proceed to aromatic ring hydrogenation [28]. With all Ni hydrotalcite catalysts, when sodium borohydride was added over 5 min duration, the reaction turned instantly black, which indicates the generation of Ni-boride is accompanied by spontaneously hydrogen is evolved. This is possibly due to nickel in association with oxide of aluminium is the active species for the formation of Ni-boride species. It appears that the rate of reductive amination depends upon the rate of NaBH<sub>4</sub> decomposition to form Ni boride and H<sub>2</sub> [48-49]. Leaching of metal from the filterate was tested for the reaction mixture and observed that there was no reaction hence this confirms that Ni metal is well formed in Ni HTLC catalytic system with this evidence its concluded that the nickel boride heterogeneous mixture is well formed and nickel species are well adhered to boride complex formed during the reaction [48-50]. Hence, the use of nickel HTLC catalysts, prepared by co-precipitation method with nickel nitrate and aluminium nitrate solutions is the most extensively method used for preparing Ni-HTLC catalysts and used for reduction reactions demonstrated by choudary et al [5-7]. To develop highly active Ni-HTLC catalytic system the influence of the operation parameters are important during the preparation of the catalysts such as order of reactants, speed of agitation, time of aging and selection of proper ratios Ni salt [5-6,48-50].

**Table 1:** Selective reductive amination of various aromatic aldehydes to aromatic amines in methanol with 2% Ni-Al Cat A # time 5-10 min

Substrate = 1.0 mmol, Amine 1.5 mmol, catalyst = 200 mg, sodium borohydride = 200 mg, room temperature.

S. No	Substituted Aldehyde +Amine	Product	Conv%	Sel%
1.	Ph-CHO + Bu <sup>n</sup> NH <sub>2</sub>	PhCH <sub>2</sub> NHBu <sup>n</sup>	100	100
2.	Ph-CHO+ PhNH <sub>2</sub>	PhCH <sub>2</sub> NHPh	100	100
3.	4MeOPhCHO + Bu <sup>n</sup> NH <sub>2</sub>	4MeOPhCH <sub>2</sub> NHBu <sup>n</sup>	65	100
4.	4MeOPhCHO+PhNH <sub>2</sub>	4MeOPhCH <sub>2</sub> NHPh	70	100
5.	4MePhCHO+PhNH <sub>2</sub>	4MePhCH <sub>2</sub> NHPh	80	100
6.	4MePhCHO+Bu <sup>n</sup> NH <sub>2</sub>	4MePhCH <sub>2</sub> NHBu <sup>n</sup>	90	100

## V. EXPERIMENTAL SECTION

### 5.1 Preparation of Ni-Al hydrotalcite (Ni/Al 2:1)

Ni-Al hydrotalcite catalysts were prepared by co-precipitation method by taking appropriate ratios of Ni and Al nitrates [5-7].

## 5.2 Preparation of Calcined Ni-Al hydrotalcite(Ni/Al 2:1, 2.5:1, 3:1)

The same procedure is mentioned in 5.1 section is repeated with ratio being changed [5-7].

## VI. CATALYSTS CHARACTERIZATION

### (a) XRD of Ni-Al 2:1hydrotalcite catalyst:

The XRD for LDHs samples such as carbonates which have one unit hexagonal cell. The peak at  $11.5^\circ 2\theta$  ( $d$  spacing= $7.7\text{\AA}$ ) of hydrotalcite carbonate are attributed to the reflections from (003) of crystallographic planes. These planes are spaced one-third per unit cell distance apart and corresponds to the interlayer [5]. The  $d$  spacing is known as the interlayer spacing which is formed from the metal hydroxide sheet (approximately  $4.8\text{\AA}$ ) and the gallery region is around  $2.8\text{\AA}$  which contains the intercalated anions. The XRD samples of the Ni-Al 2:1 calcined hydrotalcite at 723 K mainly shows the presence of mixed cubic oxide phases, which is obtained by the loss of water and carbon dioxide from the anionic interlayer of hydrotalcite precursors. Ni-Al HTLC 2:1, 2.5:1, 3:1 hydrotalcite shows the characteristic crystalline pattern and shows excellent catalytic activity for oxidation of alcohols with Ni-Al HT with molecular oxygen [5]. The used catalysts retained similar hydrotalcite XRD pattern. The XRD of the Ni-Al HTLC calcined shows the formation of NiO phase and which is the active species for reductive amination reaction [5-7,15-16].

### (b) Infrared Spectroscopy of Ni-Al 2:1 hydrotalcite catalysts:

The infrared spectra for Ni-Al HTLC 2:1, 2.5:1, 3:1, shows hydroxy stretching vibrations same as of standard Mg-AlCO<sub>3</sub> HTLC, with different M (II) cations and Ni-Al HTLC showed the absorption at  $3500\text{-}3600\text{cm}^{-1}$ , which is attributed to the H-bonding stretching vibrations of the OH group is present in the brucite like sheets. Mostly the shifting of this bond depends upon the  $X$  for Mg(OH)<sub>2</sub>. When  $X=0$  the absorption of this band shifts to higher frequency of  $3700\text{ cm}^{-1}$ . Kaneda et al [1,5-7] reported as the ( $M^{2+}/M^{3+}$ ) ratio increases the hydrogen stretching & bending corroborated with the changes in the layer spacing. A shoulder is present around  $3000\text{cm}^{-1}$ , is mainly attributed to hydrogen bonding between H<sub>2</sub>O and the anion in the interlayer and H<sub>2</sub>O bending vibration which occurs at  $1600\text{ cm}^{-1}$ . In Ni-HTLC three bands appears at  $1350\text{-}1380\text{cm}^{-1}$  ( $\nu_3$ ),  $850\text{-}880\text{ cm}^{-1}$  ( $\nu_2$ ), and  $670\text{-}690\text{ cm}^{-1}$ . IR spectra of various compositions of Ni-Al HTLC display vibrational stretching frequency of hydrogen atom in hydroxide group of Ni-Al 2:1 ratio appears at lower wavelength  $3420\text{ cm}^{-1}$  and has a smaller half width than the other compositions which indicates there is a more ordered cation distribution in the former [1,5,14-15].

### (c) TPR Characterization of Ni Al 2:1 hydrotalcite catalyst:

The TPR profile of Ni HTLC catalysts indicates that free NiO is reduced at lower temperature and NiO in association with oxide of aluminium is reduced at higher temperature and ammonia display both free NiO and NiO in association with oxide of aluminium and is the active species for reductive amination reactions and nickel aluminium HTLC displays a shoulder at lower temperature that grows on free nickel oxide content. These TPR results are in good agreement with the results reported by Choudary et al [5-9]. The activation of Ni species generated by all the samples of Ni-Al HTLC, as evident for the reductive amination of aldehyde to amines is attributed to the presence of Ni in association with aluminium oxide displays both free NiO and NiO in association with aluminium oxide. The TPR for nickel hydrotalcite was further studied for Mg-Ni of varying ratios, showed two peaks of H<sub>2</sub> consumption. The first peak around 570 K corresponds to the release of NO<sub>3</sub> anions as NO<sub>2</sub> and the subsequent reduction of NO and N<sub>2</sub>O. The second peak with maxima at 705, 920 and 1000 K for respective samples to the reduction of NiO particles. When Mg content is increased the reduction of the nickel oxide decreases it can be compared with the decrease of the NiO crystal size. This behaviour is attributed to the formation of Ni aluminate band of nickel spinel type and decreasing the size the crystallite and hence it hinders their reducibility [47-50]. The excellent results of these catalysts from characterization studies encourage author to investigate reductive amination of benzaldehyde to amines with highly active Ni-Al 2:1 HTLC catalyst.

## VII. CONCLUSIONS

The scientific results presented in this article indicates that Ni-HTLC catalysts belonging to the family of anionic clays are versatile catalysts for reductive amination of aldehydes and its wide industrial applications, notably layered double hydroxides have attracted attention in the area of polymer/LDH nano-composites have become a new promising class of materials because of their exceptional thermal and mechanical properties, and in the area of drugs LDHs acts as hosts for a variety of drugs to stud its biological activity. The efficiency of Ni-Al hydrotalcite catalysts for reductive amination of benzaldehyde is evaluated with Ni-Al HTLC in NaBH<sub>4</sub> as reducing agent and *insitu* generates Ni-B species in association with oxide of aluminium is the active species for reductive amination reaction of benzaldehyde which resulted 100% conversion effectively and single product in 10 mins duration at room temperature. This process is viable for industrial applications. The Ni catalysts is eco-friendly, atom economy, easy means of recovery and reusable. Ni HTLC catalysts which is prepared by co-precipitation method and characterized by XRD, IR and TPR instruments With special reference to the Raney nickel catalyst, Ni-Al HTLC can be charged into reactor without pre-treatment of the catalyst and the handling of present catalyst does not require any special precautions and it can be used directly by charging into the reactor.

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