Intercalation and Complexation of Ni (II) by Schiff Base Ligands Incorporated into Mg-Al Layered Double Hydroxides

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Abstract

A novel complexes Ni(II) Schiff base N, N' -bis(salicylidene)-3,4-diaminobenzoic, denoted (Ni (LH)) has been synthesised and characterised by UV, IR and XRD then Mg-Al layered double hydroxides (LDH) intercalated by Ni (LH) complex were prepared by co-precipitation and reconstruction of a mixed oxide catalyst (Mg-AlC).The characteristics of the modified LDH -Ni(LH) were characterized by X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric (TGA) and BET surface area . The IR spectral study of Ni(LH) complex showed that the metal ion coordinate through the two nitrogen atoms of the azomethine group and the two oxygen atoms of the deprotonated hydroxyl group of the salicyaldehyde moiety, in addition the IR spectral study of modified LDH -Ni(LH) indicated that most of the interlayer carbonate anions were replaced by Ni(LH) anions to form LDH-Ni(LH) and we see the rebuilding of the LDH phase after intercalation.

Keywords: LDH, Shiff base complexes, Complex formation, intercalation, electro catalytic oxidation.

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1. Introduction

Many studies have been conducted on the study of organic-inorganic hybrid materials, such as layered double hydroxides (LDH), in which the interlamellaires anions can be easily changed and the basal spacement of the hydroxide layer can be adjusted. LDH are typically represented by the general formula $[M^{II}{}_{1-x} M^{III}{}_{x}(OH)_2]^{x+} (A^{n-})_{x/n}\ mH_2O$, where M^{II} and M^{III} are divalent and trivalent cations, x is the molar ratio of $M^{III}/(M^{II}+M^{III})$, and A is the interlayer anion of valence n (Huan YU et al., 2019). LDH have attracted increasing attention in the recent years due to their potential application in a wide range of fields such as catalysis, (Jana, S.K. et al., 2008) adsorbent electrochemistry, and environmental remediation. Their large surface area, high number of active alkali sites, high anion exchange capacity, and expansion properties have piqued their interest, and they have been used as immobilization supports for a variety of metallic complexes, (Elena Pérez Barrado., 2015, Cornelia-Magda Puscasu et al., 2013) and widely used as catalyst supports and in catalytic reactions. (Debecker, D.P et al., 2009, Urdă, A.; et al., 2013). LDH with a space between the layers are thought to be an appropriate host for the intercalation of planar catalysers of transition metal complexes containing ligands of porphyrine, phtalocyanine, or Schiff base. (Parida K.M et al., 2010) Schiff bases are formed by the condensation of primary amines and carbonyl compounds. Many Schiff base complexes exhibit excellent catalytic activity over a wide range of reactions at high temperatures (>100°C) and in the presence of moisture (Navneet et al., 2013). And there have been many reports in recent years on their use in homogeneous and heterogeneous catalysis as in various biological systems, polymers and dyes, (Patrizia et al., 2012) due to the excellent selectivity, sensitivity and stability of Schiff bases for specific metal ions such as Ag(II), Al(III), Co(II), Cu(II), Gd(III), Hg(II), Ni(II), Pb(II), Y(III) and Zn(II), Furthermore, research into the catalytic properties of Schiff bases has revealed catalytic activity in hydrogenation. The most intriguing application for these compounds is the possibility of using them as effective corrosion inhibitors (Katarzyna Małgorzata.et al., 2014).

Our goal in this work was to obtain a catalyst by intercalating a schiff base complex into a layered double hydroxide to be used as heterogeneous catalysts, so we report the synthesis and characterization of Ni (II) metal complexe of Schiff base derived from the condensation of 3,4-Diaminobenzoic acid and salicyl aldehyde, and we also synthesized the catalyst MgAlC-Ni(LH) using the reconstruction method.

2. Materials and methods

2.1. Chemicals

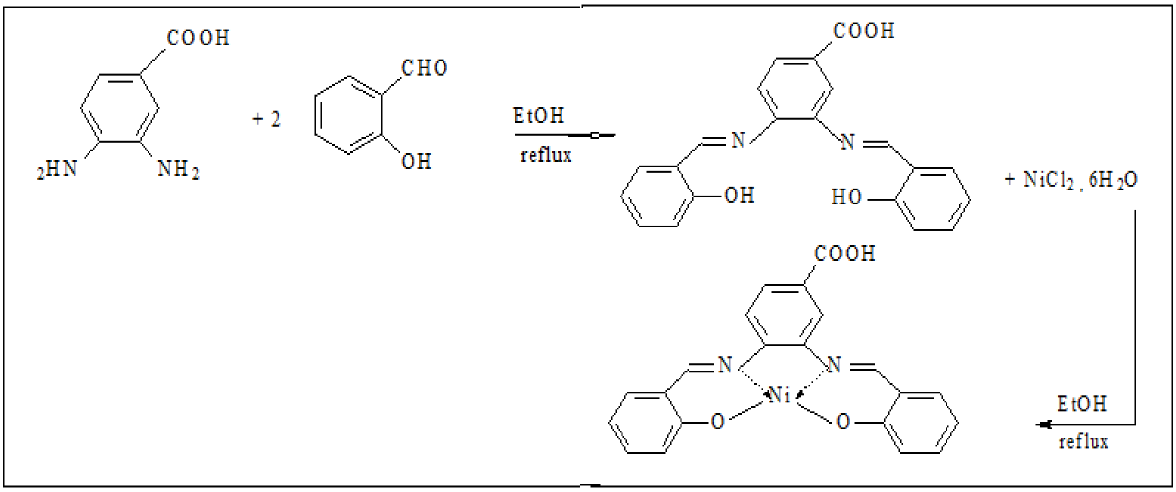
All solvents (ethanol absolute, dichloromethane, dimethyleformamide (DMF) and dimethylsulphoxide (DMSO)) were obtained by Fluka, while 3,4-diaminobenzoic acid and salicyl aldehyde, Nickel (II) chlorure hexahydrate ($Ni\ (Cl_3)_2\ 6H_2O$ 99 %, Magnesium (II) chlorure hexahydrate ($Mg\ (Cl_3)_2\ 6H_2O$ 99 %), Aluminium (III) chlorure hexahydrate ($Al\ (Cl_2)_3\ 6H_2O$ 97 %, sodium carbonate (Na_2CO_3 99.5%)and sodium hydroxide (NaOH 99 %), were obtained from Sigma Aldrich.

2.2. Synthesis of Mg-Al–CO_3 by coprecipitation

To synthesize MgAl-CO_3, The Youwen and al method (W.T. Reichle,. 1985) was used by co-precipitating two Mg^{2+} and Al^{3+} salts with a basic solution of NaOH and Na_2CO_3. A solution of 100 ml $Mg(Cl_3)_2$ $6H_2O$ (0.66M) and $Al(Cl_2)_3$ $6H_2O$ (0.33M) is added to a solution containing 100 ml of NaOH (2M) and Na_2CO_3 (1M). The addition is accomplished dropwise and mixed for 6 hours at room temperature and pH=10, to facilitate crystallization of the precipitate, the vial content (white amorphous product) was heated to 65°C with stirring for 18 hours. Following that, the precipitate obtained was washed several times with distilled water to eliminate chloride ions and sodium content. After purification, the sample was dried at 65°C for 48 hours before being ground to a homogeneous white powder. The powder was then calcined in an oven at 500°C for four hours. A mixed oxide catalyst was obtained and denoted Mg-AlC.

2.3. Preparation of the Ni complex of N, N' -bis(salicylidene)-3,4-diaminobenzoic acid (Ni(LH))

A solution of 3,4-diaminobenzoic acid (1 mM, 0.152 g) in absolute ethanol (10 mL) and 2mM NaOH (5 mL) was slowly added to a solution of salicyl aldehyde (2 mM, 0.244 g) in absolute ethanol (15 mL). The reaction mixture was refluxed for 4 hours at 60-65 °C. The reaction was allowed cooled and the grey coloured precipitate formed, we have tested the formation of ligand (LH) by Chromatography on small plates (CSP), than we add a solution of $NiCl_26H_2O$ (0.225g) in absolute ethanol (5mL) and refluxed for 4 hours at 65 °C. The reaction was allowed cooled and the brown coloured precipitate formed collected by gravity filtration. The precipitate was washed with cold ethanol (3x10 mL) and dried to a constant mass to give 0.496 g, 80% yield. Melting Point: 250 °C (CHIZOBA I. et al., 2013).



Scheme 1: Synthesis of the Ni complex of N, N' -bis(salicylidene)-3,4-diaminobenzoic acid.

2.4. Synthesis of Mg-AlC intercaled by Ni (LH)

Mg-AlC-Ni(LH) was synthesized by the reconstruction method (K.M. Parida., 2010, Zujian H et al., 2012 and Shirley Nakagaki,et al., 2014) by dissolving 1 g of Mg-AlC catalyst in 30 ml of ethanol for 1 hour to create an ethanolic suspension , then 0.5 mmol (0.274 g) of Ni(LH)complex was added, and the reaction system was refluxed at 60 °C with constant stirring for 24 hours; Afterwards, the resultant product was filtered, cleaned with ethanol, and vacuum-stored at 70 °C for an overnight period, yielding Mg-AlC-Ni(LH).

2.5. Characterization techniques

Textural measurements were performed using a BET device (CLOUTER SA3100) at 77K. Initially, the samples were vacuum degassed at 250 ° C. for 3h, and previously desorbed at reduced pressure (< 10^{-4} Torr). The BET method is used to calculate specific surface areas at different relative pressures ranging from 0.05-0.35 (Lowell, S.et al., 2004). The total pore volume, Vpore, was calculated directly from Nitrogen adsorption at P/P0=0.98.

UV–vis spectra were captured in 1cm quartz cells using the Unicam 300 and software vision 32 at wavelengths ranging from 200 to 800 nm.

Fourier transform infrared (FT-IR) spectra were recorded using a (FTIR -8400S Shimadzu (Japan) spectrophotometer) from 400 to 4000 cm^{-1}), using KBr pellets (1 mg of sample in 100 mg of KBr).

Thermogravimetric analysis (TGA) were measured in air using a PCT-1A thermal analysis system with a heating rate of 10 °C/min.

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ=0.154 nm) at 40 kV, 30 mA, a scanning rate of 0.02 Chromatography on small plates (CSP) on silice plates is used to control the purity of the ligand and complex, with dichlorométhane as an eluent for the ligand and a mixture (1/9, v/v) of methanol and dichlorométhane for the complex, followed by detection with a UV multi bands 365 nm model VL-6.L.

3. Results and discussion

The synthesized products are solid in the form of powder and have a very low solubility in organic solvents with the exception of DMF and DMSO. The LH ligand is grey and has a yield of 38% ($m_{product}$ / $m_{reagents}$)*100. It has a melting point of 245°C (as measured by banc kofler 7779). The Ni (LH) complex is brown and has a melting point greater than 260°C.

3.1. Texture measurements (BET Method)

BET surfaces were calculated in the range (0.05<P/P0<0.35). We found that the BET surface area of calcined LDH is larger than that of non-calcined LDH. (Figure.1) depicts the isotherms of N_2 adsorption and desorption at 77K on MgAl-CO_3 and MgAl-C samples. According to IUPAC recommendations, the isothermal observed is type II with H3 hysteresis loops (S. J. Gregg., 1982). BET surfaces (S_{BET}), pore volume (V_{Pore}), and pore diameter (D_P) values for MgAl-CO_3 and MgAl-C are (31,3 m^2/g, 7,2 cm^3/g, 13,7nm) and (209,8 m^2/g, 48,2cm^3/g, 1,9nm) respectively. We found that the BET surface area of calcined LDH is larger than that of non-calcined LDH. This increase in specific surface area was promoted by heat treatment (calcination at 500°C for 4 hours) which is consistent with previous research (Y.W.You et al., 2002).

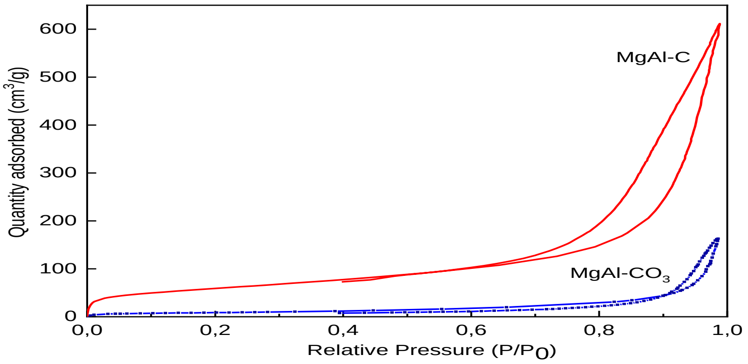


Figure 1: Adsorption isotherms of N_2 on MgAl-CO_3 and MgAl-C

3.2. Ultraviolet UV visibility (DMSO)

UV-vis spectra of the ligand (LH) and the complex Ni (LH) (10^{-4}M) are recorded in a diméthylsulfoxyde (DMSO) environment in the range of 200-800 nm (Figure.2) shows the absorption bands of the ligand LH at 297 nm, 324 nm, and 338 nm, which are characteristics of electronic transitions of the imine function (C=N) of type $\pi-\pi^*$ and n$-\pi^*$. This final band expresses the electronic transitions caused by the azomethine grouping's presence of non-bonding azote atoms (J.P. Collman et al., 1980). The bands of the Ni(LH) complex are as follows (Figure.3): λ_1 = 298 nm transition $\pi-\pi^*$, λ_3 = 381 nm transition n$-\pi^*$, and λ_4= 482 nm transition d-d.

In terms of spectrophotometric properties, the appearance of two new raies in comparison to the electronic spectrum of the ligand that gave rise to the prepared nickel complex is noteworthy. These raies characteristics, which emphasize the coordination of the nickel atom to the schiff base ligand, express metal-ligand charge transfer. (Ni(LH) λ =381 and λ = 482) are the complex frequencies.

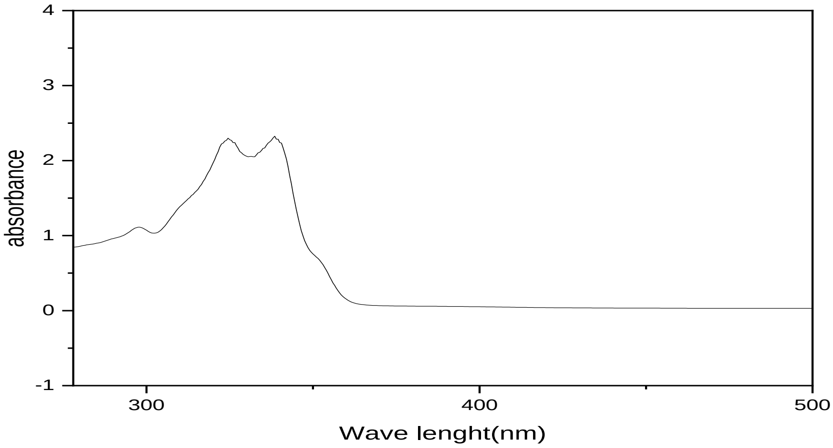


Figure. 2. UV–Vis spectra of the ligand LH in DMSO.

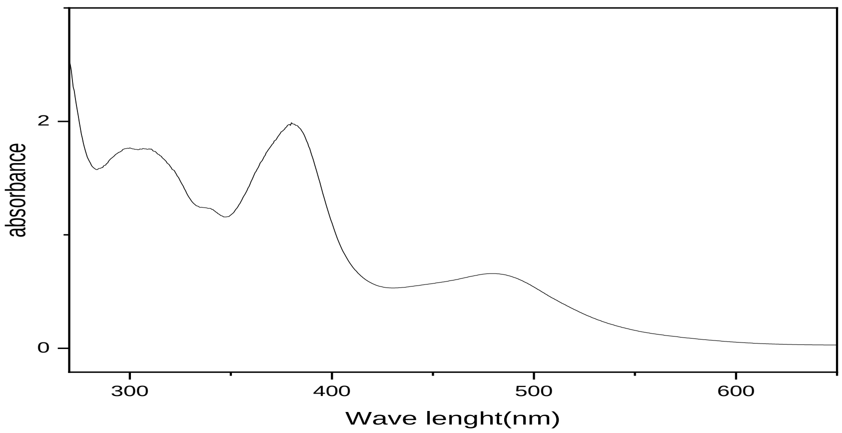


Figure.3. UV–Vis spectra of the complex Ni(LH)in DMSO.

3.3. Thermogravimetric analysis

The (Figure.4) shows the TGA curves of MgAl-CO_3, MgAl-C and MgAl-C-Ni(LH) complex. Generally, four steps are observed in the thermal evolution of LDH. Desorption of physically adsorbed water, removal of interlayer structural water, dehydroxylation of the brucite-like sheets, and decomposition of the interlayer anions (V. Rives., 2001).

For MgAl-CO_3 and MgAl-C-Ni(LH): The first weight loss (10% and 13%) occurs from room temperature to 200 °C which is due to the removal of crystallization water. A mass loss of 30% and 32% takes place in the temperature range 200- 500 °C, attributed to decomposition of the brucite-like layer and removal of interlayer anions (M. Mureşeanu et al., 2014). A second step is observed from 250 to 500 °C, assigned to partial dehydroxylation of the double hydroxide layers. Complete dehydroxylation of the lattice takes place from 390 to 590 °C, accompanied by elimination/decomposition of the organic anion (destruction of the lamellar structure), above 500°C up to 700°C, the formation of mixed oxides. This is confirmed by XRD.

On the basis of these thermograms, it is interesting to note that the mass loss of the calcined phase is significantly lower than that of the uncalcined phase over the entire temperature range studied. These mass losses are due to hydration of the sample during storage.

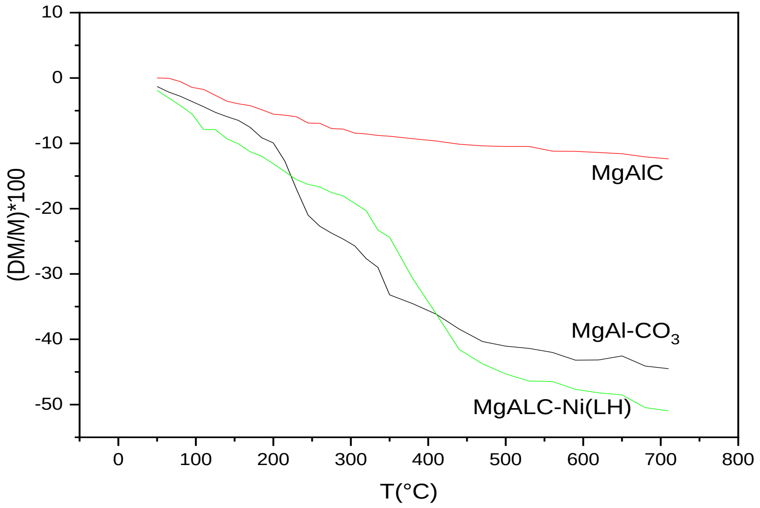


Figure 4. TGA curves of MgAl-CO_3, MgAl-C and MgAl-C-Ni(LH) complex.

3.4. FTIR Spectroscopy analysis

In the FT-IR spectral data of the complex (Figure. 5), a band around 1580cm^{-1} is assigned to an azomethine (C=N), the band at 1254cm^{-1} can be related to the phenolic (C-O) group vibrations. The bands observed at 1600–1662 cm^{-1} are due to acidic (C=O) group vibrations. The broad band appearing at 3300–3600 cm^{-1} is attributed to the acidic (O-H) group of the complex. The ring skeletal vibrations (C=C) were in the region of 1430–1500 cm^{-1} (Gehad G et al., 2005). The bands observed at 668 and 469 cm^{-1} are attributed to the ν (Ni-O and Ni- N). The characteristic bands indicating the successful preparation of the amino acid schiff base complex (Ni(LH)), namely, υ(C = N), υ_{as}(COO–), υ_s(COO–), υ(Ni-O) and υ(Ni-N), were all present in the FTIR spectra of the homogeneous complex, and the band positions agree well with published data (Khosro Mohammadi et al., 2014).

For the LDH support, the broad absorption between 3600 and 3280 cm^{-1} is due to the ν(OH) mode of the hydroxyl groups, both from the brucite-like layers and from interlayer water molecules. Interlayer water also gives rise to medium-intensity δ(H_2O) absorption close to 1635 cm^{-1}. The band at 1368 cm^{-1} is assigned to the stretching vibration of interlayer CO_3^- (M. Mureşeanu et al., 2014). The bands at wavenumber lower than 800 cm^{-1} are due to the M-O and O-M-O vibrations of the hydrotalcite (Parida K.M. et al., 2010). In the FTIR spectra of the immobilized complex, apart from the bands in the overlapping regions of the LDH support, only the $\upsilon_{as}(COO^-)$ band is clearly present at 1613 cm^{-1} indicating the immobilization of the homogeneous complex onto the LDH.

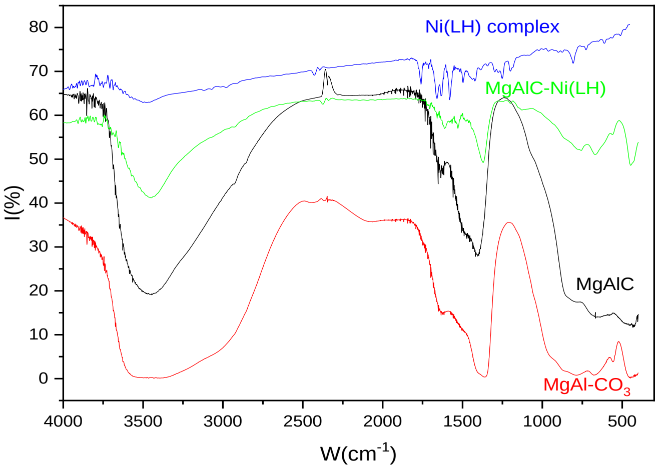


Figure 5: Infrared spectroscopy (IRTF) for the Ni(LH) complex, MgAl-CO_3, MgAl-C and MgAl-C-Ni(LH).

3.5. X-rays diffraction (XRD)

X-ray diffraction patterns (XRD, Figure. 6) confirmed the crystal structure (003), (006), (012), and (110) reflections were indexed to typical LDHs materials. Based on the d-spacing of (00L) planes ([d(003) + 2d(006)]/2), the basal spacing of LDHs could be calculated. The basal spacing value of MgAl CO_3 LDH was approximately 7.56 °A, which corresponded well with the values for CO_3 intercalated LDHs materials (Parida, K et al., 2010). They remained the phase of LDH after modification, with a slightly greater degree of crystallinity and a basal spacing (7.69 °A). As a result, the overall structure of LDH is preserved after Ni(LH) immobilization, and it is clear that newly formed hybrid composites are MgAlC-Ni(LH). This could indicate that the Nickel(II) complex is immobilized on the surface or at the edges, as well as crystal surface defects, as suggested by (M. Mureşeanu et al., 2014) in related systems.

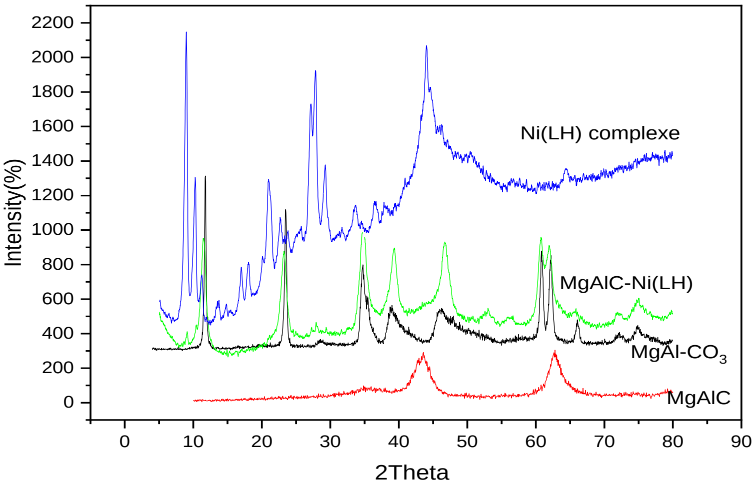


Figure.6. XRD patterns of Ni(LH) complex, MgAl CO_3, MgAl C and MgAl C-Ni(LH).

Conclusion

The primary goal of the work was to prepare A new heterogeneous catalyst by intercalation of Ni(LH) Schiff base complex derived from 3,4-diaminobenzoic acid and salicyl aldehyde into LDH for use as a catalyst in electrocatalytic oxydation reactions of alcohols. We demonstrated that it is possible to synthesize the Mg-Al-CO_3 and Mg-Al-C Ni(LH) from metal ions (trivalent and divalent) and the complex Ni(LH) for use in various fields. These solids have been characterized using various techniques (XRD, BET, FTIR, and TGA). The findings indicate that synthesized clay belongs to the LDH family. The XRD and IR analyses confirm the intercalation, while the textural analysis using the BET method confirmed the presence of high surfaces and that thermal treatment promotes their expansion. The IR absorption bands confirm the presence of the initial CO_3^{2-} anions prior to calcination and the complex's absorption band after reconstruction of the initial phase.

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