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Novel Efficient Pd-free Ni-Layered Double Hydroxide Catalysts for Suzuki C-C Coupling Reaction

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Abstract

Suzuki cross-coupling reaction has developed one of the furthermost effectual approaches for the synthesis of biaryls or substituted aromatic moieties from aryl halides and arylboronic acids with a palladium-catalyst in the past two eras. Herein, Pd-free layered double hydroxide (LDH) containing nickel catalysts were prepared by co-precipitation method under ultrasonic irradiation and N_2 atmosphere with different molar ratios of Ni: Mg: Al and coded as (1NiLDHs-Dr), (1.5NiLDHs-Dr) and (2NiLDHs-Dr). A series of reduced catalysts under 5% H_2/N_2 at 200°C were coded as 1NiLDHs-R200, 1.5NiLDHs-R200 and 2NiLDHs-R200. Deep investigation of all catalysts was done using different techniques such as inductively coupled plasma optical emission spectroscopy (ICP-OES), x-ray photoelectron spectroscopy (XPS), powder x-ray diffraction (XRD), thermogravimetric analyses (TGA), Fourier transfer infrared (FTIR), scanning electron microscope (SEM) connected with energy dispersive x-ray (EDX), transmission electron microscopy (TEM) and N_2-physisorption at -196 °C. The results attained verified that α-$Ni(OH)_2$ was fashioned for 2NiLDHs-Dr catalyst and the enclosure of nickel ions in the cationic sheet of layered structure were responsible for the fascinating catalytic efficacy rather than the basic nature of material. The Ni-containing LDHs catalysts encourage forthcoming studies in Pd-free catalysed C-C coupling reactions.

Keywords: Suzuki coupling reaction; Layered double hydroxides (LDH); Solid base catalyst.

1. Introduction

Suzuki coupling reaction includes coupling of boronic acid with aryl halides in the presence of Palladium (0) and a base (**Scheme 1**) [1]. It is generally carried out at temperatures range of 60 - 180°C with excellent yield results when palladium was used in homogenous catalyzed system which is considered the most powerful and most applicable method for carbon-carbon bond formation. It is the backbone for biaryl and heterobiaryl compouds that are important in natural products, dyes, liquid crystals and dendrimers formation, ligands for catalysis and organic light-emitting polymers synthesis, pharmaceuticals and agrochemicals industries.

Furthermore, homogeneous catalysis is not preferably used due to the lack of reuse, the problem catalyst recycling leads to loss of noble metals and metals residual in the products and the purification becomes necessarily required especially when it use in pharmaceutical production. Therefore, there is needing to remove residual metals impurities in products and losing the expensive metals by palladium substitution, partially or totally, with cheap metals like non-noble metals [2]. On the other hand, heterogeneous catalysis is a promising option because it offers several advantages like high catalyst stability, the catalyst is easily removal from mixture of the reaction by simple filtration and reusing the catalyst many times with a frequent activity loss minimum and considered one of the important ways to attain sustainability.

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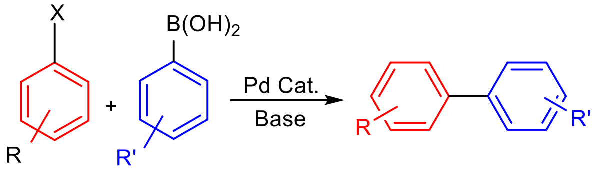
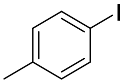
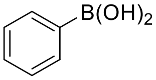
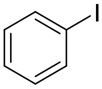
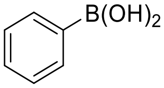
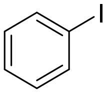
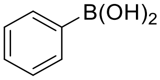
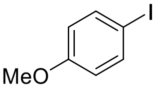
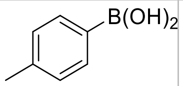
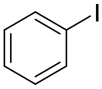
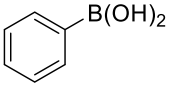
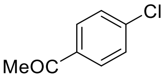
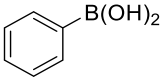
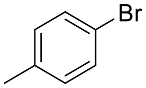
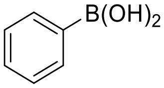
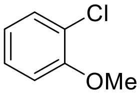
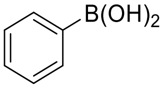
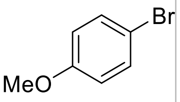
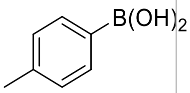
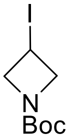
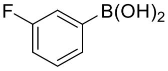
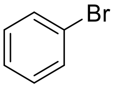
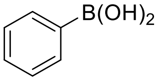
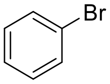
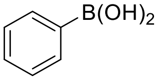
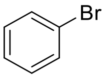
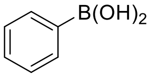
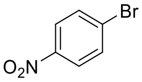
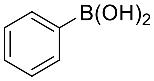
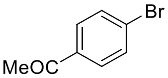
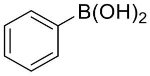
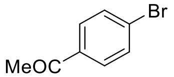
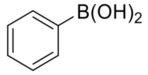
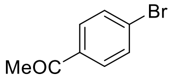
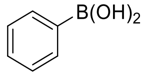
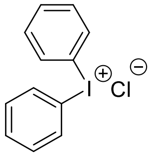
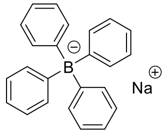
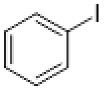
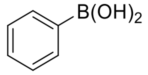
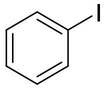
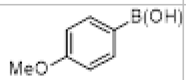


Scheme 1. General scheme for Suzuki coupling reaction.

Keen revision of the literature regarding the heterogeneous catalysts used in Suzuki coupling reaction show that, different types of transition metals were used to catalyse Suzuki coupling reaction. For instance, Volpe and co-workers [3] reported that a series of ceria catalysts used in Suzuki cross-coupling reaction between 4-iodotoluene and phenylboronic acid. The reaction was carried out at 150 °C, under nitrogen atmosphere and DMF as the solvent which resulting in corresponding biphenyl in high selectivity percentage (**Table 1, Entry 1**). Gold nanoparticles – graphene hybrids have been prepared and used as catalyst by Li and his group [4]. They found the catalytic activity of gold nanoparticles–graphene hybrids which expressed as a value of selectivity was influenced by the size of the gold nanoparticles (**Table 1, Entries 2,3**). Kim and co-workers [5] demonstrated that the Pt single atoms on thiolated multi-walled carbon nanotubes (Pt-S-MWNT) has a remarkably high activity and recyclability for the ligand-free Suzuki coupling reaction. (**Table 1, Entry 4**). In 2008, Mao and co-workers [6] developed an effective catalytic system from copper powder with K_2CO_3 as the base that was extremely effective catalyst for Suzuki coupling reaction performed in polyethylene glycol 400 (PEG-400) (**Table 1, Entry 5**). Lipshutz and co-workers have used nickel on charcoal (Ni/C) [7] that worked as an effective heterogeneous catalyst for coupling chloroarenes and phenylboronic acids (**Table 1, Entry 6**). In addition to, nickel-on-graphite (Ni/C_g) have been reported [8] as a safe and especially inexpensive material, which used to catalyse cross couplings with various boronic acids and aryl under Microwave (MW) conditions (**Table 1, Entries 7, 8**). Wang and co-workers [9] have developed an efficient, simple and economic catalyst system for the Suzuki reaction of aryl iodides and bromides with aryl boronic acid without the need of phosphine ligands by using nickel–metal colloid supported on TBAB (tetra-n-butylammonium bromide). Ni(0)/TBAB exhibited high activity for aryl bromides and iodides. In case of less reactive aryl chlorides, the phosphine ligand was required for more efficient reaction (**Table 1, Entry 9**). Recently, Willand and co-workers [10] improved procedure in the Suzuki Miyaura cross coupling reaction between N-BOC protected 3-iodoazetidine and a large variety of heteroaryl and arylboronic acids. The reaction was catalyzed by Nickel in the presence of strong base and is promoted by microwave heating (**Table 1, Entry 10**). Guo and his co-workers [11] studied the effect of elevated pressure in the liquid phase on the Suzuki-Miyaura cross-coupling of aryl halides and aryl boronic acids using cheaper Fe(III), Co(II), and Ni(II) metal salts as catalysts. The yields were improved (**Table 1, Entries 11-13**) at 15 kbar but this procedure was disgraced with high loading of catalysts. Leadbeater and Marco [12,13] claimed that the Suzuki Miyaura coupling of boronic acids and aryl halides is possible without the need for a transition-metal catalyst (**Table 1, Entry 14-17**). In order to investigate the possibility of catalyst-free Suzuki reaction, Yan and his co-workers reported in 2006 a novel and efficient method for coupling reaction of sodium tetraphenylborate with iodonium salts in acidic water [14]. This method was simple, mild, high-yielding, and more environmentally benign (**Table 1, Entry 18**).

Table 1. Survey on different catalysts for Suzuki coupling reaction.

	Aryl halide	**Boronic acid derivative**	**Cat.**	**Base**	**Solvent**	**Conditions**	**Time**	**Yield (%)**
1			HSA-CeO_2	K_2CO_3	DMF	150 °C, 0.1 MPa	3h	89 Selectivity
2			Au–graphene (2-3 nm)	NaOH	H_2O	100 °C	4h	85.8 Selectivity
3			Au–graphene (7.5 nm)	NaOH	H_2O	100 °C	4h	11.2 Selectivity
4			Pt-S-MWNT	Cs_2CO_3	THF	70 °C	24h	99.5
5			Cu(0)	K_2CO_3	PEG-400	110 °C	12h	99
6			Ni/C	K_3PO_4, LiBr	Dioxane	135 °C	18h	92
7			Ni/Cg	K_3PO_4, LiBr	Dioxane	135 °C	9h	87
8			Ni/Cg	K_3PO_4, LiBr	Dioxane	MW, 180 °C	42 min	87
9			Ni(0)/ TBAB	Na_2CO_3	EtOH	80 °C	6h	95
10			NiI_2	NaHMDS	iPrOH	MW, 80 °C	30 min	82
11			$NiCl_2$/ Ligand	KF/ KOH	THF	100 °C, 15 kbar	48h	99
12			$CoCl_2$/ Ligand	KF/ KOH	THF	100 °C, 15 kbar	48h	99
13			$FeCl_3$/ Ligand	KF/ KOH	THF	100, 15 kbar	48h	97
14			Catalyst-free	Na_2CO_3, TBAB	H_2O	MW, 150 °C	5 min	99
15			Catalyst-free	Na_2CO_3, TBAB	H_2O	MW, 150 °C	5 min	98

16			Pd, 0.25 ppm	Na_2CO_3, TBAB	H_2O	MW, 150 °C	5 min	94
17			Pd, 0.25 ppm	K_2CO_3, TBAB	H_2O	MW, 150 °C	5 min	57
18			Catalyst-free	Base-free	H_2O / p-TsOH	50 °C	0.5h	95
19			LDH-Pt(0)	K_3PO_4	Dioxane / H_2O	100 °C	12h	90
20			LDH-Rh(0)	NaOAc	DME/ H_2O	100 °C	12-18h	96

Furthermore, a class of anionic clay is called layered double hydroxides (LDHs) or hydrotalcite (HTs) has attracted considerable interest from industrial and academic fields. LDHs are lamellar mixed hydroxides which have structured-layer and have hydroxide and carbonate ions intercalated in common, which usually restrict C-C coupling reactions. Mixed metal oxide could be obtained from these materials when subjected to thermal treatment and they can become a promising candidate for C-C coupling reactions. Furthermore, the separation is easier than before after the end of reaction, that way makes LDHs an important alternative to homogeneous catalysts because of the potential of its recycling [15]. Mg-Al-layered double hydroxide (LDH) has been used successfully as solid support for Suzuki reaction by Choudary and his co-workers. In the absence of ligand, LDH-Pt(0) [16] and LDH-Rh(0) [17] catalysts were prepared and utilized for Suzuki coupling of different aryl halides with a large number of arylboronic acids to give the corresponding biaryls in good to excellent yields (**Table 1, Entries 19, 20**). Carbon–carbon bond formation was investigated by our group using LDHs alone [18, 19] and supported on other materials such carbon nanotubes [20] and graphene oxides [21].

Extensive survey about LDHs-containing nickel using as catalyst in Suzuki coupling reaction in absence of ligands has been done and to our knowledge no publications have been found. Therefore, in this study we will introduce a simple generic and efficient protocol for the preparation of NiLDHs for Suzuki reaction. This has proven successful for biaryl products derived from different aryl halides and aryl boronic acids using microwave irradiation methodology. Herein we report the results of our investigation which showed that NiLDHs behave as a very efficient catalyst of the Suzuki reaction in a Pd and ligands-free.

2. Experimental Details

2.1. Materials

$Al(NO_3)_3$. $9H_2O$, $Ni(NO_3)_2.6H_2O$ and Iodobenzene were purchased from Fluka. $Mg(NO_3)_2.6H_2O$ was purchased from Koch-Light. Chlorobenzene and Na_2CO_3 were purchased from BDH, England. Bromobenzene was purchased from MCIB, USA. NaOH was purchased from Riedel-de Haën. 4-Tolylboronic acid, 97% was purchased from Acros Organics. Pre-coated TLC sheets silica gel 60 F-254 from Merck to monitor the reaction process.

2.2. Preparation of NiLDHs

NiLDHs with molar ratio 1:1:1, 1:0.5:1.5 and 1:0:2 of Al: Mg: Ni (with constant molar ratio of M(II)/M(III) by 2:1) synthesized using co-precipitation method. At 50 °C in sonicated bath, mixture of $Al(NO_3)_3$, $Mg(NO_3)_2$ and $Ni(NO_3)_2$ as a SLOUTION A was added simultaneously with a mixture of 1.0 mol of NaOH and 0.5 mol of Na_2CO_3 as a SOLUTION B in a beaker contained reservoir solution of 0.02 M NaOH. The mixture of prepared NiLDHs mixed by mechanical stirrer. pH was fixed at 11 by controlling the flow rate of solutions A and B. After the end of precipitation process, the mixture was washed until pH reached to 7 or showed no Na+ ions were contained by ICP-AES. Then, the mixture was filtered, dried in oven at 80 °C for 20 hours and it was coded as 1NiLDHs-Dr, 1.5NiLDHs-Dr and 2NiLDHs-Dr depending to anticipated molar content of Ni.

2.3 Preparation of reduced NiLDHs

Hydrogen reduction of NiLDHs-Dr for different chemical compositions at 200 °C were carried out in a U-shaped quartz reactor. The reduction of NiLDHs-Dr was occurred in 5% H_2/N_2 atmosphere (90 ml/min) for 3h using CHEMBET 3000, Quantachrome, USA. After reduction, the samples coded as 1NiLDHs-R200, 1.5NiLDHs-R200 and 2NiLDHs-R200.

2.4. Measurements and Characterization

Powder X-ray diffraction (XRD) measurements were carried out using a Bruker diffractometer (Bruker D8 advance target, Karlsruhe, Germany) at room temperature. The patterns were obtained using Cu Kα1 and a monochromator ($\lambda = 1.5405$Å) at 40 kV and 40 mA, with 2θ varying between 2° and 80°.X'Pert HighScore Plus software was used to analyze the spectra.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was performed using PerkinElmer Optima 7000 DV. ICP-OES data were used to determine the molecular formula of the samples. The better selected wavelengths were 309.271 nm for Al, 227.022 nm for Ni and 279.077 nm for Mg.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out by using a SPECS GmbH X-ray photoelectron spectrometer. Prior to analysis, the samples were degassed under vacuum inside the load lock for 16 h. The binding energy of the adventitious carbon (C 1s) line a 284.6 eV was used for calibration, and the positions of other peaks were corrected according to the position of the C 1s signal.

Thermogravimetric analysis (TGA) runs were carried out on TA instrument apparatus (model TGA-Q500). In each run 6-10 mg was placed in the TGA pan and heated to 800 °C at a heating rate of 10 °C min^{-1} and an N_2 atmosphere (flow rate of 40 ml min^{-1}).

Fourier transfer infrared (FTIR) spectroscopy in transmission mode was performed using a PerkinElmer UATR Two FT-IR spectrometer. The measurements were carried out in the wavenumber range 4000 −400 cm^{-1} with 4 cm^{-1} resolution.

High resolution field emission (FEG quanta 250) scanning electron microscope (SEM) connected with Energy Dispersive X-Ray (EDX) detector which allows the chemistry of NiLDHs to be investigated on the sub-micron scale.

Transmission electron microscope (TEM) (Type JEOL JEM-1230) operating at 120 kV, attached to a CCD camera used to investigate morphology, particle size of the prepared samples was examined and calculated using Image J software.

Determination of strength of basic sites for NiLDHs samples was done qualitatively by Hammett indicators [22]. 25 mg of NiLDHs was shaking with 1 mL of Hammett indicator solution (0.1 % in methanol) and left to equilibrate for 2 h. The changing colour of NiLDHs was then recorded. The Hammett indicators that listed in **Table 2** were used. To determine the basicity for NiLDHs quantitatively, the titration method using benzoic acid was attained [22, 23]. 150 mg of NiLDHs was stirred in 2 mL, 0.1 mg/mL of toluene solution of phenolphthalein for 30 min then titrated with 0.01 M of toluene solution of benzoic acid. The total basicity was determined from molarity and the consumed volume of titrant. The leachable basicity [22] was also determined by shaking 500 mg of NiLDHs in 50 mL water for 1h at room temperature. After that, the NiLDHs was separated by centrifuge then 5 mL, 0.1 mg/mL of methanol solution of phenolphthalein was added to the filtrate then was titrated with 0.01 M of methanol solution of benzoic acid.

Nitrogen adsorption/desorption measurements at 77 K using NOVA3200e automated gas sorption system (Quantachrome, USA) was carried out to investigate the textural properties of LDHs samples. Prior to the measurement, each sample was degassed for 6 h at 200 ◦C. The specific surface area, S_{BET}, was calculated by applying the Brunauer–Emmett–Teller (BET) equation [24]. Pore size distribution over the mesopore range was generated by the Barrett–Joyner–Halenda (BJH) [25] analysis of the desorption branches, and values of the average pore size were calculated.

Microwave experiments were performed using CEM Discover & Explorer SP microwave apparatus (300 W), utilizing 35 mL capped glass reaction vessels automated power control based on temperature feedback.

Table 2. List of Hammett indicators used to determine basic sites.

No.	**Hammett Indicators**	**pKa**	**pH Range**	**Changing Color**	
				Acidic	**Basic**
1	Thymol blue (First change)	1.5	1.2 – 2.8	Red	Yellow
2	Methyl yellow	3.3	2.9 – 4.0	Red	Yellow
3	Methyl red	5.1	4.2 – 6.2	Red	Yellow
4	Bromothymol blue	7.0	6.0 – 7.6	Yellow	Blue
5	Thymol blue (Second change)	8.9	8.0 – 9.6	Yellow	Blue
6	Phenolphthalein	9.4	8.3 – 10.0	Colorless	Pink
7	Tropaeolin-0	11.9	11.1 – 12.7	Yellow	Orange

2.5. Experimental Procedure for Suzuki reaction

To a mixture of boronic acid derivative **2** (15 mmol) and the appropriate aryl halides **1a-c** (10 mmol) in dioxane/water (5:1) (10 mL), potassium carbonate (25 mmol) and 150 mg of Ni LDHs catalyst were added. The total mixture was placed in a process vial in the microwave and was irradiated with a power of 300 W to reach a reaction temperature of 140°C under auto generated pressure. The vial was exposed to microwaves for the required time to complete the reaction. The progress of the reaction was monitored by TLC (eluent; ethylacetate: chloroform). Upon completion of the reaction, the catalyst was removed by filtration and washed 3 times with hot 70% ethanol. The filtrate was concentrated in vacuo under reduced pressure. The obtained solid product was recrystallized using hexane to afford the corresponding pure 4-methyl-1,1'-biphenyl derivative **3**. Washing again of the pre-used catalyst with hot ethyl acetate and sonicated for 5 min to desorb all adsorbed product on the surface of catalyst then filtration and drying prior to new catalytic test was systematically followed.

3. Results

3.1. Catalyst characterization

3.1.1. X-ray diffraction (XRD)

X-ray diffraction pattern of prepared NiLDHs-Dr are presented in **Figure 1**. The peaks are sharp with high intensity signals at low 2θ values and weak signals at high 2θ values representing a layered double hydroxide structure. The patterns intensity in the *c*-plane reduced while increased in *a* and *b* planes upon increasing the Ni-content in LDHs. The pronounced reduction in peak intensities assigned to small particle size of LDHs samples rich in Ni-species. TEM analysis in the next section should judge the particle sizes of the synthesized samples precisely. Usually, Ni could be represented either in β-$Ni(OH)_2$ (strictly packed brucite type layers in which Ni^{2+} is in the middle of hydroxyl octahedral structure), and α-$Ni(OH)_2$ of foremost attention due to its tuneable assembly (oxidation state, interlayer species, interlayer distance) [26, 27]. The obvious growth in the *a* and *b*-planes intensity of diffraction pattern of the layered structure of the 2NiLDHs-Dr (of high Ni content) without substantial shift in the peak position endorse the α-$Ni(OH)_2$ creation.

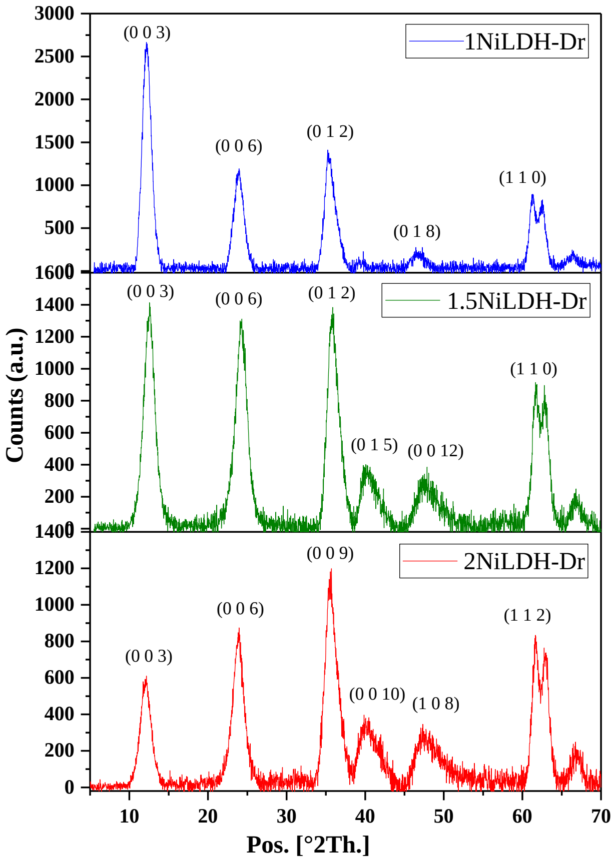


Figure 1. XRD patterns of different NiLDHs-Dr.

3.1.2. Elemental Chemical analysis (ICP-OES)

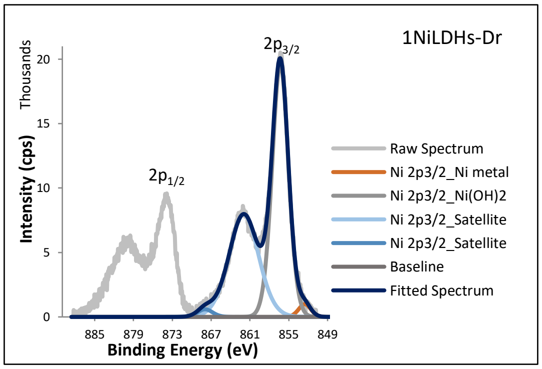
ICP analysis of NiLDHs-Dr samples was done to determine their chemical composition. The analysis showed that the M^{II}/M^{III} molar ratio in the solid form of 1NiLDHs-Dr, 1.5NiLDHs-Dr and 2NiLDHs-Dr were 2.11, 2.17 and 2.28 respectively (**Table 3**). The molar ratios of NiLDHs-Dr samples indicate the efficiency of the preparation method because they are almost equal to the minimal molar composition of the as-synthesized Ni+Mg/Al molar ratio of 2 in the precipitate that prove also that LDHs phases are pure due to their stoichiometries formation is in the range $0.20 < x < 0.33$, i.e. M^{II}/M^{III} ratios in the range 2–4 [26].

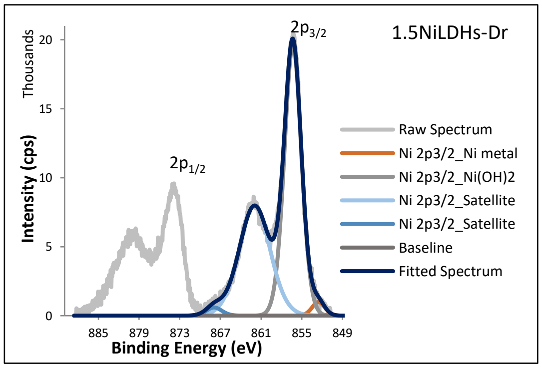
Table 3. Elemental chemical, XPS data and basic properties of NiLDHs-Dr samples.

	Ni+Mg/Al		**Basic strength mmol/g**	**Ni^{2+} isolated species sample**	
	Solution	**Soild**		**Binding energy (eV)**	**%**
1NiLDH-Dr	2.0	2.11	0.333	856.1	96.4
1.5NiLDH-Dr	2.0	2.17	0.173	855.6	96.5
2NiLDH-Dr	2.0	2.28	0.073	855.8	97.7

3.1.3. X-ray photoelectron microscopy (XPS)

XPS investigation was conducted to gain further insight into the location and nature of the Ni species present in NiLDHs-Dr samples. Deconvoluted Ni $2p_{3/2}$ XPS spectra for 1NiLDHs-Dr, 1.5NiLDHs-Dr and 2NiLDHs-Dr samples are shown in **Figure 2**. XPS spectra of samples have the same Ni species nature. The Ni $2p_{3/2}$ XPS spectrum from $Ni(OH)_2$ with the two obvious satellite intensities fit by broad peaks with binding energy at main line 852.0 eV (**Table 3**). The peaks have been deconvoluted into two contributions with binding energies at 855.8 eV and 861.4 eV respectively [28]. The first peak can be assigned to isolated Ni^{2+} species. It is interesting to note that the 2NiLDHs-Dr sample contained the highest amount of isolated Ni^{2+} species (97.7 %). Isolation of nickel species indicates a good abundance of Ni^{2+} ions on the surface more than the bulk of synthesized 2NILDHs sample.





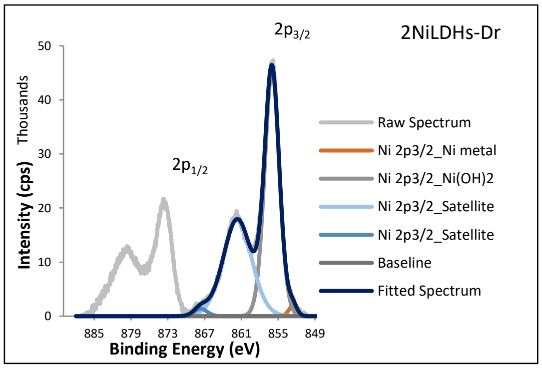


Figure 2. Deconvoluted Ni 2p3/2 XPS spectra for NiLDHs-Dr samples.

3.1.4. Thermogravimetric analysis (TGA)

Thermogravimetric analyses of NiLDHs-Dr are shown in **Figure 3**. The thermograms of 1NiLDHs-Dr, 1.5NiLDHs-Dr and 2NiLDHs-Dr were analyzed to obtain information about percentage weight loss at different temperatures. The results of these analyses are presented in **Table 4**. In the 1NiLDHs-Dr and 2NiLDHs-Dr thermograms, they showed five stages of weight loss while 1.5NiLDHs-Dr shows only four stages. The analysis of all stages could be put into three main categories. First range of weight loss (37-110 °C) is attributed to the loss of water molecules at the surface by desorption process and the dehydration of the sample. The second range of weight loss (180 - 220 °C) which is attributed to loss interlayer water molecules. At the third range of weight loss (250 – 350 °C) which is attributed to the removal of OH^{-} groups and decarbonation of carbonate anions present in the interlayer space of LDHs that leading to the formation of metal oxides [29].

Table 4. TGA data for NiLDHs-Dr samples.

	Temperature °C / Weight loss %		
Weight loss steps	**1NiLDHs-Dr**	**1.5NiLDHs-Dr**	**2NiLDHs-Dr**
1	36.7 / 1.7	44.8 / 2.1	40.6 / 1.3
2	98.3 / 6	100.6 / 5.5	81.0 / 3.3
3	180.9 / 8.9	185.2 / 6.8	107.0 / 2.2
4	300.8 / 10.2	349.9 / 17.3	189.9 / 6.9
5	340.2 / 6.6		331.2 / 16.3

doi:10.20944/preprints201809.0458.v2

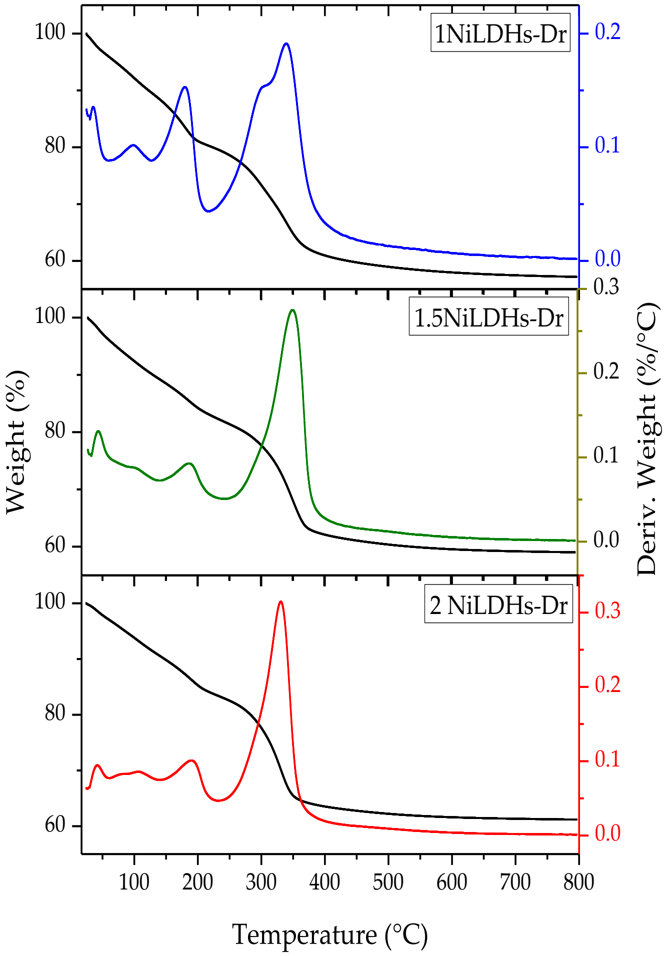


Figure 3Thermograms of NiLDHs-Dr samples.

3.1.5. Fourier-transform infrared spectroscopy (FT-IR)

Figure 4 shows the FTIR spectra of 1NiLDHs-Dr, 1.5NiLDHs-Dr and 2NiLDHs-Dr samples which they have similar IR bands. The signal at 3400 cm^{-1} is the O-H stretching band, arising from interlayer water molecules and metal-hydroxyl groups [30]. The small band centred around 1600 cm^{-1} can be ascribed to the bending vibration of water. Additionally, the band at 1350 cm^{-1} can be assigned to the vibration of interlayer CO_3^{2-} and NO_3^{-} anions. The broad peak at 630 cm^{-1} can be assigned to the M–O, O–M–O, and M–O–M (M =Al, Mg and Ni) vibrations.

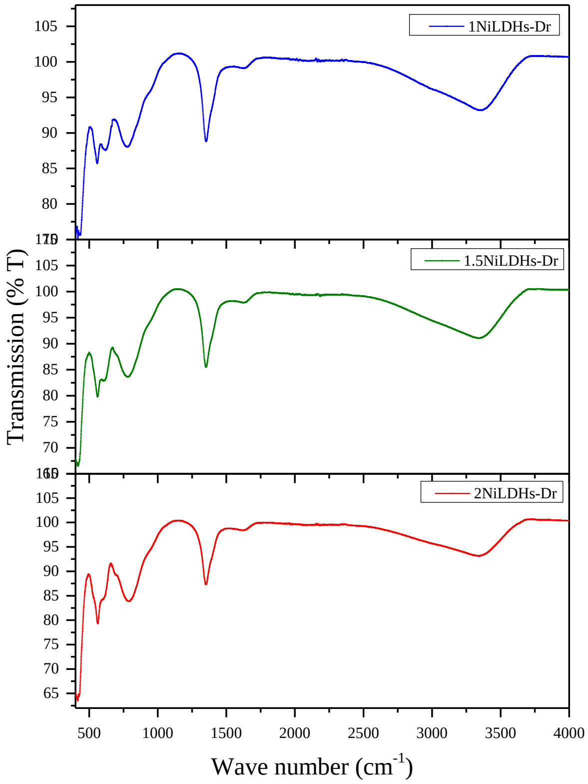


Figure 4. FTIR spectra of NiLDHs-Dr samples.

3.1.6. Scanning electron microscopy (SEM-EDX)

The SEM images of NiLDHs-Dr ravel out the morphology which stacked platelets shape. **Figure 5** shows that the layered flakes are clearer in 1NiLDHs-Dr than the other Ni- containing materials. It seems that isomorphic substitution of Mg^{2+} ions by Ni^{2+} ions in the cationic sheet and the nucleation of α-$Ni(OH)_2$ phase resulted in the distinct thickness progress of the flakes. 2NiLDHs-Dr, of high Ni-content disclosed accumulated gloomy like stacked sheets as a result of α-$Ni(OH)_2$ foundation.

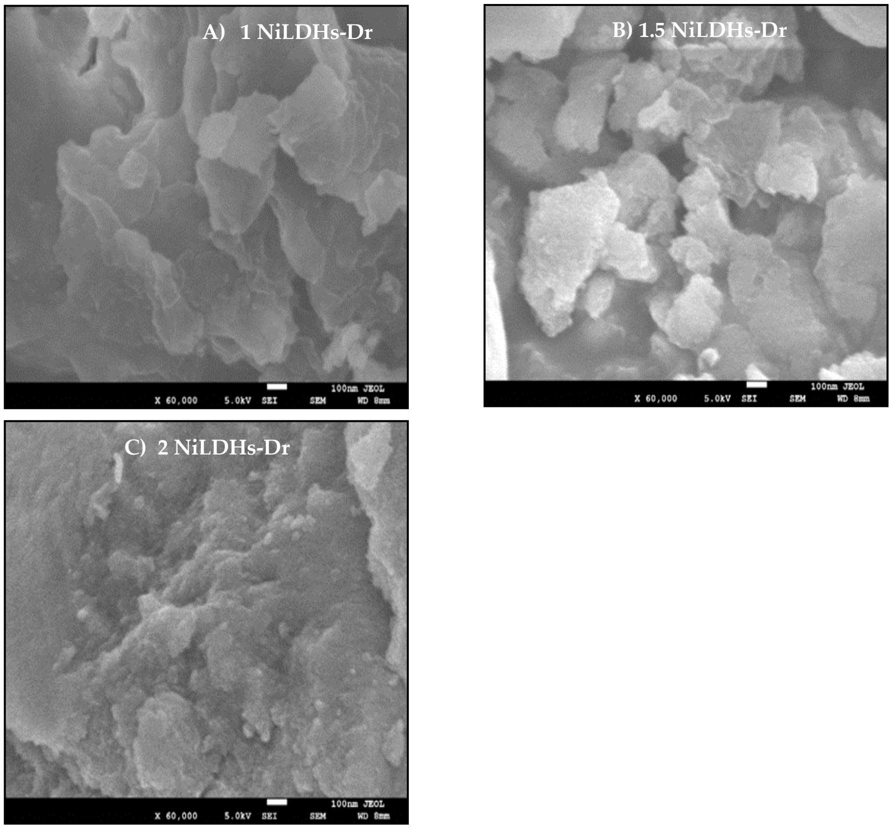


Figure 5. SEM images of all the examined NiLDHs-Dr catalysts.

3.1.7. Transmission electron microscopy (TEM)

In TEM images of NiLDHs-Dr, **Figure 6**, shows the particles are in layers with semi-hexagonal shape. The agglomerated particles appear when nickel content increased [31]. The mean particle size was calculated using Image J software and it was noticed that the as-synthesized NiLDHs solids are in the nanoscale with small particle sizes. The sample acquires high nickel content had smaller mean particle size (~3 nm).

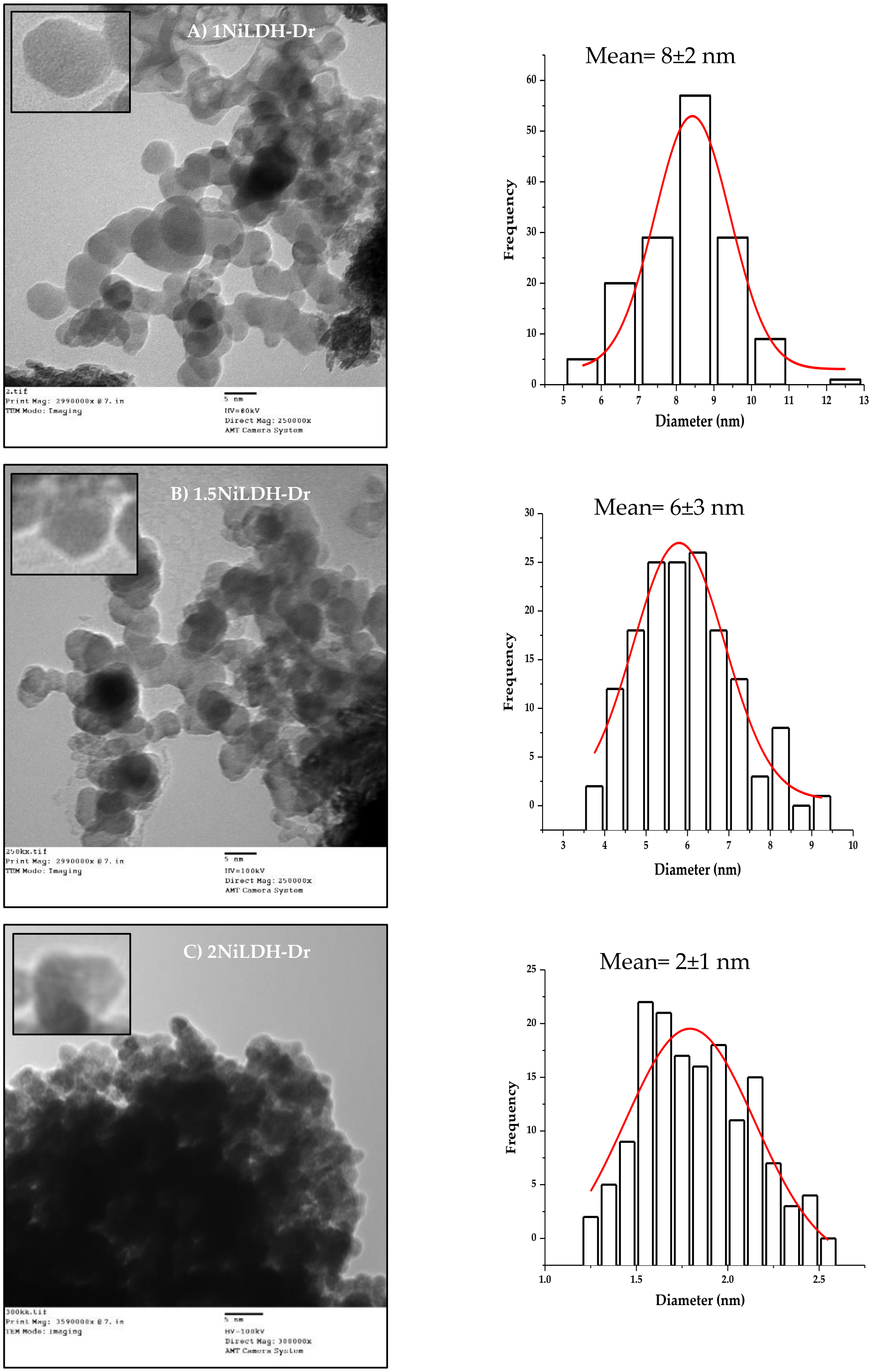


Figure 6. TEM images and histogram of particle size distribution of A) 1NiLDH-Dr, B) 1.5NiLDH-Dr and C) 2NiLDH-Dr; **inset** magnified particles.

3.1.8. Basic properties of NiLDHs-Dr

The strength of basic sites and their amounts were measured using acid–base titration and the Hammett indicator methods. Since the catalysts are considered have basic properties, the number of moles of basic sites were calculated and it was found in order of 1NiLDHs-Dr > 1.5NiLDHs-Dr > 2NiLDHs-Dr. Where the base strength of 1NiLDHs-Dr, 1.5NiLDHs-Dr and 2NiLDHs-Dr are found in range of pK_{BH+} = 11.1 – 12.7 (**Table 2**). There is no change in colors of catalysts filtrate which mean there were no leachable basicity from all the samples. The reduction in basic sites upon substitution of Mg^{2+} ions by Ni^{2+} ions in the NiLDHs samples could be credited to the departure of Lewis basic sites or formation of new phase structure of α-$Ni(OH)_2$, which is less basic than brucite β-$Ni(OH)_2$ phase [32].

3.1.9. N_2 physisorption

Figure 7 depicted that nitrogen adsorption/desorption isotherm of all samples are of type IV according to IUPAC classification [33]. The hysteresis loops in the isotherms indicate the mesoporous nature of NiLDHs-Dr. Hysteresis shapes are attributed to the presence of cylindrical, slit and blind hole pores according to Sing et al [34]. BET surface area for NiLDHs-Dr catalysts have no obvious trend (**Table 5**). The pore volume and average pore radius decline with growing of Ni content. The formation of α-$Ni(OH)_2$ greatly affect the pore nature by possible aggregation.

Table 5. Textural properties of different NiLDHs-Dr from N_2-physisorption.

	BET surface areas (m^2 /g)	**Pore volume (cm^3 /g)**	**Av. Pore radius (Å)**	**C-constant**
1NiLDHs-Dr	68.28	0.14	22.71	14.27
1.5NiLDHs-Dr	57.33	0.09	19.84	10.24
2NiLDHs-Dr	58.03	0.08	18.97	5.95

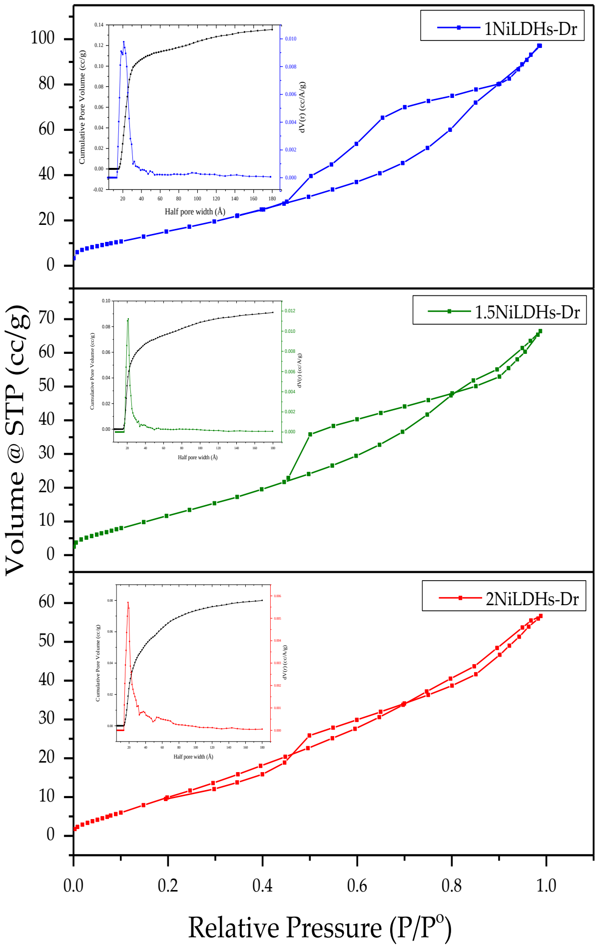
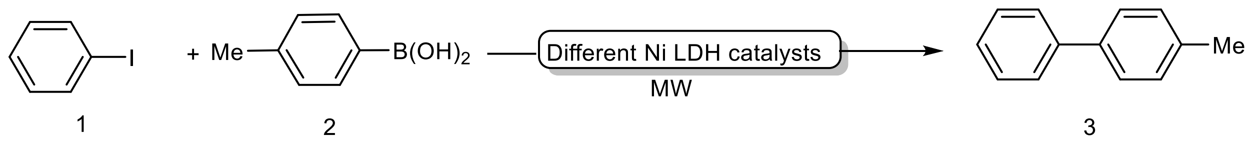


Figure 7. N_2 isotherms and Pore size distribution (inset) patterns of different ratio for NiLDHs-Dr.

3.2. Catalytic activity

At the outset, the different forms of NiLDHs catalysts (150mg) were scanned to the reaction of a mixture of iodobenzene (10mmol) **(1)**, and 4-tolylboronic acid (15 mmole) **(2) Table 6** (**Scheme 2**) which taken as model reaction for synthesis of biaryl derivative **3** utilizing microwave irradiation.



Scheme 1. Suzuki coupling reaction of Iodobenzene with 4-tolylboronic acid in presence of different catalysts under microwave irradiation.

Table 6. Synthesis of compound 3 using different Ni LDH catalysts under microwave irradiation*.

Entry	**Catalyst**	**Time (min.)**	**Yield of compound 3 (%)**
1	Catalyst-free	120	No reaction
2	1NiLDH-Dr	45	31
3	1NiLDH-R200	60	23
4	1.5NiLDH-Dr	45	55
5	1.5NiLDH-R200	60	37
6	2NiLDH-Dr	30	99
7	2NiLDH-R200	60	50

* % product yield utilizing different NiLDHs catalyst composition in reduced and dried forms; reaction conditions: 150 mg of catalyst, 10 mmol of iodobenzene, 15 mmol of 4-tolylboronic acid, 25 mmol K_2CO_3 and 10 mL of dioxane/H_2O (5:1), 300W, 140°C and 15 min.

It is clear from results cited in **Table 6** that, under microwave irradiation even after 120 min., no product formed in absence of catalyst, (**Entry 1**). In addition, all Ni LDH samples showed substantial catalytic activity, the best yield 99% of the desired product **3** was reached using 2Ni LDH-Dr catalyst in 30 min. (**Entry 6**). Furthermore, a lower product's yield in longer period of time was attained using NiLDH-R200 catalyst samples (**Entries 3,5 and 7**). In general, NiLDH-Dr catalyst samples showed superior catalytic activity than NiLDH-R200 samples. The pronounced advantages in catalytic efficacy could be assigned to the presence of Ni^{2+} ions on NiLDHs-Dr catalyst's surface in great abundance as evidenced by XPS data.

The structure of the product **3** was confirmed according to elemental analysis and spectral data, in which the obtained spectroscopic data of the reaction product and the satisfactory elemental analysis supported the structure 4-methyl-1,1'-biphenyl (**3**) (*cf.* supporting information part).

Since 2NiLDHs-Dr was the superlative catalyst, it was selected to explore the optimization conditions for Suzuki coupling reaction. To optimize the reaction conditions using the best NiLDHs catalysts, a run of experiments was carried out under changeable catalyst quantities and the reaction progress was monitored by using thin layer chromatography (TLC) for a representative reaction (**Scheme 2**) under Microwave irradiation. The results obtained from the catalytic test reaction are cited in **Table 7**.

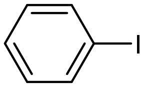
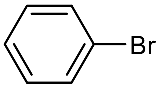
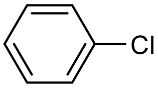
Table 7. Optimization of reaction condition for synthesis of **3** utilizing 2NiLDH-Dr catalyst

Entry	Catalyst wt. (mg)	Time (min)	Yield (%)	M.W power (watt)
1	50	60	81	300
2	100	45	90	300
3	150	30	99	300
4	200	30	99	300
5	150	90	64	100
6	150	75	69	150
7	150	60	76	200
8	150	30	92	250

Initially, for optimization of catalyst's mass, different amounts of 2NiLDH-Dr catalyst were tested under the identical reaction conditions, where the greatest yield was found using 150 mg of the catalyst and running the process for 30 min. (**Table 7, Entry 3**). Moving forward to the investigation of the effect of microwave power on this catalytic system, five reactions were performed with 100, 150, 200, 250, 300 W of the best catalyst amount (**Entries 5-8**). The best microwave power for this reaction protocol proved to be 300 W (**Entry 3**), in which the desired product **3** was isolated in 99% yield.

In addition, we extended our work to check effect of the halide atom in aryl halides as depicted in **Table 8**. **Table 8** shows that the 2NiLDHs-Dr catalyst displays a high percentage yield and TOF for iodobenzene (**Entry 1**), an increase by 1.2 and 1.4-fold when compared to the results obtained for bromobenzene and chlorobenezne, respectively. Coupling with 4-tolyl boronic acid shows the order Ar-I > Ar-Br > Ar-Cl which agreed with other studies [5, 35-36].

Table 3. Synthesis of compound **3** using 2NiLDH-Dr catalysts under M.W irradiation and different substrates*.

Entry	**Substrate**	**Time (min.)**	**Yield (%)**	**TOF (h^{-1})**
1		30	99	77475
2		45	82	42781
3		45	69	35999

* Reaction conditions: 150 mg of catalyst, 10 mmol of aryl halide, 15 mmol of bronic acid, 25 mmol of K_2CO_3, 10 mL of dioxane/H_2O (5:1). Microwave irradiation = 300 W, 140 °C.

Turn over frequency (TOF) values were calculated and given in **Table 8** are indicative to the superior catalytic activity of the catalyst, which is related to the good dispersion of Ni^{2+} species on its outermost surface and the small particle size of this particular catalyst as evidenced by XPS and TEM analyses.

Snice the Suzuki coupling reaction is important in pharmaceutical industries, obtaining the biphenyl compounds with no residual of Ni, or at least not above the legal limit, is necessary. The products of Suzuki reaction were tested for Ni content using ICP analysis. The results should be agreed with Permitted Daily Exposure (PDE) of Ni which is 22 ppm parenteral, 6 ppm inhalation and 220 oral [37]. Fortunately, the Ni was not detected at all (0 ppm) in product mixture which makes 2NiLDHs-Dr catalyst is a sustainable and promising candidate for Suzuki coupling reaction. It seems that the inclusion of Ni ions in the cationic sheet of layered material fix a comfortable octahedral coordination that resist Ni ions depletion.

3.3. Reusability of 2NiLDHs-Dr

The potential of reusability of a catalyst is an important key in catalytic activity assessment. The reusability of the 2NiLDH-Dr catalyst was checked for several reaction cycles for the synthesis of **3** under the optimized reaction conditions, the catalyst removed after the completion of the reaction by filtration. The used catalyst washed with hot ethanol (70%), hot ethyl acetate and sonicated for 5 min to desorb all adsorbed product on the surface of catalyst then its filtered and dried under vacuum. The recovered catalyst was reused for five times using the same reaction conditions. **Figure 8** shows that the regenerated catalyst performs the reactions efficiently even after being used till fifth times. The slight decay observed in the catalytic activity of the 2NiLDH-Dr catalyst on the fifth time could be attributed to the weight loss of the catalyst during the working up in each time.

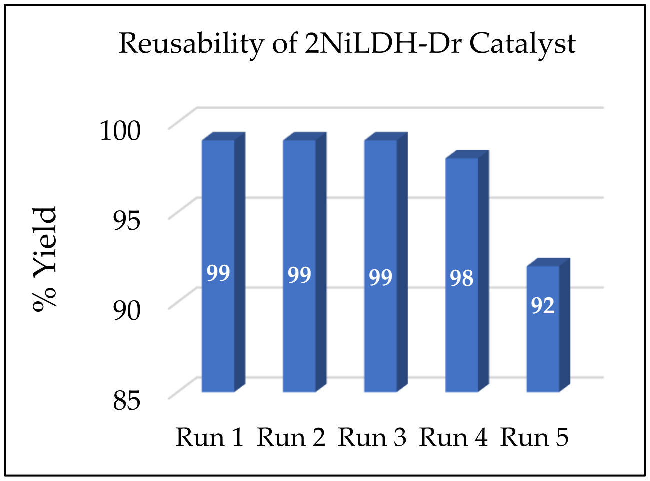


Figure 8. Reusability of 2NiLDH-Dr catalyst, reaction conditions in every cycle: 10 mmol of iodobenzene, 15 mmol of 4-tolylboronic acid, 25 mmol K_3PO_4 and 10 mL of dioxane/H_2O (5:1), 300W, 140°C and 30 min.

3.4 Tentative Mechanism

The mechanism for the nickel catalyzed Suzuki coupling reaction includes three steps: oxidative addition (OA), transmetalation (TM), and reductive elimination (RE). and according to XPS results, the plausible mechanism for the NiLDHs catalysed Suzuki coupling reaction is depicted in Figure 9. Which suggest that the key steps of the Suzuki coupling reaction proceeding through arylnickel(II) complexes which formed via OA of aryl halid and 2NiLDH-Dr, then TM occur, and finally RE. the suggested mechanism is in line with the recent reported study [38].

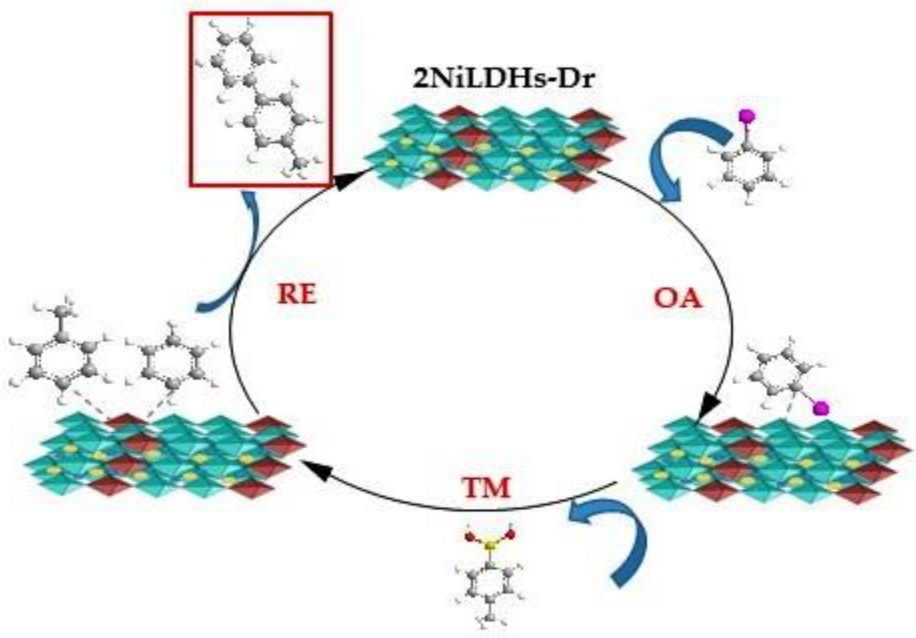


Figure 9. Plausible mechanism for the NiLDHs catalysed Suzuki coupling reaction

4. Conclusion

In this study, Ni-layered double hydroxides (NiLDHs) were prepared by co-precipitation method under ultrasonic irradiation. Isomorphic substitution of Mg^{2+} by Ni^{2+} ions was proved by XRD. All the investigated NiLDHs catalysts exhibited capable catalytic activity towards Suzuki carbon-carbon coupling reaction. The dried as-synthesized 2NiLDHs-Dr was of higher catalytic efficacy comparing to other synthesized/treated catalysts due to high content of surface Ni^{2+} species and small particle size of the catalyst. The results obtained claimed that the catalytic efficacy was correlated to Ni-content more than the basicity of the catalysts. Different aryl halides were used in catalytic activity test and coupling iodobenzene with 4-methyl boronic acid gave the highest percent yield and TOF. The reusability test of the catalyst showed a slight decay in catalytic activity after fifth use as a result of Ni weight loss during the working up. Pd-free and sustainable catalyst with high catalytic efficacy towards Suzuki C-C coupling was attained.

Note

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