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Synergistic Effect of NiLDH@YZ Hybrid and Mechanochemical Agitation on Glaser Homocoupling Reaction

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Abstract: Herein, we report the synthesis of nickel-layered double hydroxide amalgamated to Y-zeolite (NiLDH@YZ) hybrids and evaluation of the synergistic effect of various NiLDH@YZ catalysts and mechanochemical agitation on Glaser homocoupling reactions. Nitrogen adsorption-desorption experiments were carried out to estimate the surface area and porosity of NiLDH@YZ hybrids. The basicity and acidity of these hybrids were determined by CO2-TPD and NH₃-TPD experiments respectively and this portrayed good acidbase bifunctional feature of the catalysts. The NiLDH@YZ catalyzed mechanochemical Glaser coupling reaction achieved best yield of 83% for 0.5NiLDH@0.5YZ hybrid after 60 mins of agitation, which revealed the highest acid-base bifunctional feature compared to all the investigated catalysts. The developed catalyst has proven itself as a robust and effective candidate that can be successfully employed up to four catalytic cycles without significant loss in catalytic activity, under optimized reaction conditions. This work demonstrated a new strategy for C-C bond formation enabled by the synergy between mechanochemistry and heterogeneous catalysis.

Introduction

Dehydrogenative coupling is a sustainable chemical process whereby a new chemical bond is formed either by hydrogen evolution or by formal removal of hydrogen from the substrate. ^[1] Many daunting obstacles have been faced while constructing a desired C-C/C-X/X-X bond by selectively cleaving a C-H/X-H bond among a plethora of similar bonds. ^[2] The dimerization of phenylacetylene is an example of dehydrogenative coupling process taking place in the presence of copper salts and air, as reported by Glaser. ^[3] Glaser coupling is a fascinating and effective tool that can be harnessed to construct C–C bonds and this has innumerable applications in materials science, molecular electronics, polymer synthesis, supramolecular materials, and drug development. ^[4] Extensive new strategies have emerged to achieve dehydrogenative coupling ^[2] along with a range of impressive catalysts, oxidants, ligands, and innovative synthetic protocols. ^[5] Although this reaction requires an organic solvent, but the risk of using an organo-volatile solvent has been minimized by exploiting supercritical carbon dioxide, ^[6] ionic liquids, ^[7] (near-critical) water^[8] and polyethylene glycol (PEG)^[9] as solvents. In addition, some solvent-free protocols were also identified^[10] which include 1) utilizing CuCl₂–pyridine complex as the catalyst^[10a], 2) microwave irradiation in presence of an excess of copper salt^[10b] and 3) utilization of copper salt in the presence of morpholine. ^[10c]

Chemistry in ball mills has gained prominence in being efficient, ecofriendly, and a greener alternative to replace some solventbased protocols. Nowadays, this is considered to be a road to sustainable synthesis because it offers relatively milder reaction conditions, increased surface area and surface energy with a solution towards the numerous defects in catalytic materials. ^[11] The increased surface energy in mechanochemical mode is an outcome of alteration in the structure, chemical composition and chemical reactivity which is a resultant of milling. ^[11e] Schmidt et al. reported a method for the ligand and solvent free Glaser coupling of alkynes in a vibrating ball mill. ^[12]

The catalytic activity of Cu catalysts is enhanced when it is combined with solid supports like reduced graphene oxide (rGO), N-doped carbon materials, polymers and zeolites, owing to the distribution of Cu on larger surface area,^[13] presence of nitrogencontaining moieties and enhanced electron transfer.^[14] For the first time, Kuhn et al.^[15] reported the use of USY-zeolite supported Cu⁽¹⁾ catalyst for the synthesis of divnes by homocoupling of phenylacetylene and revealed the role of zeolite acidic sites in this reaction. Furthermore, they pointed out a significant influence of the pore size and topology of zeolite as higher yields were obtained with zeolites having large internal cages. Transition metals are involved in a wide range of chemical transformations namely dehydrogenative reactions,[16] cross couplings[17] and in C-H activation processes.^[18] Selection of a suitable metal salt is quite challenging and consequently it is recommended to generate M⁽⁰⁾ with suitable ligand that could possibly minimize the

formation of undesired byproducts.^[19] It has been found that Ni(cod)₂ is one of the most widely used catalysts employed in many reactions, when dehydrogenative coupling is considered. Ni catalyzed Glaser coupling reaction of two terminal alkynes is already well developed using THF as solvent, in aerobic conditions.^[20]

In this context herein, we are interested for the development of Ni-layered double hydroxides (NiLDH) catalysts^[21] which are prepared through the intercalation with cage framework zeolite. This work is aimed to develop a sustainable version of Glaser reaction by employing synergistic use of NiLDH@Y-zeolite (YZ) hybrid as heterogeneous catalyst and mechanochemical agitation to afford homocoupling of terminal alkynes (Glaser type reaction), under solvent free conditions utilizing ball milling technique.

Results and Discussion

Catalysts characterization

In the present study a series of NiLDH, YZ, and amalgamated NiLDH @YZ catalysts were synthesized with the aim of testing their efficiency in the Glaser reaction. The selection of such catalytic materials based on the expected acidic/basic bifunctional characteristic that could be necessary for improving the catalytic process.

X-ray diffraction (XRD)

X-ray diffraction patterns of NiLDH, YZ and their hybrids are presented in Figure 1. The characteristic peak of LDH is at low value of $2\theta \approx 12^{\circ}$ and is sharp with high intensity for NiLDH and 0.67NiLDH@0.33YZ. While relatively lower intensity peaks are observed for 0.5NiLDH@0.5YZ and 0.33NiLDH@0.67YZ. The highly intense patterns in a and b planes of NiLDH were gradually suppressed in the hybrids. In contrary, the XRD pattern of the 0.5NiLDH@0.5YZ hybrid completely matches with that of the corresponding synthesized YZ (JCPDS 76-110).^[22] The diffraction peaks of YZ were indexed as per previous report. ^[23] There were no significant changes in the number of diffraction peaks with respect to YZ except the peak at $2\theta = 12.3^{\circ}$, 23.4° , 35.3° and 61.9° , which refer to NiLDH peaks, indicating that NiLDH could be coated inside the YZ pores. ^[24]

Scanning electron microscopy (SEM-EDX)

The morphology of parent YZ, NiLDH and their hybrids were investigated by scanning electron microscopy. The YZ sample displays a very well-defined and polished shape (Figure 2a), while the morphology of the layered NiLDH flakes was typical of layered double hydroxides (Figure 2i).^[21] The influence of the intercalation of NiLDH on the Y-zeolite structure can be confirmed from SEM images. In 0.33NiLDH@0.67YZ, irregular spots begin to deposit on the outer surface of the zeolite material (Figure 2c). The YZ still retained the original form in 0.5NiLDH@0.5YZ (Figure 2e) with the outer surface roughened from widely dispersed NiLDH, without an aggregation of NiLDH on YZ surface. The degree of dispersion increases monotonically with the increase in NiLDH content, where 0.67NiLDH@0.33YZ showed the maximum roughness of the zeolite surface (Figure 2g).



Figure 1. XRD patterns of NiLDH, YZ and their hybrids.

Transmission electron microscopy (TEM)

The TEM image (Figure 3a) shows that YZ has a defined shape with sharp edges. Nevertheless, despite the vague picture taken for this particular sample, YZ's instability under HRTEM power was not omitted.^[27] TEM image (Figure 3c) for 0.5NiLDH@0.5YZ catalyst shows the presence of a significant degree of NiLDH coverage on the surface of the YZ crystallites. In Figure 3d, the HRTEM image of 0.5NiLDH@0.5YZ shows a non-uniform lattice fringe compared to YZ in Figure 3b, which proves the existence of NiLDH on the YZ surface. In addition, the width of the adjacent lattice fringe (Figure 3d) is approximately 0.751 nm which is similar to *doos* spacing of the NiLDH phase (0.727 nm) ^[24a] and this is further consistent with the above discussion. NiLDH sample shows extra d-spacing at 0.185 nm, which is specific to the layered material (Figure 3f).

N₂ physisorption measurement

Nitrogen adsorption-desorption for a series of NiLDH@YZ hybrid samples was examined in order to estimate their specific surface area and porosity. The results of N2 adsorption-desorption isotherms are displayed in Figure 4a. According to IUPAC classification,^[26] all samples show type IV isotherm except YZ that exhibits typical type I isotherm. The H4-type hysteresis loop indicates the presence of mesoporous slit like shape. ^[27]

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Figure 2. SEM and EDX images of NiLDH, YZ and their hybrids.



Figure 3. TEM image of YZ (a, b), 0.5NiLDH@0.5YZ (c, d) and NiLDH (e, f).

Textural properties for NiLDH, YZ and NiLDHs@YZ hybrids have been summarized in Table 1. The pore size distribution analysis, using DFT method, displayed that all the samples have bimodal distribution curves in the microporous and mesoporous ranges (Figure 4b). The pore size of YZ was decreased after coating process from 2.8 to 1.1 nm in 0.5NiLDH@0.5YZ hybrid (Table 1). Similar phenomenon was reported when different metals were introduced on porous materials. [28] The decrease in pore size of the 0.5NiLDH@0.5YZ catalyst compared to the original YZ could be due to NiLDH layers blocking the pores during the process of Y-zeolite surface coating. Both BET and micropore surface areas decreased with NiLDH addition, while the opposite occurred in mesoporous areas. YZ showed the highest BET surface area and micropore area values and pure NiLDH sample showed the opposite values. The micropore volume of YZ decreased while the mesopore volume increased after addition of NiLDH in the hybrid materials. The pronounced decrease in micropore volume in YZ after the coating process may be due to the coating of pores by NiLDH particles. ^[29] The calculated hierarchy factor recorded 0.12 for 0.5NiLDH@0.5YZ hybrid catalyst which is double to the value of YZ (0.06) and NiLDH (0.06) samples individually. The suitable hierarchy factor can lead to the creation of shorter diffusion path lengths and lower diffusion resistance in this particular catalyst. In addition, the sustainable number of mesopores could resist the formation of coke. [30]

X-ray photoelectron microscopy (XPS)

The XPS spectrum allows an analysis of the surface structure and provides information about the presence of Ni, Al, O and Si within the surface of catalysts along with the oxidation state of the metals. Figure 5a illustrates an envelope for the Al 2p band at 75.1 eV in YZ sample and 0.5NiLDH@0.5YZ hybrid and this refers to the presence of Al³⁺ ion that gets bonded to oxygen and silicon (Al-O-Si) in zeolite structure ^[31]. The binding energy of Al 2p in pure NiLDH sample resulted in a peak at 73.8 eV, while the peak that appeared at 68.2 eV should contribute to Ni 3p. ^[32] The deconvoluted Al 2p peaks at 73.8 eV indicates the presence of Al³⁺ bonded to hydroxide layers (Al-OH). ^[33]

Figure 5b displays the deconvoluted XPS band of *1s* of O in YZ, 0.5NiLDH@0.5YZ and NiLDH samples and that showed the presence of isolated oxygen (O²⁻), the lattice oxygen (OH⁻) and oxygen from the adsorbed water. Figure 5c shows that the peak intensity of *2p* of Si in YZ and 0.5NiLDH@0.5YZ, which is reduced after coating with NiLDH indicating that the Si content on the surface decreased significantly ^[24a]. In Figure 5d, NiLDH spectrum shows the two obvious shakeup satellites at 856.0 and 873.7 eV which can be identified as signals for *2p*_{3/2} of Si and *2p*_{1/2} of Ni²⁺, respectively. These satellite lines are the fingerprints of Ni²⁺ ions in an environment of oxide ions (O²⁻).^[34]



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Figure 4. (a) N_2 adsorption-desorption isotherms; (b) pore size distribution curves of NiLDH, YZ and their hybrids

Table 1. The textural properties of	f YZ, NiLDH and	their hybrids.						
	S _{вет} ^[а] (m²/g)	S _{micro} ^[b] (m²/g)	S _{meso} ^[c] (m²/g)	V _{total} ^[d] (cc/g)	V _{micro} ^[e] (cc/g)	V _{meso} [f] (cc/g)	Pore Size Distribution (nm)	HE [a
YZ	564.4	517.7	39.8	0.34	0.27	0.06	2.8	0.06
0.33NiLDH@0.67YZ	424.2	347.4	71.6	0.29	0.18	0.11	1.9	0.10
0.5NiLDH@0.5YZ	379.3	297.2	79.7	0.28	0.16	0.12	1.1	0.12
0.67NiLDH@0.33YZ	164.0	60.9	105.2	0.19	0.03	0.15	3.0	0.11
NiLDH	124.7	12.8	126.4	0.18	0.01	0.17	4.3	0.06

[a] Surface area from BET isotherm \approx S_{meso} + S_{micro}; [b] Micropore area (From t-plot method); [c] Mesopore area (From BJH method); [d] Total pore volume = V_{meso} + V_{micro}; [e] Micropore volume (From t-plot method); [f] Mesopore volume (From t-plot method); [g] Hierarchy factor = (V_{micro}/V_{total}) × (S_{meso}/S_{BET})

In XPS spectrum of 0.5NiLDH@0.5YZ hybrid (Figure 5d), the Ni $2p_{3/2}$ peak shifted to higher binding energy from 856.0 eV to 857.1 eV.

The position of Ni 2p peak is usually influenced by the local chemical or physical environment around Ni species besides the formal oxidation state. The Ni 2p peak shifts to higher binding energy when the charge density around it decreases. The existence of the acidic sites of YZ (Al and Si) around the Ni species leads to a decrease in the charge density around Ni and the slight increase in binding energy.^[35]

Temperature-programmed desorption (TPD-CO₂)

The basicity of the different catalysts was determined by CO_2 -TPD because the types of basic sites could be detected by CO_2 adsorption. The chemisorbed peaks can be compared according to the temperatures at which the peaks were shown. Bicarbonate and bidentate species decompose at low and moderate temperatures (~100 - 420 °C) and can be traced to relevant peaks. The peak that decomposed at higher temperature (≈ 540 °C) can be attributed to the presence of monodentate species. ^[36] Figure 6 revealed that each of the hybrids have different types of basic sites, whereas TPD-CO₂ profile of YZ catalyst shows just one peak at 340 °C. The TPD-CO2 of 0.67NiLDH@0.33YZ and NiLDH have identical profiles that are distinct from 0.5NiLDH@0.5YZ, which has a unique profile. The TPD-CO₂ profile of all hybrids (except 0.33NiLDH@0.67YZ) and NiLDH show peaks within the range of 100-355 °C due to the desorption of weakly bond CO2 and the breakdown of carbonate ions existing in the interlayer of LDH samples. In the TPD-CO₂ profiles of 0.5NiLDH@0.5YZ and 0.33NiLDH@0.67YZ, the peaks extend to up to 520 °C and this can be related to tightly bonded species of monodentate or bidentate carbonate. In addition, there is a peak at about 420 °C

Al 2p **O**1s b) a) Experimental ΥZ ΥZ Experimental 250 6 75.1 01s 02 Al 2p_1_Al 2p Al 2p_2_Al 2p Ols Off 5 200 O 1s_ads O/H₂O Background_Al 2p Fitted Spectra 4 532 Baseline Fitted Spectra 150 3 532.5 100 2 50 531.6 1 72.7 6 0 140 Raw Spectrum O 1s_O²⁻ Raw Spectrum 0.5NiLDH@0.5YZ 0.5NiLDH@0.5YZ Intensity (a.u.) 75.1 Intensity (a.u.) 120 Al 2p_Al³⁴ O 1s_OII O 1s_adsO/H₂O Baseline 100 Fitted Spectrum Baseline Fitted Spectru 532. 80 532 60 40 1 20 531.8 0 70 Raw Spectrum O 1s_O²⁻ NiLDH aw Spectrum NiLDH Ni 3p (68.2 eV) 531.5 Al 2p_Al metallic Al 2p_Al,(OH), 60 O ls_OII 4 50 O 1s adsorbed H.C Ni 3p overlapping 73.8 Baseline 3 40 Baseline Fitted Spectrum Fitted Spectrum 30 2 20 529.8 10 533.8 1 0 534 0 528 530 532 536 538 526 65 75 80 85 **Bonding Energy (eV) Bonding Energy (eV)** Si 2p c) Ni 2p d) 50 ΥZ Experimental 0.5NiLDH@0.5YZ Raw Spectrum 30 103.2 Si 2p_1_Si 2p Si 2p_2_Si 2p Ni 2p3/2 Ni² Ni 2p _{3/2}(857.1) Ni 2p3/2_Ni²⁴ 40 Background Si 2r 25 Ni 2p3/2_sattelite Ni 2p3/2_sattelite Fitted Spectra Baseline 20 30 Fitted Spectrum 15 862.7 20 10 Intensity (a.u.) Intensity (a.u.) 859 5 868.1 0.5NiLDH@0.5YZ NiLDH Raw Spectrum Raw Spectrum Ni 2p3/2_Ni metal Ni 2p3/2_Ni(OH)₂ 103.4 Si 2p Ni 2p 3/2 (856.0) 6 Baseline Ni 2p3/2_Satellite Fitted Spectrum 40 5 Ni 2p3/2 Satellite Baseline Fitted Spectrun 30 Ni 2p 1/2 (873.7) æ 861.9 20 879.7 2 10 1 852 867.7 0 0 860 880 102 104 106 850 870 98 100 108 **Bonding Energy (eV) Bonding Energy (eV)**



that is attributed to bicarbonate species bonded to weak or medium basic strength sites. ^[37] The profiles of TPD-CO₂ for all catalysts were integrated to measure the amount of CO₂ formed from the subtraction of the corresponding profiles. From Table 2, it is clear that 0.5NiLDH@0.5YZ catalyst has higher total number of basic sites (40.4 µmol/g), which reveals the stronger dispersion of NiLDH in the YZ cavities.

Temperature-programmed desorption (TPD-NH₃)

The acidity of catalysts was studied by NH₃-TPD profiles. The overall acidity of the catalysts can be measured from the amount of ammonia desorbed at different temperatures. The strength and number of acidic surface centers can be estimated from the

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maximum temperature intensity and location, respectively. Ammonia desorption profile of the catalysts could be divided into three regions namely (1) weak (100-250 °C), (2) medium (250-400 °C) and (3) strong (400-700 °C) acid strengths. ^[38] The TPD-NH₃ profiles of NiLDH, YZ and hybrid catalyst are shown in Figure 7. The NiLDH exhibited two peaks at 329 °C and 378 °C which are under medium temperature range corresponding to moderate acid sites.



Figure 6. TPD-CO₂ profile for NiLDH, YZ and their hybrids.

Catalyst	Ni (% w/w) ^[a]	Total CO₂ uptake (μmol/g)	Total acidity (µmol/g)
YZ	-	9.3	277.1
0.33NiLDH@0.67YZ	0.6	20.9	310.2
0.5NiLDH@0.5YZ	0.7	40.4	549.1
0.67NiLDH@0.33YZ	0.8	24.4	269.4
NiLDH	0.81	29.4	256.8

[a] From ICP analysis

The TPD-NH₃ profile of 0.67NiLDH@0.33YZ catalyst is similar to NiLDH but the maximum temperature and peak intensities are lesser in 0.67NiLDH@0.33YZ than NiLDH which suggests lesser acidity. YZ catalyst also has two different peaks at lower maximum temperatures (107 °C and 274 °C) suggesting both weak and moderate acid sites.



Figure 7. TPD-NH₃ profile for NiLDH, YZ and their hybrids.

The TPD-NH₃ profile of 0.33NiLDH@0.67YZ also shows two different peaks corresponding to poor and moderate acid sites at higher temperatures (117 and 350 °C) relative to YZ. The TPD-NH₃ profile of 0.5NiLDH@0.5YZ has exhibited five peaks at different temperatures such as 110 °C (weak acid site), 252 °C, 299 °C , 372 °C (moderate acid sites) and at 428 °C (strong acid sites) as depicted in Figure 7. The acidic-basic features of various catalyst derived from NH₃-TPD and CO₂-TPD profile analysis are displayed in Figure 8. The 0.5NiLDH@0.5YZ hybrid reveals the highest acid-base bifunctional feature relative to all the investigated catalysts. Higher acid-base bifunctional feature of catalysts not only provides the surface to interact with organic molecules but also results in it being the site for C–C coupling reactions. ^[39]



Figure 8. Acid-base bifunctional features of NiLDH, YZ and their hybrids derived from NH_3 -TPD and CO_2 -TPD profiles.

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Catalytic activity of NiLDH@YZ hydrids on Glaser homocoupling reaction

Prepared catalysts have been used to develop a protocol for heterogeneous nickel catalyzed Glaser homocoupling reaction under mechanochemical agitation in a ball mill. The challenge is to study the catalytic activities of the prepared NiLDH@YZ catalysts that allowed the transformation of terminal alkyne **1** into the corresponding 1,4- buta-1,3-diynes derivative **2**, (Scheme 1) in a time- and energy-efficient manner.



Scheme 1. Heterogeneous Ni catalyzed Glaser type reaction.

At the outset, NiLDH, YZ, 0.67NiLDH@0.33YZ, 0.5NiLDH@0.5YZ and 0.33NiLDH@0.67YZ catalysts were tested for their catalytic activity in ball mill, under solvent free conditions and results were cited in Table 3. These catalysts have the advantages that they have a minimal impact to the environment and can be easily recycled. Surprisingly, only trace product was formed using NiLDH and YZ alone (Table 3, Entries 2 & 3).

Table 3. Optimization of reaction	conditions	(catalyst	and	time)	for	Glaser
coupling of terminal alkynes. ^a						

Entry	Catalyst	Time (min.)	Yield (%)
1	Catalyst-free	360	0
2	NiLDH	180	10 (trace)
3	YZ	180	12 (trace)
4	0.67NiLDH@0.33YZ	130	61
5	0.5 NiLDH@0.5YZ	60	83
6	0.33NiLDH@0.67YZ	180	23
7 ^b	0.5 NiLDH@0.5YZ	60	15

^aReaction conditions: catalyst (400 mg), phenylacetylene (2 mmol), pyrrolidine (1 mol %) and ball mill frequency (30 Hz). ^b Without pyrrolidine.

Notably, the catalytic materials used in this reaction act as grinding auxiliaries in addition to its role as a catalyst where all the reactants are liquid. It is clear from results depicted in (Table 3) that even after utilizing a ball mill even after 6 h, no desired product 2a was formed in absence of catalyst (Table 3, Entry 1). In addition, the best yield of 83 % of the desired product 2 was reached using 0.5NiLDH@0.5YZ catalyst in 60 min (Table 3, Entry 5). Furthermore, a lower yield with longer period of time (61 % at 130 min. and 23 % at 180 min.) was observed using 0.67NiLDH@0.33YZ and 0.33NiLDH@0.67YZ catalysts (Table 3, Entry 4 & 6), respectively. Here pyrrolidine acts as a base and without pyrrolidine the reaction gives lower yield (Table 3, Entry 7). Both the pyrrolidine and hybrid catalyst are required, however only pyrrolidine does not give any significant effect. Further, effect of time and frequency of ball mill on catalytic system were examined (Table 4) with same amount of catalyst. The best frequency for this reaction protocol was noted at 30 Hz (Table 4,

Entry 3), in which the desired product 2a was isolated in 83 % yield and no other product was noticed.

NiLDH catalyst alone was not adequate for activate the terminal alkyne and obtain Glaser product with significant yield even though it has acid-base properties as shown from TPD-CO2 and TPD-NH₃ results. The **2a** yield enhanced for the 0.33NiLDH@0.67YZ catalyst by about 23%. This is actually attributed to the acid-base active sites were distributed over the larger surface area (424 m²/g) for 0.33NiLDH@0.67YZ. The highest yield was obtained by 0.5NiLDH@0.5YZ hybrid catalyst that has the equal ratio from NiLDH and YZ (83%). The superior activity of the former hybrid catalyst was attributed to their unique basic properties than other hybrid catalysts. Moreover, the acidity of YZ and its characteristic topology that appeared from high hierarchy factor value (0.12) engaged on giving the hybrid catalysts the exceptional catalytic activity. However, the efficiency of the hybrid catalyst was slightly suppressed when the amount ratio of NiLDH was more than YZ (0.67NiLDH@0.33YZ, vield 61%) which could be explained by the aggregate of NiLDH particles inside the pores of YZ.

 Table 4. Optimization of reaction condition (time and ball mill frequency for homocoupling of terminal alkynes.

Entry	Time (min.)	Yield (%)	Ball-mill frequency (Hz)
1	120	62	20
2	90	70	25
3	60	83	30

Reaction conditions: 0.5NiLDH @0.5YZ catalyst (400 mg), phenylacetylene (2 mmol) and pyrrolidine (1 mol %).

For the synthesis of symmetrical diyne molecules, the scope and generality of this protocol were investigated with various types of terminal alkyne derivatives including electron donating group and electron withdrawing group using 0.5NiLDH@0.5YZ catalyst under the optimized conditions (Table 5). And the reaction proceeds efficiently in both cases without any compatibility.



Reaction conditions: 0.5NiLDH@0.5YZ catalyst (400 mg), phenylacetylene (2 mmol) and pyrrolidine (1 mol %), ball mill frequency (30 Hz), time 1 h.

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We have performed a reaction with a combination of electronically different alkynes, 1-ethynyl-4-methylbenzene and phenvl acetylene for the synthesis of 1-methyl-4-(phenylbuta-1,3-diyn-1yl)benzene under the same reaction condition. We have obtained poor yields of the unsymmetrical product, which indicates mixture of symmetrical divne formation is favored rather than unsymmetrical ones (Table 5, entry 6).

The results cited in Table 5 revealed that this catalyst showed the same reactivity whether the substrates were bearing electron donating or withdrawing groups. Similar results were reported in the literature using poly styrene supported copper catalyst. [40]

All the products were well characterized using NMR spectral data. In the ¹H NMR spectra, disappearance of singlet peak of acetylenic hydrogen confirms the formation of desired coupled products (2a-f). (Supporting Information).

Reusability of 0.5NiLDH@0.5YZ catalyst

The reusability of the 0.5NiLDH@0.5YZ catalyst was tested for several reaction cycles for Scheme 1 under optimized reaction conditions, the catalyst removed after filtration, washed with hot ethyl acetate and dried under vacuum. The recovered catalyst was used under the same reaction conditions four times. Figure 9 shows that the regenerated catalyst conducts the reaction efficiently under the same conditions even after a four-fold use. A slight decay in the catalytic activity of the 0.5NiLDH@0.5YZ catalyst was observed in third and fourth cycles which was studied by comparing XRD (Figure 10) of the original catalyst with the corresponding regenerated catalyst after first and last cycle of Glaser reaction. XRD analysis shows regenerated catalysts losing crystallinity under mechanochemical force while maintaining their layered structure. It is clear from Figure 10 that the intensity of diffraction peaks that originated from Y-zeolite decreased dramatically due to the breakup of Si-O-Si and Si-O-Al bonds as reported by previous studies [41]. Although peaks due to NiLDH showed to be distinctly resistant to mechanical force of ball milling, the intensities of its distinguished XRD peaks in regenerated catalysts are significantly decreased. [42] XRD pattern of regenerated catalyst after the first cycle showed marked peak



Figure 9. Results of recyclability of 0.5NiLDH@0.5YZ catalyst under optimized reaction conditions.

broadening that became wider after the last cycle, suggesting reduction of crystallinity and deformation of particle size induced by the milling action. The crystallite size was calculated for the original and regenerated catalysts (after first and last cycles) to demonstrate the degree of deformation of layered structure, which was found as 53.6, 16.5 and 5 nm, respectively but layered structure was retained even after the last cycle. We conclude herein that the slightly decay in catalytic activity of 0.5NiLDH@0.5YZ could be attributed to weight loss during the workup process, deformation in regenerated catalysts and surface defects.

Tentative Mechanism

Results obtained from utilizing both NiLDH and YZ as individual catalysts for the Glaser reaction shows almost no catalytic activity. On the other hand, a noticeable catalytic activity has been observed in the case of using the hybrid catalyst that has dual acid-base properties. Therefore, the proposed tentative mechanism (Scheme 2) is based upon results of catalytic tests and characterization of hybrid catalysts.

The transmetallation reaction between the hybrid catalyst and the acetylide ion (catalyst-assisted generation of nucleophile) gives the alkynyl complex (1), which then converts to a dialkynyl-Ni complex intermediate (2). In the presence of oxygen, the latter complex (2) gets readily converted to the final product 1,3-diyne via reductive elimination and regenerates the catalyst. [20, 43]



Figure 10. XRD of used 0.5NiLDH@0.5YZ catalysts after first and fourth cycles.

Pyrrolidine facilitates hydrogen abstraction from the terminal alkyne to form acetylide ion (Scheme 2). Notably, the last step is facilitated by the Lewis acid sites of the hybrid catalyst. The superiority of the 0.5NiLDH@0.5YZ catalyst among all the investigated catalysts can be explained on the basis of its highest acid-base bifunctional properties as witnessed by CO2-TPD and NH₃-TPD

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Scheme 2. The proposed mechanism for Glaser homo-coupling reaction.

Conclusion

In summary, NiLDH@YZ hybrid catalysts with different percentage compositions were synthesized and successfully harnessed to carry out Glaser coupling utilizing solvent-free ball mill technique. The catalytic activities of the catalysts were examined by their ability to transform terminal alkyne into the corresponding 1,4- buta-1,3-diynes derivatives in a time- and energy-efficient manner. The results of NH₃-TPD and CO₂-TPD profiles of 0.5NiLDH@0.5YZ hybrid catalysts revealed the highest acid-base bifunctional feature relative to all the investigated catalysts. The unique acid-base behavior of this particular hybrid was an outcome of good dispersion and interaction between NiLDH and YZ as witnessed by SEM, and HRTEM. The effect of the mechanochemical agitation can lead to the reduction of the particle size and creation of active sites by generating fresh active surfaces, which maintains the chemical activity of the recycled materials.

Experimental Section

Synthesis of NiLDH@YZ hybrids

NiLDH was prepared by co-precipitation method ^[21] and Y-zeolite was pretreated to obtain its H form (HY-zeolite) as per reported method ^[22] which were then intercalated using ion exchange method to yield NiLDH@YZ hybrids. For this, 1 g of NiLDH was suspended in 100 mL of ultrapure water using a magnetic stirrer for 20 minutes. 1 g of HY-zeolite was applied to suspended NiLDH solution, which was suspended in 100 mL ultrapure H₂O for 20 minutes. Subsequently, the solution was refluxed at 50 °C under N₂ atmosphere for 5 days. The resulting precipitate was filtered and washed with distilled water then dried at 80 °C for 16 h. By using same method three hybrids namely 0.33NiLDH@0.67YZ, 0.5NiLDH@0.5YZ and 0.67NiLDH@0.33YZ having different weight percent of NiLDH and YZ, were prepared.

General procedure for Glaser reaction

The terminal alkyne (2 mmol), pyrrolidine (1 mol %) and NiLDH@YZ catalysts (400 mg) were injected into a 25 mL stainless steel jar fitted with two stainless steel balls (15 mm in diameter). The jar was locked, and milling was carried out at different frequencies in a ball mill (Retch CryoMill, Hanna, Germany) and progress of the reaction was checked by TLC after

every 15 minutes. The milling process was repeated until the reaction is thoroughly completed. Then the milling Jar was opened and allowed to stand in an air atmosphere for 60 minutes. After the post-reaction oxidation, the crude products were extracted using ethyl acetate (3x10 mL) and sonicated for 5 minutes to desorb all adsorbed liquid on the catalyst surface followed by filtration. The filtrate was concentrated under reduced pressure and the residual crude products were purified by column chromatography using n-hexane/ethyl acetate mixtures (7:3).

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Keywords: Acid-base bifunctional catalyst; Ball milling; Glaser reaction; NiLDH@Y-zeolite hybrid catalyst; Synergistic effect

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In the present study NiLDH, YZ and amalgamated NiLDH@YZ catalysts were tested for the Glaser homocoupling reaction. The catalyst with 0.5 NiLDH@0.5 YZ showed the superior catalytic efficiency under mechanochemical agitation. A robust catalyst used for four times provide a new strategy in C-C coupling reactions using mechanochemistry.

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