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# Nickel-Catalyzed Solvent-Free Three-Component Coupling of Aldehyde, Alkyne and Amine

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**Keywords:** Nickel / Solvent-free reaction / Multicomponent / Heterogeneous catalysis / Propargylamines

A versatile three-component coupling of aldehydes, alkynes and amines has been developed, catalyzed by $Ni^{2+}$-exchanged Y-zeolite, which acts as an environmentally benign, recyclable, efficient and heterogeneous catalyst. This three-component ($A^3$) coupling (reported for the first time to proceed under nickel catalysis) is carried out under solvent-free conditions, and the corresponding propargylamines are obtained in good to excellent yields.

## Introduction

Multicomponent reactions[1] of simple molecules provide a very versatile and efficient method to construct desired molecules, as they allow several starting materials to be combined in a one-pot operation exhibiting economy of steps and often atom economy. These reactions have been achieved mostly by making use of transition-metal catalysts. For example, the three-component coupling of aldehyde, alkyne and amine ($A^3$ coupling) gives propargylamines, which are important synthetic intermediates for potential therapeutic agents and polyfunctional amino derivatives.[2] Recently, enormous progress has been made in expanding the scope of this $A^3$ coupling by employing various transition metal catalysts such as Ag,[3] Au,[4] Cu,[5] Ir,[6] $Hg_2Cl_2$,[7] Zr,[8] Re,[9] and Cu/$Ru^{II}$ dimetallic systems.[10] Although several catalytic methods for the construction of propargylamines are reported, most of them require an inert gas, high temperatures and expensive metals such as Au, Ag, Ir, or Zr as catalysts. Thus, the development of a milder, cheaper, reusable, highly efficient as well as environmentally benign method for constructing propargylamines is desirable.

Since the seminal work of Wilke,[11] nickel has been shown to catalyse many transformations associated with alkyne functionalization including the addition of alkynes to 1,3-dienes,[12] styrenes,[13] methylenecyclopropanes,[14] enones,[15] arylcyanation,[16] reductive coupling with aldehydes,[17] hydrothiolation,[18] hydrosilylation,[19] multicomponent coupling,[20] homodimerization[21] and cross-trimerization of alkynes.[22] Several excellent studies on nickel-catalysed transformations including cycloadditions, Negishi cross-coupling, *N*-arylation of nitrogen nucleophiles, *S*-arylation of thiols, Heck, Suzuki and Sonogashira couplings are also reported, reflective of the growing interest in nickel catalysis.[23] In several cases, it is shown that the less toxic and inexpensive nickel can indeed replace traditional Pd, Ru, Au, Ag and Cu catalysts, making these processes more practical and economically viable. Also, the mechanisms involved in Ni-catalyzed processes can be different from the reaction pathways that are dominant in Pd-catalyzed cross-coupling reactions due to the ability of nickel to give radical species. In addition, Ni complexes can undergo a facile switch among several oxidation states, resulting in a rich reactivity with surprising catalytic cycles and promising new possibilities.

## Results and Discussion

Recently, Suginome et al., have reported the nickel-catalyzed addition of C–H bonds of terminal alkynes to C=C bonds using a nickel catalyst with different phosphane-substituted ligands.[12–14] Very recently, use of iron-[24] as well as indium-catalyzed[25] $A^3$ coupling were reported. To the best of our knowledge, the Ni-catalyzed three-component coupling of aldehyde, alkyne and amine has not been reported so far. Herein, we report the first example of a nickel-catalyzed synthesis of propargylamines by addition of sp C–H bonds to C=N bonds.

The development of heterogeneous catalysts for fine chemicals synthesis has become a major area of research recently, as the potential advantages of these materials (simplified recovery and reusability, potential for incorporation in continuous reactors and microreactors) over homogeneous systems can make a major impact on the environmental performance of a synthesis. Using this combination of heterogeneity and catalysis, which reinforce the greenness of organic reactions, we sought to develop a heterogeneous catalytic system that can have several advantages, such as

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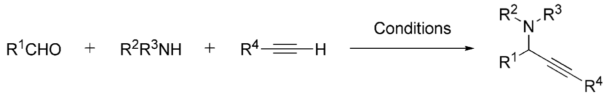
fast and simple isolation of the reaction products by filtration as well as recyclability and minimization of metallic waste. Our interest in heterogeneous catalysis[26] focuses on the use of clays and zeolites as solid supports, which are readily impregnated with metal ions. It is also relevant to note that recent environmental concerns about solvent-based chemistry have stimulated a renewed interest in the study of chemical reactions under solvent-free conditions.[27]

For the optimization of the reaction conditions and the identification of the best nickel source and solvent, cyclohexanecarbaldehyde, morpholine and phenylacetylene were chosen as model substrates. Catalytic activities of various nickel sources for propargylamine synthesis were studied, and the three-component coupling provided the desired product in low but promising yields. The results are summarized in Table 1. Use of organic solvents resulted in a lower conversion (Table 1, Entries 1–4), and the reactions proceeded cleanly under solvent-free conditions. Use of solid supports led to sharply ascending efficiencies in $A^3$ coupling except for Ni/Al-HT (Table 1, Entry 9). Nickel supported on zeolite was found to be a much better catalyst than others and gave nearly quantitative yields of propargylamines. Nickel-exchanged zeolite was prepared by an ion-exchange method.[28] The nickel-modied zeolite was characterized by powder XRD, EDX, and UV-DRS. The total nickel content was found to be 4.46 atom-% by EDX analysis (see Supporting Information). In control experiments with an unmodified solid support, no reaction took place (Table 1, Entry 13), clearly highlighting the specific role of nickel in the solid support. The optimal conditions for the nickel-catalyzed $A^3$ coupling involve nickel-exchanged zeolite under solvent-free conditions at 80 °C for 4 h (Table 1, Entry 12).

Table 1. Optimization of reaction conditions.[a]

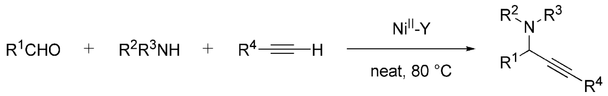


| Entry | Nickel source | Solvent | Yield (%)[b] |
|---|---|---|---|
| 1 | $Ni(OAc)_2·4H_2O$ | DMF | 25[c] |
| 2 | $Ni(OAc)_2·4H_2O$ | toluene | 21[c] |
| 3 | $Ni(OAc)_2·4H_2O$ | THF | 20[c] |
| 4 | $Ni(OAc)_2·4H_2O$ | MeCN | 26[c] |
| 5 | $Ni(OAc)_2·4H_2O$ | none | 63 |
| 6 | $Ni(Cl)_2·6H_2O$ | none | 53 |
| 7 | $Ni(SO_4)_2·6H_2O$ | none | 55 |
| 8 | $Ni(NO_3)_2·6H_2O$ | none | 36 |
| 9 | Ni/Al-HT | none | 31 |
| 10 | Ni-K10 clay | none | 64 |
| 11 | Ni-Al-MCM 41 | none | 73 |
| 12 | Ni-Y zeolite | none | 97 |
| 13 | H-Y zeolite | none | 0 |

[a] Cyclohexanecarbaldehyde (1.0 mmol), morpholine (1.2 mmol), phenylacetylene (1.2 mmol), Ni-Y (20 mg), 80 °C for 4 h. [b] Yield of isolated product. [c] 100 °C for 15 h.

In order to ascertain that Ni-Y zeolite is able to catalyse the process without leaching of $Ni^{2+}$ ions into the solution[3d] and thus the catalysis is truly heterogeneous, a Sheldon test was also performed. Aldehyde (10 mmol), amine (12 mmol) and alkyne (12 mmol) were treated with 150 mg of Ni-Y zeolite at 80 °C for 1 h. The reaction mixture was cooled to room temperature, and the catalyst was filtered. The filtrate was further heated at 80 °C for additional 2 h. To the recovered solid catalyst, reactants (aldehyde, alkyne and amine) were added, and the mixture was heated at 80 °C for 3 h. The obtained results indicate that there was no appreciable leaching of metal ions under the present reaction conditions (Table 2). To gain additional evidence for the heterogeneity of the catalyst, a mercury poisoning experiment was performed (see Supporting Information). After about 40% completion in a typical reaction, elemental Hg (2.0 g, ca. 300 equiv.) was added to the solution whilst stirring. The complete cessation of the reaction provides strong support for the heterogeneous nature of the catalyst.

Table 2. Sheldon test carried out with Ni-Y catalyzed $A^3$ coupling.[a]



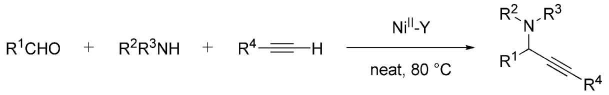
| Catalyst | Yield (%)[b] | | |
|---|---|---|---|
| | 1 h | 1 + 2 h | Reused catalyst |
| Ni-Y | 37.9 | 40.4 | 86.2 |

[a] Aldehyde (10 mmol), amine (12 mmol), alkyne (12 mmol), Ni-Y (150 mg), at 80 °C. [b] HPLC yield.

This nickel-catalyzed three component coupling is also successfully extended to different combinations of alkynes, aldehydes and amines. As depicted in Table 3, this reaction works very well for a wide range of substrates with very good to excellent yields. A variety of alkynes are coupled with cyclohexanecarbaldehyde and morpholine as the other components (Table 3, Entries 1–8). Aliphatic, aromatic, cyclic and heterocyclic alkynes are studied and in all the cases, the reactions proceed smoothly to give the corresponding propargylamines in a yield of 84–97%. Aromatic as well as aliphatic aldehydes, including cyclic and acyclic ones, display high reactivity under the present reaction conditions (Table 3, Entries 1 and 9–19).

To extend the scope of the reaction to amine substrates, various amines, including primary, secondary cyclic, acyclic and aromatic amines were examined by using cyclohexanecarbaldehyde and phenylacetylene as model substrates (Table 3, Entries 1 and 20–28). The coupling proceeded smoothly to afford the corresponding propargylamines in excellent yields under standard conditions. To clearly demonstrate the potential of this method for preparative purposes, we performed the reaction on a gram scale. The reaction was readily applicable to a gram scale process giving isolated yields almost comparable to those in the small-scale reactions. Meanwhile, the recovery and reuse of Ni-Y were also investigated, and the recovered catalyst exhibited a constant activity for up to 8 consecutive cycles (Table 4).

Table 3. Nickel-catalyzed three-component coupling of aldehydes, alkynes and amines.[a]



| Entry | Aldehyde ($R^1$) | Amine ($R^2$, $R^3$) | Alkyne ($R^4$) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | cyclohexyl | morpholine | Ph | 97, 94[c] |
| 2 | cyclohexyl | morpholine | 4-($n$-$C_5H_{11}$)$C_6H_4$ | 96 |
| 3 | cyclohexyl | morpholine | 2-pyridyl | 91 |
| 4 | cyclohexyl | morpholine | $n$-hexyl | 84 |
| 5 | cyclohexyl | morpholine | $CH_2OH$ | 92 |
| 6 | cyclohexyl | morpholine | cyclohexenyl | 92 |
| 7 | cyclohexyl | morpholine | cyclopropyl | 84 |
| 8 | cyclohexyl | morpholine | 6-MeO-2-naphthyl | 95 |
| 9 | isovaleraldehyde | morpholine | Ph | 96 |
| 10 | PhCH=CH | morpholine | Ph | 94 |
| 11 | Ph | morpholine | Ph | 85[d] |
| 12 | 4-$ClC_6H_4$ | morpholine | Ph | 90,[d] 88[c] |
| 13 | 4-$MeOC_6H_4$ | morpholine | Ph | 81[d] |
| 14 | 4-$MeC_6H_4$ | morpholine | Ph | 96[d] |
| 15 | 4-$FC_6H_4$ | morpholine | Ph | 92[d] |
| 16 | 4-$i$Pr$C_6H_4$ | morpholine | Ph | 88[d] |
| 17 | 3-$O_2NC_6H_4$ | morpholine | Ph | 93[d] |
| 18 | 2-$ClC_6H_4$ | morpholine | Ph | 91[d] |
| 19 | 2-$HOC_6H_4$ | morpholine | Ph | 95 |
| 20 | cyclohexyl | piperidine | Ph | 95 |
| 21 | cyclohexyl | pyrrolidine | Ph | 96 |
| 22 | cyclohexyl | $R^2 = R^3$ = ethyl | Ph | 95 |
| 23 | cyclohexyl | $R^2 = R^3$ = allyl | Ph | 97 |
| 24 | cyclohexyl | benzylamine | Ph | 81 |
| 25 | cyclohexyl | $R^2 = CH_2Ph$; $R^3 = CH_3$ | Ph | 94 |
| 26 | cyclohexyl | $R^2$ = Ph; $R^3 = CH_3$ | Ph | 96, 92[c] |
| 27 | cyclohexyl | $R^2 = R^3 = CH_2Ph$ | Ph | 98 |
| 28 | cyclohexyl | $R^2 = R^3 = i$Pr | Ph | 95 |

[a] Reaction conditions: aldehyde (1.0 mmol), amine (1.2 mmol), alkyne (1.2 mmol), Ni-Y (20 mg), 80 °C for 4 h. [b] Yield of isolated pure product. [c] Yield of gram-scale reaction with aldehyde (10 mmol), amine (12 mmol), alkyne (12 mmol). [d] For 10 h.

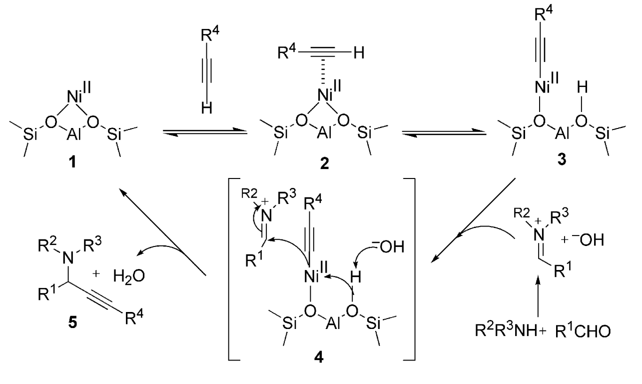
Table 4. Reusability of Ni-Y in the three-component coupling of aldehydes, alkynes and amines.[a]

| Reuse | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th | 8th |
|---|---|---|---|---|---|---|---|---|
| Yield[b] | 97 | 95 | 96 | 95 | 95 | 94 | 95 | 94 |

[a] Cyclohexanecarbaldehyde (3.0 mmol), morpholine (3.2 mmol), phenylacetylene (3.2 mmol), Ni-Y (60 mg), 80 °C for 4 h. [b] Yield of isolated product.

In Ni-catalyzed cross-couplings, both $Ni^0$ and $Ni^{II}$ reagents are normally employed as Ni sources, though the $Ni^0$ species is generally regarded as being the catalytically active one. Although utilization of $Ni^0$ reagents, such as $Ni(COD)_2$ and $Ni(PPh_3)_4$, as catalysts is the simplest and most direct route,[12–14,16,21] these nickel sources are difficult to handle because of their high air sensitivity and thermal instability. By contrast, $Ni^{II}$ compounds, which are readily available and are convenient to handle, are more preferred as pre-catalysts from a practical point of view. However, in some instances[29] these $Ni^{II}$ catalysts need to be activated (i.e, converted in situ to zerovalent nickel). On the other hand, reports are available for direct $Ni^{II}$-catalyzed reactions.[30] Most of these nickel-catalyzed couplings[12–14,16,29e] involve the following three steps: sequential oxidative addition, transmetalation and reductive elimination.

By analogy with these reports, a plausible reaction pathway is proposed as shown in Scheme 1. In the present study $Ni^{II}$-Y itself acts as the active catalyst generating an initial nickel(II) acetylide intermediate **3** by the reaction between a $Ni^{II}$ species in zeolite with a terminal alkyne with subsequent cleavage of one of the oxo bridges in the zeolite. This nickel acetylide intermediate reacts with the iminium ion generated in situ from aldehyde and amine to give the corresponding propargylamine, and the $Ni^{II}$-Y catalyst is regen-



Scheme 1. Possible mechanism of $Ni^{II}$-Y-catalyzed three-component coupling.

erated for subsequent reactions. The fact that $Ni^{2+}$ essentially remains unchanged, is evident from an analysis by UV-DRS, which shows the presence of only $Ni^{2+}$ before and after the reaction.

## Conclusions

A very highly efficient nickel-catalyzed three-component coupling of aldehyde, alkyne and amine by C–H activation has been achieved under solvent-free conditions. Whereas previous protocols require an inert gas, the present methodology proceeds readily in the presence of atmospheric oxygen. This procedure is also environmentally friendly as it does not require any organic solvents. Excellent yields, milder reaction conditions and a solvent-free protocol are other notable advantages of this method. Besides, catalyst recovery and reusability are also achieved by using this procedure. Detailed studies on the mechanism and applications of the current Ni-catalyzed additions to carbonyl compounds are underway.

## Experimental Section

**General Procedure for the Ni-Zeolite-Catalyzed Condensation of Aldehydes, Amines, and Alkynes:** Aldehydes (1.0 mmol), amines (1.2 mmol), and then alkynes (1.2 mmol) were successively added to Ni-Y (20 mg). After stirring at 80 °C for the respective time, the mixture was diluted with dichloromethane. After removing the catalyst by filtration, followed by solvent evaporation, the resulting crude product was finally purified by column chromatography (silica gel). The recovered catalyst was thoroughly washed with ethyl acetate and used for the next run.

**Supporting Information** (see footnote on the first page of this article): Experimental procedure and spectroscopic data for all compounds.

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