A Novel Approaches For Organic Compound Reactions By Using Nickel Catalyst

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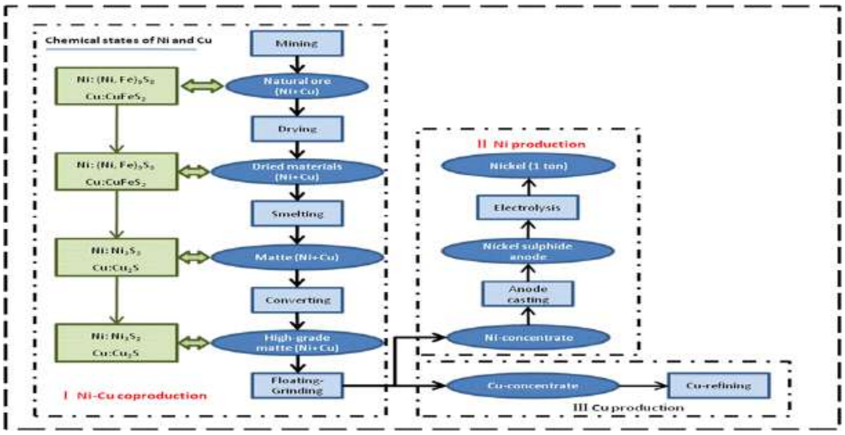
Abstract- **A nickel catalyst is a substance containing that speeds up chemical reactions is a element it has symbol [Ni] and atomic number 28. Nickel is one of four elements others are iron, cobalt, and gadolinium) Nickel has two atomic electron configurations, [Ar] $3d^8 4s^2$ and [Ar] $3d^9 4s^1$,Used for the selective hydrogenation of dienes and alkynes in processes Catalyze the decomposition of ammonia and urea to produce hydrogen, often integrated with renewable energy sources for green hydrogen production by Organic synthesis: Widely used in cross-coupling reactions to form carbon-carbon and carbon-heteroatom bonds.**Where as utilization for **Industrial processes for breaking down methane into hydrogen and carbon dioxide, and for hydrogenating unsaturated fatty acids. There are many forms exist in numerous forms, such as alloys, nickel supported on metal oxides, Raney Nickel, nickel salts, and organometallic complexes. Nickel catalysts are known for being inexpensive, accessing multiple oxidation states of Nickel catalysts are known for being inexpensive, accessing multiple oxidation state Ni(0), Ni(II), Ni(III), Ni(IV), and coming in various forms, including alloys, metal oxides, and the porous form known as Raney Nickel.Otherwise used for Nickel boride is the common name of materials composed chiefly of the elements nickel and boron that are widely used as catalysts in organic chemistry. The H_2/Ni_2 system will not hydrogenolyse ethers, alcohols, aldehydes, amines and amides as it reduces alkenes in preference, even under forcing conditions.**

Key Words: Nickel(Ni),Organic Reactions, Ni-combined-Reaction, Ni-catalyst.

I. INTRODUCTION

There are some metals which required for plant growth at a low concentration but they are toxic at higher concentration health risks associated. Nickel is a solid silver white hard transition element and common uses are in stainless steel, coin, jewelry and in various forms of dental care. Few metals likewise nickel easily accumulated in plant, exhibiting toxic effects on germination and plant growth. Metal toxicity depends upon the level and duration of dose.



Nickel is emitted in the environment due to industrial, cement manufacturing, metal smelter, refineries and anthropogenic activities. The excess level of nick germination and plant growth.

The development of new methods for forming carbon–carbon bonds is essential for advancing the synthesis of biologically active molecules. Achieving high selectivity in these reactions remains a significant challenge in organic chemistry.

Here we show that a nickel-catalyzed β-arylation and benzylation of 2′-hydroxychalcones enables the efficient synthesis of chalcone derivatives. This transformation is directed by the substrate’s intrinsic hydroxy group, resulting in high chemoselectivity and avoiding unwanted by products.This approach offers a promising strategy for developing therapeutic agents and functional materials based on the chalcone structure.

II. OBJECTIVE

Nickel is a versatile catalyst used in a wide range of organic reactions, including.
1) HYDROGENATION,
2) CROSS-COUPLING,
3) DEHYDROGENATION,
4) POLYMERIZATION
5) PHOTOREDOX CATALYSIS
6) β-ARYLATION

Common nickel catalysts:

- ✓ Raney nickel
- ✓ Homogeneous nickel catalysts
- ✓ Heterogeneous nickel catalysts
- ✓ Nickel (0) & Nickel (II)

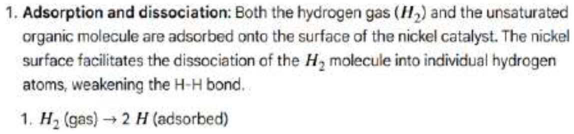
1) HYDROGENATION:

Hydrogenation is the chemical process of adding hydrogen to a compound, typically to convert an unsaturated molecule with double bonds into a saturated one with single bonds. This reaction is often performed using a catalyst, such as nickel.

Horiuti-Polanyi mechanism:

Describes nickel-catalyzed hydrogenation: hydrogen molecules and unsaturated compounds adsorb onto the nickel catalyst surface. The nickel weakens the H-H bond, causing the hydrogen molecule to dissociate into two hydrogen atoms. These hydrogen atoms add sequentially to the carbon atoms of the double bond, forming a half-hydrogenated intermediate before adding the second hydrogen to create a saturated product.

Step-by-step mechanism:



1. **Adsorption and dissociation:** Both the hydrogen gas (H_2) and the unsaturated organic molecule are adsorbed onto the surface of the nickel catalyst. The nickel surface facilitates the dissociation of the H_2 molecule into individual hydrogen atoms, weakening the H-H bond.

1. H_2 (gas) → 2 H (adsorbed)

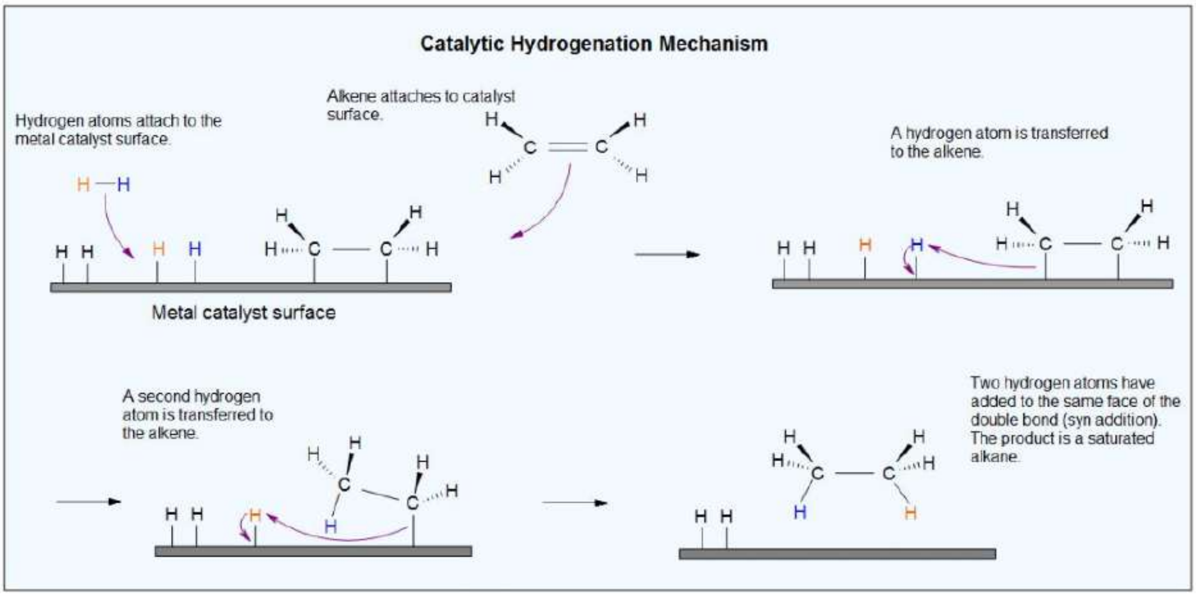
2. Half-hydrogenation: A single hydrogen atom adds to one of the carbon atoms in the double bond. The other carbon atom remains bonded to the catalyst surface, creating a "half-hydrogenated" intermediate.

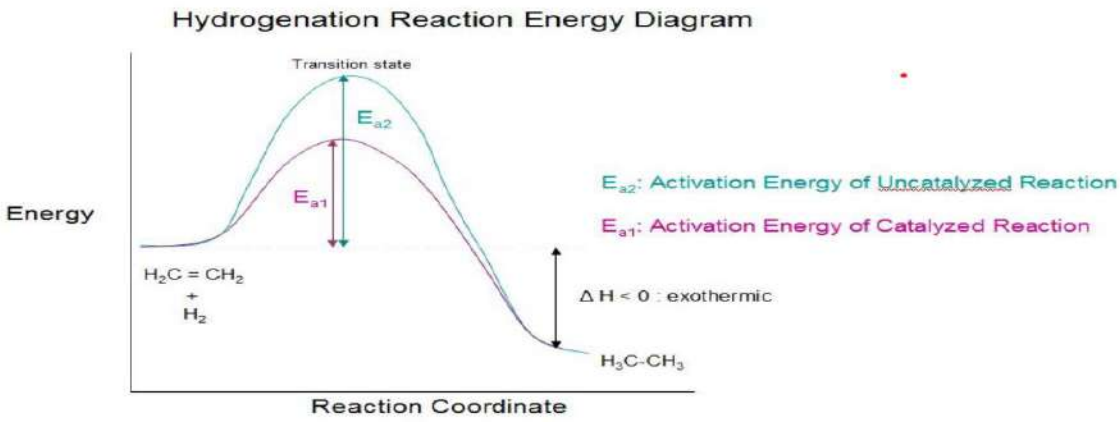
3. Second hydrogenation: A second hydrogen atom from the catalyst surface adds to the other carbon atom of the original double bond.

4. Product desorption: The now saturated molecule detaches, or desorbs, from the catalyst surface, freeing up the active site for the next reaction cycle.

5. Catalyst regeneration: The catalyst is regenerated and ready to start the process again, as it is not consumed in the reaction.

- Catalyst role: The nickel catalyst provides a surface to bring the reactants together and lowers the activation energy, allowing the reaction to proceed more quickly and under milder conditions than it otherwise would.
- Syn addition: The adsorption of the molecule onto the flat catalyst surface leads to the addition of the two hydrogen atoms to the same side of the double bond, a process called *syn* addition.
- Reduction: This process is a reduction reaction, as the alkene gains hydrogen atoms and the carbon atoms' oxidation state decreases.





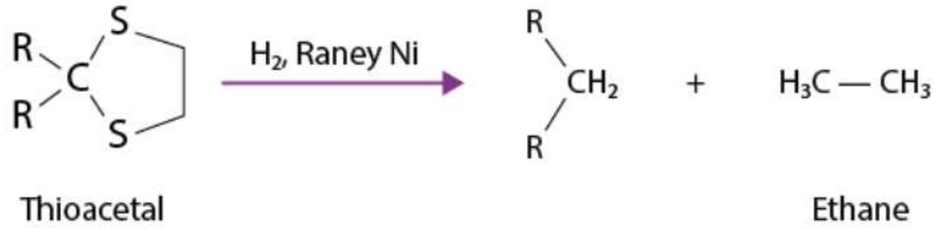
Reaction: Benzene reacts with hydrogen gas over a nickel catalyst (often Raney nickel) to form cyclohexane.

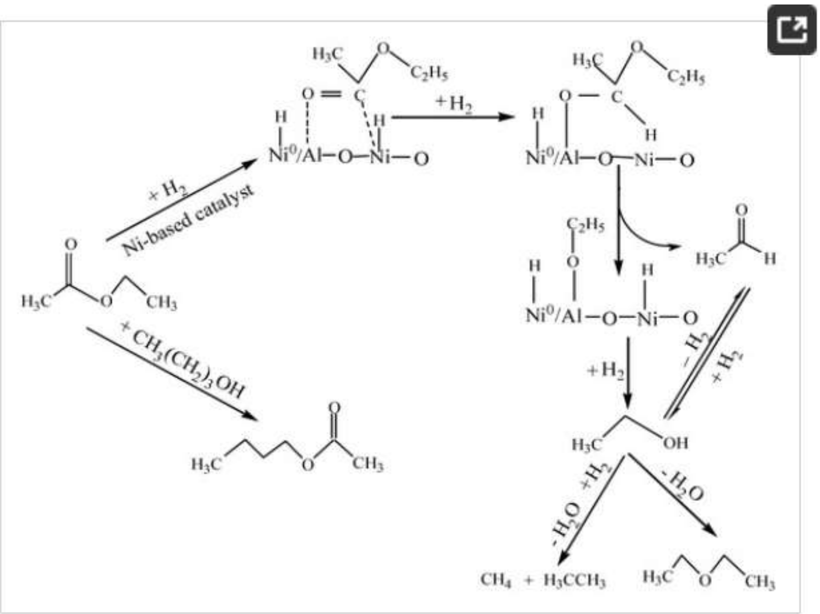
$$C_6H_6 + 3H_2 \xrightarrow{Ni} C_6H_{12}$$

Dinitrotoluene to Diaminotoluene: Raney nickel is used to hydrogenate dinitrotoluene, a key intermediate in the production of polyurethane foam.

Glucose to Sorbitol: The sugar substitute sorbitol is produced by hydrogenating glucose, with Raney nickel acting as the catalys

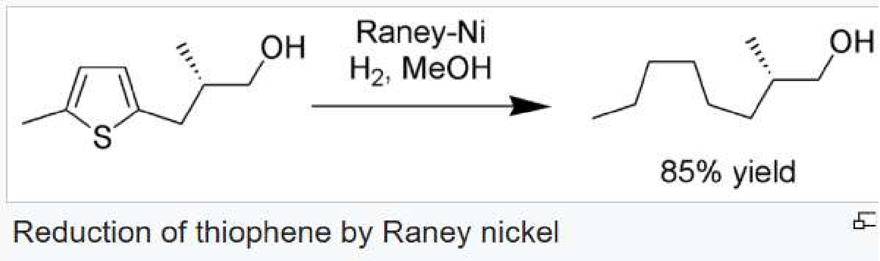
Raney nickel also has the ability to catalyse certain desulfurization reactions. For example, hydrocarbons can be obtained from the reduction of thioacetal with the help of Raney nickel (illustrated below).





Scheme 2. The proposed reaction pathway for hydrogenation of ethyl acetate

According to the experimental results and the related literatures, a plausible reaction pathway for hydrogenation of ethyl acetate to ethanol is proposed as Scheme 2. In the pathway, ethyl acetate is firstly absorbed on the active Ni^{2+} cation sites in association with aluminium oxide through a relatively weak acyl structure, the metal active sites in the catalysts are responsible for the carbonyl activation, which also seems to be the reason for the increased conversion.



Reduction of thiophene by Raney nickel

Raney nickel will remove the sulfur of thiophene to give a saturated alkane

CROSS-COUPLING

Mechanistic aspects

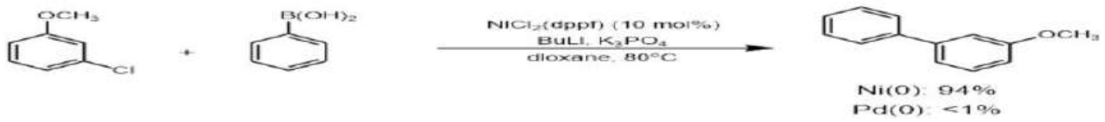
- Nickel(0) is often the catalytically active species.
- The catalytic cycle typically involves oxidative addition of an organohalide to a nickel(0) species.
- For C(sp³)-C(sp²) coupling, the mechanism can involve a radical intermediate pathway, where nickel(0) adds to an electrophile, then undergoes reductive elimination.
- In some reactions, an exogenous reductant like manganese or zinc is necessary to turn over the catalyst and complete the cycle

Common nickel-catalyzed coupling reactions

- Negishi coupling: A reaction between an organozinc reagent and an organohalide, catalyzed by nickel or palladium, to form a new C-C bond.

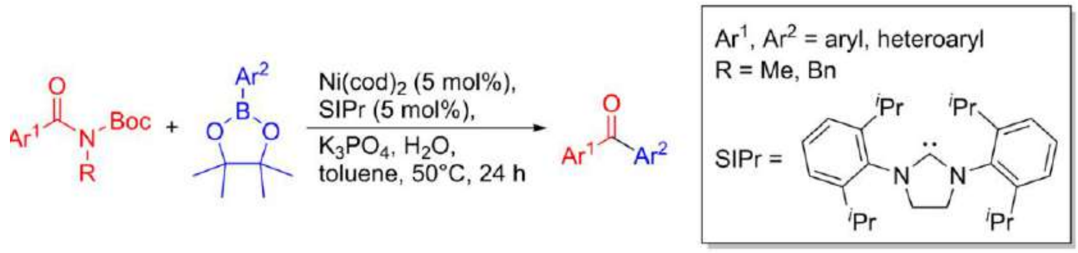
- Suzuki-Miyaura coupling: While traditionally associated with palladium, nickel catalysts have been developed for this reaction, including coupling with previously challenging substrates like aliphatic mesylates.

- Various catalytic uses of metals other than palladium (especially nickel) have been developed.[29] The first nickel catalyzed cross-coupling reaction was reported by Percec and co-workers in 1995 using aryl mesylates and boronic acids.



Amide coupling

Nickel catalysis can construct C-C bonds from amides. Despite the inherently inert nature of amides as synthons, the following methodology can be used to prepare C-C bonds. The coupling procedure is mild and tolerant of myriad functional groups, including: amines, ketones, heterocycles, groups with acidic protons..

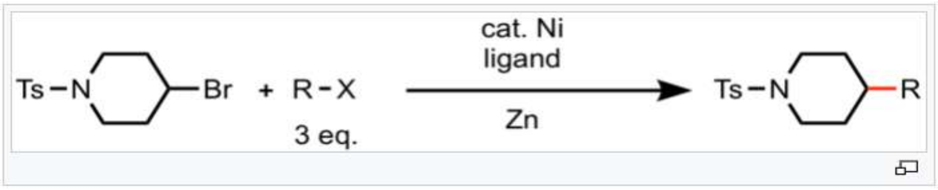


The synthesis of a tubulin-binding compound (antiproliferative agent) was carried out using a trimethoxybenzamide and an indolyl pinacolatoboron coupling partner on a gram scale.

Cross-electrophile coupling: A more recent development where two electrophiles are coupled together in the presence of a nickel catalyst and a reductant, such as zinc.

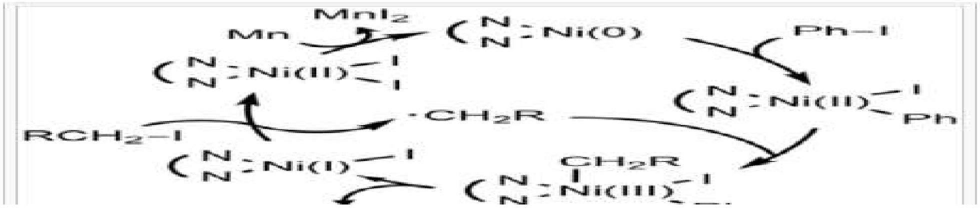
This description refers to a significant advancement in synthetic organic chemistry, often called reductive cross-electrophile coupling (RCEc) or cross-electrophile coupling (XEC)

Using excess amount of one reagent can provide synthetically useful yields of cross-coupled product when the starting reagents have similar reactivity. (e.g. coupling between two alkyl halides). This strategy has been used with a Ni catalyst and zinc as reductant. Dimerization of the more reactive alkyl halide was the major byproduct.

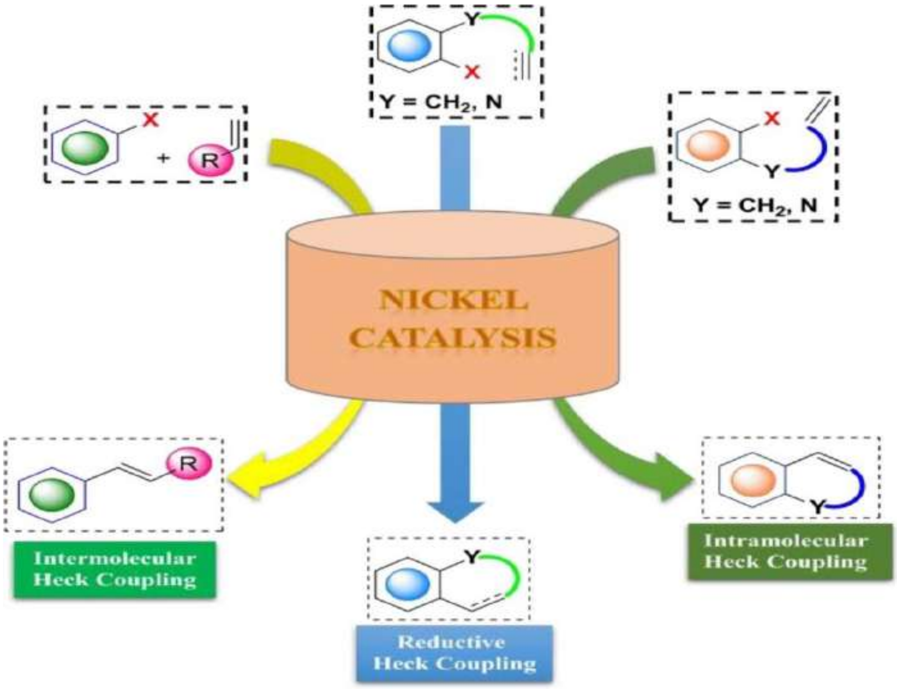


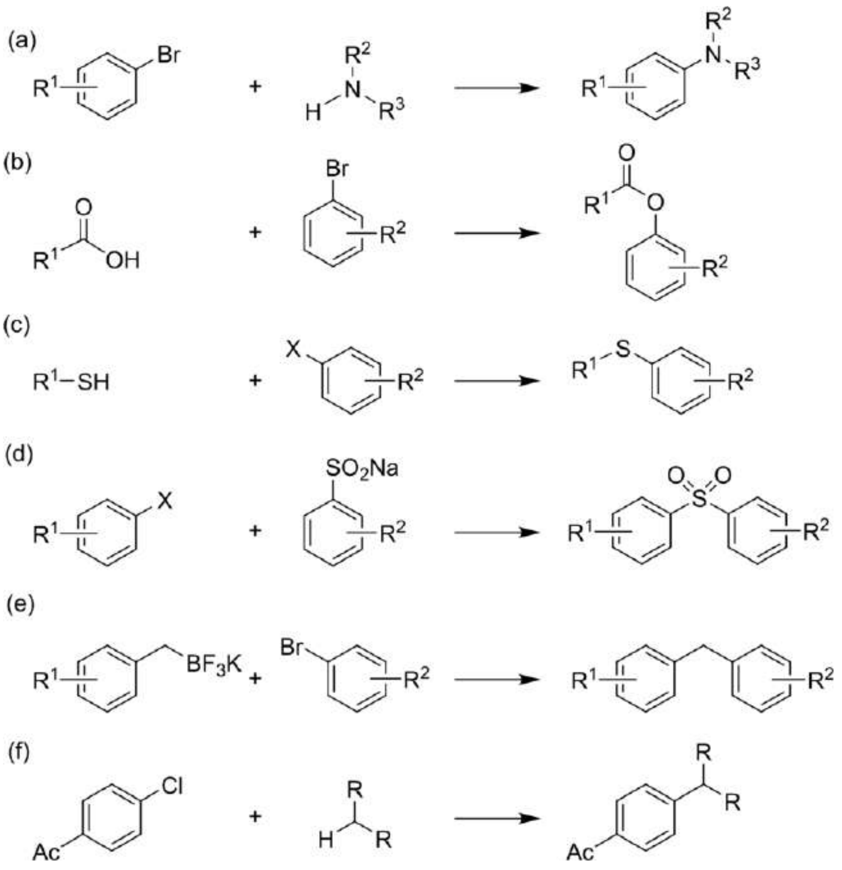
Alkyl-alkyl (Csp3-Csp3) cross electrophile coupling using metallaphotoredox catalysis has also been achieved.[6] In this case, small alkyl electrophiles were used excess amount. Tris(trimethylsilyl)silanol can be employed as a halogen abstractor in combination with photoredox and Ni catalysis.

- Coupling of Two Electrophiles: Unlike traditional cross-coupling reactions (like Suzuki, Stille, or Negishi couplings) which join an electrophile and a nucleophile (organometallic reagent), this method couples two different electrophiles .
- Catalyst: A nickel catalyst is typically employed to facilitate the reaction.
- Reductant: An external terminal reductant, such as zinc metal or manganese, is used in a stoichiometric amount to drive the catalytic cycle.



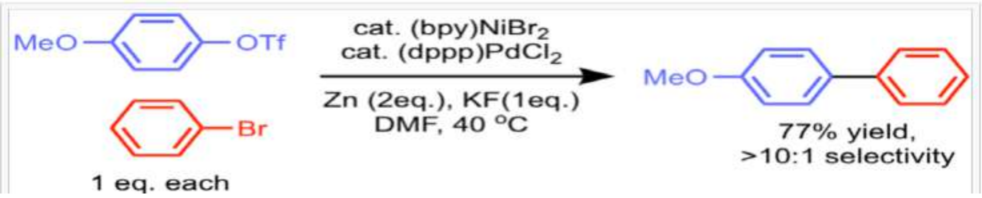
Transition metal catalyzed cross-coupling reactions are important in chemical synthesis for the formation of C−C and C-heteroatom bonds. Suitable catalysts are frequently based on palladium or nickel, and lately the cheaper and more abundant first-row transition metal element has been much in focus. The combination of nickel catalysis with photoredox chemistry has opened new synthetic possibilities, and in some cases electronically excited states of nickel complexes play a key role. This is a remarkable finding, because photo-excited metal complexes are underexplored in the context of organic bond-forming reactions, and because the photophysics and the photochemistry of first-row transition metal complexes are underdeveloped in comparison with their precious metal-based congeners. Consequently, there is much potential for innovation at the interface of synthetic-organic and physical-inorganic chemistry. This Minireview highlights recent key findings in light-driven nickel catalysis and identifies essential concepts for the exploitation of photoactive nickel complexes in organic synthesis.





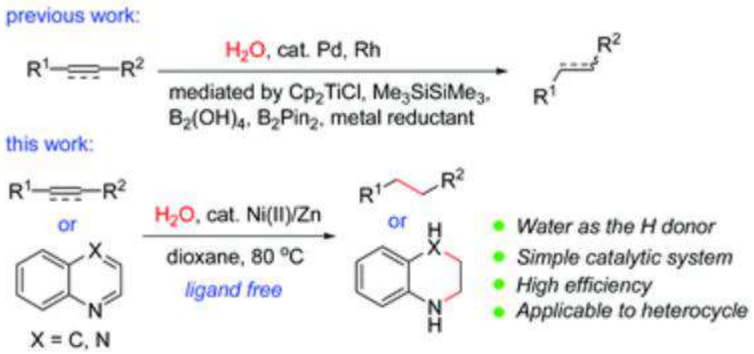
Since the development of Buchwald-Hartwig amination as a convenient methodology applicable to a wide range of substrates under relatively mild conditions, typically using palladium catalysts, further variations of this methodology were developed over the years, aiming to engage nonprecious metal catalysts, especially nickel.

Reductive cross coupling of two different aryl (pseudo)halide was achieved. Use of two different metals (Ni and Pd) was essential for the observed cross-selectivity of chemically similar two reactants. Aryl triflates generally prefer oxidative addition to the electron-rich Pd(0) catalyst whereas Ni(0) selectively reacts with aryl bromides.



DEHYDROGENATION

nickel-catalyzed transfer hydrogenation reaction of alkenes and alkynes using water as the hydrogen source has been developed. The method features the use of inexpensive and air-stable nickel(II) salt as the pre-catalyst and zinc powder as a reducing agent, allowing the TH reaction to occur under mild reaction conditions with a wide substrate scope and functional group tolerance. No ligand was required for this reaction. The reaction has also been applied successfully to the reduction of nitrogen-containing heterocycles.



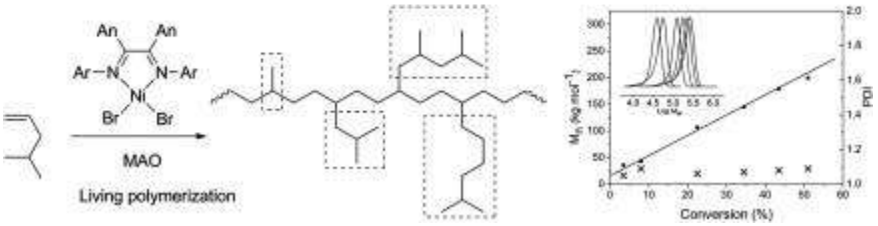
The method proceeds with high generality, a wide substrate scope and good functional group tolerance. Remarkably, the reaction is also applicable to the reduction of nitrogen-containing heterocycles, which has not been achieved in nickel-catalyzed TH reactions using water.

POLYMERIZATION

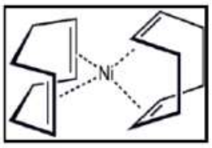
A common example of a nickel catalyst for polymerization is the α-diimine nickel complex, used to polymerize monomers like 4-methyl-1-pentene. Another example is (I) α-diimine nickel catalysts, which are a key type of catalyst for ethylene polymerization, as described in nature.

α-Diimine nickel complexes

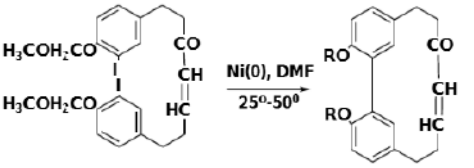
- Function: These catalysts are used for the polymerization of olefins, such as 4-methyl-1-pentene.
- Mechanism: They can perform "living/controlled" polymerization under specific conditions, allowing for control over the polymer's structure.
- Structure: They often work with an activator like methylaluminoxane (MAO).
- Phosphine-phenolate nickel catalysts: These are effective for ethylene polymerization and copolymerization with polar monomers like acrylates.
- SHOP-type nickel catalysts: This is a specific type of nickel catalyst used in ethylene polymerization.
- Salicylaldimine nickel catalysts: These are another class of catalysts used for ethylene polymerization.



- Nickel(II) α-diimine catalysts: These are a widely studied class of catalysts for olefin polymerization.
    - For ethylene: Nickel(II) α-diimine catalysts can produce highly branched polyethylenes with high molecular weights, even at high temperatures. Highly reactive, air-sensitive source of zero-valent nickel Ni(0)Ni open parent close parent- Ni(0)widely used in organic synthesis and catalysis. Its key reactions involve ligand exchange and oxidative addition, making it a versatile precursor to other nickel complexes and a powerful catalyst.



The reaction was first used for the synthesis of an antileukemic lignan, amulsone (1.045), obtained from the wood of Reduction becomes a competing reaction and moderate yields in case of ortho-substituted aryl iodides such as (1.044) is obtained. However, o,o-disubstituted aryl halides cannot be coupled in these conditions.Addition of a proton source forms the reduction product. recorded details of vinyl and aryl halides with Ni(0) complexed



1.044

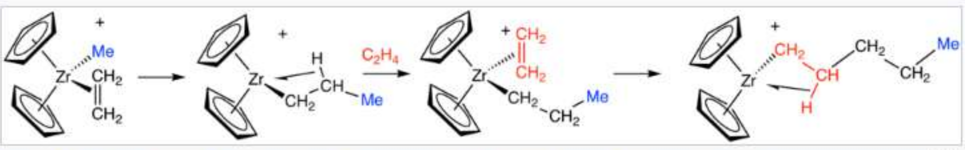
1.045(R = CH_2OCH_3), 46%
1.046 (R = H), 72%

- For 4-methyl-1-pentene: They are used to polymerize this branched olefin, leading to amorphous elastomers with a variety of branch structures depending on the catalyst's design and reaction conditions.complexes that are used for specific types of polymerization, such as:
- Bis(1,5-cyclooctadiene)nickel(0): This can be a precursor for creating other nickel catalysts used in polymerization and cross-coupling reactions.
- Nickel(II) catalysts with phosphine ligands: These can be used to catalyze the living polymerization of certain monomers like diazoacetates, forming polycarbene homopolymers.

Chart 1. Strategies To Improve the Performance of Phosphine-Sulfonate Nickel Catalysts

- Ziegler-Natta-type systems: Nickel compounds, such as Ni(OOC 8H 15)$_2$, can be used in multi-component Ziegler-Natta catalyst systems for the polymerization of dienes like butadiene to produce polybutadiene.
- Ziegler-Natta catalyst systems are a class of coordination catalysts used in the industrial polymerization of olefins to produce high molecular weight and stereoregular polymers like polyethylene and polypropylene. They are fundamentally important to the modern plastics industry, responsible for millions of tons of polyolefin production annually.
- Mechanism

The polymerization process generally proceeds through a coordination-insertion mechanism, where the olefin monomer coordinates to the vacant site on the transition metal center and then inserts into the growing polymer chain attached to the metal. The process creates highly linear polymers with controlled molecular weights and specific stereochemical properties (e.g., isotactic or syndiotactic).

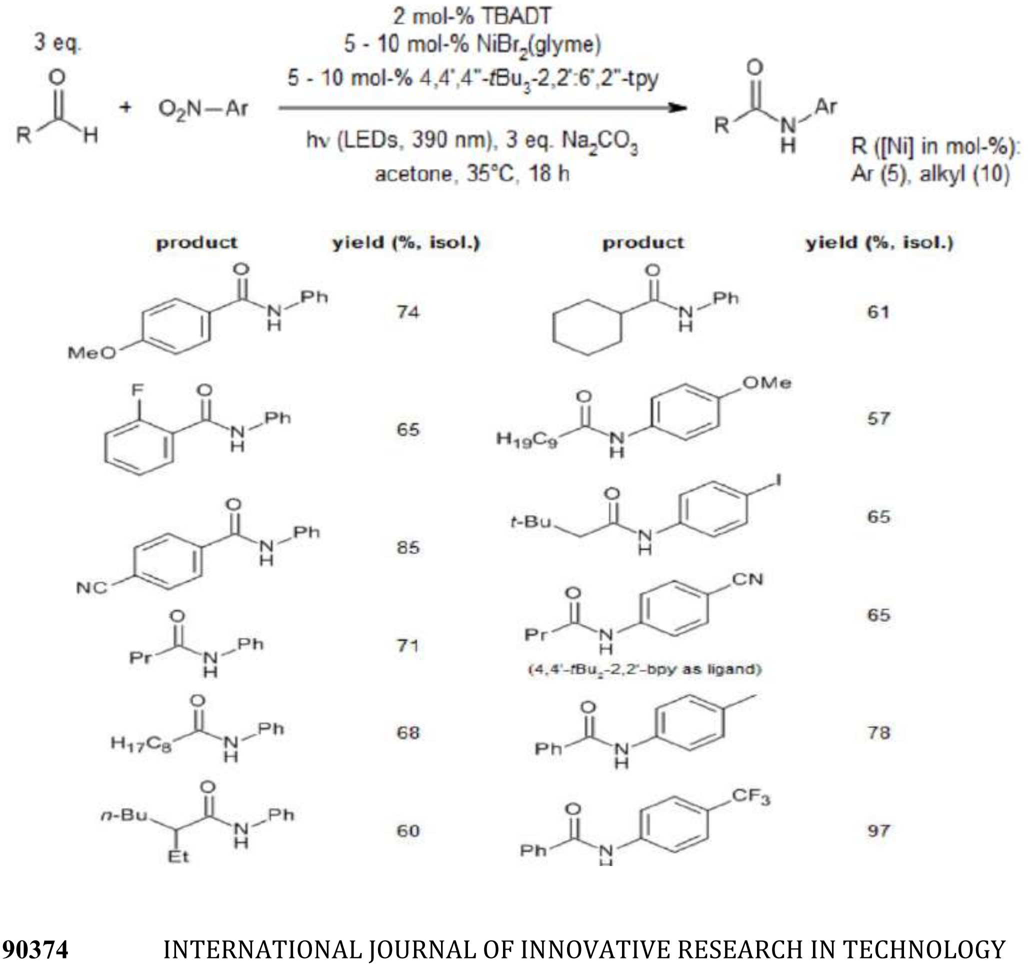


Simplified mechanism for Zr-catalyzed ethylene polymerization.

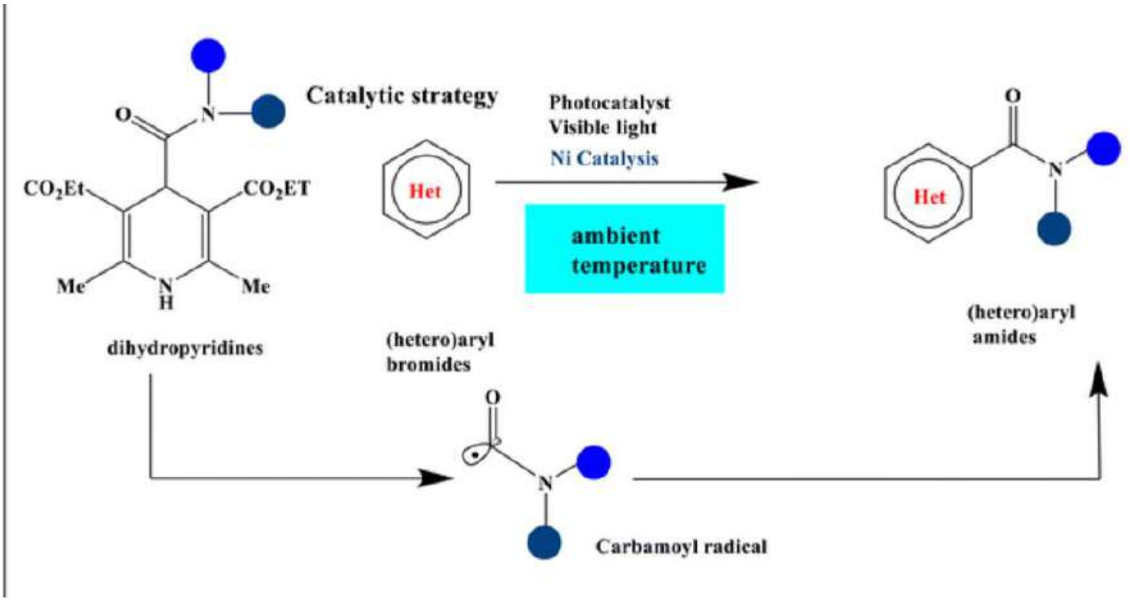
PHOTOREDOX CATALYSIS

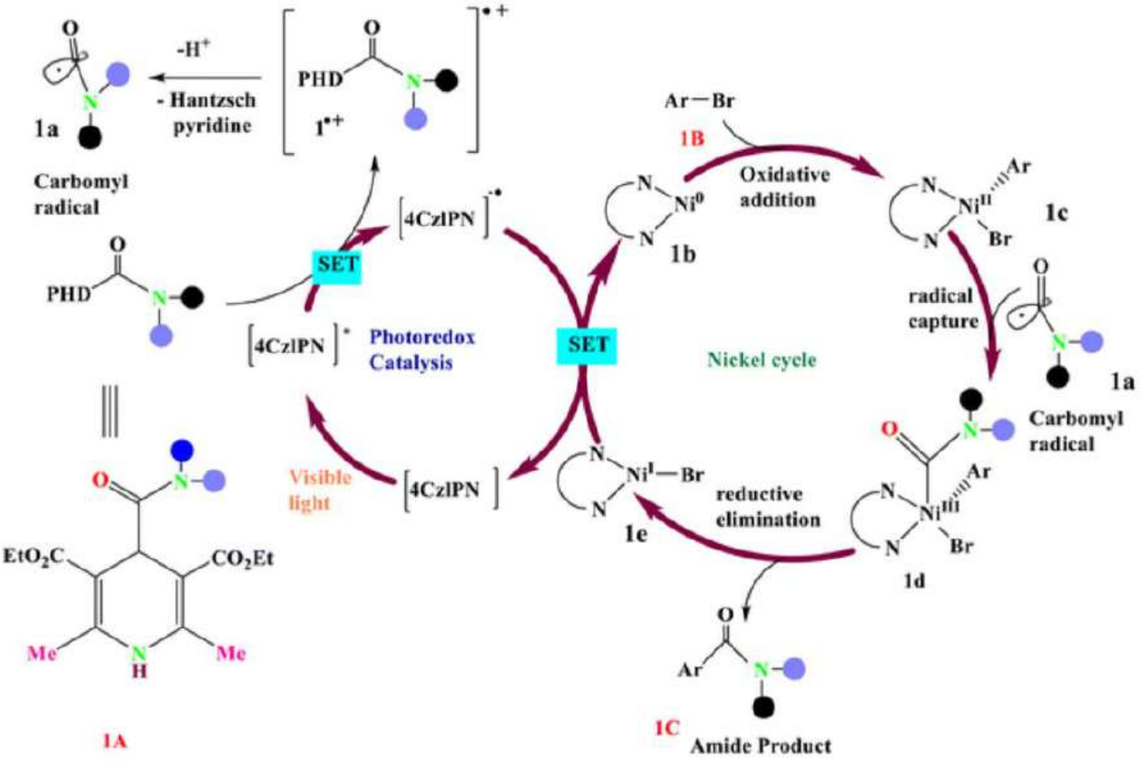
Photoredox nickel organic reactions combine nickel catalysis with photoredox catalysis to drive organic synthesis, enabling reactions under mild conditions by using visible light to activate substrates via single-electron transfer (SET). This synergistic approach uses nickel's ability to access multiple oxidation states and form new carbon-carbon and carbon-heteroatom bonds, while photoredox catalysts generate reactive intermediates from light energy. The synergy allows for the activation of traditionally inert bonds, leading to diverse transformations like coupling, amidation, and C–H functionalization.

- Dual catalysis: Combines a nickel catalyst with a photocatalyst to work together in a single reaction cycle.
- Mild conditions: Reactions can be run under visible light at room temperature, often without the need for strong reductants or oxidants.
- Efficient bond formation: Creates new bonds, particularly carbon–carbon and carbon–heteroatom bonds, in a highly efficient manner.
- Versatile oxidation states: Nickel can cycle through multiple oxidation states. Dual catalysis: Combines a nickel catalyst with a photocatalyst to work together in a single reaction cycle.
- Mild conditions: Reactions can be run under visible light at room temperature, often without the need for strong reductants or oxidants.
- Efficient bond formation: Creates new bonds, particularly carbon–carbon and carbon–heteroatom bonds, in a highly efficient manner.
- Versatile oxidation states: Nickel can cycle through multiple oxidation states to facilitate different steps in the catalytic cycle.
- Broad substrate scope: The reactions can tolerate a wide variety of functional groups and include diverse substrates like aldehydes, alkyl halides, and nitro arenes.
- Coupling reactions: Used for aryl alkylation, C–S cross-coupling, and the formation of C(sp2)-C(sp3) bonds.
- Amidation: Direct amidation of aldehydes with nitroarenes to form amides, using nickel and a photoredox catalyst to activate both substrates.
- C–H functionalization: A tool for activating and functionalizing C–H bonds under milder conditions compared to traditional methods.
- Alkene carbofunctionalization: A novel strategy for adding carbon-based groups across double bonds in alkenes.

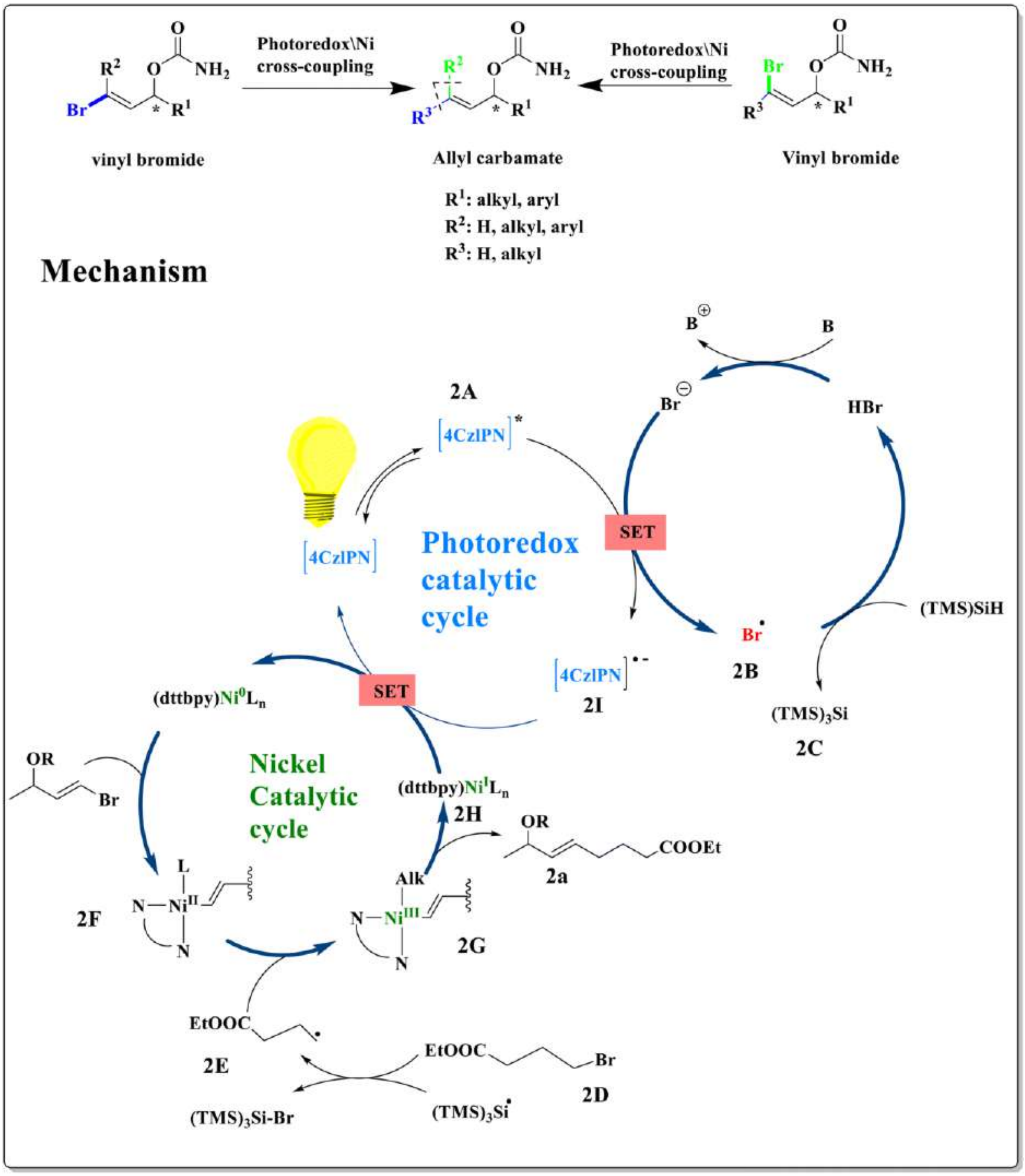


Nurtalya and coworkers described a one-electron method for catalytic amide (1C) synthesis that uses photoredox and nickel dual catalysis[5] to allow for the direct carbamoylation of (hetero) aryl bromides (1B).[4] The ability of the nickel catalyst to participate in radical capture activities and undergo oxidative addition with aromatic bromides 1B guaranteed the synthesis of the cross-coupled amide products 1C

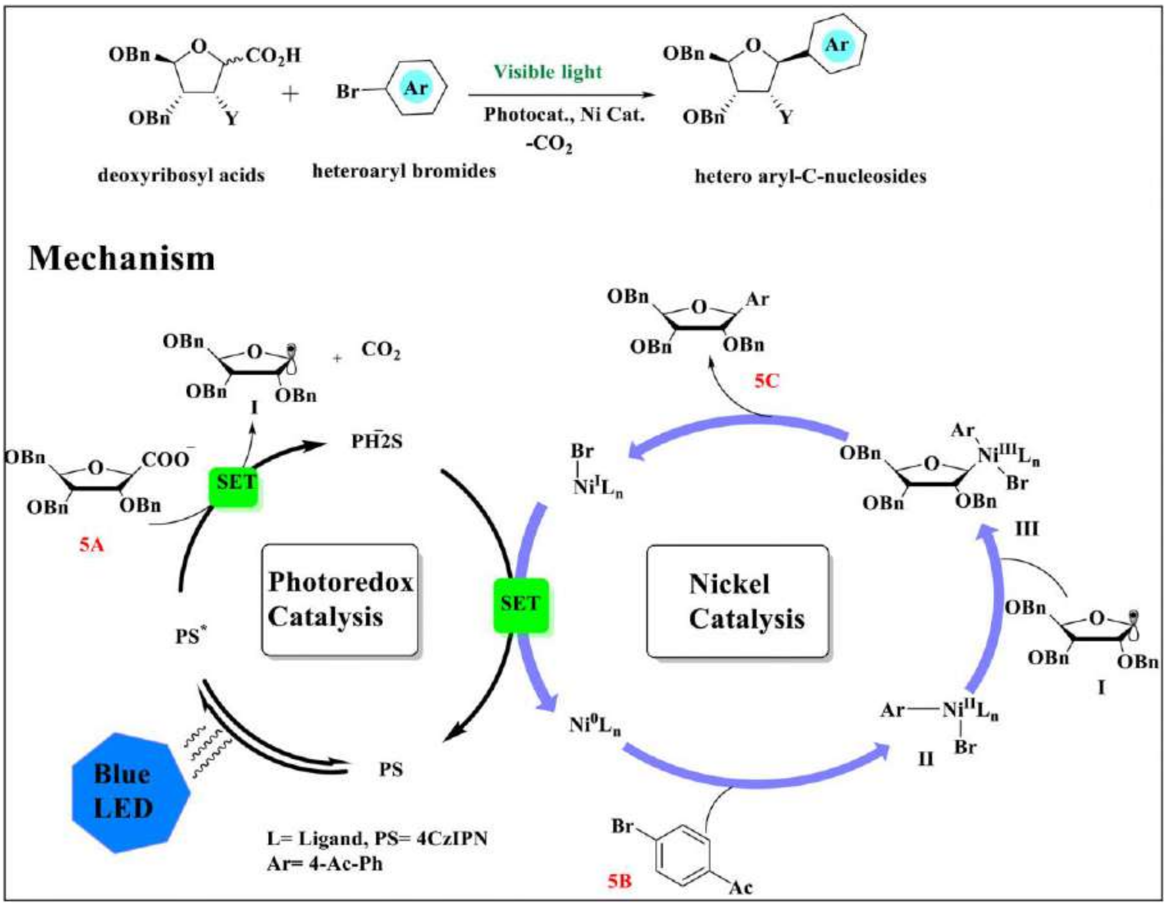




Proposed mechanism for the carbamoylation process catalyzed by photoredox and Ni catalysts.



nstead of photoredox-catalyzed decarboxylative cross-coupling, anomeric ribosyl/deoxyribosyl acids and aryl/heteroaryl bromides were converted to aryl\hetero-aryl-*C*-nucleoside. Initial excitation results in the production of the 4CzIPN (PS) in a photoexcited state (PS*).[41] The production of a sp^2 hybridized anomeric radical I and the photooxidative decarboxylation processes of 5A is made possible by the high reduction potential of the photoexcited state[37] of 4CzIPN (PS*).[44] The electrophilic Ni^{II}-aryl intermediate II is expected to be created in combination with that photoredox cycle by oxidatively adding to the aryl bromides 5B by two SET reductions of $(bpy)Ni(II)Br_2$ produced by the photocatalyst PS, generating active Ni^0 species (Ni^0Ln) *in situ* (Scheme 5). This Ni^{II} species produced a Ni^{III}-aryl-ribosyl complex III by quickly capturing anomeric ribosyl radical I. Following reductive elimination, this combination produced the Ni^I complex $(bpy)Ni^IBr$ and the intended product 5C

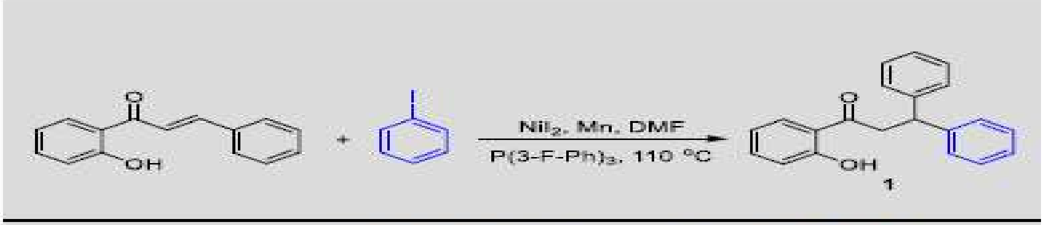


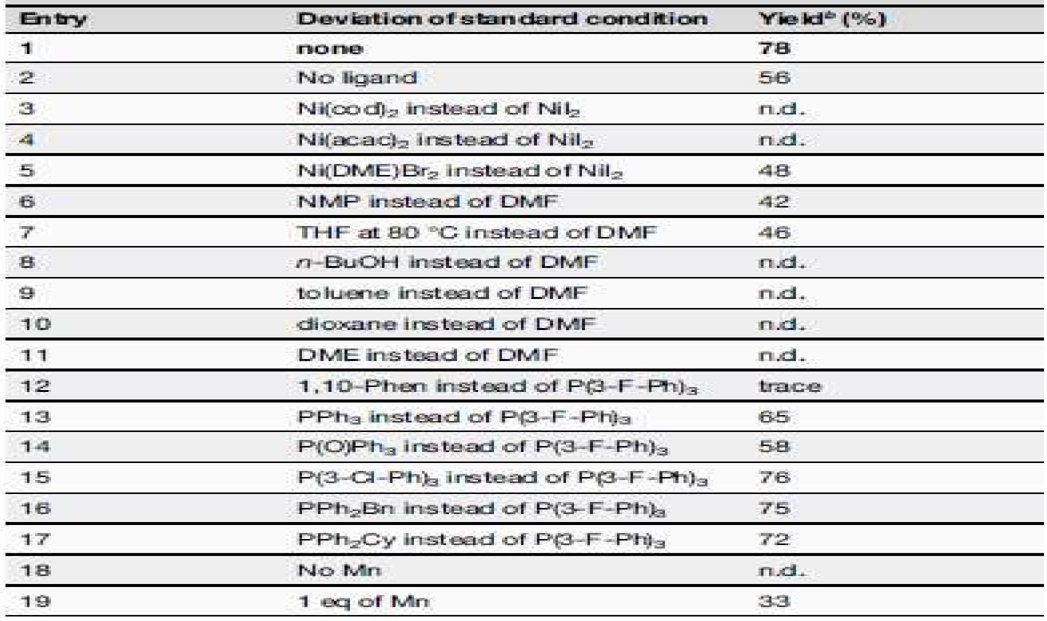
β-ARYLATION

Nickel-catalyzed β-arylation and benzylation of 2′-hydroxychalcones to access warfarin analogues.

Optimization of Reaction Conditions:

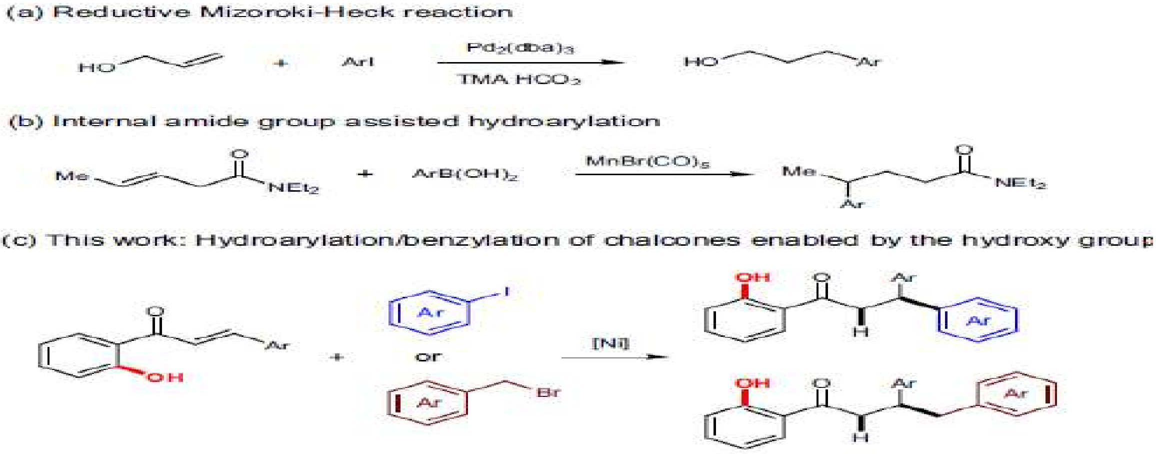
We selected 2’-hydroxychalcone and iodobenzene as model substrates for our study and conducted a comprehensive investigation of various parameters affecting the reaction (Table 1).The type of Ni catalyst was found to significantly influence the reaction yield. For example, neither $Ni(cod)_2$ nor $Ni(acac)_2$ produced any detectable product,whereas NiI_2 increased the yield to 56%, outperforming $Ni(DME)Br_2$ (Entries 1–5). DMF emerged as the optimal solvent, as substituting it with toluene, dioxane, n-BuOH, or DME inhibited the reaction, and both NMP and THF resulted in a notable decrease in yield (Entries 6–11, see Table S1 for more details). Although a ligand was not strictly necessary for this model reaction, the addition of an appropriate ligand further enhanced the yield and minimized byproducts from direct alkene reduction. Optimization revealed that nitrogencontaining ligands inhibited the reaction, while meta-substituted triphenylphosphine derivatives performed favorably (Entries 12–17). Additionally, both Mn and the Ni catalyst were essential, and reducing the equivalents of iodobenzene, orMn below 2.5 eq. significantly decreased the yield. Other types of reducing reagents were also explored, including Zn, $HSiEt_3$, $PhSiH_3$, andHCOOK. However, none of these alternatives provided a higher yield thanMn(see Table S2 for more details).Under the optimized conditions (Entry 1), product 1 was obtained with excellent selectivity and an isolated yield of 78%.



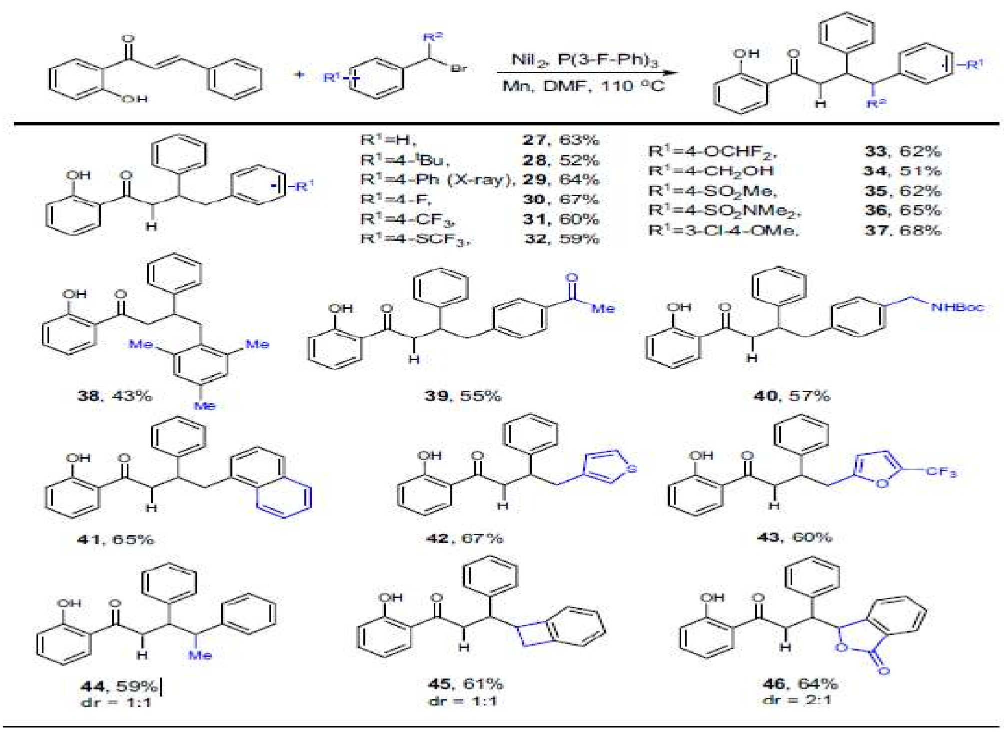


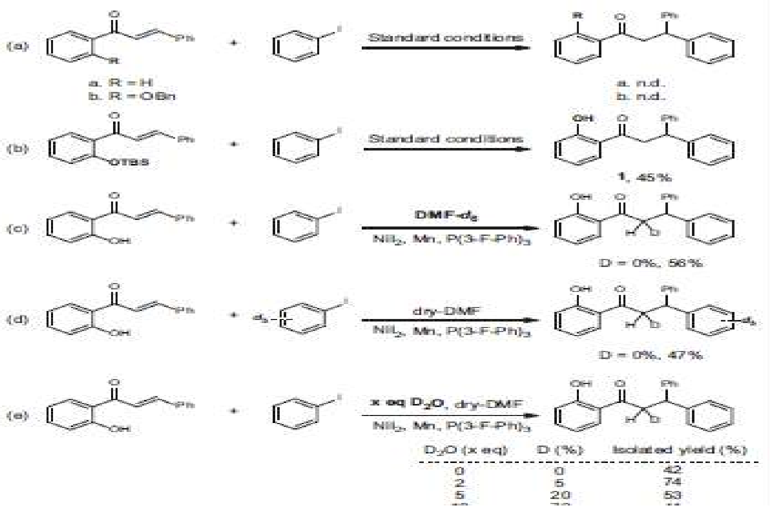
Entry	Deviation of standard condition	Yield^b (%)
1	none	78
2	No ligand	56
3	Ni(cod)$_2$ instead of NiI$_2$	n.d.
4	Ni(acac)$_2$ instead of NiI$_2$	n.d.
5	Ni(DME)Br$_2$ instead of NiI$_2$	48
6	NMP instead of DMF	42
7	THF at 80 °C instead of DMF	46
8	*n*-BuOH instead of DMF	n.d.
9	toluene instead of DMF	n.d.
10	dioxane instead of DMF	n.d.
11	DME instead of DMF	n.d.
12	1,10-Phen instead of P(3-F-Ph)$_3$	trace
13	PPh$_3$ instead of P(3-F-Ph)$_3$	65
14	P(O)Ph$_3$ instead of P(3-F-Ph)$_3$	58
15	P(3-Cl-Ph)$_3$ instead of P(3-F-Ph)$_3$	76
16	PPh$_2$Bn instead of P(3-F-Ph)$_3$	75
17	PPh$_2$Cy instead of P(3-F-Ph)$_3$	72
18	No Mn	n.d.
19	1 eq of Mn	33

Hydroarylation of alkenes. a Reductive Mizoroki-Heck reaction. b Internal amide groupassisted hydroarylation. c This work: Hydroarylation/ benzylation of chalcones enabled by the hydroxy group.

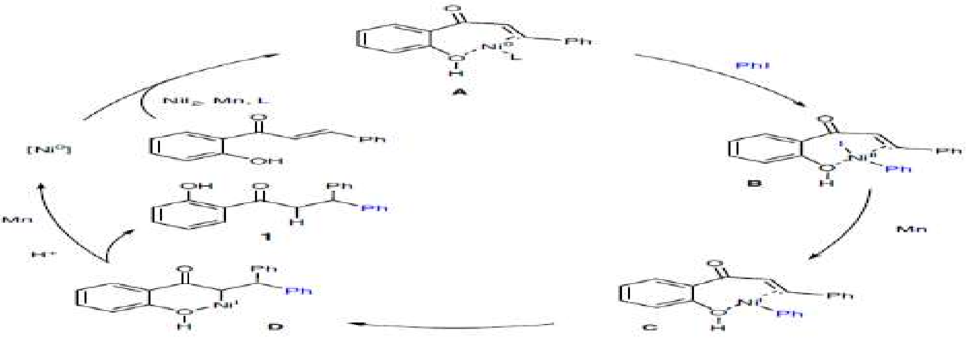


Based on the aforementioned control experiments and relevant literature Reports .we propose a possible reaction pathway, using the formationof compound 1 as an example (Scheme 7). Initially, the Ni(II) catalyst is reduced by Mn and coordinates with the substrate to form complex A. This complex then undergoes oxidative addition with iodobenzene, resulting in complex B. Subsequently, complex Bis further reduced by Mn, followed by migratory insertion into the olefin to generate the sixmembered metallacyclic intermediate D. Finally, intermediate Dundergoes protonation to yield product 1 and release the Ni(I) catalyst, which can be reduced by Mn to initiate the next catalytic cycle.





study via control experiments. a No product formation observed in the absence of the free 2'-hydroxy group. b Hydrolyzable protection of the 2'-hydroxy group (TBS) allows product formation. Control experiments with deuterated solvent or d reagent indicate that neither the solvent nor the substrate serves as the proton source. e Results suggest that water is the primary proton source incorporated into the product.



Raney nickel:

The nickel catalyst developed by Murray Raney, known as Raney nickel or "spongy nickel," is a highly porous, fine-grained solid widely used as a versatile catalyst in various industrial and organic synthesis applications. Its primary uses revolve around hydrogenation, dehydrogenation, and desulfurization reactions.

In the activation process, the alloy, usually as a fine powder, is treated with a concentrated solution of sodium hydroxide. The simplified leaching reaction is given by the following chemical equation:

$2 Al + 2 NaOH + 6 H_2O \rightarrow 2 Na[Al(OH)_4] + 3 H_2$

The formation of sodium aluminate ($Na[Al(OH)_4]$) requires that solutions of high concentration of sodium hydroxide be used to avoid the formation of aluminium hydroxide, which otherwise would precipitate as bayerite.[6] Hence sodium hydroxide solutions with concentrations of up to 5 M are used.

Alloy preparation

Raney nickel is pyrophoric and must be handled with care. This shipping container is filled with vermiculite to protect the sealed bottle inside.

The Ni–Al alloy is prepared by dissolving nickel in molten aluminium followed by cooling ("quenching"). Depending on the Ni:Al ratio, quenching produces a number of different phases. During the quenching procedure, small amounts of a third metal, such as zinc or chromium, are added to enhance the activity of the resulting catalyst. This third metal is called a "promoter".[6] The promoter changes the mixture from a binary alloy to a ternary alloy, which can lead to different quenching and leaching properties during activation

Macroscopically, Raney nickel is a finely divided, grey powder. Microscopically, each particle of this powder is a three-dimensional mesh, with pores of irregular size and shape, the vast majority of which are created during the leaching process. Raney nickel is notable for being thermally and structurally stable, as well as having a large Brunauer-Emmett-Teller (BET) surface area. These properties are a direct result of the activation process and contribute to a relatively high catalytic activity

Applications of Raney Nickel Catalyst

Raney nickel is valued for its high activity, structural stability, and cost-effectiveness compared to precious metal catalysts like platinum or palladium.

Industrial Applications

- Production of nylon precursors: Raney nickel is used to hydrogenate benzene to cyclohexane, which is then oxidized to adipic acid, a key raw material for producing polyamides like nylon.
- Food industry (hydrogenation of oils): It was originally developed for the industrial hydrogenation of liquid vegetable oils to produce solid fats, such as margarine and shortening, improving their texture and shelf life.
- Production of sorbitol: This catalyst is used to hydrogenate dextrose (glucose) into sorbitol, a sugar substitute used in many food and personal care products like toothpaste and sugar-free gum.
- Manufacturing of industrial solvents: It catalyzes the conversion of sulfolene to sulfolane, a solvent used in petroleum refining and natural gas production.
- Agrochemicals, pharmaceuticals, and personal care products: It is used in the synthesis of various intermediates for these industries, such as converting 2,4-dinitrotoluene to 2,4-toluenediamine for polyurethane foam production.
- Fuel cells: Raney nickel-based electrodes are used as a non-noble metal catalyst alternative for hydrogen electrodes in alkaline fuel cells due to their high activity and stability.

Organic Synthesis and Laboratory Applications

- Hydrogenation of multiple bonds: It is typically used for the reduction of compounds containing multiple bonds, such as:

  - Alkenes and alkynes to alkanes.
  - Nitro compounds ($R-NO_2$) to amines ($R-NH_2$).
  - Nitriles (R-CN) to primary amines ($R-CH_2NH_2$).
  - Carbonyl compounds (aldehydes/ketones) to alcohols.
- Desulfurization: A key application is the removal of sulfur from organic compounds, as seen in the Mozingo reduction of thioacetals into hydrocarbons. It is unique among catalysts for its tolerance to some sulfur compounds during a reaction, although the sulfur is consumed by the nickel.
- Dehydrogenation reactions: Raney nickel can also be employed for dehydrogenation processes, such as the dehydrogenation of menthadienes or isopropanol.

HOMOGENEOUS NICKEL CATALYSTS

A homogeneous catalyst is a substance that speeds up a chemical reaction by being in the same physical state (phase) as the reactants, typically dissolved in a solvent (liquid phase), allowing for uniform mixing, high activity, and excellent selectivity, with common examples including acid catalysts (H- raised to the positive power$H+$ions) and soluble transition metal complexes, though separating them post-reaction can be tricky.

Homogeneous nickel catalysts are soluble nickel complexes (often with phosphine or N-heterocyclic carbene ligands) that work in the same phase as reactants, offering high selectivity for forming C-C & C-Heteroatom bonds, hydrogenation, and various reductions, despite challenges in separation from products, with examples like Ni(0) complexes and Ni(II)-NHC systems being key in modern organic synthesis.

- The nickel catalyst and reactants exist in the same liquid phase (solution), allowing for intimate contact and precise control.
- Versatility: Nickel's ability to switch oxidation states makes it excellent for many transformations, including C-C coupling, hydrogenation, and hydroamination.
- Ligands are Key: Ligands (like phosphines, NHCs) tune nickel's reactivity, forming highly active species for specific reactions, such as Ni(0) or Ni(II)-NHC complexes.

MECHANISM:

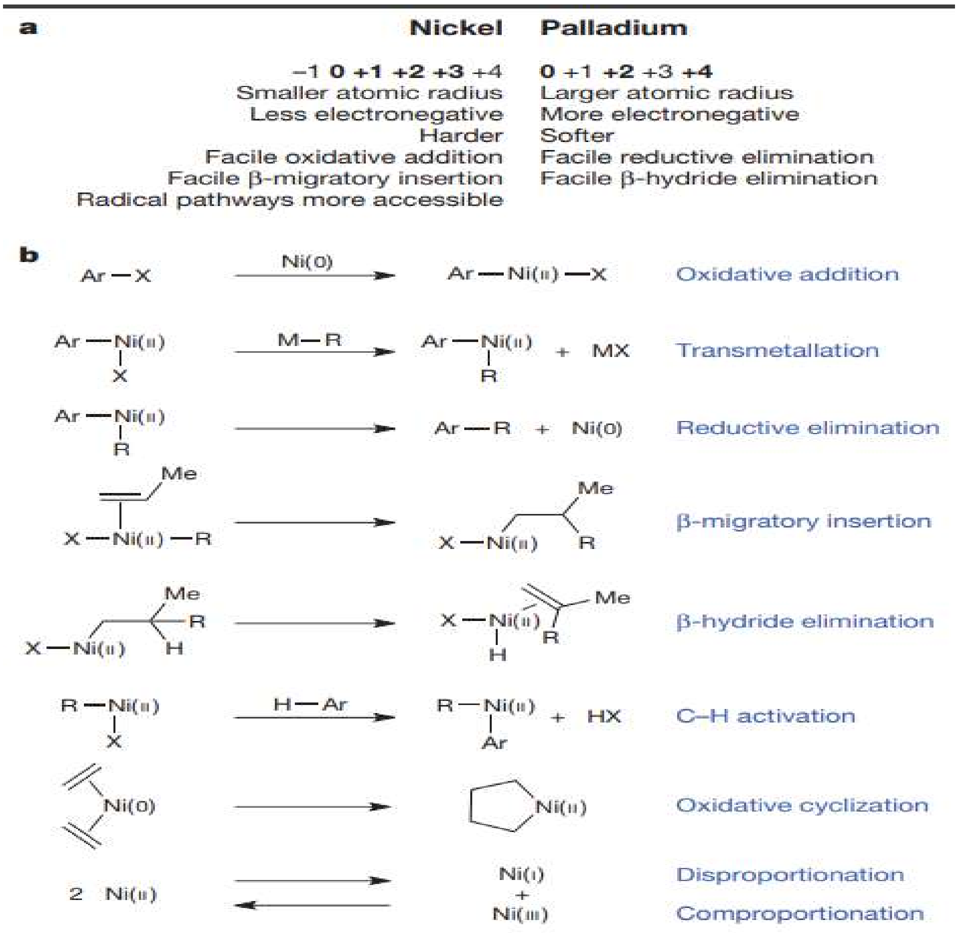
- Activation The nickel precatalyst (often a stable Ni(II) complex) is reduced *in situ* to the active catalytic species, which is frequently a low-valent Ni(0) or Ni(I) complex. This activation often requires an external reducing agent.
- Substrate Coordination/Oxidative Addition The active nickel species coordinates with a reactant (substrate) and undergoes oxidative addition, breaking a bond in the substrate (e.g., a C-X bond where X is a halide) and forming new Ni-C and Ni-X bonds. This step may proceed through a two-electron pathway or a one-electron radical pathway, depending on the substrate and ligands involved.
- Transition metal / Migratory Insertion A second reactant (or an internal part of the first) coordinates to the nickel center. The two organic fragments then link together, forming the new carbon-carbon (or carbon-heteroatom) bond. This process is called migratory insertion or reductive coupling.
- Reductive Elimination The newly formed product is released from the metal center, and the nickel catalyst returns to its original active oxidation state to begin another catalytic cycle.

- Applications:
  - Reductive Amination: Converting ketones to amines (e.g., using Ni/triphos systems).
  - Hydrogenation/Dehydrogenation: Adding or removing H_2.
  - Hydrothiolation: Adding thiols to alkynes.
  - C-C/C-Heteroatom Bonds: Building complex molecules.

HOMOGENEOUS NICKEL CATALYSTS

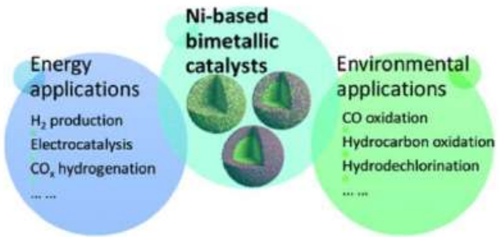
Mechanism and elementary steps Before discussing each class of transformation, a survey of nickel's characteristic modes of reactivity, particularly in regard to some of the elementary steps of transition metal catalysis (Fig. 1) is needed. Nickel is a relatively electropositive late transition metal. Therefore, oxidative addition, which results in loss of electron density around nickel, tends to occur quite readily (though, conversely, reductive elimination is correspondingly more difficult). This facile oxidative addition allows for the use of cross-coupling electrophiles that would be considerably less reactive under palladium catalysis, such as phenol derivatives7–9, aromatic nitriles10 or even aryl fluorides11.

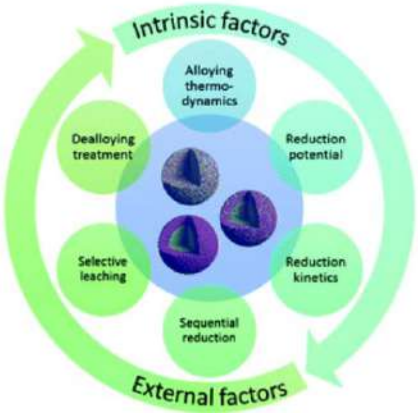
Nickel also has a number of readily available oxidation states commonly invoked in catalysis. The majority of palladium-catalysed reactions are based on a Pd(0)/Pd(II) catalytic cycle, and most often proceed through polar (that is, non-radical) mechanisms. Likewise, Ni(0)/Ni(II) catalytic cycles are widespread, but the easy accessibility of Ni(I) and Ni(III) oxidation states allows different modes of reactivity and radical mechanisms. As a result, many transformations are based on Ni(I)/Ni(III), Ni(0)/Ni(II)/Ni(I), or even cycles in which nickel remains in the Ni(I) state for the entire catalytic cycle. Nickel fundamentals. a, Comparison of basic characteristics of nickel and palladium, including accessible oxidation states (top row, states in bold are more commonly involved in catalysis) and trends in reactivity. b, Prototypical examples of elementary organometallic reaction steps, highlighting changes in oxidation state at nickel. Additional ligands bound to nickel not involved in each transformation are omitted for clarity. Ar, aryl; M, metal; Me, methyl.



Milestones in cross-coupling reactions of aryl ethers and esters. A) Kumada–Corriu-type, nickel-catalysed biaryl formation from aryl ethers and organomagnesium (Grignard) reagents. B) Suzuki–Miyaura-type, nickel-catalysed biaryl synthesis from aryl ethers and boronic esters. C) Suzuki–Miyaura-type, nickel-catalysed biaryl synthesis using aryl esters and aryl boronic acids or aryl boroxines. Ph, phenyl; t-Bu, tert-butyl; Et, ethyl; cod, 1,5-cyclooctadiene; i-Pr, isopropyl; Mes, 2,4,6-trimethylphenyl.

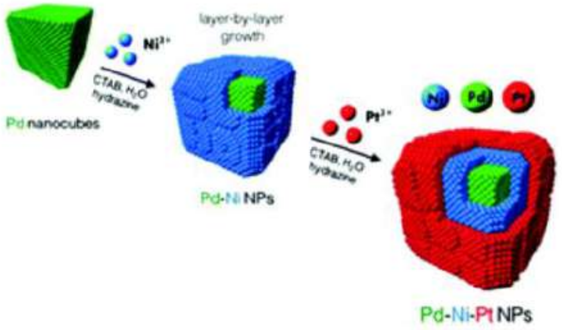
Ni-based bimetallic heterogeneous catalysts for energy and environmental applications:





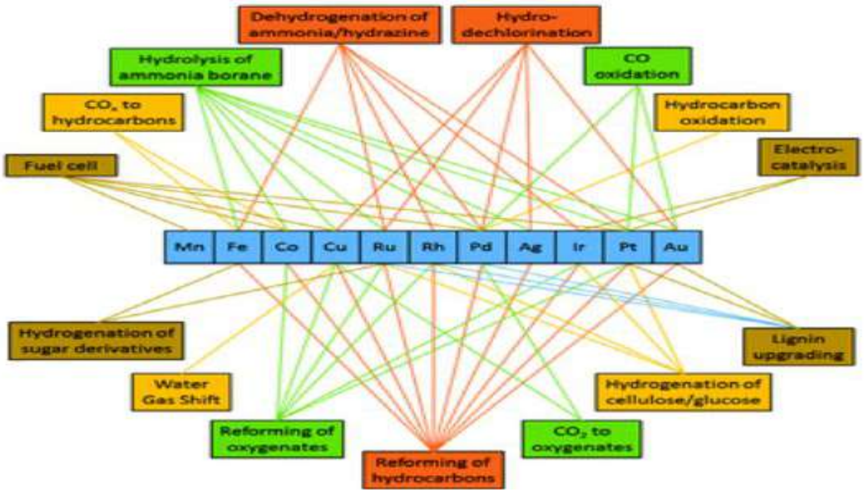
Bimetallic core–shell structures can be obtained either by seed-mediated growth or by one-pot co-reduction of metallic precursors. In particular, for the bimetallic Ni@noble metal core–shell structure, Ni serves as a core and the noble metal serves as a shell. This kind of structure is generally prepared using a seed-mediated growth process, where Ni cores are prepared by reducing their salt precursor prior to the deposition of the noble metal on their surface. In most cases, capping ligands are used in this step to prevent aggregation. It should be noted that the one-pot co-reduction method cannot form this structure because of the higher reduction potential of noble metals than that of Ni. In this case, noble metals will be reduced first and Ni will be deposited subsequently as a shell over the noble metal core.

Demonstrates how Pd cubes function as shaped crystal substrates to catalyze and direct the oriented overgrowth of Ni. Pt ions were added after the Ni overgrowth to "trap" the metallic Ni phase and complete the layer-by-layer synthesis of the shaped ternary metal NPs.



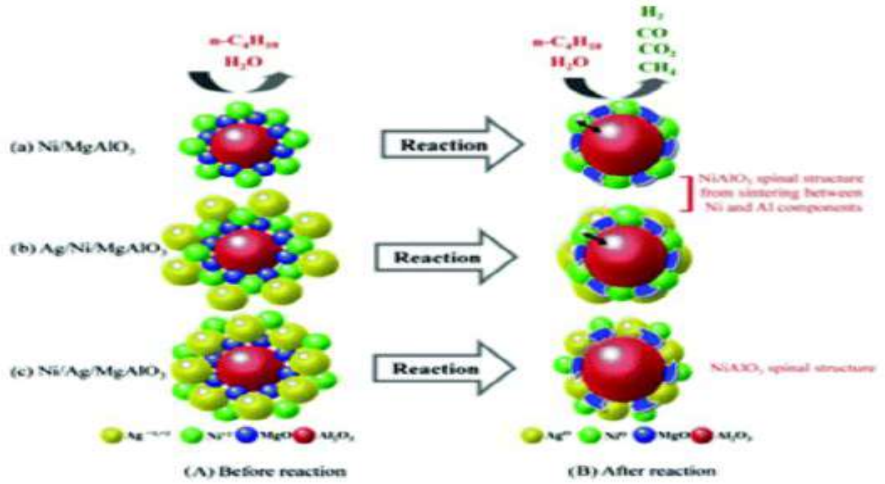
Scheme 1 Schematic illustration for the synthesis of cubic Pd–Ni–Pt core–sandwich–shell NPs.

Catalysis applications of bimetallic Ni catalysts



Since Ni has similar electronic properties as Pd and Pt, its application is widely explored in similar reactions as the other two. Here we will critically discuss recent advances in bimetallic Ni catalysts where both noble metals (Ru, Rh, Ir, Pd, Pt, Au, and Ag) and transition metals (Fe, Co, and Cu) have been used as guest metal counterparts. However, in some cases Ni also acts as a guest metal or promoter to modify the catalytic activity of reactive noble metals.

REFORMING OF HYDROCARBONS:

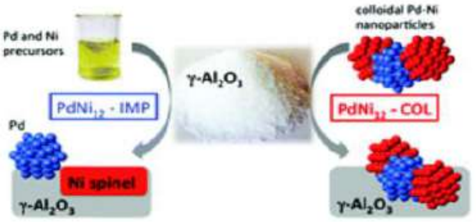


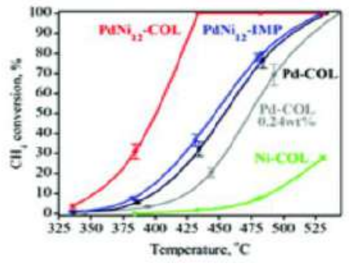
Steam reforming and dry reforming of light hydrocarbons, such as methane and butane provide a promising method for hydrogen production. Although steam reforming of methane yields synthesis gas with a high $H_2 : CO$ ratio of about 3 : 1, dry (CO_2) reforming of methane has certain advantages since it utilizes two abundantly available green-house gases to produce industrially important syngas and can reduce net emissions of these gases.[57] However, compared to H_2O reforming, CO_2 reforming causes more severe coke formation because of the increased C/H molar ratio in the feedstock. Therefore, the development of a coke-resistant catalyst is the major challenge for CO_2 reforming of hydrocarbons.

the increased C/H molar ratio in the feedstock. Therefore, the development of a coke-resistant catalyst is the major challenge for CO_2 reforming of hydrocarbons.

Oxidation of hydrocarbons

Few examples on bimetallic Ni–Pd catalysts have been reported for the removal of hydrocarbon through oxidation. Three-way catalysts based on Ni–Pd supported on Al_2O_3 were reported for the oxidation of C_3H_6 under stoichiometric conditions.A recent study by Shen *et al.* investigated the role of different preparation methods of Ni–Pd catalysts in inducing different structures of the catalysts with different activities for methane combustion.The traditional impregnation–calcination method produced monometallic Pd particles on a binary $NiAl_2O_4$ support, and in this case, no improvement of activity was observed as the Ni was consumed to form an inactive $NiAl_2O_4$ spinel. In contrast, the colloidal approach produced Pd and Ni NPs on the parent Al_2O_3 support and exhibited better activity. Furthermore, the addition of Ni to Pd during colloidal synthesis prevented the over-growth of Pd NPs, thereby improving the stability against sintering at a high-temperature in oxidation processes.





Schematic diagram for the preparation of bimetallic Ni–Pd catalysts and their catalytic performances in the methane combustion. Reaction conditions: 4100 ppm methane, 5 mol% water, a pressure of 1.1 bar, 1.2 mg of Pd, and 7.6 mg of Ni (0.029 wt% Pd and 0.190 wt% Ni loading in relevant catalysts, except for the 0.24 wt% Pd catalyst).

III. RESULTS AND DISCUSSION

1) Catalytic Activity of Nickel Complexes:

The nickel-based catalytic system demonstrated significant efficiency in promoting organic compound reactions under comparatively mild conditions. Across a range of substrates, the reactions proceeded smoothly, indicating that nickel acts as an effective and versatile catalyst. The observed catalytic performance highlights nickel's ability to activate key bonds such as C–C, C–N, and C–O, which are often challenging to transform using conventional catalysts.

Compared to traditional noble metal catalysts, the nickel catalyst exhibited comparable reactivity while operating at lower catalyst loadings. This suggests that the developed approach offers an economical and sustainable alternative for organic synthesis.

2) Reaction Scope and Substrate Compatibility:

The developed methodology showed broad substrate compatibility. Both electron-donating and electron-withdrawing substituents on the organic compounds were well tolerated, with minimal impact on reaction efficiency. Aliphatic as well as aromatic substrates successfully underwent transformation, indicating the robustness of the nickel-catalyzed system.

Notably, sterically hindered substrates also participated in the reaction, though with slightly reduced conversion. This reduction may be attributed to limited access of the substrate to the nickel active center, suggesting that steric effects play a role in reaction kinetics.

IV. CONCLUSION

Nickel-catalyzed methodologies have emerged as a powerful and versatile platform for driving a wide range of organic transformations, offering both economic and environmental advantages over traditional precious-metal catalysts. The novel approaches explored in this study highlight nickel's unique ability to facilitate diverse cross-coupling, reductive, and C–H activation reactions with high efficiency, broad substrate scope, and tuneable selectivity.

By leveraging nickel's rich redox chemistry, compatibility with mild conditions, and adaptability to electrochemical or photochemical systems, these strategies open new pathways for sustainable synthesis of complex organic molecules. Such advancements not only reduce reliance on costly and scarce metals but also pave the way for greener, scalable, and more energy-efficient chemical processes.

In essence, nickel catalysis stands as a promising frontier in modern organic chemistry—bridging innovation with sustainability, and offering transformative potential for pharmaceuticals, materials science, and fine chemical industries.

Conflicts of interest

The authors declare that they have no competing interests.

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