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Heck reaction over palladium supported on nickel ferrite as an efficient and inexpensive catalyst

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The palladium supported on nickel ferrite found to be highly active catalyst for the Heck olefination of aryl iodides and activated aryl bromides providing an excellent yield in an aerobic condition, in shorter reaction time.

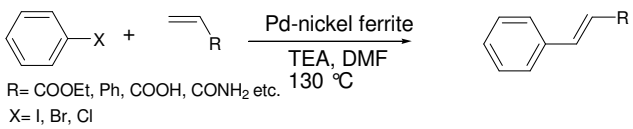
Keywords: Heck reaction, palladium, nickel ferrite, catalyst, olefins

The palladium catalyzed coupling reaction between aryl halide and olefins is known as the Heck reaction[1]. In the last decade, it has become an important C-C coupling reaction in modern organic synthesis due to the broad availability of substrates (aryl-iodides, -bromides, and -chlorides) and the tolerance to the wide range of functional groups. The use of homogeneous palladium catalysts is well documented in the literature[2], and it has high activity and selectivity than heterogeneous catalyst but, it is associated with many problems such as (a) often expensive and sensitive ligands (usually phosphine) necessary to activate palladium (b) the catalyst separation or recovery of expensive palladium metal from the reaction-mixture is not easy (c) cost of the catalyst is important especially when it is used in industry and (d) at higher temperature, deactivation of the palladium catalyst is observed[3a-b]. From the economic point of view, these problems are getting much importance. The comparatively high stability of Pd on solid supports works well even under normal ambient conditions, that is without the exclusion of air[3c].

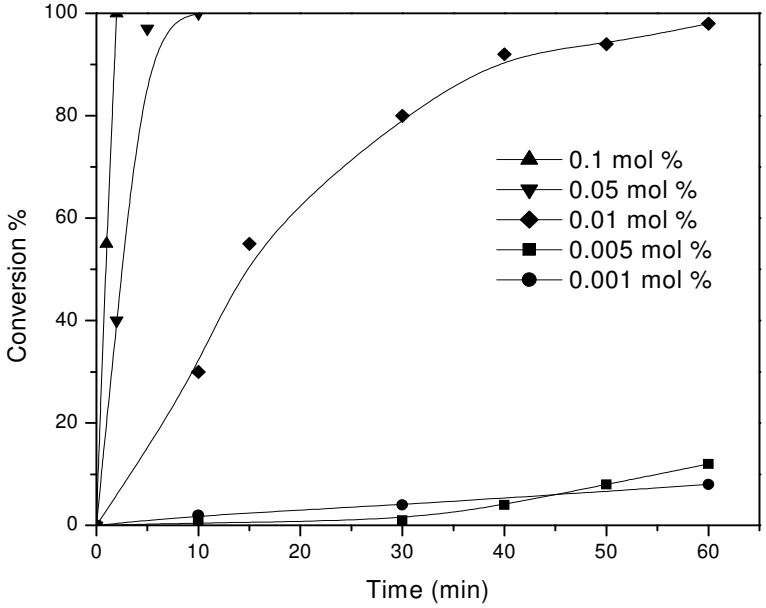
In the recent years, much attention has given to overcome these problems by employing many heterogeneous palladium systems[4], such as Pd supported on different supports like carbon[5], mesoporous silica[6], zeoliets[7], metal oxides[8], clays[9], polymer[10], diatomite[11], ionic liquids[12] and surface modified nickel ferrite[13]. Ferrite is a family of oxide that plays an important role in the field of heterogeneous catalysis and proved to be a suitable support[14]. Nickel ferrite with an inverse spinal structure shows ferromagnetism and therefore it can be easily separated from the reaction- mixture by employing an external magnetic field. Herein, a new Pd (II) supported catalyst on magnetically recoverable nickel ferrite and its catalytic activity for the Heck reaction with various substrates and optimization of reaction conditions is reported.

The synthesis and characterization of nickel ferrite have been reported previously[15]. The powder XRD pattern and surface area is well corroborates with the literature. Loading of Pd (II) were carried out over nickel ferrite (Pd-Ni) by wet impregnation method. The catalytic activity of Pd-Ni catalyst was studied for the Heck reaction, where in iodobenzene was substrate, and ethyl acrylate as a reagent, in presence of triethylamine base, over 0.05 mole% Pd at 120°C in an aerobic condition shown in **Scheme I**.

The effect of temperature over the Pd-Ni was studied at various temperatures ranging from 80 to 130°C. The **Figure 1** shows catalytic activity of Pd-Ni at different temperatures. The conversion increases with temperature, 31% conversion was observed at 80°C within 60 min. It is also observed that as the temperature increases reaction time reduces drastically from 60 to 2 min, with excellent yield and selectivity for the *trans* product at 80 and 130°C, respectively.



Scheme I



[a]Conditions: iodobenzene (1 mmole), ethyl acrylate (2.5 mmole), triethylamine (2.5 mmole), DMF (4.0 mL), 130 °C at various concentrations.
Conversions were determined by GC ($\Delta_{rel} = \pm 5\%$).

Figure 1 — The effect of Pd-concentration on the Heck reaction[a]

Table I — The effect of different solvents on the Heck reaction[a]

Entry	Solvents	Time (min)	Conversion (%)[b]
1	DMF	10	100
2	NMP	30	94
3	DMAc	15	100
4	Ph-O-Ph	15	95
5	Diglyme	30	44
6	Xylene	30	24
7	Toluene	30	7
8	H_2O	60	NR

[a] Conditions: iodobenzene (1 mmole), ethyl acrylate (2.5 mmole), triethylamine (2.5 mmole), solvent (4 mL), Pd (0.05 mole %), 120 °C.
[b] Conversions were determined by GC ($\Delta_{rel} = \pm 5\%$).
NR- no reaction.

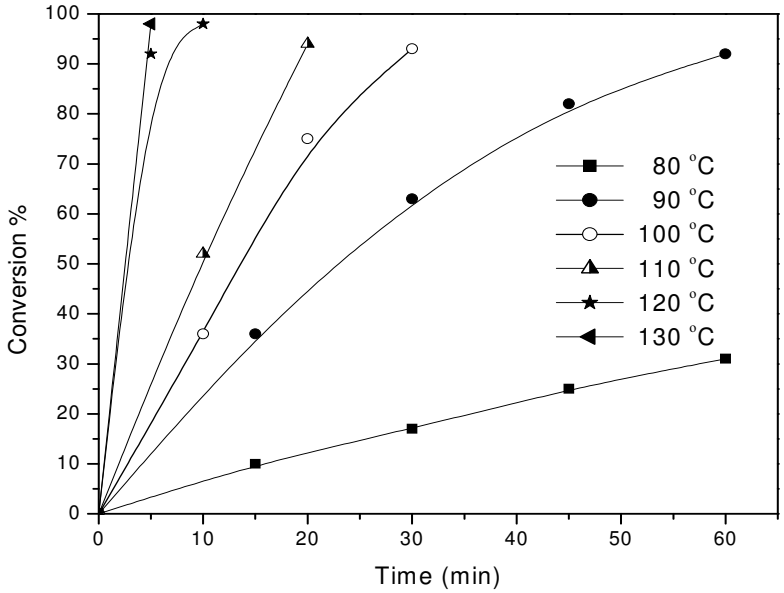
Table II — The effect of various bases on the Heck reaction[a]

Entry	Base	Time (min)	Conversion (%)[b]
1	TEA	10	100
2	TBA	10	100
3	K_2CO_3	30	75
4	Na_2CO_3	30	54
6	NaOAc	30	50
7	$NaHCO_3$	30	65
8	$Ca(OH)_2$	30	48
9	Cs_2CO_3	30	34

[a] Conditions: iodobenzene (1 mmole), ethyl acrylate (2.5 mmole), base (2.5 mmole), DMF (4.0 mL), Pd (0.05 mole%), 120°C.
[b] Conversions were determined by GC ($\Delta_{rel} = \pm 5\%$).

The effect of different solvents on the Heck reaction was studied and the results are summarized in **Table I**. The polar aprotic solvents, gave excellent conversion and selectivity for *trans* product (**Table I**, entries 1-4). Among the various solvents studied dimethyl formamide (DMF), dimethyl acetamide (DMAc), *N*-methyl 2-pyrolidone (NMP) and diphenyl ether (Ph-O-Ph) shows excellent activity. On the contrary, a non-polar solvents (toluene and xylene) show poor conversion (entries 6-7). The general trend for solvents was in the order: DMF > DMAc > Ph-O-Ph > NMP > diglyme > xylene > toluene > water.

The influence of different bases was studied and the results are given in **Table II**. Among the various bases examined triethyl amine (TEA) and tributyl amine (TBA) were found to be the best (**Table II**, entries 1-2). The organic bases are superior to inorganic bases. This may be due to the partial inhomogenity of inorganic bases into the organic substrate, reagent, and solvent, which lowered the conversion and requires longer reaction time (entries 3-9).



[a]Conditions: iodobenzene (1 mmole), ethyl acrylate (2.5 mmole), triethylamine (2.5 mmole), DMF (4.0 mL), 0.05 mole% Pd catalyst at various temperatures. Conversions were determined by GC (Δ_{rel} = ±5%).

Figure 2 — The effect of different temperatures on the Heck reaction[a]

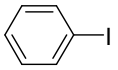
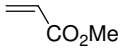
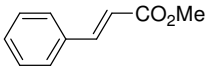
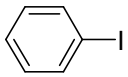
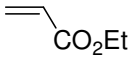
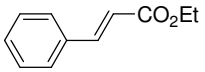
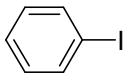
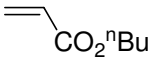
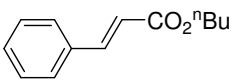
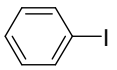
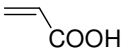
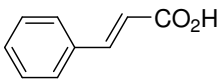
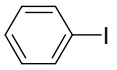
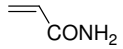
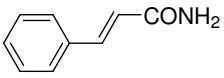
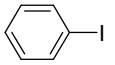
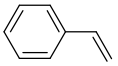
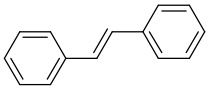
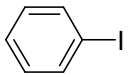
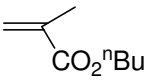
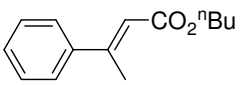
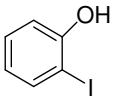
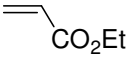
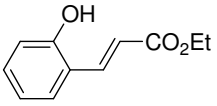
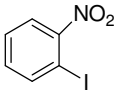
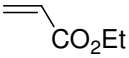
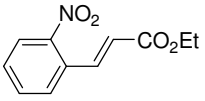
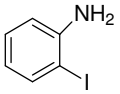
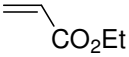
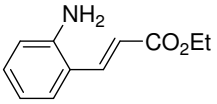
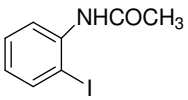
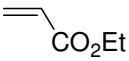
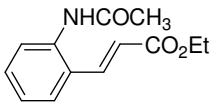
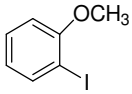
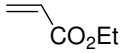
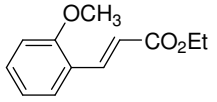
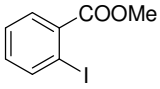
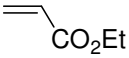
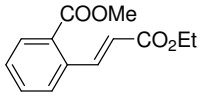
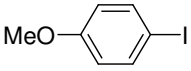
The effect of Pd concentration on the conversion of iodobenzene was studied and the results are shown in **Figure 2**. The result shows that catalytic activity increases with Pd content, reaction completed within 2 min. with excellent conversion and selectivity for β arylated *trans* product over 0.1 mole% Pd. By decreasing Pd concentration from 0.1 to 0.01 mole% did not influence the rate of reaction to a greater extent. Further decrease in Pd content gave only 9% conversion over 0.001 mole% Pd within 60 min.

Using the optimized reaction conditions, the general applicability of Pd-Ni for different olefins and aryl halides with electron withdrawing or donating substituents was explored. The activity of different olefins and substrates are shown in **Table III**. The iodobenzene can react with various olefins like acrylate, acrylic acid, acryl amide, and styrene delivering the corresponding products in good to excellent yield (**Table III**, entries 1-7). Ethyl acrylate was found to be the most reactive among the studied olefins (entry 2). As expected, the most electron rich olefin styrene reacts slower than other acrylates whereas the methyl butyl acrylate reacts very sluggishly, may be due to the steric hindrance (entry 7). Among the various substituted aryl iodides both the deactivated (electron rich) and activated (electron poor) efficiently converted to the desired product in good to excellent yield within 10 to 45 min (entries 8-17). The *ortho* substituted aryl iodides require higher reaction temperature than *para* substituted (entries 8-13).

The catalytic activity of aryl bromides and chloride with butyl acrylate are given in **Table IV**. The comparatively less reactive aryl bromide gave less conversion over 1.0 mole% Pd in presence of additive TBAB (tetra butyl ammonium bromide) within 4 h (Table IV entries 1-3). The activated 4-bromo acetophenone gave 52% conversion of the corresponding product within 15 min, but conversion did not increase even after reaction continued for 2 h without additive. Whereas, in the presence of additive 4-bromo acetophenone gave 87 and 90% conversion with butyl acrylate and styrene, respectively within 15 min. (entries 5-7). The 4-chloro acetophenone gave very poor yield over 2.5 mole% Pd and at 150°C temperature (entry 8).

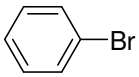
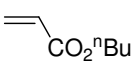
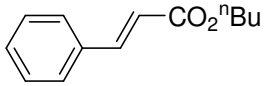
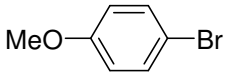
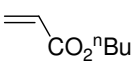
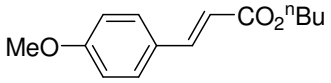
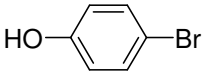
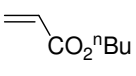
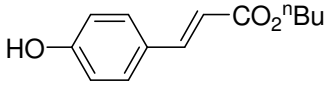
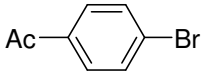
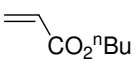
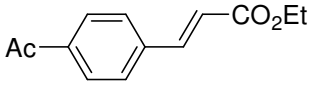
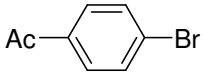
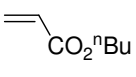
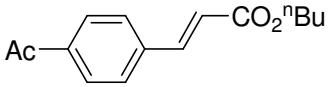
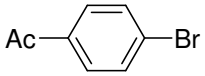
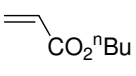
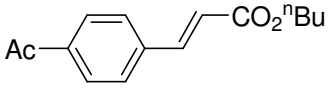
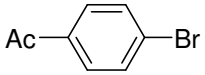
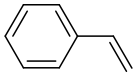
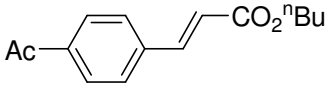
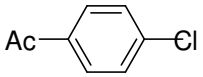
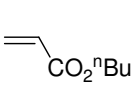
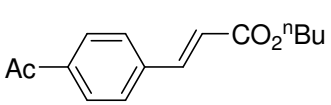
The leaching study was carried out to verify the heterogeneity of reaction. The Pd-Ni catalyst was not reduced by any means since it is expected to be present mainly as Pd (II) species. After the completion of typical reaction, catalyst was separated from the reaction-mixture by filtration and washed with DCM and water several times. The oven dried (110°C) catalyst was used for second run under the similar reaction condition. It gave 98% conversion within 10 min. To confirm, the Pd leaching in the filtrate of first run, 4-iodo toluene, ethyl acrylate and

Table III — The Heck reaction of substituted aryl halides with olefins using Pd-Ni catalyst[a]

Entry	Aryl halide	Olefins	Products	Time (min)	Conversion[b] (%)
1				10	100
2				5	98
3				10	100
4				15	100
5				15	98
6				30	68
7				60	12
8				10	91
9				20	100
10				30	94
11				10	96
12				20	100
13				45	93
14				10	100
15				15	91
16				10	94
17				15	100

[a] Conditions: aryl halide (1 mmole), olefin (2.5 mmole), triethylamine (2.5 mmole), DMF (4.0 mL), 0.05 mole% Pd catalyst, 120 °C. *ortho* iododerivatives: Temp- 130 °C.
[b] Conversions were determined by GC ($\Delta_{rel} = \pm 5\%$).

Table IV — The Heck reaction of substituted aryl bromides and chlorides with olefins using Pd-Ni catalyst[a]

Entry	Aryl halide	Olefins	Products	Time (min)	Conversion[b] (%)
1				4 h	20
2				4 h	33
3				4 h	21
4[c]				2.5 h	80
5[d]				15 2 h	52 52
6				15	87
7				15	90
8[e]				2 h	25

[a] Conditions: aryl halide (1 mmole), olefin (2.5 mmole), tributylamine (2.5 mmole), DMF (4.0 mL), TBAB (0.5 mmole), 1.0 mole% Pd catalyst, 140 °C.
[b] Conversions were determined by GC ($\Delta_{rel} = \pm 5\%$).
[c] 0.5 mol% Pd. [d] Without additive (TBAB)
[e] Reaction were carried out at 150 °C on 2.5 mol% Pd.

triethylamine was added. The composition of the reaction-mixture was determined by GC and amount of 4-iodo toluene was set to 100% and the reaction carried out at typical reaction condition. It is observed that, 13% 4-iodo toluene was converted to corresponding product within 10 min. But, on further continuation of reaction gave 99% conversion within 45 min. The difference observed in the GC determination gave the qualitative information about leaching. This method did not allow the absolute quantification of the Pd species (active or inactive) dissolved in filtrate and redeposit on to the solid support. This method confirmed that presence of active Pd species into the filtrate. Therefore, qualitatively we conclude that, some of the Pd (II) species are not redeposit on the nickel ferrite surface after the completion of reaction. Further studies are in progress to minimize leaching and recycle the Pd-Ni catalyst.

Experimental Section

Preparation of nickel ferrite: The synthesis of nickel ferrite was carried out by using the reported literature method[15]. The metal oxalate precursor was prepared by adding 32 mL N_2 purged solution of $NiSO_4.6\ H_2O$ (3.0 g, 0.0114 mole) $FeSO_4$: 7 H_2O (6.82 g, 0.0228 mole) to the 80.0 mL N_2 purged $(COONH_4)_2\ H_2O$ (3.65 g, 0.0228 mole) with vigorous stirring. The resulting yellowish green suspension was chilled and decanted before filtering the solid. The precipitate was washed with ~ 250 mL distilled water and dried in oven at 110 °C for 1 h. The nickel ferrite phase was achieved by heating the precursor in air for 4 h at 550 °C in a pre heated muffle furnace in silica crucible.

Synthesis of 1 wt% Pd on nickel ferrite (Pd-Ni): The solution of palladium chloride (made from 10 mg of $PdCl_2$ in 5 mL distilled water) was added to 1.0 g

of nickel ferrite support, and the mixture was vigorously stirred for 10 h at room temperature. The water was evaporated under reduced pressure on rota evaporator. The catalyst was dried in oven at 110 °C for 2 h.

Typical experimental procedure for the Heck reaction: In a 20 mL two neck round bottom flask was placed aryl halide (1 mmole), olefin (3 mmole), triethylamine (3 mmole), and Pd (0.5 mole%) in 4.0 mL of DMF. The reaction-mixture was heated at temperature 130°C for appropriate time. The reactions were monitored by gas chromatography (HP-5890). After the completion of reaction-mixture, was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulphate, and then analyzed by GC, GCMS, FTIR and NMR

Conclusion

The palladium loaded on nickel ferrite efficiently catalyses the Heck olefination of aryl iodides, activated aryl bromides with acrylates and styrene over low loading of precious palladium in an aerobic condition in shorter reaction time, and qualitatively it was found that, the active species is leaching from support into the solution.

Acknowledgement

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