Review on Microwave Assisted Suzuki- Miyaura Biaryls Coupling Reactions Using Palladium Catalysts

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Abstract

Microwave-assisted organic synthesis provides a novel and efficient method of achieving thermal organic reactions. It is about to change the practice of synthesis performed in many academic and industrial laboratories. Biaryls are very important compounds used in the pharmaceuticals and have several industrial applications. This review focuses on reactions of microwave assisted synthesis of biaryls using Palladium catalyst. In this context the reactions are categories on the basis on catalyst recycled, power consumption and time required. In this current article, the state of the art and comparative study of Suzuki- Miyaura biaryls coupling reactions reported in last few years are summarized.

***Key words**:* Microwave, biaryls, aryl halide, aryl boronic acids, Pd catalyst

Introduction

Carbon-carbon bond formation by the Suzuki cross-coupling reactions is versatile tool in organic chemistry.[1] The Suzuki reaction (the palladium-catalyzed cross-coupling of aryl halides with boronic acids) is perhaps one of the most versatile and at the same time also one of the most often used cross-coupling reactions in modern organic synthesis.[2] Pd/C can be considered as a versatile and suitable source of Pd for many reactions among the heterogeneous catalysts. It is easy to recover, and the products obtained are usually not contaminated by traces of Pd. Palladium is very important metal catalysts used in organic synthesis for cross-couplings and related reactions.[3]

These catalysts are easy for the preparation, good performance in recyclability and large time efficiency of such Pd catalysts are generally more desirable for industrial applications. Microwave-assisted synthesis are the alternative methods to conventional thermal methods because microwave (MW) irradiation provides fast, uniform and selective heating in the chemical reactions.[4] The synthesis of biaryl compounds using Suzuki-Miyaura coupling between aryl halides and phenylboronic acids is one of the most common powerful methods. These are biaryl compounds are used as intermediates in the various organic syntheses of advanced materials and also in the pharmaceutical industries under mild reaction conditions.[5]

As per the green chemistry principles, in the microwave irradiation methods, there is a reduction in the excess use of solvent, energy, moreover it gives high reaction yields in a short reaction time requirement for the chemical reactions.[6,7] Pd-catalyzed Suzuki coupling reactions are one the important synthetic methods to synthesize biaryl compounds.[8,9] In the Suzuki coupling reactions, different Pd catalysts have been prepared and utilized by various researchers as catalysts for production of biaryls.[10,11] The homogeneous catalysts also have some disadvantages during recycling of catalyst, purification of the desired product and higher operational cost in the large-scale productions.[12]

Nowadays researchers are focused on the use of MW-irradiation methodology during chemical reactions for the heating source because it remarkably assists in achieving desirable products rapidly. This organic synthesis showed numerous industrial applications.[13-15] Microwave technology has been broadly used for the development of eco-friendly and solvent-free syntheses of polyfunctional compounds.[16] MW-assisted syntheses are widely used because of its low costs and its experimental simplicity in the reaction conditions. MW techniques are giving chemoselective products along with improved yields and purity compared to conventional methods because it allows homogeneous heating of the solution mixtures.

In this article we have discussed Suzuki-Miyaura cross coupling between aryl halides and aryl boronic acids studied by various researchers by using different palladium catalysts in a MW irradiation method. Here we have reviewed important coupling reactions of biaryl preparations reported in recent years.

General mechanism of homogeneous and heterogeneous catalysis:

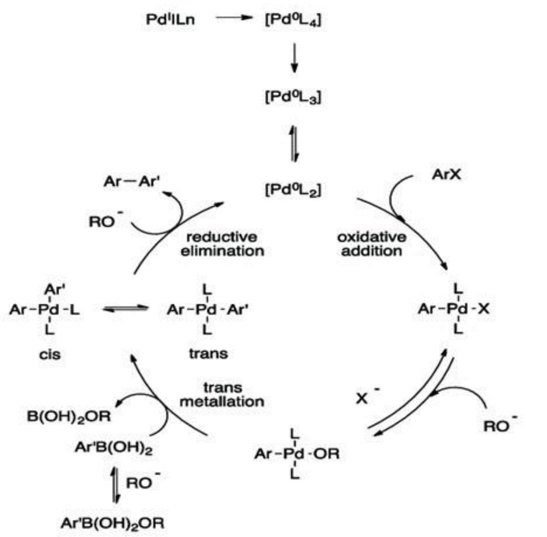


Figure: 1

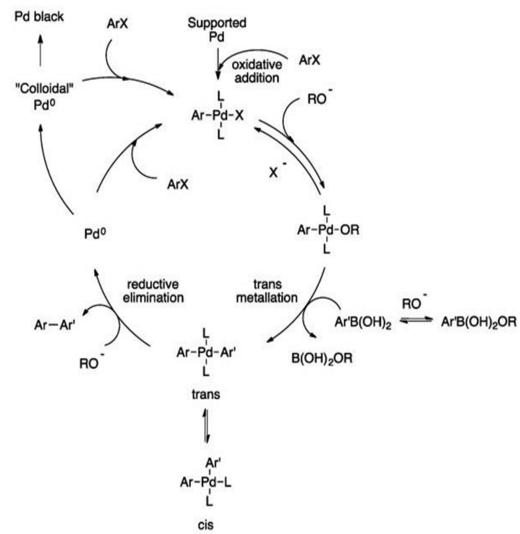
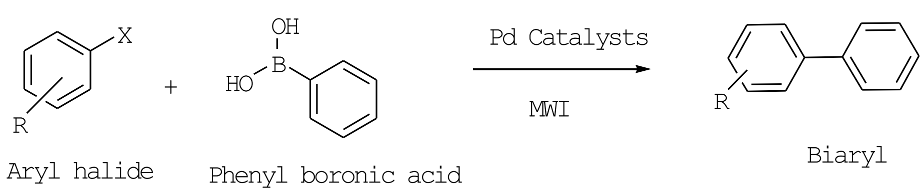


Figure: 2

As shown in figure 1 (homogeneous catalysis) and 2 (heterogeneous catalysis) **t**he general catalytic cycle of Suzuki-Miyaura cross coupling[17,18] consists three steps such as oxidative addition, transmetalation and reductive elimination. In oxidative addition, aryl halide Ar-X interacts with Pd catalyst to form complex ArPdXLn. In transmetalation, complex ArPdXLn in the presence of the base converted to nucleophilic palladium complex ArPdORLn followed by reaction with aryl boronic acid Ar'B$(OH)_2$ gives diaryl complex ArPdAr'Ln in a cis–trans equilibrium form and in reductive elimination the cis form gives the biaryl derivative Ar–Ar' and Pd(0).[1,19,20]

Suzuki-Miyaura cross coupling reactions

i) Coupling reactions of Aryl halides and phenyl boronic acids:



Scheme 1: Coupling of Aryl halides and phenyl boronic acids

Suzuki-Miyaura cross coupling between aryl halides and phenyl boronic acids studied by various researchers using varied palladium catalysts in a MW irradiation (Scheme 1). Some of the important coupling reactions of biaryls in the last three years are discussed bellow.

Sandra Ramirez-Rave et al.[21] synthesized biaryls using halobenzene, phenyl boronic acid, Na_3PO_4 and Pd catalyst (0.1 mol %) stirred and heated at 110 °C under MW irradiation for 5 min in a MW reactor. MW assisted coupling carried out using all different catalysts 1(R = Me), 2(R = Ph), 3(R = Bn) and 4($C_6H_4NO_2$) in the presence of Na_3PO_4 as base. The coupling reactions were accelerated under MW radiation as compared to conventional heating. In case of R = 4-$C_6H_4NO_2$ showed the highest catalytic activity with more than 99% yield. The catalytic activity of complex was further examined in the two cross-couplings with a series of para-substituted bromo-benzenes. It showed yields from 63-99%. Catalytic experiments were performed under the same reaction conditions using different bases such as Na_2CO_3, K_2CO_3, Rb_2CO_3, Cs_2CO_3, NaOH.

Talat Baran et al.[22] reported MW-assisted environmentally safe, fast and simple method in presence of Schiff base-modified sporopollenin microcapsules and palladium salt (Na_2PdCl_4) as a catalyst (0.0025 mol%) with aryl halide, phenyl boronic acid, K_2CO_3 added in a Schlenk tube and mixture irradiated in a microwave oven for 6 min (at 50 ^{0}C). Biaryl coupled product obtained after reaction and the catalyst recovered from reaction mixture. FT-IR, SEM, Thermo gravimetric analysis and X-ray diffraction and EDAX analyzed for sporopollenin microcapsule. MW assisted-synthesis reaction optimized for the of 4-bromoanisole, phenyl boronic acid gives 4-methoxybiphenyl as a model reaction. Catalyst sporopollenin microcapsules supported Pd(II) in the presence of base K_2CO_3 for 6 min reaction time gives biaryls with good yields. Reusability of sporopollenin microcapsules supported Pd(II) catalyst also monitored and shown good yields. Reaction also Optimized using different basees for coupling reaction.

Nuray Yilmaz et al.[23] synthesized biphenyls using aryl halides, phenyl boronic acid, potassium carbonate and Pd nanocatalyst (0.004 mol%) were added and irradiated via MW heating system under solvent-free media at 400 W for the time 5 min. Catalyst prepared from Chitosan, cellulose and Na_2PdCl_4. The reaction optimized between p-bromoanisole and phenyl boronic acid studied using various bases such as NaOH, KOH, Na_2CO_3, Cs_2CO_3, K_2CO_3. Nuray Yilmaz et al proposed Suzuki-Miyaura cross coupling reactions by using an economical, simple, fast, and green MW technique palladium nanocatalyst on chitosan/cellulose composite. Pd-nanocatalyst showed excellent catalytic performance along with high biphenyl yields. The reaction yields was found as R-I> R-Br >R-Cl. Effect of different substituents such as electron-withdrawing and electron-donating on biphenyl yields are studied under optimal conditions.

Nuray Yilmaz Baran[24] synthesized biaryls from aryl halides, phenyl boronic acid in presence of base K_2CO_3 using O(PMPA)-Pd (Oligo(N-(pyridin-2-ylmethylene)pyridin-2-amine))(0.05 mol %) in a Schlenk tube irritated with MW (400W) in solvent-free media for 6 min. This MW irradiation method is nontoxic, solvent free, simple and fast. The catalyst produced high biaryl yields. Characterization of the catalyst done using UV, FT-IR and ^{1}HNMR. Thermal degradation performed for O(PMPA)-Pd catalyst. Catalyst O(PMPA)-Pd prepared from Na_2PdCl_4 and O(PMPA) in ethanol under reflux for 24h at 70 °C. K_2CO_3, Cs_2CO_3, NaOH and KOH were tested as a bases and the highest biaryl yield was reached using K_2CO_3 up to 99%.

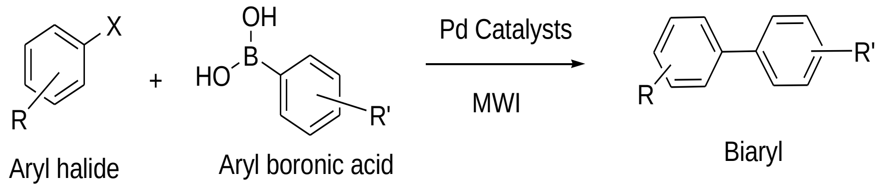
Influence of MW power on yield also analyzed and shown maximum yield at 400W. A catalyst has showed good catalytic performance even up to eight subsequent recycles.

Talat Baran[25] synthesized biphenyl compounds using solvent-free media under MW from aryl halides and phenylboronic acid in presence of base K_2CO_3 and catalyst Pd NPs@APC (agar/pectin composite (APC) Nano particles) 1.8×10^{-3} mmol in a Schlenk tube irradiated at 350W for 5 min under oxygen atmosphere. Yields are recorded from 52 to 99%. Catalyst Pd NPs@APC prepared by stirring agar, pectin in water at room temperature followed by addition of $PdCl_2$ solution then refluxed. It has characterized using FT-IR and thermo gravimetric analysis (TG/DTG). Recovery and reusability of a metal catalyst is investigated for Suzuki–Miyaura coupling reactions. The influence of time, percentage of catalyst, type of bases and MW power on the yield of reaction were studied. Optimization of coupling studied using bases such as K_2CO_3, Na_2CO_3, Cs_2CO_3, KOH and NaOH. Highest yields are found in case of K_2CO_3.

Nuray Yilmaz Baran et al.[26] synthesized biaryls from aryl halide, phenyl boronic acid, Pd NPs@Sch-boehmite (0.005 mol%) and K_2CO_3 irradiated in a Schlenk tube in a MW for 6 min at 400 W under solvent-free conditions. Catalyst Pd NPs@Sch-boehmite prepared from NH_2-boehmite and 2,4-dihydroxybenzaldehyde in EtOH heated at 70 ^{0}C for 72 h, then formed Sch-boehmite was mixed with $PdCl_2$ in EtOH and heated at 70 ^{0}C for 4 h. It was characterized using FT-IR, FE-SEM, TG/DTG, EDS and XRD (X-ray diffraction) techniques. Recyclability studied for Pd NPs@Sch-boehmite for number of cycles. After completing reaction Pd NPs@Sch-boehmite was separated and directly reused for the next successive runs for eight cycles by providing 82% yield. All the aryl halides shown good yields in coupling reaction even for compounds bearing the ortho-substituents showed that Pd NPs@-Sch-boehmite possesses good catalytic effect.

Talat Baran[27] synthesized biaryls using aryl halides, phenyl boronic acid, base, and 0.06 mol % Pectin(Pct)-Pd catalyst in a Schlenk tube and irritated in a MW at 400 W for 8 min under solvent-free medium. Optimization of reaction achieved with K_2CO_3 as base in the presence of 0.06 mol% AC-Pd catalyst for 8 min and it yields 99%. Pct-Sch and Na_2PdCl_4 were stirred in water at room temperature for 5 h to give catalyst. The effectiveness of catalyst was investigated in the Suzuki-Miyaura coupling reactions for different halides (I, Br, and Cl) and various R-groups with phenylboronic acid. Characterization of the Pct-Pd catalyst was performed by FT-IR, TG/TGA, XRD and EDAX analysis. Pct-Pd catalyst used in the synthesis of biphenyl compounds with excellent reaction yields. The recovery and reproducibility of AC-Pd catalyst was checked in subsequent runs. Observed that even after 12 runs it produced 91% of conversion yields. It showed easy recovery, facile recyclability, low Pd leaching and high stability in air.

ii) Coupling reactions of aryl halides and aryl boronic acids:



Scheme 2: Coupling of aryl halides and aryl boronic acids

Suzuki-Miyaura cross coupling between aryl halides and aryl boronic acids reported by various researchers using different palladium catalysts in a MW irradiation (Scheme 2). Some of the important coupling reactions of biaryls in the last three years are discussed bellow.

Hany A Elazab et al.[28] synthesized biaryls from aryl halide which was dissolved in environmentally benign solvent system H_2O:EtOH (1:1) followed by addition of aryl boronic acid, potassium carbonate in the presence of catalyst Pd/CuO (1 mol%) then heated under MW irradiation at power 250W at different temperatures of 80, 120, and 150°C for 10 min. Pd supported on CuO nanoparticles (Pd/CuO) catalysts prepared with different weight percents of 5, 10, 20, 30 % of Palladium loading on CuO. Catalysts characterized using TEM, GC–MS analysis, X-ray photoelectron spectroscopy (XPS) analysis. The X-ray diffraction patterns were measured at RT. The reaction yield was increasing with the temperature. Maximum conversion obtained at 150°C. This trend is same for all prepared Pd/CuO catalysts (5, 10, and 20 wt %). It was found that increasing the catalyst weight percent on the solid support, product conversion increases at different temp. Highest yield 100% for 20wt% Pd-loaded catalyst at 150 ^{0}C. But at Pd content 30 wt% shown sharp drop in the catalytic performance and lowers yield to 65%. Recycling experiments shown good yields with 0.5 mol% Pd/CuO.

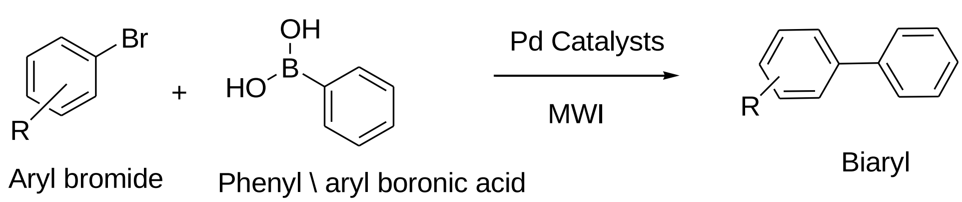
Hany A. Elazab[29] synthesized biaryls from aryl bromide dissolved in a H_2O: EtOH (1:1), aryl boronic acid and potassium carbonate along with catalyst (0.5 mol%) of palladium supported on magnetite nanoparticles (Pd/Fe3O_4) heated under MW irradiation at 250 W, 2.45 MHz. Catalyst Pd/Fe_3O_4 prepared in different ratios (5, 10, 20, 30 wt %) of palladium supported on iron oxide from ferric acetyl acetonate, $Fe(C_5H_7O_2)_3$ to different % of Palladium (II) acetyl acetonate. Catalysts are characterized using GC-MS, X-ray photoelectron spectroscopy (XPS) analysis and TEM. Reaction optimized at different temperatures such as 80, 100, 120, and 150 °C using a MW at 250 W power for 10 min in the presence of iron oxide supported palladium nanoparticles as a catalyst (1 mol%). At 10 wt % Pd supported on the iron oxide catalyst shown 100% conversion in 10 min at 120 °C but the conversion was less than 50 % when testing Pd nanoparticles or magnetite nanoparticles independently. Catalytic activity of Fe_3O_4 was enhanced by using palladium. Recycled and reused up to seven times with good performance.

Motakatla Novanna et al.[30] reported synthesis of 2-amino-3-carboxamide 1, 1'-biaryls using Suzuki coupling. It was synthesized using Anthranilamide and iodine in water, sodium bicarbonate then treated with arylboronic acids, catalyst Pd(dppf)Cl_2.DCM, base 0.5 N K_2CO_3 in a solvent dioxane-MeOH and were MW irradiated at 200 W for 10 min. Iodoamino amides treated with variety of aryl and hetero aryl boronic acids and under optimized condition gave 2-amino-3-carboxamide 1,1'-biaryl derivatives and 4'-amino-[1,1':3',1"-terphenyl]-5'- carboxamide in very good yields, except some of boronic acids did not react due to steric hindrance.

Talat Baran et al.[31] synthesized biaryls using Pd NPs@CAP(nanoparticles@microcapsules) catalyst (0.1 mol%), Phenyl boronic acid, aryl halide and K_2CO_3 in a Schlenk tube irradiated at power 400 W for 6 min. Various bases such as KOH, Na_2CO_3, Cs_2CO_3 and K_2CO_3 were investigated in the model reaction and the yields were analyzed. Maximum yields found for K_2CO_3 and it was 98%. K_2CO_3 was selected as the base for coupling due to higher yields. Comparison showed for Pd NPs@CAP with previously reported catalysts for the reaction between 4-bromoanisole and phenylboronic acid. Pd NPs@CAP. Shown better performance in terms of higher yields and in shorter time duration under solvent-free conditions. Reusability and Catalyst were recycled, reused with high and easy separation with good performance.

Abdurrahman Sengul et al.[32] synthesized diaryls using Suzuki cross- couplings between aryl chlorides and aryl boronic acids in the presence of [Pd(L)]Cl catalyst. The aryl chloride, phenylboronic acid, K_2CO_3, catalyst Chloro-2,6bis (1-(3-propylsulfonate)benzimidazol-2'-yl) pyridinepalladium (II)chloride [Pd(L)]Cl (0.02 mmol) in H_2O were irradiated at 850 W for 10 min in a MW oven. Abdurrahman Sengul et al also optimized base K_2CO_3 along with reaction time .The reaction time was optimized 15 min at 850 W MW irradiation and 2 h for conventional heating at 80 °C. The optimum concentration of catalyst benzimidazole – Pd complex ([Pd(L)]Cl was found to be 0.1 mol%. This is a new water soluble Pd catalyst containing sulfonated imidazole ligand showed excellent Suzuki Coupling reactivity with aryl chlorides in water under MW irradiation. Good to excellent yields of cross coupling products were obtained when the ionic groups are K^+, TBA^+ (tetrabutylammonium) and $Bmim^+$ (**1**-Butyl-3-methylimidazolium) were used . The catalysts K ([Pd (L)]Cl **,** TBAB ([Pd(L)]Cl**,** Bmim([Pd(L)]Cl were used for coupling.

iii) Coupling reactions of aryl bromides and phenyl or aryl boronic acids:



Scheme 3: Coupling of aryl bromides and phenyl or aryl boronic acids.

Suzuki-Miyaura cross coupling between aryl bromides and aryl boronic acids reported by various researchers using different palladium catalysts in a MW irradiation (Scheme 3). Some of the important coupling reactions of biaryls in the last three years are discussed bellow.

Felipe Lopez-Saucedo et al.[33] reported Suzuki-Miyaura Couplings using catalysts palladium complexes Pyridylthiother-ligated Pd(II):Pd-NS1, Pd-NS2, Pd-SNS. They synthesized biphenyls using Pd-cat(Pd-SNS) (Pyridyldithiother)(0.01 mmol), Aryl bromides, $PhB(OH)_2$, Na_2CO_3, in the solvent DMF/H20 irradiated at 120 W for the time 15 min. Optimization by using different catalysts such as Pd-NS1, Pd-NS2, Pd-SNS Pd-cat. (0.01 mmol), Bromobenzene, $PhB(OH)_2$, Na_2CO_3, DMF at 120 ˚C and 120 W for 15 min. Yields were recorded through GC-MS analysis. Efficacy of catalysts depends on the donor nature of the substituent on the bromobenzenes. Pyridylthiother ligands were synthetized by solution of the corresponding RSH and NaH. Then 2-(bromomethyl)pyridine (NS1, NS2) or 2,6- bis(bromomethyl)pyridine (SNS) derivatives gives ligands (NS1, NS2, SNS). These ligands are dissolved in DCM and added $[Pd(Cl)_2(MeCN)_2]$ yields pure palladium complexes catalysts. Catalytic experiments were performed.

Kamal M. Dawood et al.[34] synthesized coupling of 3-(5-bromobenzofuran-2-yl)-1*H*-pyrazole with arylboronic acids in aqueous media under thermal heating and MW irradiation using catalyst Pd(II)-complex-benzothiazole-oxime palladium(II) (0.25 mol%) for 15 to 30 min and in thermal heating for 6 to 14 h. 1-(5-Bromobenzofuran-2-yl)ethanone converted to 3-(5-bromobenzofuran-2-yl)-1*H*-pyrazole by subsequent reactions. Characterization of 3-(5-bromobenzofuran-2-yl)-1*H*-pyrazole done using FT-IR, 1HNMR, 13CNMR etc. Coupling reactions were optimized and compared yields in the presence of bases such as KOH and Cs_2CO_3 in H_2O-DMF solvent system under MW and conventional heating.

Afaf Y. Khormi et al.[35] synthesized biaryls using aryl bromide and phenylboronic acid, TBAB, K_2CO_3 in water with nanoformamidine-based palladium complex catalyst in a MW at 300 W (95 ˚C) for 10 min. Coupling reaction optimized using different bases, solvent and co-catalysts at different MW power. They also optimized Suzuki cross-coupling of 4-bromoacetophenone with phenylboronic acid and Pd-complex (0.75 mol%) under thermal heating at 100 ˚C for 3 h. The formamidine-based palladium (II) complex was prepared by dissolving N,Ndimethyl- N'-(pyrimidin-2-yl)formimidamide in methanol with of Na_2PdCl_4 at room temperature. Characterized using SEM, EDX and XRD analysis. Effect of concentration of precatalyst, solvent and base on the yield were analyzed.

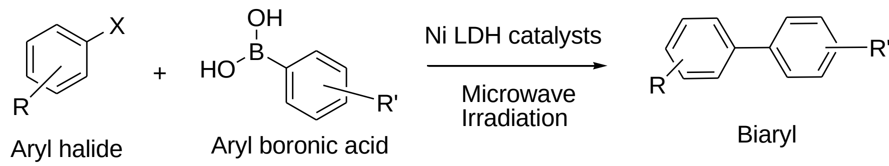
Table 1. Details of reaction conditions and catalysts in cross coupling reactions

Author	Reactant	Catalyst	Temp or Watts	Time (min.)
Ramirez-Rave, Morales-Morales et al. 2017	Halobenzene, phenyl boronic acid	Pd catalyst [PdCl{C6H4(Ph2P = NC6H4SR-j3-C,N,S)}]	60W	5
Şengül and Hanhan 2018	Aryl chloride and aryl boronic acids	water soluble benzimidazole – Pd complex ([Pd(L)]Cl)	850 W	15
Dawood, Darweesh et al. 2018	3-(5-bromobenzofuran-2-yl)-1*H*-pyrazole and arylboronic acids	benzothiazole-oxime-based Pd(II) complex	250W	15-30
Khormi, Farghaly et al. 2019	Phenyl boronic acid and 4-bromoacetophenone/ aryl bromide	nanoformamidine-based palladium complex	300 W	10
López-Saucedo, Flores-Rojas et al. 2018	Aryl bromides with phenyl boronic acid.	Pd-NS1, Pd-NS2, Pd-SNS	120 W	15
Novanna, Kannadasan et al. 2020	2-amino-5-iodobenzamide and 2-amino-3, 5-diiodobenzamide arylboronic acids and Aryl boronic acid	$Pd(dppf)Cl_2$	200 W	10
Catalyst reused or recycled				
Baran 2019	Aryl halide and $PhB(OH)_2$	Palladium nanoparticles (Pd NPs)	400 W	6
Baran, Baran et al. 2018	Aryl halides, phenyl boronic acid	New palladium nanocatalyst on chitosan/cellulose composite.	400 W 50 ˚C	5
Baran, Sargin et al. 2017	Aryl halide, phenyl boronic acid	Na_2PdCl_4, $PdCl_2(CH_3CN)_2$, poropollenin microcapsules	50 ˚C	6

		supported Pd(II) catalyst		
Yılmaz Baran 2019	Aryl halides and phenyl boronic acid	PMPA, O(PMPA) and O(PMPA)-Pd catalyst	400W 50 ˚C	6
Baran 2018	aryl halides and phenylboronic acid	palladium nanocatalyst (Pd NPs@APC)	350 W.	5
Elazab, Sadek et al. 2018	aryl halide and aryl boronic acid	Pd supported on CuO nanoparticles (Pd/CuO).	250W at 80, 120 and 150 ˚C	10
Elazab 2019	aryl halide and aryl boronic acid	Iron Oxide Supported Palladium Nanoparticles	250 W	10
Baran, Baran et al. 2019	Aryl halide and Phenyl boronic acid gives biaryls	Palladium nanoparticles (Pd NPs)	400 W	6
Baran 2019	aryl halide and phenyl boronic acid	Pectin supported palladium catalyst (Pct-Pd)	400W.	8
Pd free Ni Catalyst				
Alzhrani, Ahmed et al. 2019	Aryl boronic acid and aryl halide	NiLDHs-R200	300 W	15

In table 1, Suzuki-Miyaura coupling is a metal catalyzed reaction such as Pd catalysts between boronic acid or boronic ester and aryl halide under basic conditions. This reaction creates carbon-carbon bonds to produce biaryl compounds. The first Suzuki-type cross coupling reaction between haloarenes and phenylboronic acid was published by Suzuki and Miyaura in 1981.[19] In above reactions various Pd catalysts are used in different concentration in Suzuki–Miyaura cross-coupling for the preparation of biaryls. All the reactions were performed in MW irradiation at different power watt and reaction time. In most of the reactions, catalysts were regenerated and reused for subsequent cycles of coupling reactions with good performance. Among the various bases used by researchers in Suzuki-Miyaura coupling, K_2CO_3 was shown maximum yields in the biaryl preparations. Support material selection for the catalytic reactions is very important parameter because this influence on catalytic activity, thermal stability, and reusability of catalyst. It is also important to resist metal leaching problem which influence the reusability of the catalyst.[36] Association and dissociation[37] of the ligands or solvent with catalysts influence on the cross coupling reaction. The relative reactivity of aryl halides decreases in the order of I > Br > Cl during oxidative addition in the catalytic cycle. The coupling of an organoboron reagent with an aryl halide gives biaryls by using the palladium or nickel catalyst.

iv) Pd free Nickel (Ni) catalysts:



Scheme 4: Coupling of aryl halides and aryl boronic acids using Ni-LDH catalysts.

Many researchers[38-42] have proposed Pd-free Ni catalysts as a safe, simple, effective and economic catalysts used to catalyses cross couplings with various boronic acids and aryl halides under thermal conditions or MW conditions.

Ghalia Alzhrani et al.[42] synthesized biaryl (Scheme 4) using mixture of boronic acid derivative and aryl halide in dioxane / water (5:1), potassium carbonate in the presence of 150 mg of Ni LDHs (layered double hydroxide) catalyst. The mixture irradiated with a power of 300 W, at 140 °C under auto generated pressure. TEM, TGA, FT-IR, elemental chemical analysis, X-ray diffraction studied for catalyst NiLDHs-Dr. The best yield 99% was achieved using 2Ni LDH-Dr catalyst in 30 min. Lower yield at longer period of time was attained using NiLDH-R200 catalyst. NiLDH-Dr catalyst showed good catalytic activity than NiLDH-R200. The important advantages in catalytic activity due to the presence of Ni^{2+} ions on NiLDHs-Dr catalyst's surface in more abundance as evidenced by XPS data. Optimization of various catalysts for coupling showed in 30min to 60 min. Product yield analyzed at different NiLDHs catalyst composition in iodobenzene and 4-tolylboronic acid in the presence of base K_2CO_3 and solvent dioxane / H_2O at 300 W, 140 °C for 15 min. Yields are Ar-I > Ar-Br > Ar-Cl. Reusability up to 5 cycles very good.

Conclusion

This review describes details of studies of the MW assisted Suzuki-Miyaura cross coupling using different Palladium catalysts. This approach offers a straightforward route to the synthesis of a diverse range of biaryls from aryl halides and aryl boronic acids with different reaction parameters or conditions such as power of MW irradiation, reaction time, molar percentage of catalyst, etc. The use of MW irradiation method significantly shortened the reaction time. From the reported results it can be concluded that palladium is less toxic, safer, more economical, eco-friendly, reusability of the catalyst and high product yields. In summary, importance and the significant use of Suzuki- Miyaura biaryls coupling reactions in organic synthesis have been seen which is highlighted by a rapid reporting of new aryl halides and aryl boronic acids in the presence of variety of Pd-catalysts for cross-coupling partners. The present review would serve the need of organic chemist to engage in searching new applications of palladium by varying reaction conditions for the organic synthesis.

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