



REVIEW

Suzuki-Miyaura Cross Coupling Reaction in Various Green Media

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Suzuki-Miyaura cross-coupling reaction is an efficient and utilized method for the direct formation of carbon-carbon bonds. The effectiveness and efficiency of Suzuki-Miyaura cross-coupling reaction and its applications have been the topic of interest for synthetic chemists for the last few decades. Green chemistry is the area where we use eco-friendly products. Suzuki coupling includes palladium or nickel catalyzed coupling reaction, which involves ester of boric acids or simply boric acids with the organic halides or pseudohalide. In recent years, these catalytic systems have been developed in a green environment for Suzuki reaction (Suzuki-Miyaura cross-coupling reaction). This review epitomizes the Suzuki-Miyaura cross-coupling reaction using efficient catalysts in various green media.

Keywords: Suzuki-Miyaura cross coupling reaction, Green media.

INTRODUCTION

According to IUPAC, the term green chemistry is characterized as the development, plan and utilization of chemical items and cycles to diminish or to dispose of the utilization and age of dangerous substances [1]. Due to environmental and medical problems, such as eco-friendly medium requirements need of an hour for both living organisms and the climate (environment) so deadly chemicals are kept away.

Green chemistry has now become the objective for spearhead research into sustainable technologies. These may diminish both, the production as well as the utilization of the substances which are hazardous in mining and the plan, manufacturing, and use of chemical products. This may likewise prompt energy saving and superior climate and wellbeing *i.e.*, a better environment. Taking into account this serious issue, scientists are continuously putting efforts to find a good and affordable sustainable replacement for the toxic, organic expensive solvents [2]. In recent years, efforts have been made by scientists to achieve Suzuki-Miyaura cross-coupling reaction (SMR) in an eco-friendly environment using an efficient catalyst and after several attempts [3], Suzuki-Miyaura cross-coupling reaction (SMR) is successfully performed in green solvents like water, ethanol,

neoteric media such as deep eutectic solvents, biomass derived solvents, ionic liquids and supercritical carbon dioxide, *etc.*

The organic synthesis involves the formation of a C-C single bond catalyzed by many transition metals. These metals mediated cross-coupling reactions are the powerful route to form a C-C bond. Among so many transition metals, palladium is the one, which is commonly used for the formation of the carbon-carbon bond. This reaction is named as palladium-catalyzed *i.e.* (Pd-catalyzed) Suzuki-Miyaura coupling reaction [2] and considered as the most exploited and powerful tool for direct formation of carbon-carbon single bond. Previously, the formation of a carbon-carbon bond, transition metal copper was preferred before the use of Pd in this cross-coupling reaction [3].

There are several other methods known for the formation of C-C bonds like Negishi coupling, Himaya coupling, Kharash coupling, Sonogashira coupling, Kumuda coupling, Buchwald-Hatwig coupling, Stille coupling, Murahashi coupling reactions [4-11]. But among all these, Suzuki Miyaura coupling was considered the most suitable methods due to (i) mild reaction conditions; (ii) availability of varieties of environmentally friendly boronic acids; and (iii) easy handling and removal of the byproducts [1].

For the synthesis of medicines, chemicals, natural products or polymeric materials, the SM cross-coupling reaction is the first choice for many chemists over many other coupling reactions. The popularity and interest in the SM coupling reaction have been reported and has been utilized as new tool for synthesis [12].

Suzuki-Miyaura cross-coupling reaction (SMR): SMR is a well-known palladium catalyst reaction for the formation of a carbon-carbon bond (C-C bond). The coupling occurs between boronic acid derivatives and organohalide (**Scheme-I**). The coupling is highly regio- and stereo-selective [13-15]. This cross-coupling reaction occurs in three steps [16] (i) **Oxidative addition:** This is the rate-determining step. The reaction is initiated by the oxidative addition of organic halides (R-X) to Pd(0) catalyst. This step leads to the formation of intermediate (R₁-Pd-X) *i.e.* organopalladium species; (ii) **Transmetalation:** Organoborane compound reacts with the intermediate [R₁-Pd-X] *via* transmetalation in the presence of a base and leads to the formation of intermediate (R₁-Pd-R₂). Organoboron compound is activated by a base. In absence of a base, transmetalation is not possible; (iii) **Reductive elimination:** In this last step, alkane is formed from intermediate (R₁-Pd-R₂) by reductive elimination palladium (0) species are regenerated (**Scheme-II**).

Currently, green solvents are used for Suzuki-Miyaura cross-coupling reaction (SMR), which are discussed as follows:

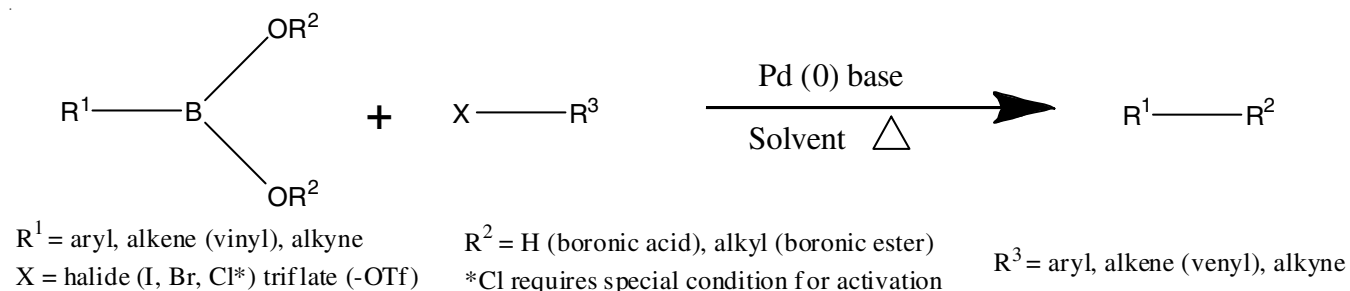
Water: Water is an abundant asset with a splendid particularity, is a safe and green solvent. In past twenty years, water is used as a solvent in a cluster of organic reactions [17]. Some

advantages to use water as a solvent are (i) it acts as the medium and as the co-catalyst in a significant number of these concurrent synthetic routes because of its hydrophobic nature and high surface tension, which emphasizes the inclination of non-polar molecules to aggregate in water [18]; (ii) has high cohesive energy; and (iii) water plays a significant role in the rate of increasing speed of reactions by setting up hydrogen bond with the particular functional groups of the reactants and initiating them in the particular process [19].

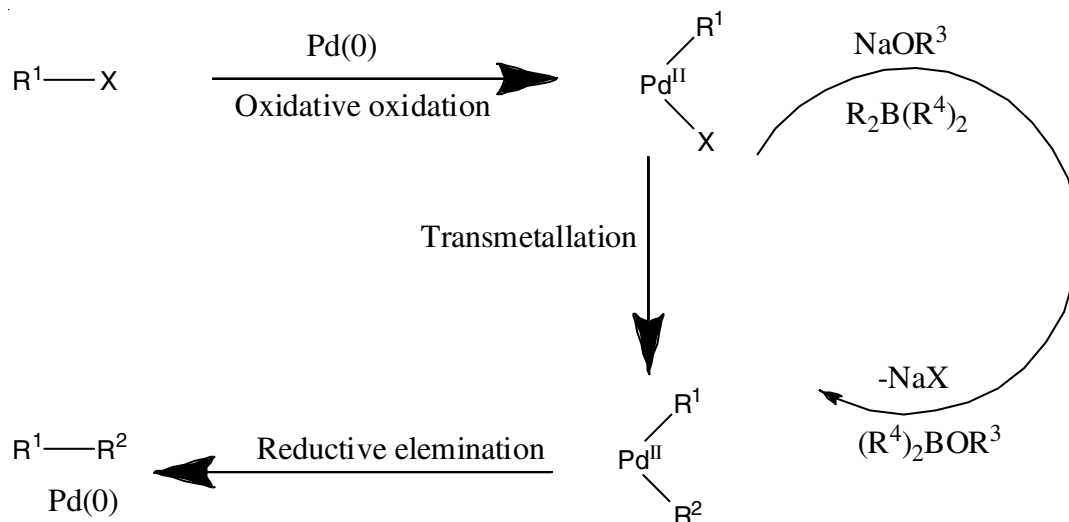
The use of water as a greener feasible reaction medium is attributed for reducing the pollution in the environment [20-23]. It has been used in the SMR combined with various uphold systems for a wide assortment of nanoparticles as the catalysts [24-26]. Significant contemplations have been stretched out to the heterogeneous and aqueous exchanging of organic conversions by amphiphilic block copolymer-promoted metal nanoparticles or the transition metal complexes [27].

Ethanol: Ethanol is another green solvent used in various organic reactions. In year 1862, ethanol was first used by two scientists Berthelot & Saint Gills performed esterification of acetic acid using ethanol [28].

Polyethylene glycol: Poly(ethylene glycol) (PEG) oligomers are considered as proficient, less volatile, eco-friendly and have been found to be effective as alternative solvents in an extensive range of chemical, mechanical and clinical applications [29]. PEGs are promptly miscible with not only water but also organic polar solvents, yet immiscible with non-polar organic solvents, aliphatic hydrocarbons and supercritical CO₂ [30-32]. Gene-



Scheme-I: SMR coupling reaction between boronic acid derivatives and organohalide



Scheme-II: Mechanism of SMR

rally, economical PEGs have been broadly utilized as greener solvents in a few organic reactions as they are almost innocuous *i.e.* harmless, being regularly utilized in drug preparations. Moreover, PEGs have an extremely low vapour pressure, high catalytic property and thermal stability [32] and also possess the stability in acidic as well as basic media, which make them appropriate media for the oxidation or reduction process. Besides, PEGs have been utilized as a productive supplement in aqueous stage cross-coupling changes to improve the cooperation between water-solvent catalysts and the organic reactants [33,34].

Ionic liquids: Ionic liquids (ILs) are progressively being utilized as well-known media in a different area of specialized applications. The outstanding physico-chemical properties of ionic liquids, for example, non-combustibility, stability and polarity (chemical, electrochemical and thermal), non-volatility can be generously adjusted by changing the cationic as well as the anionic components [35], which can offer several advantages to ionic liquids with certain properties through a various combination of cations and anions. Ionic liquids have been utilized in SMR as productive and feasible media [36].

Deep eutectic solvents: Deep eutectic solvents (DES), presented at first by Abbott *et al.* [37], which are significant choices to room temperature ionic fluids (RTIL), because of their fascinating properties and advantages. Generally, DES are made through the complexation of quaternary NH_3 salts as the hydrogen-bond acceptors with a hydrogen bond contributor, for example, urea, amino acids, sugars, carboxylic acids, and glycerol or M^{2+} ions [38]. Due to their high viscosity, DES contains broad hydrogen-bonding lattice, moderately big particle sizes and electrostatic force [39]. DES as green media have been utilized for some chemical processes [40,41] and different organic and inorganic transformations [42-44].

Suzuki-Miyaura coupling using green media: As the organic solvents and Pd catalyst used in the Suzuki-Miyaura coupling reaction are expensive, and also the palladium reagents are difficult to recycle. So, these problems lead to the discovery of green conditions for Suzuki-Miyaura cross-coupling reaction [45]. Bussolari & Rehbour [46] reported that the reaction between the arylboronic acid and bromothiophenes or bromofurans) in presence of $\text{Pd}(\text{OAc})_2$, if treated in aqueous media,

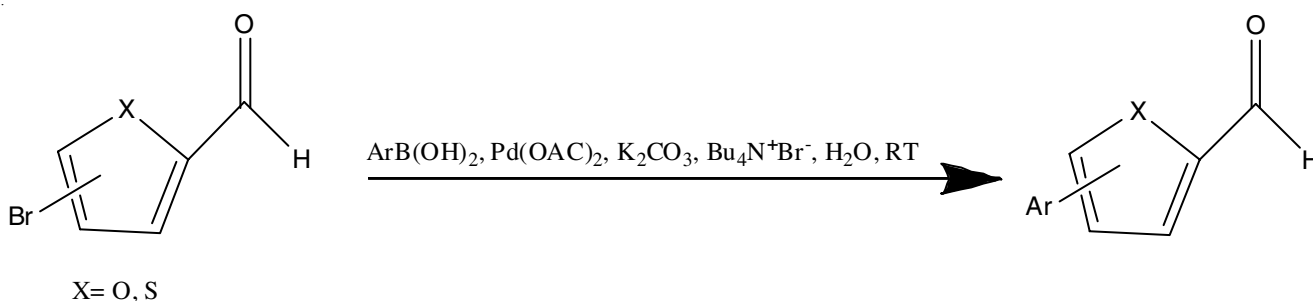
occurs very fast, even though the mixture was non-homogeneous, the yield of the reactions was good (**Scheme-III**). The main features of this reaction was the easy disposal of the side reactions emerged from phosphine ligands while using a Pd catalyzed mediated SM cross-coupling reaction.

Kirsch *et al.* [47] coupled β -chloroacrobins with various boronic acids leads to the formation of tetrasubstituted alkenes. Despite the fact that aryl chlorides are less reactive because of their inactive nature in the oxidative addition step, the Suzuki-Miyaura cross-coupling of vinyl chloride is simpler when contrasted with the aryl and alkyl chlorides (**Scheme-IV**).

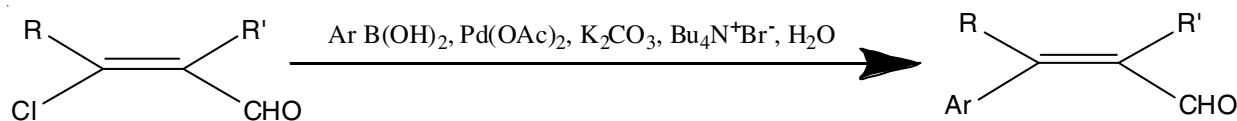
Villemin *et al.* [48] carried out the Suzuki-Miyura cross-coupling reactions with a variety of heteroaryl halides in monomethylformamide (MMF), which shows a high polarity in the microwave irradiation and this polarity is very high in comparison to H_2O and other amides. In this reaction, sodium tetraphenylborate ($(\text{C}_6\text{H}_5)_4\text{BNa}$) was used either in H_2O or in MMF for phenylation of respective heteroaryl halides (**Scheme-V**).

The homogeneous catalyst pyridinium-attuned β -cyclodextrin (Pyr: β -CD) is extremely soluble in water when contrasted with the native β -CD and can be used again multiple times (< 6 times) without critical loss of the catalytic activity. The detailed study about the preparation and applications of an ionic Pd(II) complex, which is stabilized by utilizing water soluble Pyr: β -CD as a proficient catalyst for the Suzuki-Miyaura cross-coupling reaction [49]. The substrate scope, under the improved conditions, was investigated for a scope of various 4-substituted aryl bromides, which contain both electron-withdrawing and electron-donating groups, which all outfitted products in great yields in a brief timeframe, except for nitro-group replacement (0.5 mol% $\text{Pd}(\text{OAc})_2$ at 80 °C in 2 mL H_2O) (**Scheme-VI**).

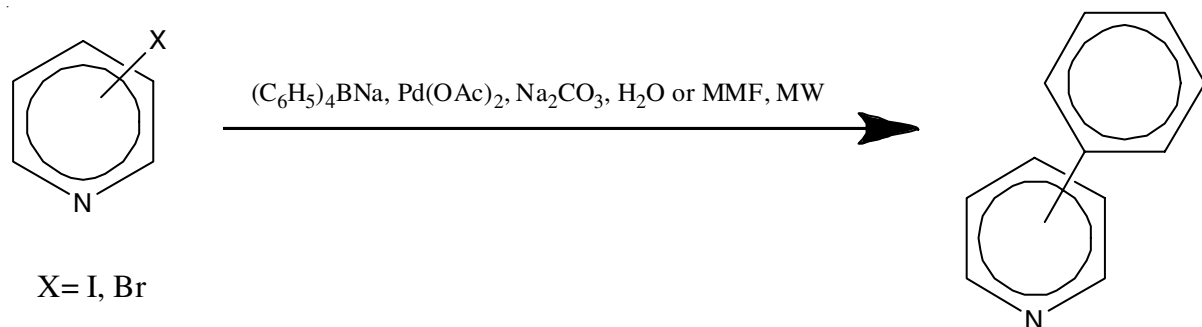
Zou *et al.* [50] prepared the Pd@MIL-101Cr-NH₂ catalyst through the immobilization of Pd nanoparticles on an amino-functionalized metal-organic framework (MOF). The catalytic activity of the different loaded catalysts (4, 8, 12 and 16 wt.% Pd@MIL-101Cr-NH₂) was assessed for the Suzuki-Miyaura cross-coupling reaction. The best catalytic execution being accomplished with the MOF consists of 8 wt.% Pd nanoparticles



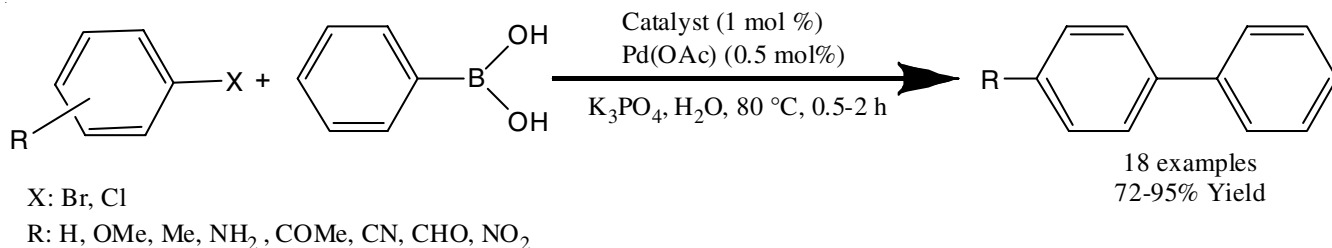
Scheme-III: SMR of arylboronic acid and bromothiophenes in presence of $\text{Pd}(\text{OAc})_2$



Scheme-IV: SMR of various arylboronic acids coupled with β -chloroacrobins



Scheme-V: SMR of various heteroaryl halides in monomethylformamide (MMF)



Scheme-VI: The SMR of variety of aryl halides with phenylboronic acid catalyzed by pyridinium-modified Cd/Pd(OAc)₂ complex

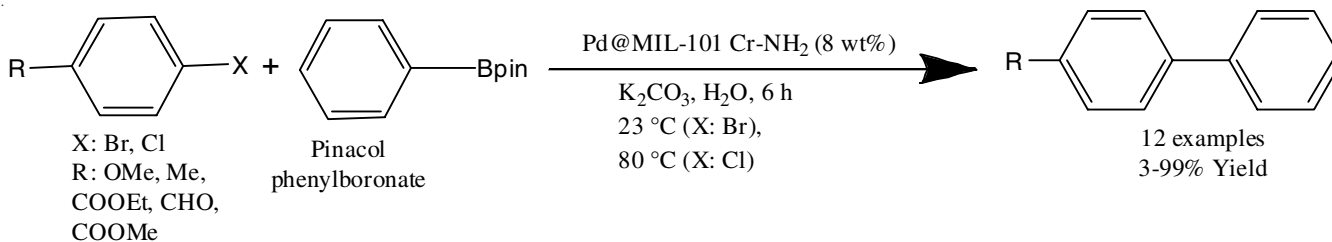
(**Scheme-VII**). Moreover, the catalyst can be reused multiple times without change of its catalytic action.

Varma *et al.* [51] depicted a flexible iron-cellulose-inferred Fe₃O₄@CPd catalyst, which has been synthesized by *in-situ* creation of nanoferrites and the consolidation of carbon from sustainable cellulose by means of calcination. In the presence of this catalyst, arylation of aryl halides conveniently completed by boronic acid under the microwave irradiation conditions inside 30 min (**Scheme-VIII**) and assists both the electron donating and withdrawing substituents.

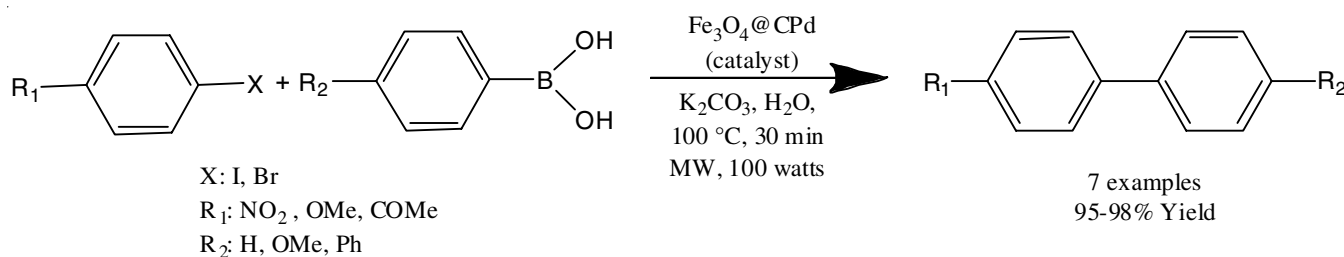
Wang *et al.* [52] synthesized (Ni, Mg)₃Si₂O₅(OH)₄ solid-solution nanotubes of a tunable structure by means of hydrothermal synthesis by shifting the molar proportion of Mg²⁺ to Ni²⁺, which were then stacked with Pd (~0.045 wt.%). The resulting catalyst exhibited good activity for the Suzuki-Miyaura

cross-coupling reaction between 4-iodotoluene and phenylboronic acid (**Scheme-IX**). Among the different proportions of Mg²⁺:Ni²⁺ explored, the hydrothermally steady stable solid-solution silicate nanotubes with Mg²⁺:Ni²⁺ proportion (1.0:1.0) gave an ideal tubular structured backing to the catalysts with low Pd stacking, great reusing execution for around 10 cycles, with the yields of ~99% and an incredibly low Pd discharge level of ~0.02 ppm was additionally noticed.

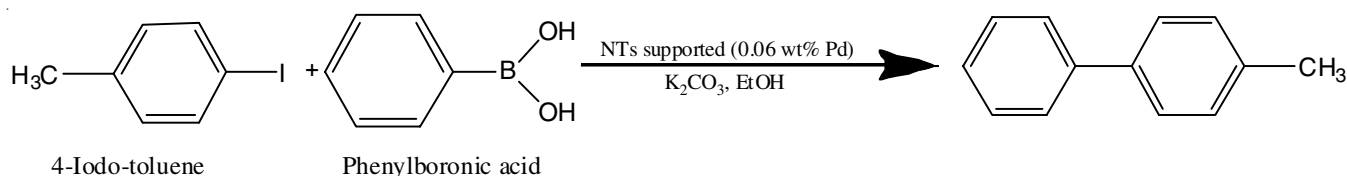
Nahra *et al.* [53] prepared the [NHC] [Pd(η³-R-allyl)Cl] complexes as easy, environmentally friendly and successful catalysts for both electron-withdrawing and donating aryl bromides and chlorides and also heteroatom containing and sterically hindered aryl halides (**Scheme-X**). The catalytic reaction was conducted in ethanol with a weak and inexpensive inorganic base.



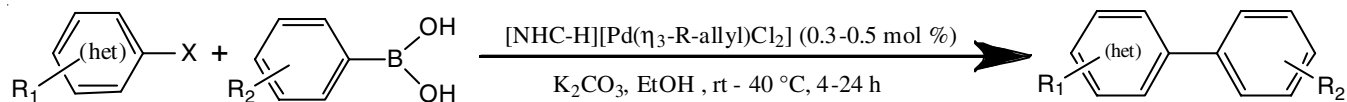
Scheme-VII: The SMR of aryl bromides/chlorides using 8 wt% Pd@MIL-101 Cr-NH₂ catalyst



Scheme-VIII: Arylation of various aryl halides using Fe₃O₄@CPd catalyst



Scheme-IX: SMR of 4 iodotoluene and phenylboronic acid



X: Br, Cl

R₁: OMe, CF₃, CN, NO₂, NH₂, Me, COMe, FR₂: H, Me, COMe, CHO, F, CF₃30 examples
66-99% yieldScheme-X: Reaction of SMR using catalyst [NHC][Pd(η₃-R-allyl)Cl] in ethanol solvent

Most recently, graphene oxide (GO) [54,55] and chemically-derived graphene (CDG) [56] have been reported as amazingly flexible carbon materials. The GO and chemically derived graphene have been utilized as supports for Pd groups and nanoparticles as predominant catalysts for the Suzuki-Miyaura cross-coupling reaction in aqueous ethanol. Rather than standard Pd/C catalysts, GO and graphene-based catalysts managed the cost of a lot higher activities with TOF surpassing 39000 h⁻¹ and extremely low Pd challenging, the most noteworthy activity being accomplished with Pd²⁺-GO and H₂-decreased derivative Pd⁰-CDG-H₂, trailed by Pd⁰-CDGEXP and Pd/C (Scheme-XI).

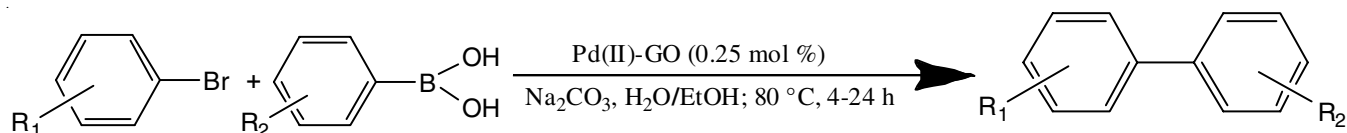
Fu *et al.* [57] revealed an effortless photodeposition procedure to synthesize a green catalyst, Pd/g-C₃N₄ nanocomposite with lower Pd substance (Pd 0.10/g-C₃N₄) for the Suzuki-Miyaura cross-coupling reaction (Scheme-XII) where the Pd nanoparticles were consistently scattered on the g-C₃N₄ surface. Incredible catalytic activity was seen at room temperature with quantitative change and a good yield of 97% for the biphenyls.

The nanostructured Pd nanoparticles were trapped on the outside of modified attractive GO by GO/Fe₃O₄/PAMPS/Pd

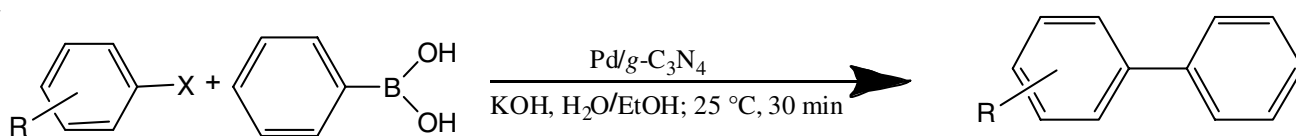
(where PAMPS = poly-2-acrylamido-2-methyl-1-propanesulfonic acid) presented as an effective nanocatalyst for the Suzuki-Miyaura cross-coupling reaction in a combination of water and ethanol as reported by Sedghi *et al.* [58] (Scheme-XIII). Predominant catalytic activity was noticed for the cross-coupling of alkyl iodides, bromides and chlorides as the difficult substrates.

It was observed that when the electron-donating substituents aryl halides and aryl boronic acid are taken, the reaction completed in very less time, though those with electron withdrawing substituents took somewhat more, probably because of the presence of polar electron-donating substituents on the surface of nanohybrid CQD catalyst (Scheme-XIV) [59]. The catalyst was discovered to be reusable up to the 3rd run, without losing the catalytic activity.

Astruc *et al.* [60] revealed the convenience of α-Fe₂O₃ nanoclusters (1.8 nm size) which were homogeneously stored on the edge of GO sheets (α-Fe₂O₃ nanocluster/GO) as an effective catalyst in ppm for the Suzuki-Miyaura cross-coupling reaction. The reaction was performed overnight at 80 °C within the sight of 150 ppm mol%. Derivatives of bromobenzene containing both electron-donating and withdrawing groups,

R₁: OH, OMe, CHO, NO₂, H, COOEt, COOH, CN, FR₂: OMe, H27 examples
81-100% Yield

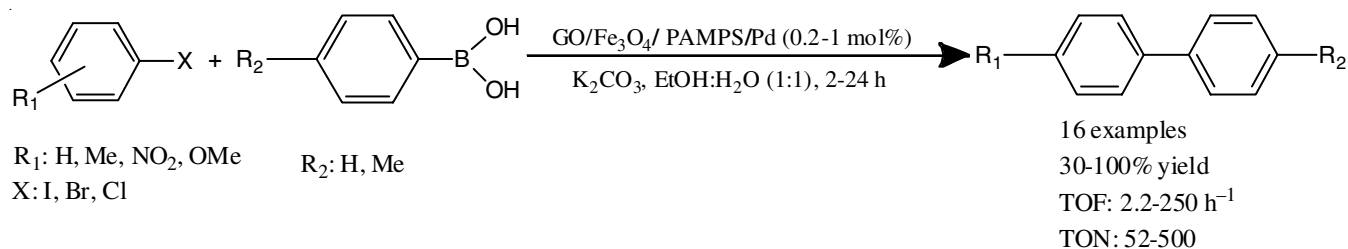
Scheme-XI: SMR of several aryl bromides in presence of 0.25 mol% Pd(II)-GO

R₁: H, Me, CHO, NO₂, OH, COOH

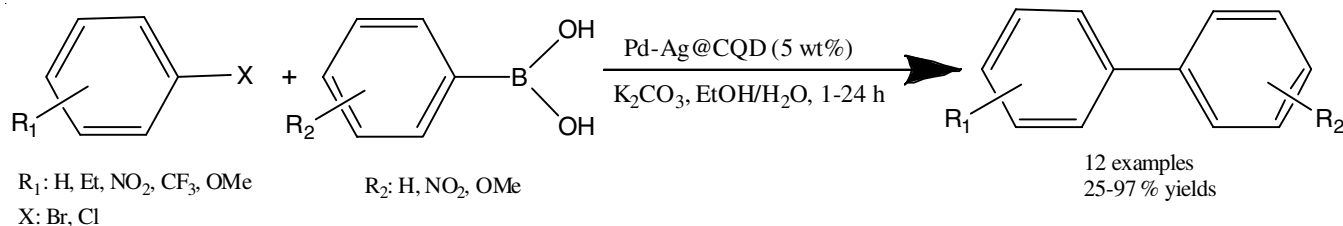
X: I, Br, Cl

12 examples
38-100% conversion

Scheme-XII: The SMR of aryl halides on the catalytic conversion to biaryls



Scheme-XIII: The SMR of several aryl halides with aryl boronic acids catalyzed by the GO/Fe₃O₄/PAMPS/Pd nanocomposite



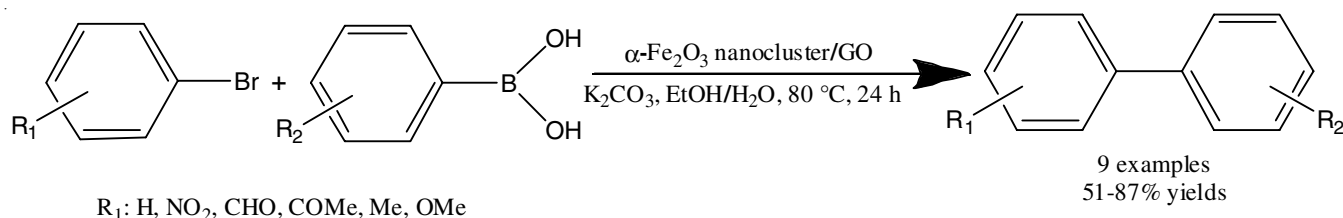
Scheme-XIV: SMR using Pd-Ag@CQD catalyst

at the *para*-positions were appropriate as the coupling partners, resulted in the product formation in great yields (**Scheme-XV**). The catalyst could be reused multiple times (almost 4 times) with great yields.

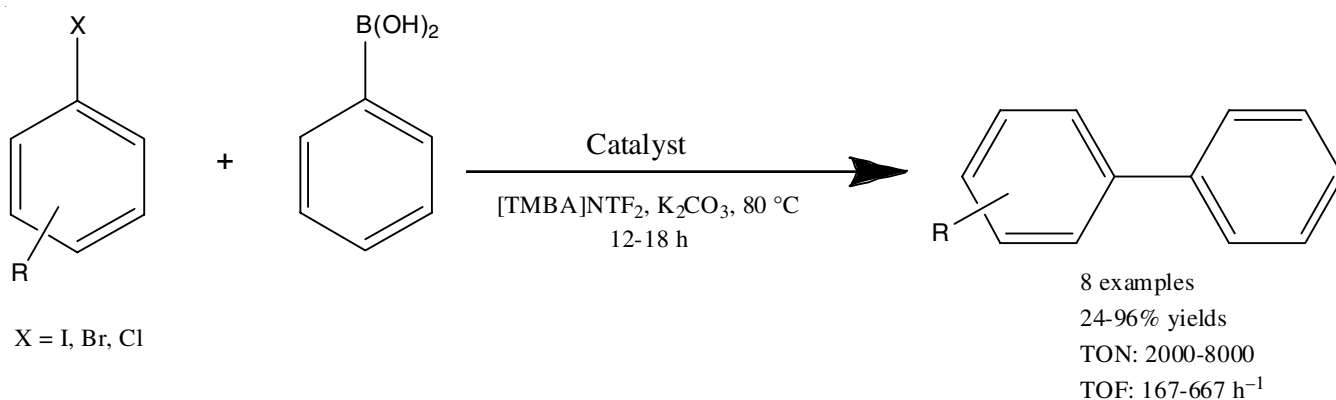
Ionic liquids (ILs) have been utilized in the Suzuki-Miyaura cross-coupling reaction as proficient and controllable media. Welton *et al.* [61] described the first investigation of ionic fluids as the solvent for Pd-catalyzed C-C cross-coupling reactions. Recently, Kaur & Singh *et al.* [62] prepared an effective recyclable mud carbapalladacycle nanocomposite for Suzuki-Miyaura cross-coupling reaction in tetramethyl butylammonium bis-(trifluoromethanesulfonyl)imide [TMBA]NTf₂ ionic liquid. Halides like chloro-, iodo-, bromo-, substituted aryl halides created the ideal products in great to brilliant yield and selectivity (**Scheme-XVI**).

Few Pd-based catalytic frameworks for the Suzuki-Miyaura cross-coupling reaction presented in various ionic liquids are specified in Table-1.

The arrangement of different biaryls utilizing the Suzuki-Miyaura cross-coupling reaction in a DES framework has been accounted for through the development of C-C bonds at 100 °C utilizing 0.1-1 mol% of PdCl₂ as a catalyst, cationic phosphine ligands and K₂CO₃ as a base (**Scheme-XVII**) [67]. Among the different eutectic mixture frameworks inspected, ideal outcomes were acquired with choline chloride and ethylene glycol, followed intently by choline chloride and glycerol. Glycerol is greener in comparison to ethylene glycol and with the negligible contrast in the acquired yield, the choline chloride and glycerol framework have become the picked medium for this reaction. After the end of the reaction, DES and the catalyst



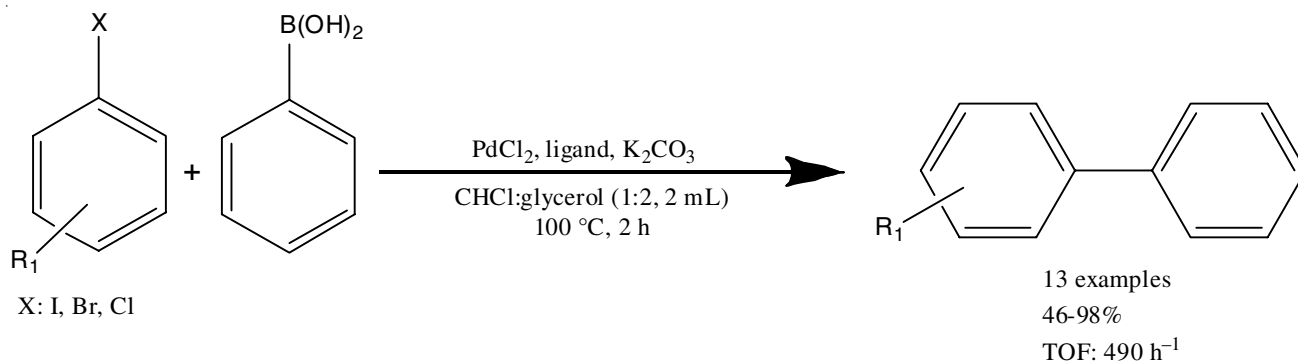
Scheme-XV: SMR using α -Fe₂O₃ nanocluster/GO catalyst



Scheme-XVI: Pd catalyzed SMR in ionic liquids

TABLE-1
COMPARISON OF VARIOUS Pd-BASED CATALYTIC FRAMEWORKS IN VARIOUS IONIC LIQUIDS FOR THE SMR

Solvent	Catalyst	Base	Temperature (°C)	Time (h)	Yield (%)	Ref.
[bmpy][NTf ₂]-water	PdCl ₂	K ₃ PO ₄	65	2	84-99	[63]
[C ₄ -DABCO] [dca]	PdCl ₂	-	110	3-6	40-99	[64]
[Aemim]Br	[[Gmim]Cl-Pd (II)]	Et ₃ N	25	1-10	65-94	[65]
[P ₆₆₁₄][NTf ₂]-water	Pd ₂ (dba) ₃	Cs ₂ CO ₃	160	48	19-99	[66]



Scheme-XVII: Pd catalyzed SMR between choline chloride and glycerol system

can be recuperated and reused multiple times almost around 5 times.

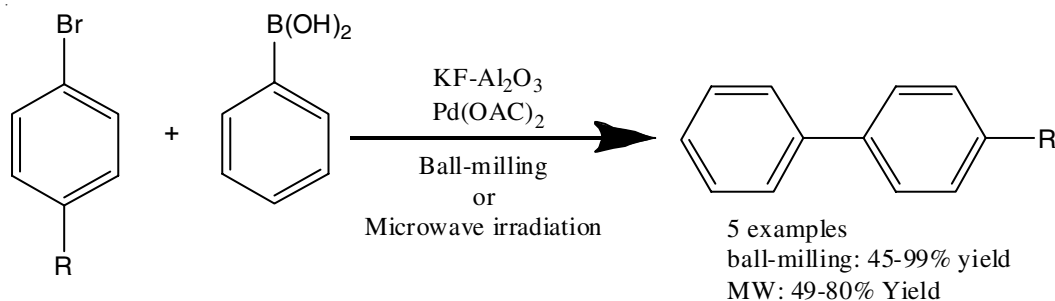
The solvent-free reactions have acquired extensive consideration as green strategies which are good options in contrast to the conventional procedures [68] regularly utilizing supported reagents under the microwave irradiation conditions [69]. These incorporate pounding techniques and high-velocity ball milling [70]. In past few years, the SMR has been performed under solventless conditions [71,72] Schneider *et al.* [73] reported a greener convention for the solvent-free Suzuki-Miyaura cross-coupling reaction within the sight of an inorganic solid (KF-Al₂O₃) and the advancement of other energy forms, for example, mechanochemical process and the microwave irradiation (**Scheme-XVIII**).

Resistance toward environmental oxygen, alluring safety aspects, better yields and more limited reaction times make this system an easy and appealing variant of the Suzuki-Miyaura cross-coupling reaction. Baran *et al.* [74] revealed a magnetically curable sporopollenin-based Pd catalyst for the immediate synthesis of biaryl compounds through the Suzuki-Miyaura cross-coupling reaction with both high turnover frequency and numbers. The catalyst recyclability was examined to 10 continuous cycles for the amalgamation of biaryls with little decrease in the reaction yields from 99 to 93%. Borchardt *et al.* [75]

portrayed the mechanochemical Suzuki polycondensation as a more powerful and greener option in contrast to the traditional media based polymerization change of poly(phenylene)s. Under improved conditions, this pioneer course can create straight polymers with a remarkable degree of polymerization, under ligand-free conditions in a short time about a half-hour. Moreover, the technique was expanded to a hyperbranched framework with high-temperature opposition in average to great yields in a short period. Several researchers [76,77] performed various reactions which led to the development of more interest in studying the application of Suzuki-Miyaura cross-coupling in green chemistry.

Conclusion

In this review article, a wide range of both homogeneous and heterogeneous catalytic frameworks, particularly nanocatalysts with metal for the Suzuki-Miyaura cross-coupling reaction (SMR) have been summed up. Various classes of heterogeneous catalysts dependent on graphene, zeolites, Fe₃O₄ and so forth, have shown their accessibility in cordial carrier going from water, ethanol, glycerol, polyethylene glycol (PEG) and ionic fluids. For the great advancement in future, a lot of research has to be done to develop sustainable chemistry. Catalytic systems which are heterogeneous are used to put forward the



Scheme-XVIII: Solvent free synthesis of biphenyl *via* Microwave irradiation and ball milling

idea of eco-friendly methods and so medium like water is being used in the reaction. Suzuki-Miyaura-cross coupling reaction using palladium are developed in both the conditions *i.e.* homogeneous as well as heterogeneous conditions. But among them heterogeneous conditions are more preferred over homogeneous.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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