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Review Article

Recent advances in cross-coupling reactions in aqueous medium

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Abstract: Transition metal catalyzed cross-couplings reactions, such as Suzuki-Miyaura, Sonogashira and Heck has emerged as important synthetic route for carbon-carbon bond formations. Various products of these reactions have wide applications in medicinal and pharmaceuticals industries. This review comprises of the use of aqueous media as a greener protocol for organic synthesis that have emerged in recent years.

Keywords: Suzuki-Miyaura; Sonogashira; Heck; cross-coupling; heterogeneous; aqueous-catalysis

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1. Introduction

Water is the nature's solvent. It exhibits exceptional physical and chemical properties. Few properties includes high heat capacity, large dielectric constant, a large temperature range in which it remains in the liquid state, potent hydrogen bonding, and low solubility of oxygen in water. Chanda, A., & Fokin, V. V., (2009). Further, water is a safe, non-flammable, cost-efficient, inexhaustible, environmentally benign and naturally abundant solvent. All these properties have attracted the attention of chemists and they have started investigating the use of water as an alternative to the various organic solvents used for organic reactions. Organic solvents such as benzene, methanol, toluene, THF, chlorinated hydrocarbons etc. are flammable, carcinogenic to human and environment (Sachdeva, H., & Khaturia, S., 2017). Thus, replacement of organic solvent with water follows an important principle of green chemistry.

In 1980s Breslow first showed the effect of water on rates and selectivities of Diels-Alder reactions. Their finding was often recognized as the "Big Bang" in organic synthesis that prompted researchers to work in this field (Lindstrom, U. M., 2002). Sharpless, Grieco and

many more have made significant contributions towards various organic transformations in aqueous medium. Few examples includes aldol reactions, allylation reactions, Claisen-rearrangements, hydrogenations of alkenes and oxidations. (Lindstrom, U. M., 2002).

In 2002, Lindstrom explained the theoretical and practical advantages of the utilization of water as solvent for organic transformations. (Lindstrom, U. M., 2002).

a) Simplified experimental procedures: For the isolation of organic products; simple phase separation technique can be followed for recovering of water-soluble catalysts and other reagents.

b) Eliminating tedious protection-deprotection steps: Various cumbersome methods such as hydrophobic derivatization can be avoided and water-soluble compounds such as carbohydrates can be used directly in their "native" form (Li and Chen, 2006).

c) The unique solvating properties of water. (Lindstrom, U. M., 2002).

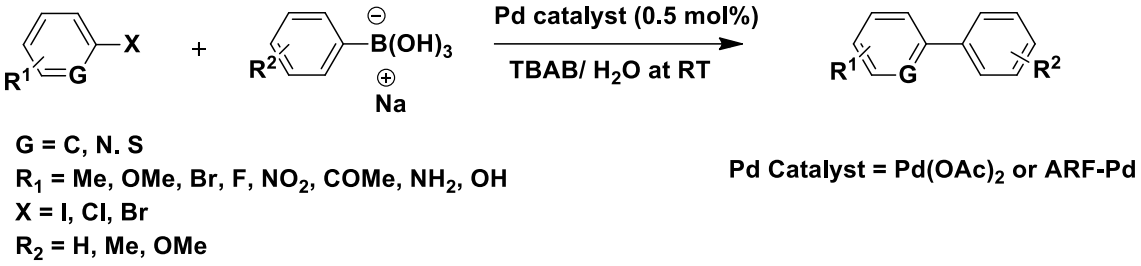
Water possesses many unique physical and chemical properties, such as large temperature window in which it remains in the liquid state, extensive hydrogen bonding, high heat capacity, large dielectric constant, and optimum oxygen solubility to maintain aquatic life forms. Chanda, A., & Fokin, V. V., 2009).

Recently water based reactions were divided as "in water" or "on water" by Butler, Coyne, and Fokin. The "on water" reactions are those where the reactants form heterogeneous mixture in water whereas "in water" reactions form a homogeneous mixture (Butler and Coyne, 2016). For on water reactions, the hydrophobic nature of the reactants brings them closer and thereby increases the reaction rates. In addition, trans-phase hydrogen bonding at organic-water interface activates the reactants and sometime stabilizes the transition states. Thus, water can play a dual role as a solvent as well as a catalyst.

2. Suzuki cross coupling reaction

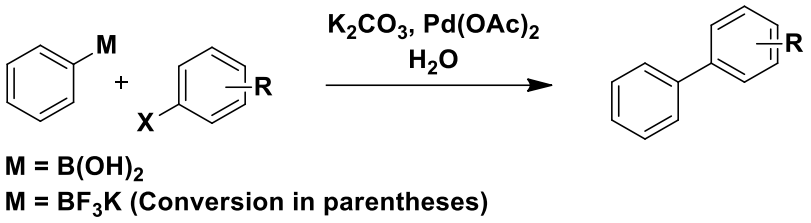
Palladium catalyzed cross coupling reaction between haloarenes and aryl boronic acids for the selective construction of C-C bonds were reported by Suzuki and Miyaura in 1981 (Suzuki *et al*, 1981); (Leadbeater and Marco, 2003). Biaryls obtained were extensively used as building block in organic chemistry in the synthesis of agrochemicals, pharmaceuticals, natural products, herbicides etc. (Knife *et al*, 2018). Since the discovery of this reaction, various modifications have been made in the reaction conditions to make the reaction cost effective and environment friendly (Knife *et al*, 2018). The phosphine based palladium catalysts and non-phosphine based Pd catalysts used for this reaction are often sensitive to air and moisture. Therefore, the reactions are performed in inert atmosphere and organic solvents. However, the availability, stability, cost of palladium complexes and ligands restricts it use (Bora and Mondal, 2012). Recent development shows the use of water as an environment friendly and economically favorable alternative to the organic solvent in organic transformations (Bora and Mondal, 2012). Herein, we wish to focus on the recent development of Suzuki-Miyaura cross-coupling reactions in aqueous media in both homogeneous and heterogeneous systems.

Basu *et al* reported the use of air-stable sodium aryl trihydroxyborates as an alternative to the organo boron species in Suzuki Miyaura cross-coupling reaction (Basu *et al*. 2010). They have carried out the reaction separately in presence of both $Pd(OAc)_2$ and heterogeneous Pd-catalyst (ARF-Pd) in water at ambient temperature.



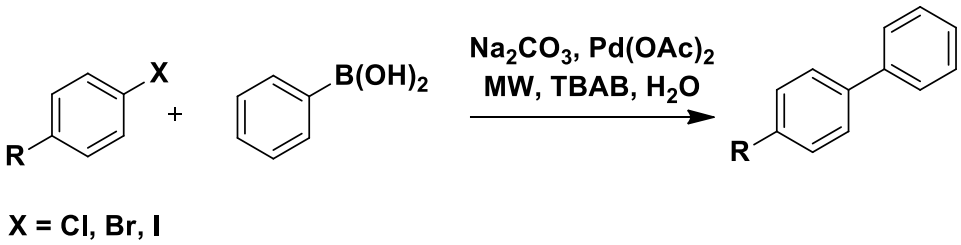
Scheme 1

A ligand free and ligand assisted Suzuki reaction in both pure water and aqueous media was reported by Schatz *et al* (Schatz *et al*. 2015). They have utilized $Pd(OAc)_2$ as catalyst in both the conditions. Initially, ligand free Suzuki reaction was carried out with aryl halide and phenyl boronic acid or potassium phenyltrifluoroborate as a nucleophilic coupling partner under aqueous medium to yield the corresponding biaryl compounds. However, there was every possibility for its improvement in yield. An imidazolium salt was used as ligand in ligand assisted Suzuki reaction, which helps for the in-situ generation of *N*-heterocyclic carbene ligands. This NHC-ligand precursors enhances the catalytic activity thereby reducing the Pd loading and without any effect on its conversion.



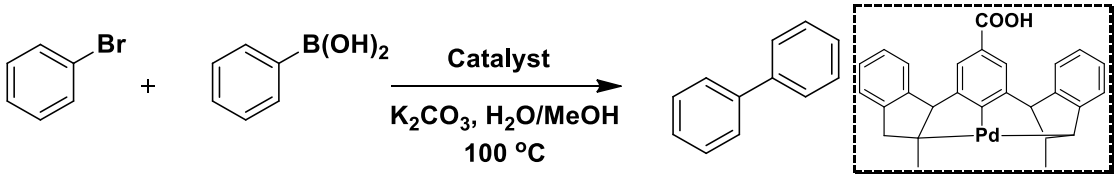
Scheme 2

Leadbeater and Marco reported the synthesis of biaryls via the coupling reaction between aryl halides and phenyl boronic acids using palladium acetate as catalyst and TBAB as additive in water (Leadbeater and Marco, 2003). The reaction was continued at ~150 ℃ for 5-10 minutes by both conventional heating and microwave methods. The products were isolated by chromatographic technique and the yield obtained by both the methods were comparable.



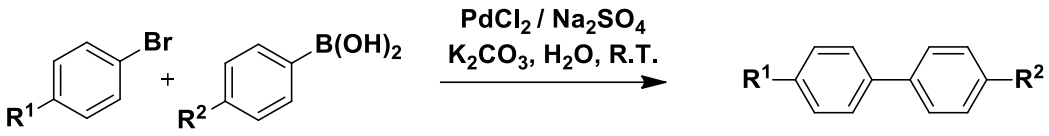
Scheme 3

A novel hydrophilic pyridine-bridged bis-benzimidazolylidene palladium pincer complex was developed by Tu *et al* (Tu *et al*. 2010). They have used the complex as a catalyst towards Suzuki–Miyaura coupling reactions in aqueous media. This protocol exhibited wide functional group tolerance even in very low catalyst loading in ppm scale.



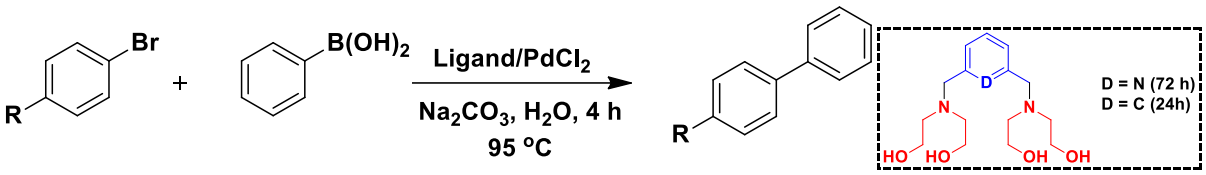
Scheme 4

Bora *et al* made a significant contribution to the Suzuki reaction (Bora and Mondal, 2012). They have reported the use of sodium sulfate, sodium chloride, sodium acetate as excellent promoter in $PdCl_2$ catalyzed Suzuki-Miyaura cross-coupling reactions in water under room temperature. The mild reaction conditions and use of cheap, non-toxic reagents, non-volatile solvent makes it more efficient and alternative method towards biaryl synthesis.



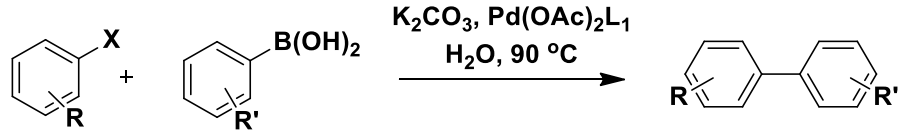
Scheme 5

In another article, Morales-Morales *et al* reported the synthesis of three novel pincer ligands based on amino alcohol components in its structure (Morales-Morales *et al*. 2013). This functional group favors its solubility in water. Thereafter these ligands were utilized with palladium as a potential catalyst for the Suzuki-Miyaura coupling reaction in water. The reaction was continued under mild reaction conditions to afford the biphenyls in excellent yields.



Scheme 6

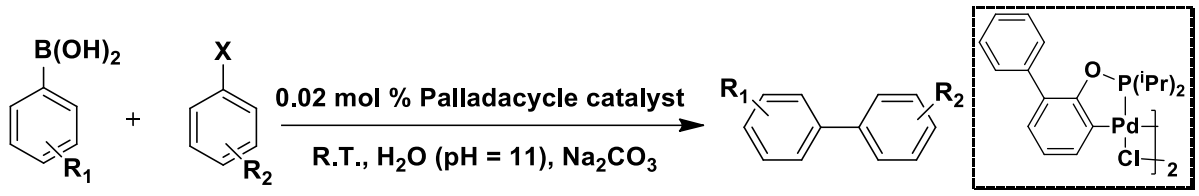
Amini *et al* reported the synthesis of water-soluble phosphazane derivatives using PCl_3 and $PhNH_2$ (Amini *et al*. 2014). Thereafter they have used phosphazane derivatives as ligand and palladium acetate as catalyst for the cross-coupling reaction of aryl halides and aryl-boronic acids in water. They have performed the reaction in a sealed tube at 90 °C. Insitu generation of Palladium(II)- phosphazane complex demonstrated good catalytic activity towards Suzuki reaction for wide range of substrates.



Scheme 7

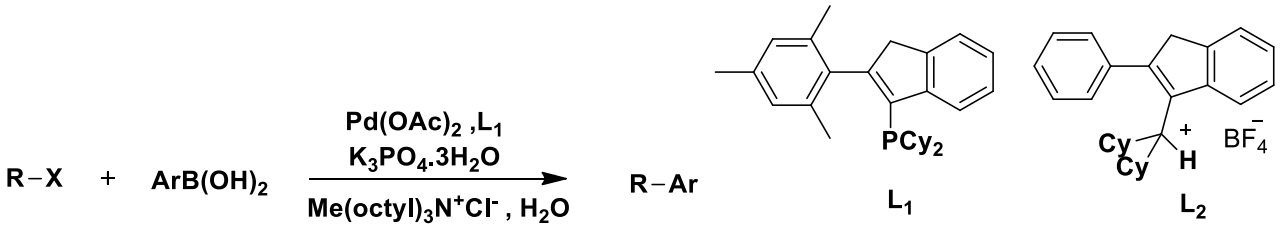
Eppinger *et al* reported a novel approach for the design and synthesis of Palladacyclic structure using ([1,1'-biphenyl]-2-yloxy)diisopropyl-phosphine and palladium chloride (Eppinger *et al*. 2011). This structure was used as catalyst for

aqueous Suzuki-Miyaura cross-coupling under air at room temperature. The isolation and purification of desired products are quite simple as the reaction takes place in absence of organic co-solvents and additives.



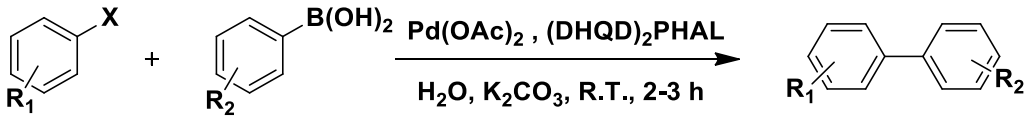
Scheme 8

A new catalytic system based on the use of $Pd(OAc)_2$, phosphine ligand: (2-mesitylindenyl)dicyclohexylphosphine, phase transfer reagent: $Me(octyl)_3N^+Cl^-$ and base: $K_3PO_4{\cdot}3H_2O$ was developed by Liu *et al* (Liu *et al*, 2012). This catalytic system was used in Suzuki coupling reaction between a variety of aryl and hetero aryl chlorides with boronic acid in water to yield the desired products.



Scheme 9

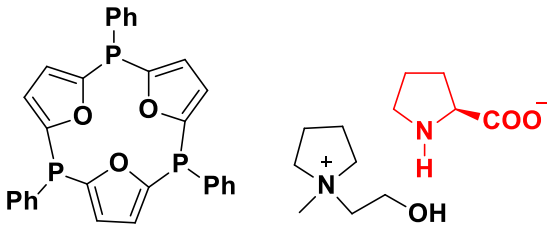
Saikia *et al* have reported a phosphine free system in palladium catalysis. Instead of phosphine ligand they have chosen $(DHQD)_2PHAL$ as a ligand and used this protocol for Suzuki-Miyaura cross coupling reaction (Saikia *et al*. 2013). The reaction was performed using $Pd(OAc)_2$ and $(DHQD)_2PHAL$ in water at room temperature. The reusability of this catalyst system for several catalytic cycles makes its superior over the other.



Scheme 10

Several other approaches for the Suzuki-Miyaura cross coupling reaction includes the use of Phenylphosphinacalix[3]trifuran, Ionic-liquids, Carborane-based NBN pincer palladium and many more. Planas *et al* reported the synthesis of *o*- and *m*- carborane based NBN pincer palladium complexes (Planas *et al*. 2014). These complexes were utilized as catalyst for the Suzuki coupling reaction in water and were found very effective in low amounts.

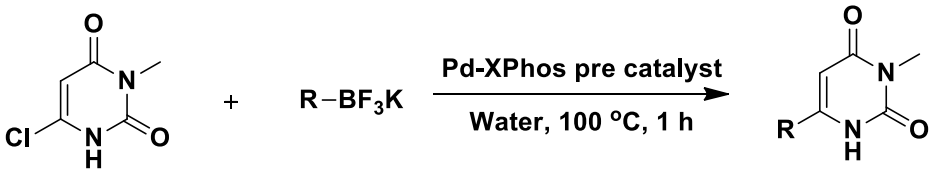
Yu *et al* reported the synthesis of Phenylphosphinacalix[3]trifuran via. one pot four step synthetic method using ^nBuLi as deprotonating agent (Yu *et al*. 2015). This compound is soluble in most solvents, stable in air and does not require special precautions to handle in laboratory. Thus, this compound along with $Pd(OAc)_2$ can be used in cross-coupling reactions of aryl halides and aryl boronic acid in water.



Scheme 11

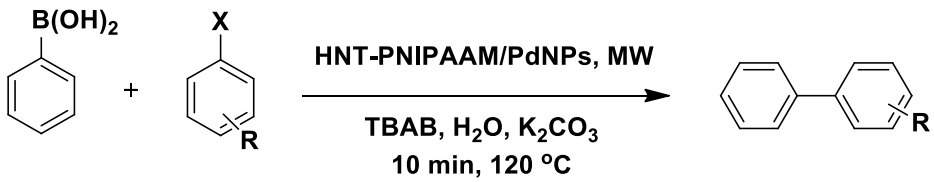
Ionic liquid, 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate was designed and synthesized by Pore *et al* from inexpensive and commercially available precursors (Pore *et al*. 2015). This IL behaved as dual functionalized task specific IL. The hydroxyl functionality of the cation boosts water solubility and prolinate functionality acts as a ligand and stabilizes the in-situ formed palladium nanoparticles. Thus, these Pd nanoparticles exhibited high catalytic activity towards Suzuki-Miyaura cross-coupling reactions in absence to phosphine ligands.

Sajith *et al* reported the use Pd-XPhos as precatalyst for the cross-coupling reaction between (hetro) aryl trifluoroborate and 6-chloro-3-methyl uracil (Sajith *et al*. 2016). This reaction resulted in the formation of (Hetero) aryl functionalized uracil derivatives in excellent yields. These products are biologically active and are commonly used as cytostatic, antiviral, antagonists etc.



Scheme 12

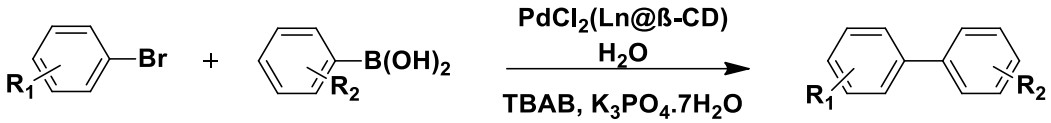
Riela *et al* designed a heterogeneous catalyst via grafting of poly(*N*-isopropylacrylamide) (PNIPAAM) on the external surface of halloysite nanotubes (HNTs) (Riela *et al*. 2016). Thereafter palladium nanoparticles were incorporated into it to yield the desired HNT-PNIPAAM/PdNPs. HNT-PNIPAAM/PdNPs was utilized as catalyst in the Suzuki reaction under microwave irradiations at 120 ℃ for 10 minutes. On completion of the reaction, the catalyst could be separated from the reaction mixture via centrifugation and could be reused for five catalytic cycles. The support i.e. HNTs used during the synthesis of catalyst are natural alumino-silicate nanomaterials with hollow tubular structures. Its low cost, biocompatibility and wide availability makes it suitable as a better alternative to carbon nanotubes.



Scheme 13

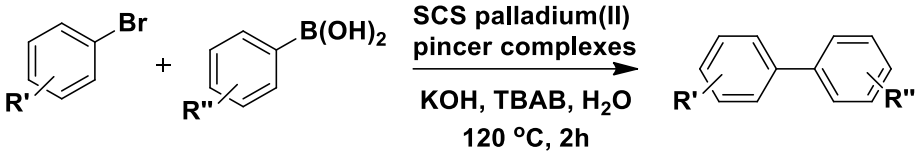
Jian *et al* reported the synthesis of $PdCl_2(L_n@\beta\text{-CD})$ using $PdCl_2$ and mono-6-(L-aminopropanol)-deoxy-β-cyclodextrin (Jian *et al*. 2018). Thereafter, they have utilized the complex as catalyst for aqueous Suzuki cross-coupling reactions.

High stability, low toxicity, low catalyst loading (0.00084 wt %), recyclability of the catalyst makes it more beneficial over other.



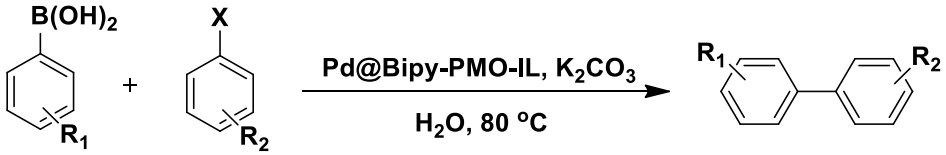
Scheme 14

Knife *et al* reported the synthesis of various water soluble cationic Pd(II) SNS pincer complexes (Knife *et al*. 2018). These ligands were used for the synthesis of biaryl compounds using aryl bromides and boronic acids as coupling partners in aqueous medium. They have also proposed a mechanism where the reaction is proposed to proceed via Pd(II) to Pd(IV) mechanism, which is opposing with the previous finding i.e. Pd(II) to Pd(0) mechanism.



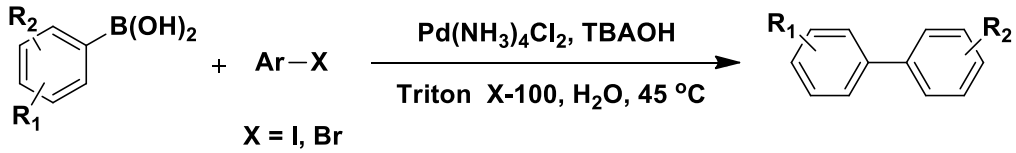
Scheme 15

Rostamnia *et al* developed a hybrid catalyst based on periodic mesoporous organosilica (PMO) (Rostamnia *et al*. 2019). PMO was functionalized with bipyridinium ionic liquid to produce Bipy–PMO. Subsequently, Pd ions were incorporated to the pore walls of Bipy–PMO to yield the desired Pd@Bipy–PMO. The catalytic efficiency of the hybrid catalyst was tested in Suzuki-Miyaura coupling reaction in water at 80 ℃.



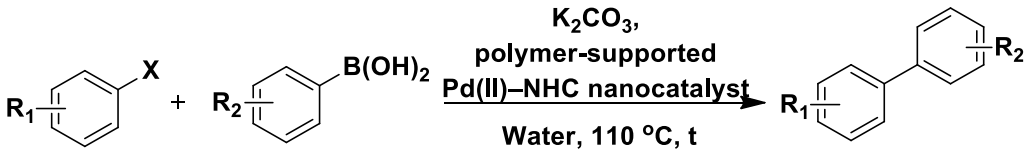
Scheme 16

Gao *et al* developed a ligand free protocol based on ppm level Pd catalyzed Suzuki-Miyaura cross-coupling reaction in aqueous solution (Gao *et al*. 2019). A surfactant, Triton X-100 has been used in the reaction to solubilize the organic substrates. The reaction was performed in presence of quaternary ammonium hydroxides as base at 45 ℃ for 1-2 h under ambient conditions to yield the desired products in moderate to excellent yields.



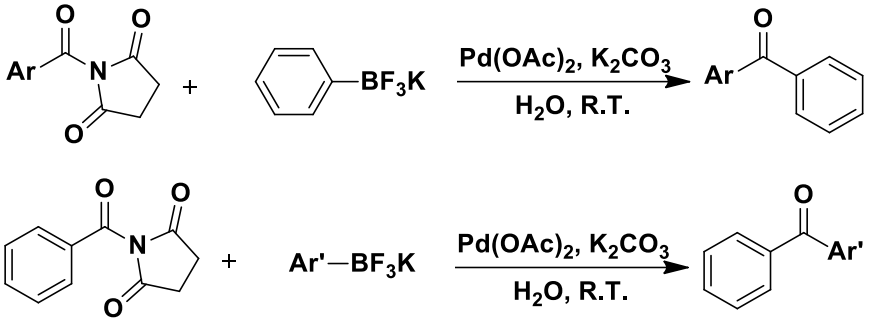
Scheme 17

Recently Taton *et al* reported the synthesis of polymer-supported Pd(II)–NHC_2 unit (NHC = N-heterocyclic carbene) and used it as efficient catalyst for Suzuki-Miyaura cross-coupling reactions (Taton *et al*. 2019).



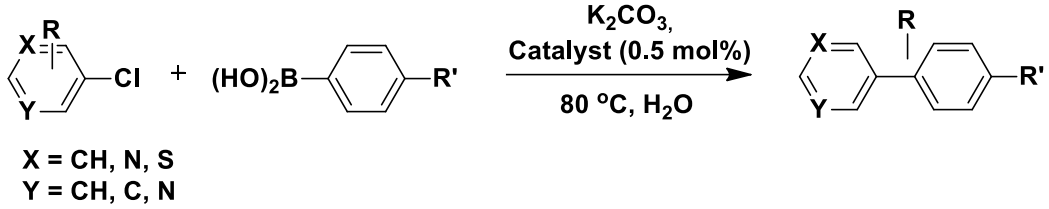
Scheme 18

Zeng *et al* were the first to report the use of highly reactive *N*-acylsuccinimides and potassium aryltrifluoroborates for the Suzuki–Miyaura coupling reaction (Zeng *et al*. 2020). They have carried out the reaction with palladium acetate as catalyst in water phase under ligand-free condition to yield the desired aryl ketone in moderate to high yield.



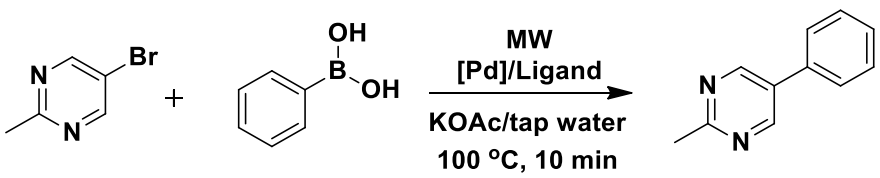
Scheme 19

Very recently, Das et al reported the synthesis of water soluble Pd (II) complex of unsymmetrical Schiff-base ligand and utilized it as a catalyst in Suzuki-Miyaura and Sonogashira reactions (Das *et al*. 2021). The catalyst was highly efficient to yield biaryls and aryl-alkynes in moderate to high yield.



Scheme 20

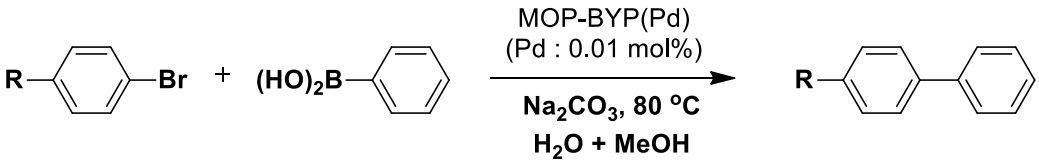
Yan *et al* reported an important synthetic pathway for the synthesis of biphenylpyrimidine scaffolds via a Suzuki-Miyaura coupling reaction (Yan *et al*, 2021). This coupling reaction was carried out under microwave irradiation in water in presence of phenylbiguanide as a ligand. Various physicochemical and pharmaceutical properties of phenylpyrimidine derivatives makes it an important moiety in drug discovery.



Scheme 21

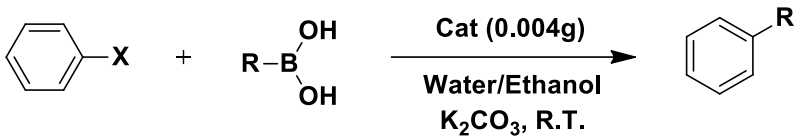
A heterogeneous catalyst based on Zirconium-Metal-organic polyhedra (MOPs) anchored with single Pd atom (MOP-BPY(Pd)) was successfully synthesized by Shin *et al* (Shin et al, 2021). Synthesized MOP-BPY(Pd) was utilized as a

catalyst in Suzuki-Miyaura coupling reaction in aqueous medium. The catalyst was found to be highly efficient compared to the molecular Pd complex and metal-organic framework (MOF) anchoring Pd atoms.



Scheme 22

Mahdavi *et al* reported the synthesis of palladium coated thiourea grafted on Fe_3O_4 magnetic nanocomposite (Mahdavi *et al*, 2021). The catalytic efficiency of the nanocomposite was tested in Suzuki-Miyaura coupling reaction in aqueous medium and the reaction facilitated the formation of biphenyl products.

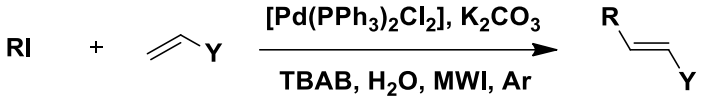


Scheme 23

3. Heck cross coupling reaction

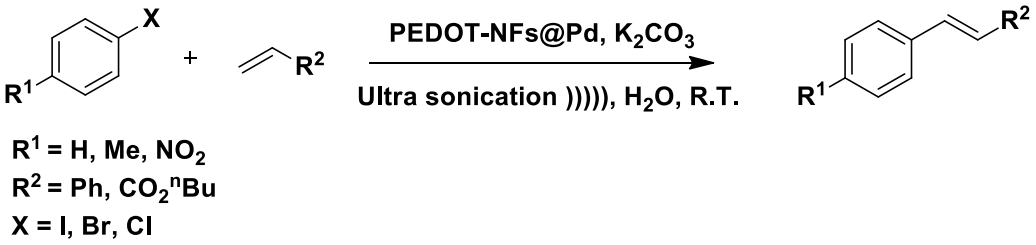
Another important palladium catalyzed cross coupling reaction between aryl halides and olefins are known to form vinyl derivatives, which was reported by Mizoroki in 1971 and Heck in 1972 (Mizoroki, 1971 & Heck, 1972). This reaction takes place in presence of ligand thereby forming coordination complexes with metal ions in solution. These ligands may be either solvent, base or bulkier organic molecules that may suitably bind with the metal ion. The recent development in this reaction considers both environmental and economic point, thus new ligand free protocols in water have been developed (Christoffel and Ward, 2017). In this review, we will focus on the reaction-taking place in aqueous medium. In 1988, Beletskaya and co-workers were the first to report the ligand-free Heck cross-coupling reaction in water (Christoffel and Ward, 2017). Thereafter Calabrese and co-workers developed a sulfonated water-soluble phosphine ligand in 1990. They have utilized it for aqueous Pd-catalyzed Heck reaction (Calabrese *et al*. 1990).

Wang *et al* reported palladium-catalyzed Heck coupling reactions in water via microwave irradiation method for the synthesis of trans-products (Wang *et al*. 2000). Compounds synthesized under microwave irradiation method is 18-42 times faster than that of conventional reflux method.



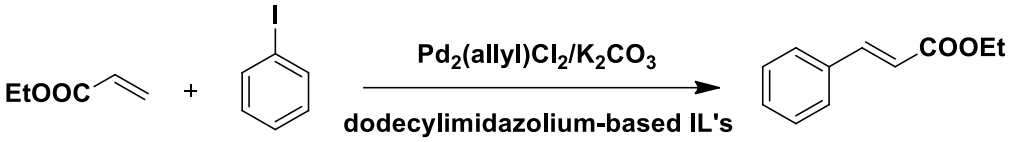
Scheme 24

An efficient reusable PEDOT nanofiber/Pd(0) composite has been developed by Rezaei for ligand free Heck reaction (Rezaei 2017). He utilized the composite as catalyst for C-C cross-coupling reactions of aryl halides with olefinic compounds under ultrasonic irradiation in water to yield a wide range of substituted alkenes. Ultrasonic irradiation method are cleaner and have various advantages over conventional heating reactions.



Scheme 25

Very recently, Bica *et al* reported the design and synthesis of dodecylimidazolium-based ionic liquids based on alkylation of N-methylimidazole or dimethylimidazole with dodecyl chloride (Bica *et al*. 2017). This ionic liquid was used as additive in palladium catalyzed Heck cross-coupling reaction between ethyl acrylate and iodobenzene in water. During the reaction, imidazolium-based IL's are able to generate carbene species, which are practically not possible using conventional cationic surfactants. The concentration of N-heterocyclic carbene species is one of the very important factor that determines the formation of catalytically active species.

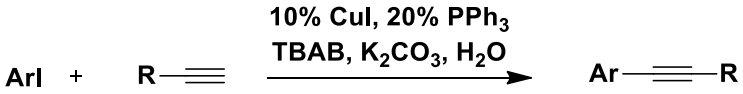


Scheme 26

4. Sonagashira reaction

In 1975, Sonogashira *et al* discovered a new cross-coupling reaction between aryl or vinyl halide and terminal acetylenes (Sonogashira *et al*. 1975). This reaction proceeds in presence of palladium complex, copper (I) catalyst, and is generally referred to as Sonogashira reaction. The use of organic solvent and amine led to environmental pollution (Chen *et al*. 2007). Thus, various modifications has been made in reaction conditions to make it environmentally benign and economic. A number of Pd-catalyzed Sonogashira reactions in aqueous media have been found in literature but very few references on Pd-free Sonogashira reaction are found. In this review we will focus on Pd-free and heterogeneous system Sonogashira reaction.

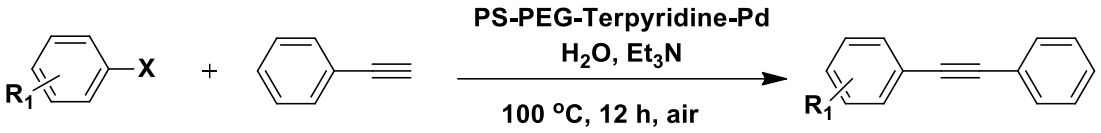
Chen *et al* reported the use of copper iodide as catalyst as an alternative to the palladium catalyst for the cross-coupling reaction between aryl iodides and terminal acetylenes in water under microwave irradiation or refluxing condition (Chen *et al*. 2007). The reaction conditions were suitable for the synthesis of alkynes in excellent yields with wide functional group tolerance.



Scheme 27

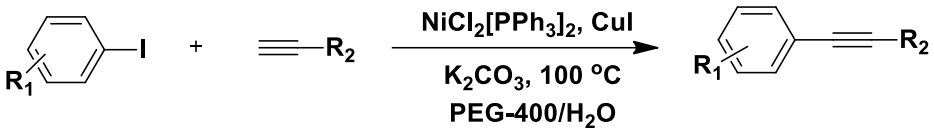
An heterogeneous Polystyrene-poly(ethylene glycol) (PS-PEG) resin supported palladium-Terpyridine complex was synthesized by Sazuka *et al* (Sazuka *et al*. 2015). This complex was used as catalyst for Sonogashira coupling reaction

between aryl halide and acetylene compound in water at 100 ℃ for 12 h to yield the desired diarylacetylene in moderate to high yields.



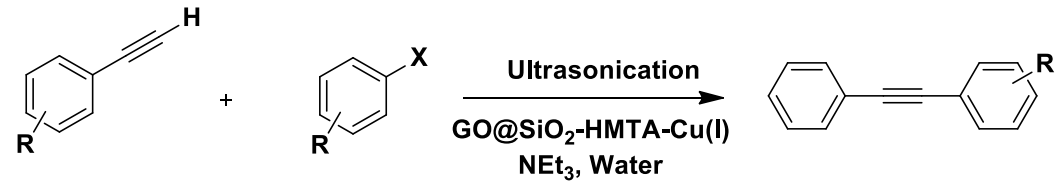
Scheme 28

Cai *et al* developed an extremely new protocol for the Sonogashira coupling reaction for the synthesis of aryl acetylenes using Nickel catalyst (Cai *et al*. 2015). They have performed the reaction of aryl halides and terminal alkynes using $NiCl_2(PPh_3)_2$ and CuI as catalyst in a mixture of PEG-400 and water at 100 ℃ under Argon atmosphere for 2 h to yield a variety of aryl acetylenes. The advantage of this catalyst over others is that it could be recycled and reused for up to six catalytic cycles without much effect in its yield.



Scheme 29

Naeimi and Kaini reported the synthesis of GO@SiO_2-HMTA-Cu(I) nanocomposite via surface functionalization of graphene oxide with hexamethylenetetramine and then immobilizing copper diiodide into it (Naeimi *et al*. 2018). This heterogeneous catalytic system was used in Sonogashira coupling reaction under ultrasonic irradiation method for the synthesis of diarylethyne compounds.



Scheme 30

5. Conclusion

In conclusion, we have reported the use of various different types of palladium catalysts including catalysts grafted over magnetic nanoparticles, MOPs etc. for Suzuki-Miyaura, Sonogashira and Heck cross-coupling reactions in aqueous medium, which has brought several benefits and innovative approaches to the synthetic chemistry. Furthermore, these supported palladium catalysts have several advantages including recyclability, low catalyst loading, mild reaction conditions, moderate to high yields etc. over the use of traditional palladium catalysts.

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