RECENT ADVANCES ON NANO-MATERIALS/PARTICLES CATALYZED CARBON-CARBON CROSS-COUPLING REACTIONS

Abstract

The main objective of this chapter is to describe the use of nanomaterials/particles as a catalyst in carbon-carbon cross-coupling reactions. Since the beginning of this century, nanomaterials/particles are being used in organic synthesis as a catalyst. Carbon-carbon bonds formation via cross-coupling reaction is one among them where nanomaterials/particles are used as a catalyst. Various types of nanomaterials/particles, such as palladium, copper, and nickel-based nanomaterials are used for this purpose. Therefore, in this review, we have discussed the use of those types of catalysts for the carbon-carbon bonds formation via cross-coupling reactions. The use of nanomaterials/particles as catalysts in organic synthesis may be considered as one step forward towards sustainable chemistry because most of the reactions are heterogeneous. Therefore, further development of more readily available nannocatalyst are highly desirable. This chapter may provide important information regarding the recent developments in this area and may help researchers to develop better nanocatalysts for the carbon-carbon bonds formation.

Keywords: organic chemistry; catalysis; synthesis; nanomaterials/particles; cross-coupling

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I. INTRODUCTION

Nanomaterials/particles are very interesting compounds having characteristic physiochemical and photo-electronic properties. Because of its unique properties, a researcher from different areas are interested in investigating and exploring its implication in various fields which makes nanoscience a broad and interdisciplinary subject [1-2].The properties of nanomaterials/particles mainly depend on and are controlled by the particles size of the materials and its constituents[1-6]. Because of its very small size and enlarged surface area, chemists are interested in investigating nanomaterials/particles as a nanocatalyst in organic synthesis [7-8]. As a result researcher have found many use of nanomaterials in synthetic organic chemistry and catalysis. In this short review, we will discuss some selective examples of metal-based nanomaterials/particles in carbon-carbon bonds formation.

Carbon-carbon bonds formation is the main objective and also the heart of organic chemistry [9]. Therefore, since decades organic chemists are developing various protocols for the construction of carbon-carbon bonds. Recently, priorities have been given on the betterment of green and sustainable reaction protocols for organic synthesis because of the environmental standpoint [10-11]. Considering the environmental impact, nanomaterials/particles are one of the alternative to normal metal catalysts because it could be recycled and reused as nanocatalysts are the heterogeneous catalyst. Herein, we have collected some selective recently developed protocols for the construction carbon-carbon bonds by employing nanomaterials/particles as a catalysts.

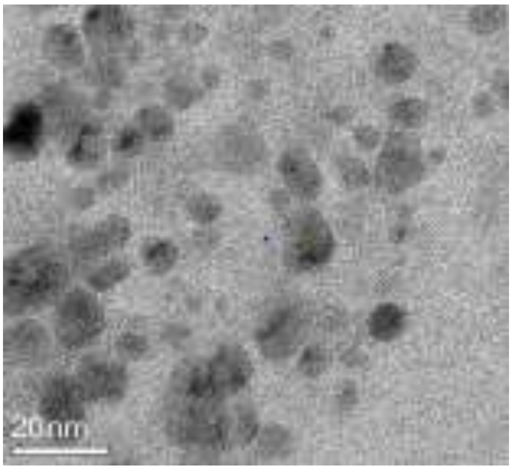
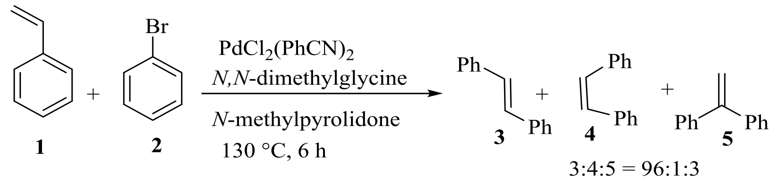


Figure 1: TEM image of Cu_2O nanoparticles.

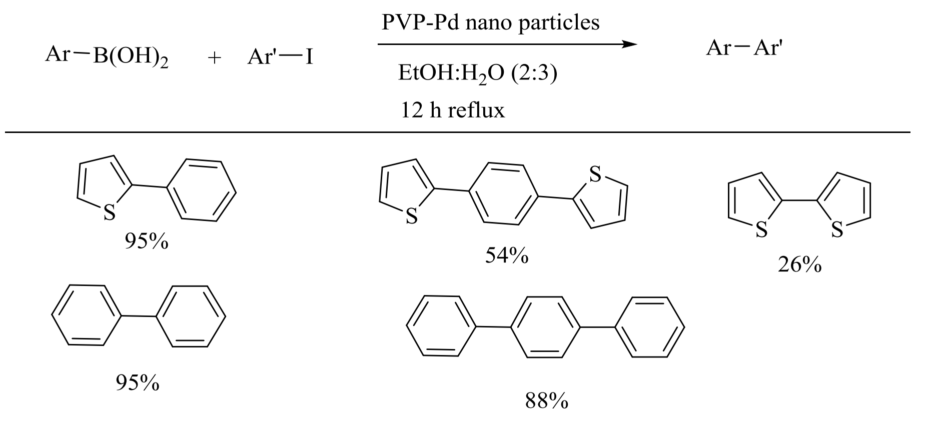
II. DISCUSSION

First, conf At the beginning of this century, Reetz and co-workers discovered the formation of palladium nanoparticles are formed and responsible in palladium-catalyzed Heck cross-coupling reactionof styrene with bromobenzene (Scheme 1) [12]. Generally such types of coupling reactions required to use $Pd(PPh_3)4$ but later report suggest that these transformation could be achieved by using simple catalyst such palladium (II) salts along with some additives. These observations influenced the authors to become interested to investigates the fate of the catalyst and they have discovered the formation of palladium nanoparticles which is catalyzing the reaction. The reaction provides a 96:1:3 mixture of *trans*, *cis*, and geminal coupled products respectively.



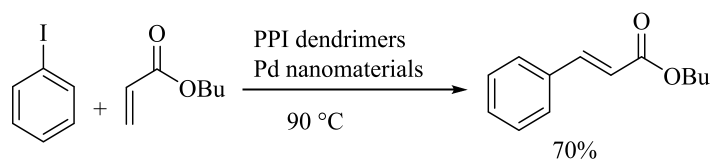
Scheme 1: Palladium-catalyzed Heck reaction.

El-Sayed and co-workers have reported colloidal poly(N-vinyl-2-pyrrolidone) (PVP) anchoredpalladium nanoparticles catalyzed carbon-carbon bonds formation between aryl iodides and aryl boronic acids [13]. The nanocatalyst was prepared by heating $H_2[PdCl_4]$ and PVP in 40% EtOH in water and the nanocatalyst obtained in this process has particle size around 3.6 nm. Reaction works well with 40% ethanol in an aqueous medium providing a very good yield of the corresponding products (Scheme 2). They have also observed that the initial rate is linearly depended on palladium concentration which means the catalysis takes place on the nanoparticle surface.



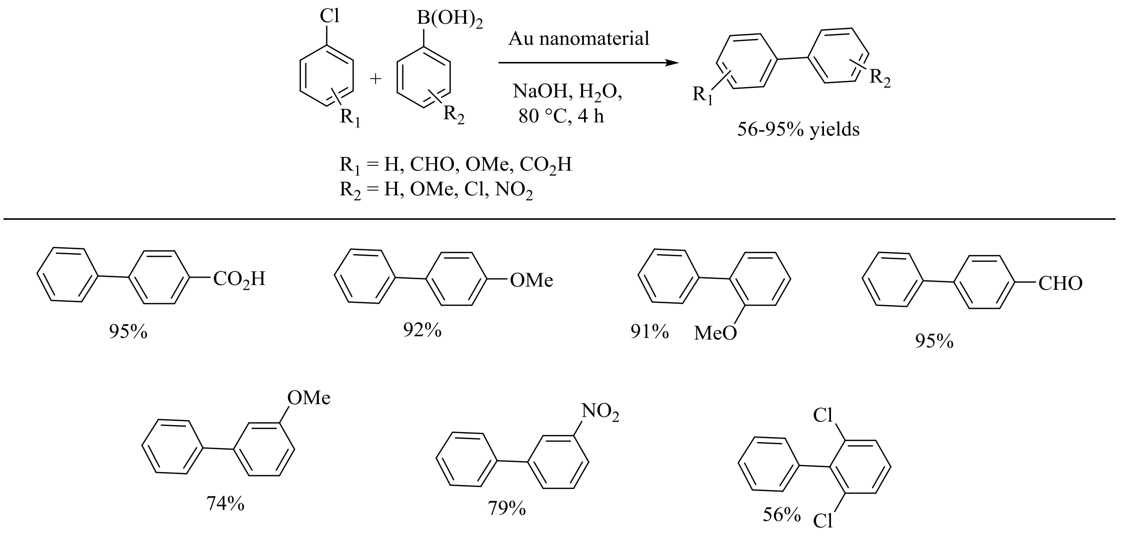
Scheme 2

The heck coupling reaction was reported by Crooks and co-workers with poly(propyelene imine) (PPI) dendrimers stabilized palladium nonmaterial [14]. It was the first report which shows that dendrimers can be used to stabilize nanoparticles. The method is operationally simple and effective at less reaction temperature i.e. at 90°C and provides a good yield of the carbon-carbon coupling product. Another advantage of this reaction protocol is the nanocatalyst could be isolated and recycled without decrease catalytic activity (Scheme 3).



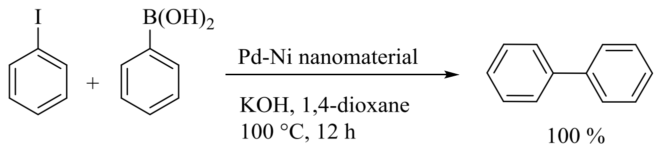
Scheme 3

Poly(2-amino thiophenol) (PATP) supported gold nanoparticles catalyzed Suzuki-Miyaura cross-coupling methods was reported by Rong Guo and co-worker (Scheme 4) [15]. This is an excellent example of a nanomaterial catalyzed organic reaction because itnotonlysubstitutes palladium-based nanocatalyts but also the mol % of the catalyst (only 0.05 mol %) required very less and it required water only as a solvent which is an environmentally benign green solvent. The reaction condition is mild enough to sustain the functional group such as acid, aldehyde, MeO, nitro and halogens. This catalytic system works in less temperature and provides very high yield and also the catalyst could be recycled, hence this could be considered as an ideal catalytic method.



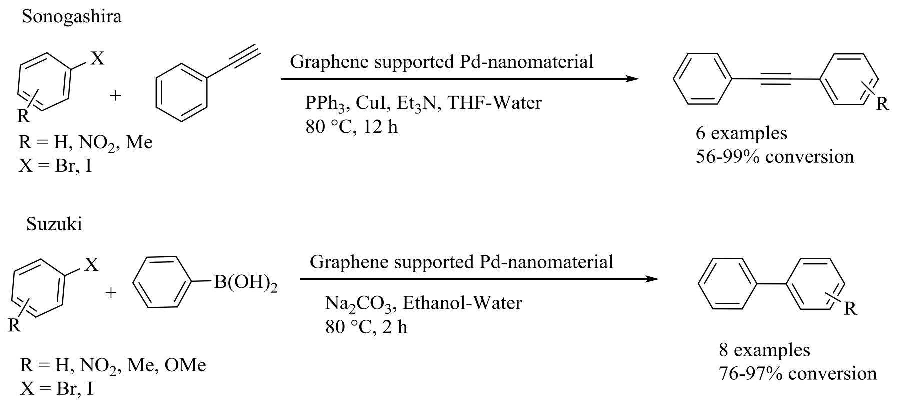
Scheme 4

A magnetically separable palladium nickel alloy nanomaterial is an effective catalyst in catalyzing Suzuki-Miyaura coupling reaction under ambient reaction condition(Scheme 5) [16]. The authors have also observed that the palladium-nickel alloy catalyst is better than that the pure palladium catalyst. This catalyst could be isolated and reused and the recycled catalyst can perform the coupling reaction up to five cycles with no quenching of catalytic efficiency.



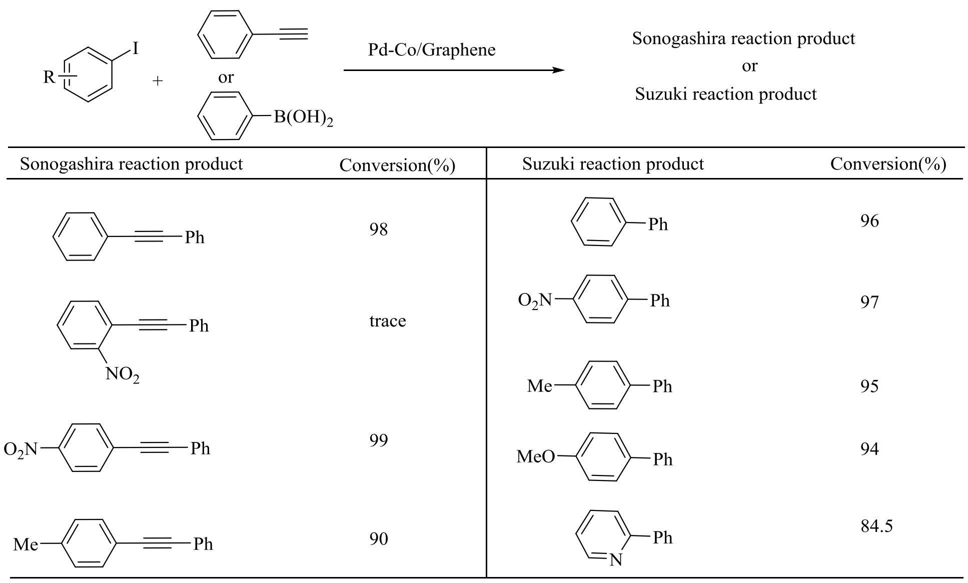
Scheme 5

Graphene-supported palladium cobalt alloy nanomaterial catalyzes both Sonogashira and Suzuki-Miyaura cross-coupling methods under ambient reaction conditions (Scheme 6) [17]. This catalyst can be separated magnetically from the reaction vessel and could be recycled for Suzuki coupling up to five cycles without quenching of catalytic reactivity. The nanocatalystis quite insensitive towards the electronic nature of the reactant and provides good yields irrespective of the substituent on reactants (Table 1). This enhanced reactivity may be attributed to the high surface area of graphene and also due tothe cobalt metal which makes palladium more easily accessible for reactants.

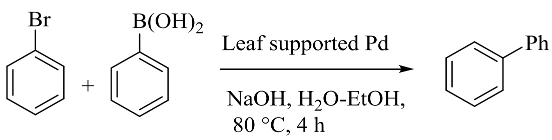


Scheme 6

Table 1: Pd-Co/Graphene nanomaterials catalyzed Sonogashira and Suzuki coupling

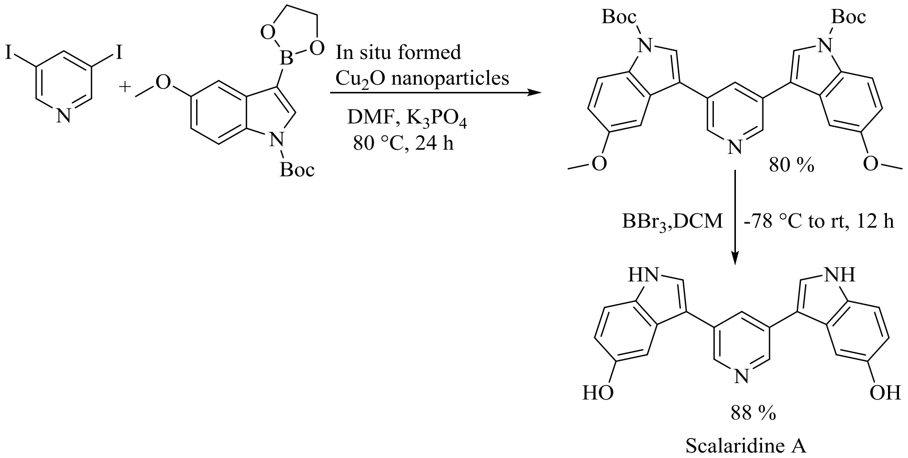


Plant leafanchored palladium nanoparticles are an effect catalyst for carbon-carbon bonds formation [18]. This protocol is a wonderful example of bio-mimetic fabrication of nanomaterial that exhibits catalytic potential and will attract researchers for the further development of environment-friendly green technology. The protocol was developed by Krishnan and coworkers (Scheme 7).



Scheme 7

Copper(I)-oxide nanoparticles which form in situ during the reaction and cross couples 3,5-diiodopyridine with aryl and indolyl boronate [19]. The cupric chloride used in reaction forms copper(I)-oxide nanocatalystwith the help of potassium phosphate and *N*, *N*-dimethylformamide. This reaction condition is widely applicable to a variety of substrate having functional groups line F, CF_3, NO_2, OMe, Me, Cl, Br, etc.The authors have used this protocol to synthesis pyridine heterocycles Scalaridine A (Scheme 8). They have also proposed a mechanism which has been outlined in figure 3.



Scheme 8

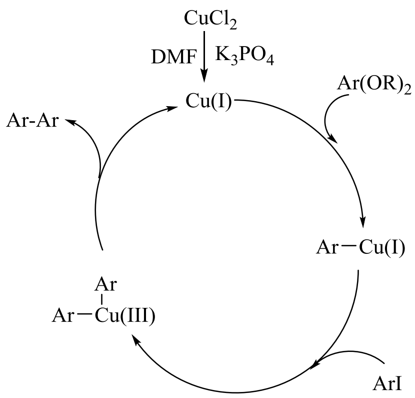
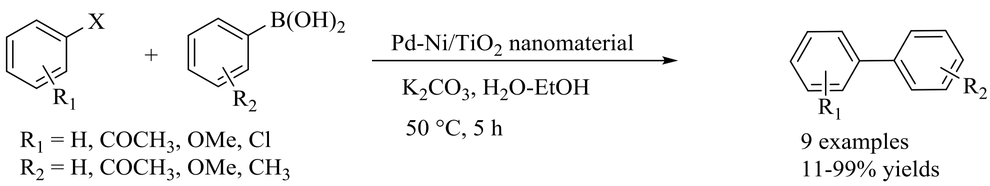


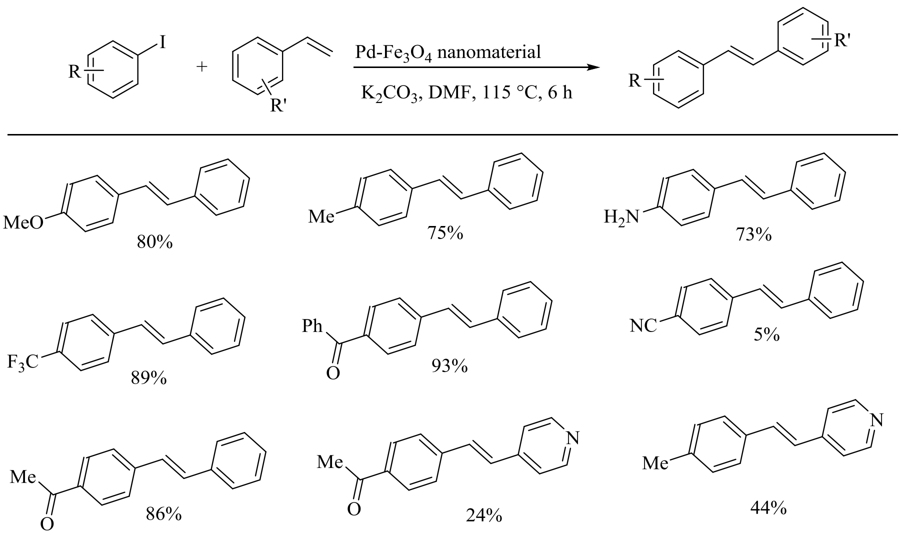
Figure 2: Mechanism of action.

Ren and co-workers have synthesized nicked doped palladium nanoparticles supported on TiO_2 nanomaterial (Scheme 9). This nanomaterial is able to catalyzed the Suzuki-Miyaura cross-coupling reaction in a water-ethanol solvent mixture at 50 °C with the help of K_2CO_3 base [20]. The catalytic method is very efficient and provides an almost quantitative yield of the corresponding products. Aryl iodides and aryl bromides works well in this reaction condition but aryl chlorides are ineffective and provide less yield of the crossed coupled products. The nanomaterial can be isolated and recycled up to four cycles without decrease in catalytic activity.



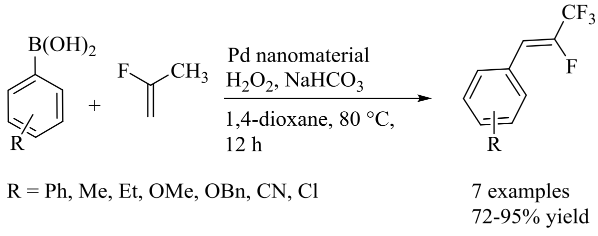
Scheme 9

Biglione and co-workers have synthesized Fe_3O_4 supported super magnetic Pd nanomaterial which acts as a catalyst for Heck-Mizoroki cross-coupling reaction (Scheme 10). A variety of the substrate can be crossed coupled to get the corresponding crosscoupled product under the established reaction conditions [21]. Aryl iodides gives better yield compared to aryl bromides which needed prolong reaction time. They have also studied the effect of stabilizer and discovered that the oleylamine is the best one to get uniformed shell nanoparticles.



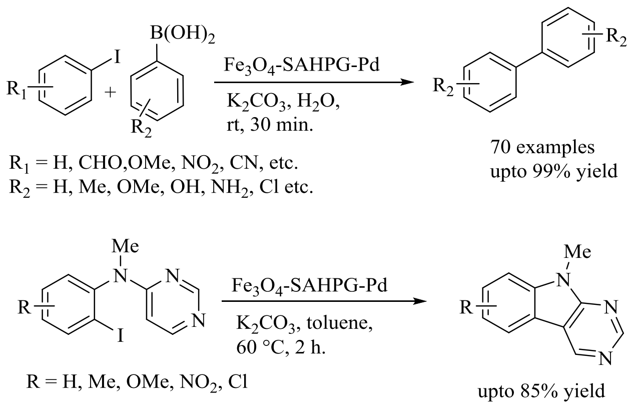
Scheme 10

The heck-type coupling reaction was developed to synthesize β-fluoro-β-(trifluoromethyl)styrene derivatives using palladium nanomaterial (Scheme 11) [22]. The reaction works well with different substrates and hydrogen peroxide plays the role of a green oxidant and provides good yield of the corresponding products. An active catalyst was obtained by the pyrolysis of the palladium acetate-phenanthroline complex.



Scheme 11

Palladium nanoparticles anchored on self-assembled hyperbranched polyglycidole (SAHPG) coated magnetic Fe_3O_4 nanoparticles was discovered by Azizollahi and co-workers [23]. This nanomaterial is an excellent nanocatalyst for the Suzuki-Miyaura cross-coupling method. The protocol works well with a very low amount of catalyst and the more interesting part of this catalysis is that the reaction works at ambient temperature and the environment-friendly water is the solvent (Scheme 12). Furthermore, this nanomaterial also catalyses oxidative carbon-carbon cross-coupling reaction to give pyrimido[4,5-*b*]indole derivatives and the reaction is faster compare to the protocol which is catalyzed by palladium acetate(Scheme 12). The mechanism of action of this oxidative coupling has been shown in figure 4.



Scheme 12

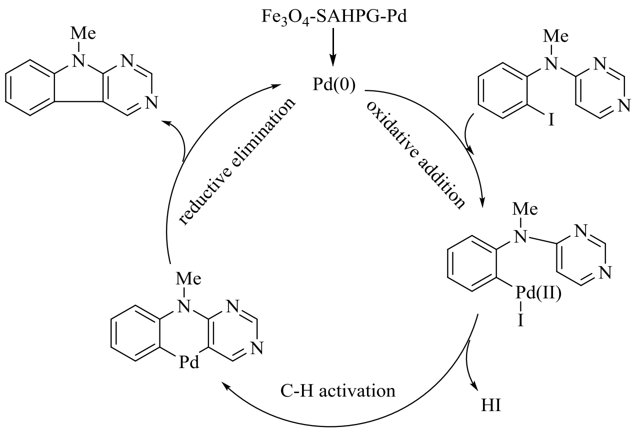
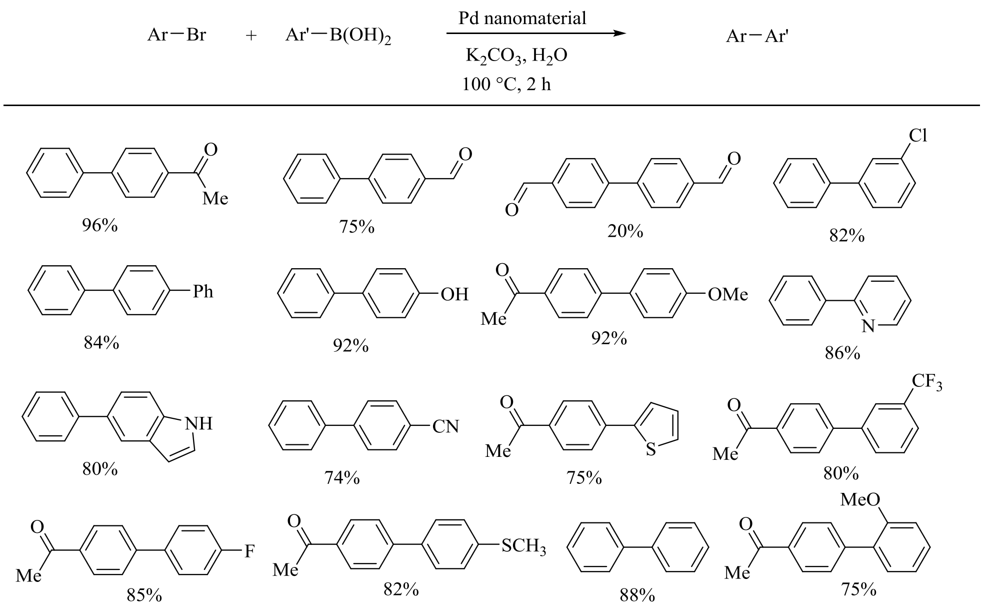


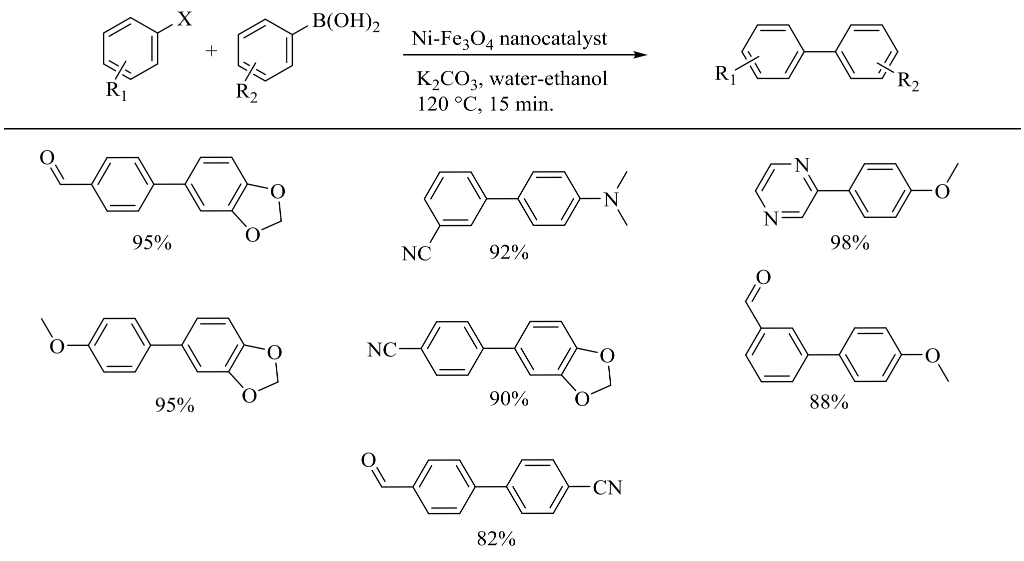
Figure 3: Reaction Mechanism

A ZnO/Fe_3O_4 based palladium nanomaterial doped with manganese ion was prepared and found effective to catalyzed Suzuki-Miyauracoupling method along with other organic reaction (Scheme 13) [24] The catalyst is recyclable and are used up to the sixth cycles and then catalytic efficacy decreases.



Scheme 13

Recently Ali R. Siamaki and coworkers [25] have reported synthetic application of multi walled carbon nanotubes supported nickel-Fe_3O_4 nanomaterial synthesized by ball-milling technology. The nanomaterial can catalyze Suzuki coupling methods with a wide range of substrate compatibility. The standardized reaction method require the use of 1 mol % of the nanocatalyst, 3 equivalent of K_2CO_3, water-ethanol mixture solvent and 120 ^oC reaction temperature. The above reaction condition can cross couple variety of aryl iodides having OMe, CHO, CN substituents with aryl boronic acids having OMe, NMe_2, CHO substituents and provides very isolated yields of the corresponding Suzuki coupling products (Scheme 14).



Scheme 14

III. CONCLUSIONS

In conclusion, this chapter has demonstrated the recent development of nanomaterials/particles catalyzed carbon-carbon bonds formations via cross-coupling methods. Variety of methods have been developed so far using the nano-catalyst and also this particular field of research has large scope for developments. For example, most of the described methods are based on palladium nanocatalyst which is not readily available and the precursor of the palladium nano-catalysts i.e. the palladium salts are very expensive. Likewise, almost all the methods required high reaction temperature and also only a handful of simple aryl substrates are effective. The development of new methods with more easily accessible and readily available and cheap nanomaterials are highly desirable and also ambient reaction condition and water as a solvent will be very interesting developments in this field. Regarding substrate scope, more complex substrates like natural product derivatives,drug candidates,cholesterols and other bioactive substrates should be tested. Therefore, researcher have good opportunities to develop this field and this chapter will provide valuable information for the same.

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