Chapter II

Section A

Heterogeneous Pd composite catalyzed Suzuki and Heck coupling reaction in water

II.A.1. Introduction

Carbon-carbon bond formation reaction is the essence of the synthesis in organic chemistry. Kolbe's fundamental laboratory-based C-C bond formation in 1845 for his well-known acetic acid synthesis played an important role in shaping chemical synthesis [1]. The enzymatic processes must take place in an aqueous environment in nature, but water has been avoided as a reaction medium in common organic synthesis. Since the historic study of Breslow for Diels-Alder reactions [2], the recognition of water as a solvent in C-C coupling reactions has been increased and proved to be advantageous over organic solvents [3]. Generally, protection and deprotection processes under aqueous solvent in organic synthesis can be simplified and there has already been great advance to understand the organic reaction in water at high temperatures and its broad scopes are varying from the source of life to energy and fuels to chemical synthesis [4]. In the 20th century, carbon-carbon bond formation reactions have shown a new paradigm that has amplified the effectiveness of organic chemists appreciably in synthesizing complex molecular frameworks, which has substituted our thinking completely about organic synthesis. Based on transition metal catalysis, the C-C bond formation reactions joining functionalized and sensitive substrates are fundamental for organic molecule synthesis and provide new opportunities in medicinal as well as nanotechnology. In organic chemistry, the C-C coupling reaction is a general term for a wide variety of organic reactions where, in the presence of metal catalysts, two fragments are combined together. Generally, two types of coupling reactions have been identified. Homo-coupling reaction occurs when two identical chemical species are joined together to afford a single product and Hetero-coupling reaction (also known as cross-coupling) occurs when two dissimilar chemical species are combined to form a

single product. Among the homo-coupling reactions, the Wurtz reaction [5], the Pinacol coupling reaction [6], Glaser coupling [7], and the Ullmann reaction [8] are important. On the other hand, the C-C cross-coupling reaction includes Cadiot-Chodkiewicz coupling [9], Castro-Stephens coupling [10], Corey-House synthesis [11], Kumada coupling [12], Heck reaction [13], Sonogashira coupling [14], Negishi coupling [15], Stille cross-coupling [16], Suzuki reaction [17], Murahashi coupling [18], Hiyama coupling [19], Fukuyama coupling [20], and Liebeskind-Srogl coupling [21]. Over the past 30 years, the development of C-C cross-coupling reactions catalyzed by transition metals has profoundly revolutionized the protocols for the synthesis of natural products, organic materials, and polymers, building blocks for supramolecular chemistry, and medicinal chemistry from simpler moieties. In 2010 E. Negishi, R. Heck, and A. Suzuki were awarded the Nobel Prize in chemistry for developing direct bond formation between carbon atoms (palladium-catalyzed C-C cross-coupling reaction). However, the growth of highly active catalysts has drawn much consideration for the development of efficient, green, and cost-effective synthesis in organic chemistry. Metal-nanoparticle (NP)-based catalysts can be assumed as an intermediate between homogeneous and heterogeneous catalysts, and they are considered half-heterogeneous catalysts [22]. Due to the small size of metal-NPs, they are not easily removed from the reaction mixture and this problem is usually solved by binding the NPs with structural support. Therefore, there is a need for heterogeneous catalysts via immobilization of metal NPs on solid supports to achieve high catalytic activity, high mechanical and thermal stability, easy regeneration, and separation procedures [23-26]. Metal NPs on structural support or metal-composite catalysts (composite materials are combinations of two or more materials having different phases) are being investigated as a new dimension of catalysis [27-29]. Normally, composites are

composed of two types of different materials, One is called a binder or matrix, which binds the fragments together and is termed reinforcement. If one of the combining elements of the composite is in the nanometer dimension, then it is called a nanocomposite [30]. In addition, as the subject is so broad in this chapter, we have shown the application of different nanostructured materials as host elements for the heterogeneous PdNPs-catalyzed Suzuki and Heck coupling reactions.

II.A.2. General outline of C-C cross-coupling reaction mechanism

The mechanism of the C-C cross-coupling reaction generally comprises three important steps
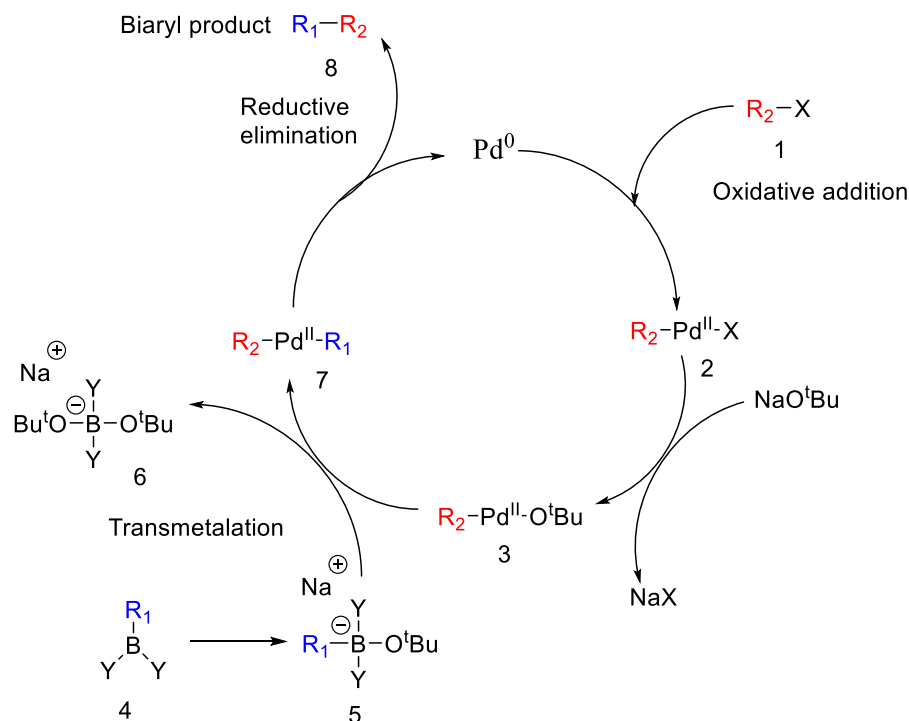
1.   Oxidative addition

2.   Transmetalation

3.   Reductive elimination

The oxidative addition and reductive elimination are generally multistep processes as they involve ligand association and dissociation processes respectively. On the other hand, the transmetalation process involves ligand exchange between two metal centers.

II.A.2.1. Suzuki coupling

The Suzuki coupling is categorized as a C-C cross-coupling reaction, where two dissimilar fragments boronic acid and organohalide or triflate are combined to yield substituted biphenyls in presence of palladium (0) complex catalyst [31]. The relative reactivity order of halides and triflate is R-I > R-OTf> R-Br >> R-Cl. Since its discovery in 1979, this reaction becomes utmost acceptable process for the carbon framework expansion in organic molecules. Suzuki-Miyaura

coupling reaction is extremely helpful for the assembly of a conjugated diene, polyene systems, and biaryl systems with high stereoisomeric purity.
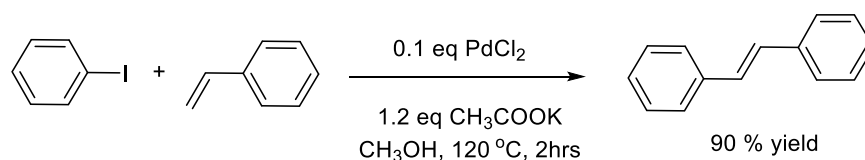

Scheme II.A.1. *Suzuki coupling reaction mechanism.*

Suzuki Miyaura coupling using inactivated alkyl halides to form C (sp^2)–C (sp^3) and even C (sp^3)–C (sp^3) bonds, has made incredible progress in the field of coupling reaction [32, 33]. The first step of the Suzuki coupling mechanism (Scheme II.A.1) is the oxidative addition of Pd (0) to the aryl halide (1) to form the organopalladium species (2). Afterthat, intermediate (3) is formed by the reaction with a base, which again forms the organopalladium species via transmetalation (4) with the complex (boronate complex) formed by the reaction of the boronic acid (5) with base. The last step is reductive elimination which yields the biaryl product (8) and brings back the original Pd (0) catalyst. The

Suzuki coupling reaction occurs in presence of the base and the base has three roles in this coupling reaction: formation of the palladium complex, formation of trialkyl borate and accelerates the reductive elimination by the reaction of alkoxide with Pd complex.
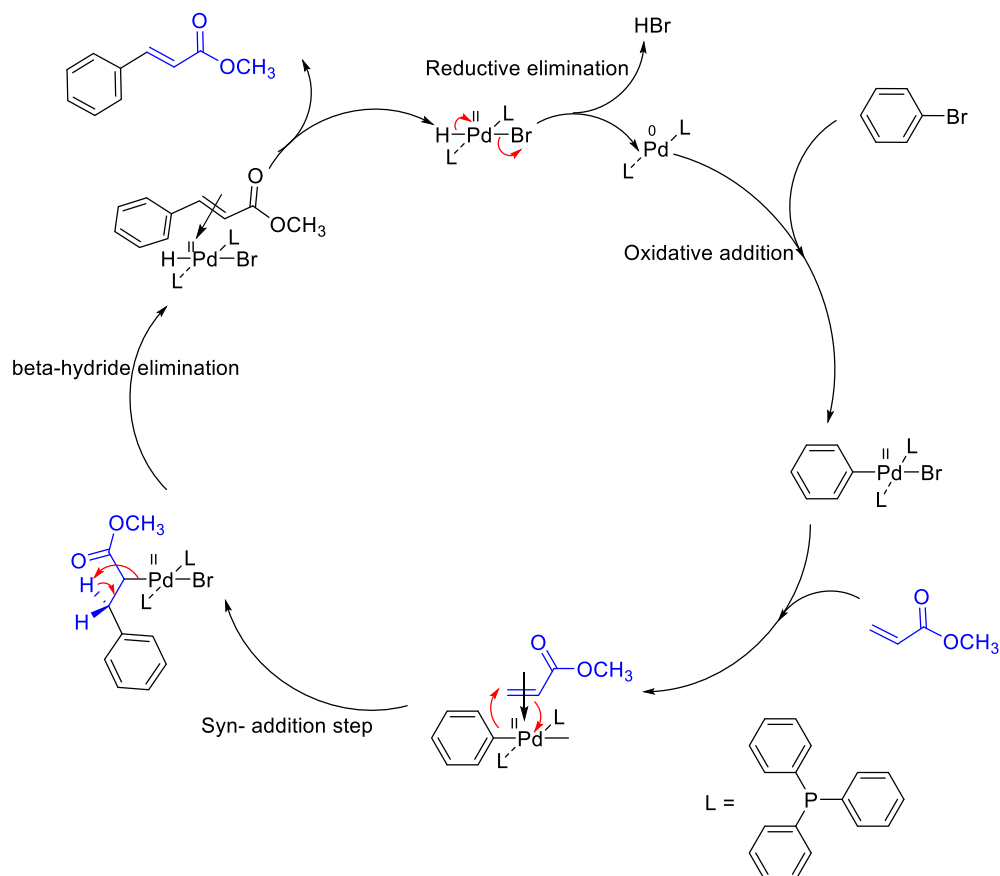
II.A.2.2. Heck reaction

The Heck reaction is the cross-coupling reaction (also known as Mizoroki-Heck reaction) where halides or triflates with unsaturation are joined with an alkene to form substituted alkene in the presence of a base and a palladium Pd(0) catalyst (or palladium nanomaterial-based catalyst) [34]. Tsutomu Mizoroki (1971) describes the synthesis of stilbene from iodobenzene and styrene in presence of potassium acetate base and $PdCl_2$ catalyst at 120 °C temperature (Scheme II.A.2.).

SchemeII.A.2. *Mizoroki-Heck C-C cross-coupling reaction*

In 1972, Heck appreciated the Mizoroki publication and independently discover the same reaction with different conditions (palladium acetate catalyst, catalyst loading 0.01 equivalent, a hindered amine base, and in absence of solvent) [34]. The mechanism of the Heck reaction involves several steps. At first, palladium (II) acetate $[Pd(OAc)_2]$ is reduced by triphenylphosphine (PPh_3) to bis(triphenylphosphine)palladium (0). Step 1 of the coupling reaction involves the insertion of Pd (0) into the aryl bromide bond (Scheme II.A.3). In step 2 alkene and Pd forms a C-Pd bond in a syn-addition step. In the third step, a Pd-alkene π complex is generated through β-hydride elimination. The Pd (0)

114

compound is then regenerated by the reductive elimination of the Pd (II) complex with the help of a base in the final step of the coupling reaction.

Scheme II.A.3. *Pd catalyzed Heck coupling reaction mechanism.*

II.B.3. Background of heterogeneous metal-composite catalyst for cross-coupling

Heck and Suzuki cross-coupling reactions are typically catalyzed by Pd-based homogenous systems that require the use of ligands (phosphine or *N*-heterocyclic) to design active catalytic systems. As a consequence, the separation of the homogeneous catalyst after reaction has been appeared as

biggest problem in the field of catalyst. Accordingly, the catalyst may incorporate in the final product, thus results the loss of catalyst in the reaction, and a devalued product is formed from a pharmaceutical point of view. The main challenge is to develop heterogeneous catalytic systems for C-C cross-coupling reactions and establish the nature of the active catalyst species. The literature of coupling reaction with homogeneous catalytic systems is well developed, but the contrary is observed for heterogeneous systems [37]. Some researchers claim to develop solid pre-catalyst of soluble catalytically active Pd species [38-40], while others recognize absolutely heterogeneous systems, where catalysis takes place on the surface of Pd-based solid heterogeneous catalyst [41, 42]. The effectiveness of a good catalytic system is generally decided by the activity, selectivity, and lifetime of the prepared catalyst [43]. The activity of the catalyst is measured by the percentage of the reactants converted into a product, however, the selectivity is measured by the percentage of the reactants that are transformed into desired final products and the lifetime of the catalyst is that time when the catalyst attain its activity and selectivity to the expected level.
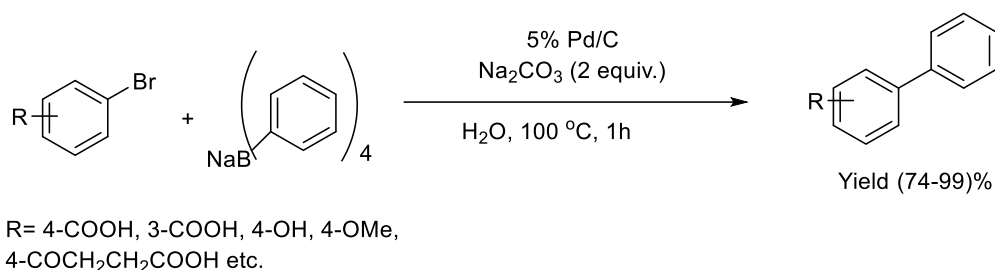
Pd NPs have become attractive forms of heterogeneous catalyst due to their size and shape dependence and efficient catalytic activity in C-C cross-coupling reaction [37, 44]. Nevertheless, their use as a catalyst has been restricted because of scantiness of efficient separation procedures and techniques like centrifugation and filtration are not much effective to recover the NPs completely. Moreover, the agglomeration and sintering property of NPs upon heating, they are leached to form the insoluble non-catalytic Pd black [37]. Supported Pd catalyst has drawn profound interest due to their easy reusability in the C-C cross-coupling reaction. Most often, PdNPs immobilized on solid support become less catalytically active and better understanding of the activity

of PdNPs leads to design more effective heterogeneous catalysts in the cross-coupling reaction. Supported metal catalyst or metal-composite catalyst can be categorized as: inorganic, organic, and inorganic-organic materials.
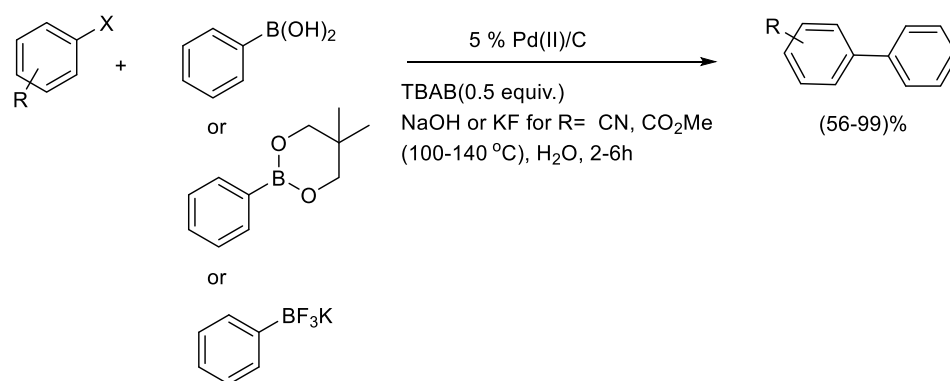
II.B.3.1. Inorganic support

II.B.3.1.1. PdNPs in carbonaceous supports

In C-C cross coupling reaction, the use of carbonaceous nanomaterial supported PdNPs opened up a new paradigm in the field of heterogeneous catalysis [45-47]. Amongst them, due to the commercial availability of activated charcoal, often (Pd/C) where Pd is immobilized on charcoal is used as heterogeneous catalyst. In addition, different solid supports like alumina and silica possess lower surface area than charcoal support [47]. From literature, it is reported that Pd/C is stable in air, water, acid, and bases and it does not require any inert atmospheric condition to be performed [47, 48]. Xu *et al.* developed a pathway for the reaction between water-soluble bromo arenes with sodium tetraphenylborate to synthesize substituted biphenyl (Scheme II.A.4) in presence of 0.0025 mol% of Pd/C under a refluxed condition in water (reaction time was varied from 1-7 h) [49]. The Comparison between inorganic bases showed that sodium bases are more effective than potassium bases in this reaction. The catalyst was recycled upto five cycles with a gradual loss of reactivity.

R= 4-COOH, 3-COOH, 4-OH, 4-OMe,
4-COCH$_2$CH$_2$COOH etc.

Scheme II.A.4. *Suzuki-Miyaura reaction by Xu et al.*

Previous reports showed that surfactants are used as additive to increase the solubility of the reactants aryl halides. Kohler *et al.* performed the coupling reaction of aryl chlorides with aryl boronic acids (Scheme II.A.5) in presence of ligand less Pd/C catalyst in water [50]. All reactions were carried out under an ambient condition to minimize the chance of homocoupling. Although a lower Pd concentration (0.2–0.5 mol%) is required for activated aryl chlorides and higher Pd concentration (2 mol%) is needed for deactivated chloroarenes. The addition of surfactant TBAB as an additive and application of NaOH amongst the inorganic bases have profound role in this reaction. Not only the aryl boronic acids but the boronated esters and potassium trifluoroborates are equally effective under this optimized reaction condition. The reactivation of the catalyst [Pd (0) to Pd (II)] using iodine as an oxidizing agent was carried out to recycle the catalyst in successive runs.
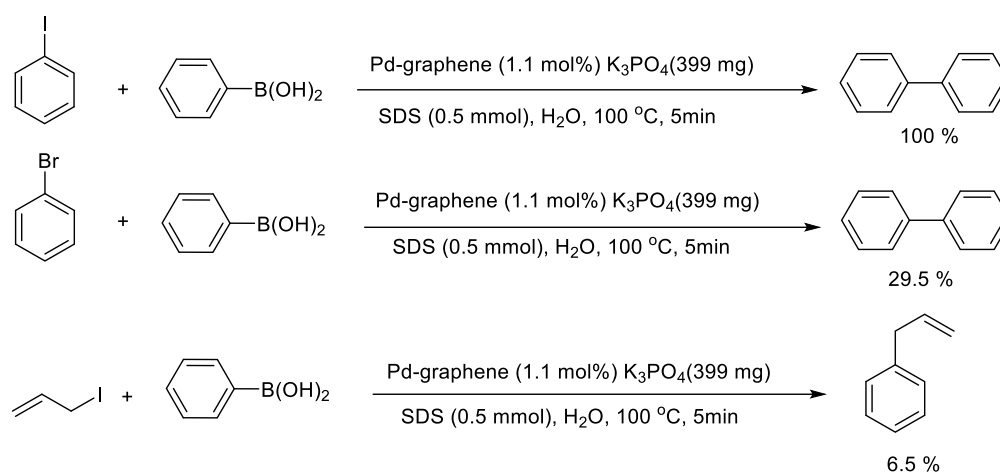

X= I, Br, Cl
R= 4-COMe, 4-CN, 2-CN, 4-COOMe, 2-COOMe
4-F, H, 4-Me, 2-Me, 4-OMe, 4-OH, 4-NH$_2$

Scheme II.A.5. *Suzuki coupling reaction by Kohler et al.*

Among the nanomaterials, graphene is solely able to stand out far ahead of all other nanomaterials because of its unique structure and exclusive

characteristics [51]. Graphene and its derivative have widely been used as catalytic support due to their high flexibility and strength like solid substrates. They exhibit a high surface area and are homogeneously embedded into metal matrices which make graphene and its derivative a viable candidate to be used as catalyst support. Due to the immobilization of metal NPs on the surface of graphene and its derivatives, the surface area of the composite material increases, thereby increasing the distance between the sheets. The catalytic activity of these metal composite materials successfully enhance the productivity of the most studied C-C cross-coupling reactions [52-57]. Zhang *et al.* reported graphene-modified PdNPs by reducing Pd(OAc)$_2$ (Scheme II.A.6) using a surfactant sodium dodecyl sulfate (SDS) [58].
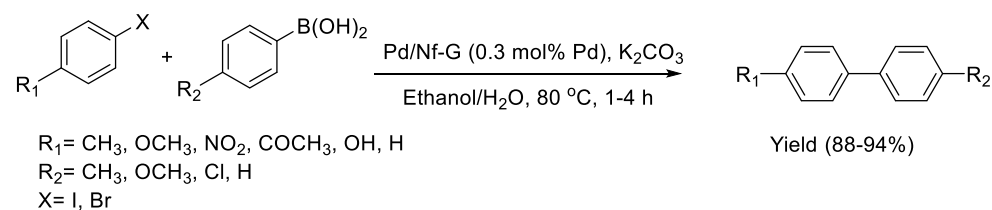

Scheme II.A.6. *Pd-graphene composite catalyzed synthetic approach by Zhang et al.*

The use of SDS can be showed as surfactant as well as a reducing agent. The prepared catalyst was highly efficient under aqueous as well as in aerobic conditions and exerted the product within 5 min. The recovery of the catalyst was done by filtration process and reused upto ten consecutive cycles. Allyl

iodides and bromobenzene were also employed in this coupling reaction but resulted in a lower yield of allylbenzene and biphenyl.

Shendage *et al.* electrochemically deposited PdNPs on nafion-graphene support (Pd/Nf-G) which showed eminent catalytic activity for the Suzuki coupling reaction to produce substituted biphenyls from substituted aryl boronic acids (Scheme II.A.7) under ethanol/water mixture at 80 °C [59]. Under the reaction temperature, Nafion is chemically and thermally stable. It is used to disperse and stabilize graphene on the electrode surface. The electrochemical process is generally heterogeneous in nature and allows easy recovery of the desired product. Besides this, no side product formation, short time of reaction, simple operation, and percentage of purity of side product make this process advantageous than conventional processes.

R$_1$= CH$_3$, OCH$_3$, NO$_2$, COCH$_3$, OH, H
R$_2$= CH$_3$, OCH$_3$, Cl, H
X= I, Br

Yield (88-94%)

SchemeII.A.7. *The Suzuki coupling reaction using Pd/Nf-G catalyst.*

The formation of PdNPs on Nf-G support was confirmed by SEM-EDAX, XRD, TEM, thermogravimetric analysis (TGA). The reaction between different aryl iodides and arylboronic acid was studied using a Pd/Nf–G catalyst. The electron-donating and electron-withdrawing aryl iodides afforded the product with excellent yield; however, aryl bromides require longer reaction time.

Gómez-Martínez *et al.* used boron-derived nucleophiles like potassium aryltrifluoroborates or boronic acid esters and aryl halide as reactants to afford biaryls for Suzuki coupling reaction using PdNPs (6 % Pd w/w) supported on

graphene (PdNPs–G) and reduced graphene oxide (PdNPs–rGO). They prepared three types of catalysts (Figure II.A.1), catalyst 1 is PdNPs immobilized on rGO sheets functionalized with octadecylamine (PdNPs–rGO/ODA), where 13 nm average size Pd (0) NPs have been immobilized. Catalyst 1 disperses better in organic solvents due to the presence of amino-functional groups.
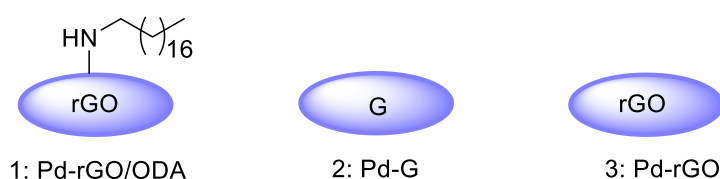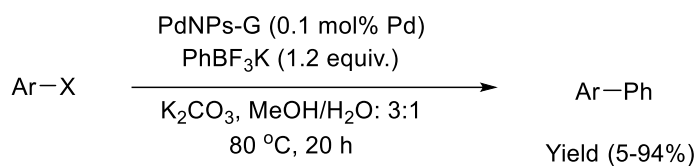

Figure II.A.1. *Pd(0) NPs supported catalyst employed in Suzuki coupling.*

Catalyst 2 is (PdNPs–G) where 5 nm average size Pd (0) NPs are distributed on the sheets of graphene oxide, while, catalyst 3, (PdNPs–rGO) contains Pd (0) NPs with an average size of 6.9 nm. Catalyst 2 and catalyst 3 are well dispersed in an aqueous medium. Due to the better dispersibility in water, both the catalysts, 2 (PdNPs–G) and 3 (PdNPs–rGO) are highly active in this process with a solvent ratio (MeOH/H2O:3/1) (Scheme II.A.8). Under the microwave irradiation, the catalyst 2 was reused upto eight consecutive cycles without the loss of its catalytic activity. Moreover, the catalytic activity dropped significantly under the conventional heating reaction conditions after five consecutive cycles.

PdNPs-G (0.1 mol% Pd)
PhBF$_3$K (1.2 equiv.)

Ar$-$X $\xrightarrow{}$ Ar$-$Ph

K$_2$CO$_3$, MeOH/H$_2$O: 3:1
80 ^{o}C, 20 h

Yield (5-94%)

Ar-X= 4-MeOC$_6$H$_4$Br, 2-MeC$_6$H$_4$Br,
1,3-(Me)$_2$C$_6$H$_3$-2-Br, 4-4-MeCOC$_6$H$_4$Br
1-Br-napthalene, 2-Br-pyridine, 2-Br-thiophene,
4-MeOC$_6$H$_4$I, PhOTf, 4-MeCOC$_6$H$_4$Cl

Scheme II.A.8. *Suzuki coupling catalyzed by Pd (0) NPs supported GO and rGO.*

II.A.3.1.2. Zeolite support (Inorganic support)

Among the catalyst support, zeolites having an anionic framework provides high surface area and it is conducive to the high dispersion and adsorption of metal species [60, 61]. As crystalline nanoporous materials, zeolite can trap or recover heavy metals including Pd from industrial water waste due to its well-distributed microporous space [62]. Wang *et al.* prepared the zeolite-supported Pd (II) catalysts by placing Pd (II) species on the solid surface of zeolite with an anion framework based on the charge balance principle (Figure II.A.2). They developed a highly efficient zeolite-supported Pd catalyst (0.84% Pd@zeolite USY) for in water C-C cross-coupling reaction using tetrapropylammonium hydroxide (TPAOH) base (Scheme II.A.9) [63]. This catalyst was successfully employed to produce substituted alkynes and biaryl from terminal alkynes and aryl boronic acids. The interaction between metal and support may be varied due to the interaction between metal-reactant and the form of the metal [64].
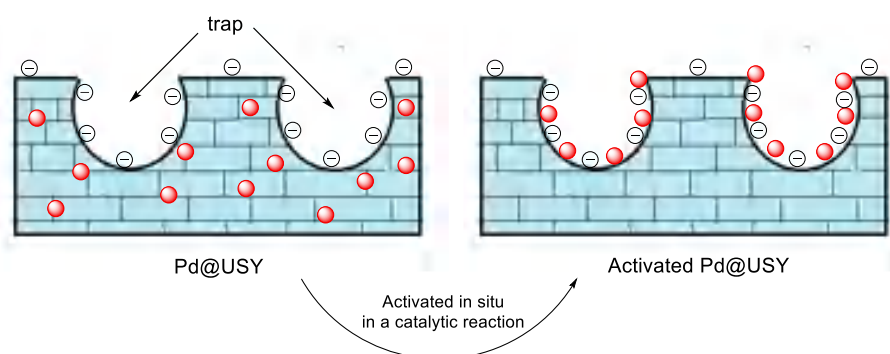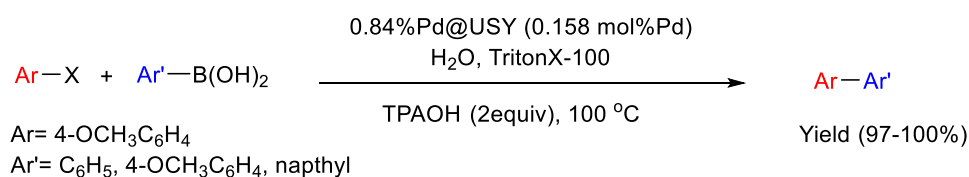
Figure II.A.2. The migration of Pd during the activation in catalysis.

In an aqueous system, the Pd species migrate in the catalytic process and the Pd (II) intermediate undergoes ion exchange with cations (Na^+, K^+ etc.) present in an aqueous medium and easily escapes from the zeolite support. Therefore, it is quite necessary for the metal species to get stabilized on the catalytic support during the reaction. They observed that in some alkaline aqueous systems, Pd (II) intermediate species uses zeolites (with an anionic framework) as a sink for coupling reaction, therefore, the position of Pd on the surface of zeolites can be controlled by release/capture capability of metal ions [65].
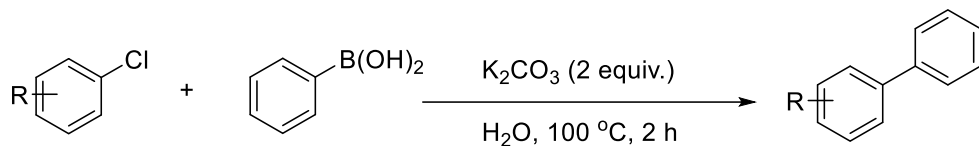

Scheme II.A.9. Pd@zeolite USY catalyzed Suzuki coupling reaction.

II.B.3.2. PdNPs on organic-inorganic support

Corma *et al.* reported the use of oxime palladacycle anchored to amorphous silica-based inorganic supports [66]. They synthesized oxime palladacycle

anchored with silica (Pd/SiO₂) or with MCM-41 (Pd/MCM-41). The schematic diagram for the preparation of this catalyst is shown in (Scheme II.A.11).
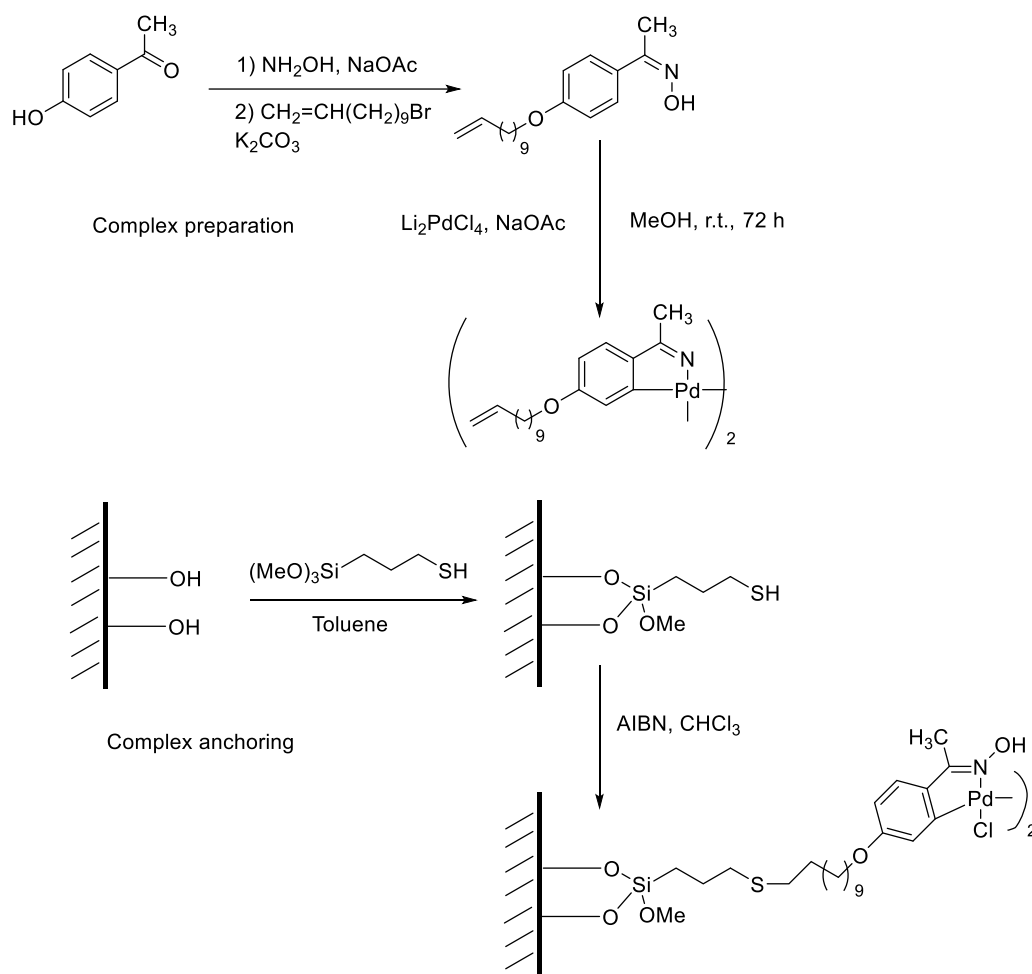

R= 4-Ac
5 mol % Pd/SiO$_2$: >99%
5 mol % Pd/MCM-41: 94%

R= 2-NO$_2$
5 mol % Pd/SiO$_2$: 89%
5 mol % Pd/MCM-41: 40%

Scheme II.A.10. *Suzuki coupling reaction described by Corma et al.*

Scheme II.B.11. *The procedure of anchoring of oxime carbapalladacycle with marcaptipropyl modified high silica surface*

However, Pd/SiO_2 showed the best result using bromoarens and activated chloroarens with 5 mol% Pd in presence of K_2CO_3 base. The same oxime palladacycle anchored to polystyrene and polyethylene glycol afforded lower yield of the coupling product (Scheme II.A.10). The Pd/SiO_2 catalyst can also be recycled without significant drop in its catalytic activity upto eight consecutive runs. They also carried out the leaching study of the catalyst through three-phase

test and observed no detectable Pd species was observed in the medium which confirms the true heterogeneous nature of the process.

II.B.3.3. Organic support

Among various polymeric supports, the natural polysaccharide of chitosan (CS) is cheap, non-toxic, and has excellent complexation capability with transition metal due to the presence of polar functional groups. Moreover, chitosan is very easy to process into different forms, such as microspheres, films, fibers, and so on. Cotugno *et al.* developed an efficient protocol for Suzuki cross-coupling reaction using Pd (0) Chitosan composite catalyst [68]. The excellent yield and selectivity were achieved using this catalyst at a relatively short reaction time (5 h). They carried out the reaction between different aryl halides and aryl boronic acids using K_2CO_3 as a base, PdNPs@Chitosan (0.1 mol%) catalyst, molten TBAB at 70-90 ^oC under aqueous solvent (Scheme II.A.12). To obtain the catalyst, in presence of TBAB, Pd(OAc)$_2$ was reduced electrochemically on the surface of chitosan. Subsequently, the PdNPs metallic core is stabilized by tetrabutylammonium cations mixed with Br- and [PdBr$_4$]$^-$ and the core-shell nanostructured catalyst is further chemically absorbed on chitosan surface (Figure II.A.3).
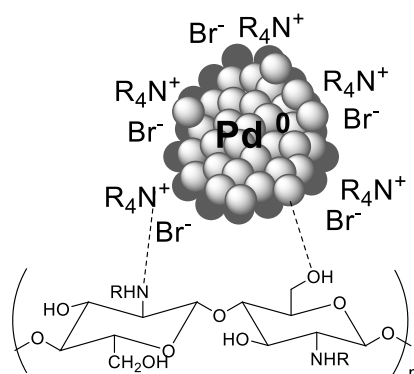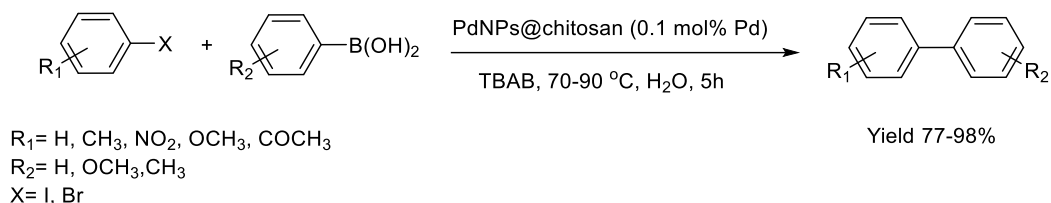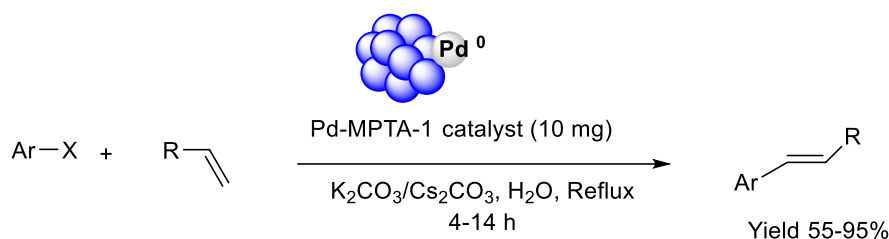
Figure II.A.3. The core-shell structure of Pd nanoparticles is chemisorbed on chitosan in tetraalkylammonium-based ionic liquids (ILs).

R$_1$= H, CH$_3$, NO$_2$, OCH$_3$, COCH$_3$
R$_2$= H, OCH$_3$,CH$_3$
X= I, Br

Yield 77-98%

Scheme II.A.12. *Suzuki cross-coupling reaction catalyzed by PdNPs@Chitosan.*

Mondal *et al.* synthesized PdNPs grafted mesoporous organic polymer catalyst by reacting (Scheme II.A.13) Pd(OAc)$_2$ and poly-triallylamine (MPTA-1) in presence of methanol [69]. The mesoporous materials generally exhibits high surface area and the active metal centrers are distributed on this large surface, thereby capable to run organic transformation effectively [70]. These materials act as an ideal tethering agent to bind the active metals strongly at their surface. Cross-linking polymers minimize the chance of metal leaching from its surface and extensively stabilizes the metal in long-term. are extensively used as long-term stabilization of the metals, which minimizes the possibility of leaching of metals under reaction conditions [71]. They observed the Heck coupling reaction between different aryl and heteroaryl halides and substituted alkenes using this heterogeneous Pd–MPTA-1 catalyst in a water medium. However, substituted chlorobenzenes underwent this C-C coupling reaction and took a longer reaction time along with a lower yield of the product compared to the corresponding bromobenzene and iodobenzene.

127

Scheme II.A.13. *Heck reaction catalyzed by Pd-MPTA-1 catalyst in water media.*
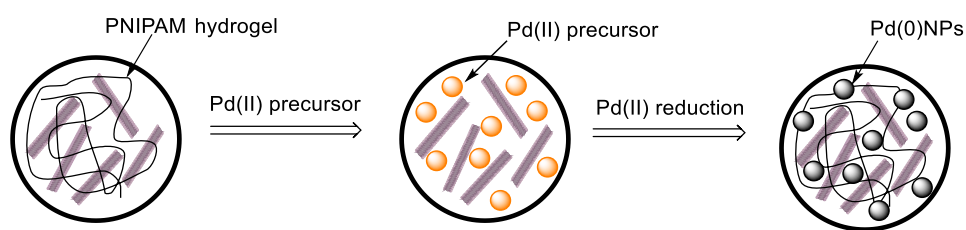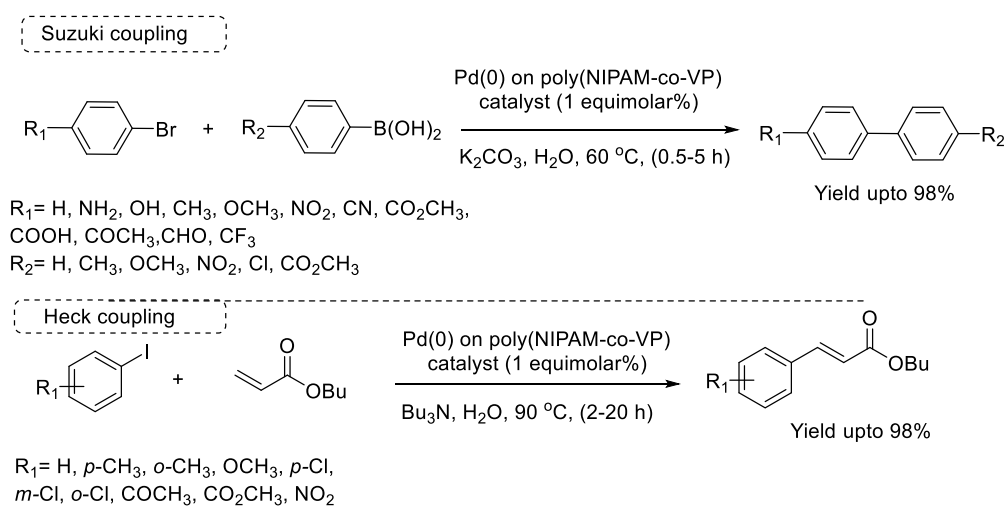

Figure II.A.4. *Pd(0) gtrafted on Poly(N-isopropylacrylamide-co-4-vinylpyridine) [poly(NIPAM-co-4-VP)] copolymer hydrogel.*

Lee *et al.* synthesized PdNPs immobilized on Poly(*N*-isopropylacrylamide-co-4-vinylpyridine) [poly(NIPAM-co-4-VP)] copolymer hydrogel for Suzuki and Heck cross-coupling reaction in water (Scheme II.A.14) [72]. Poly(*N*-isopropylacrylamide) (PNIPAM) is an example of temperature-responsive polymer which shows a phase transition from coil-to-globule in an aqueous solution at 32 °C which is the lower critical solution temperature (LCST) [73]. The swelling of PNIPAM polymer hydrogels is due to changes in the H-bonding of the PNIPAM polymer with water molecules [74]. Above LCST of PNIPAM, some H-bonds are dissociated and hydrophobic interactions are dominant among the PNIPAM network. Therefore, it is possible to carry out Suzuki coupling

reaction with hydrophobic substrates in absence of surfactants and organic solvents. Moreover, PNIPAM can be easily recovered from an aqueous medium by simple filtration above its LCST. Due to the versatile properties of PNIPAM, PdNPs immobilized on it have been utilized as recyclable heterogeneous catalysts [75, 76]. They observed that the PNIPAM matrix could not be restored after recycle and the leaching of Pd occurred.

Scheme II.A.14. *Suzuki, Heck coupling reaction catalyzed by Pd(0) [poly(NIPAM-co-4-VP)] catalyst.*

To resolve this difficulty they have utilized temperature-responsive poly(*N*-isopropylacrylamide-co-4-vinylpyridine) [poly(NIPAM-co-4-VP)] co-polymers [77] as the PdNPs support (Figure II.A.4). The poly(NIPAM-co-4-VP) copolymer stabilized PdNPs were prepared by reducing the Pd(II) precursor on the copolymer surface using $NaBH_4$ as reducing agent in MeOH solvent.

II.B.4. Conclusion

The Suzuki and Heck, cross-coupling reactions have been widely exploited for decades for the expeditious C-C, C=C, C≡C bond formation which is used for

the development of organic compounds, polymers and natural products in drug discovery. From the industrial point of view, Pd catalyzed coupling reactions in greener way using alternative reaction media are the current area of interest. Among green solvents, the utmost choice is water due to its environmental benefits, safeties, and cost. The use of homogeneous Pd catalyst is not appropriate in industrial purposes due to their lower stability, higher cost of synthesis, problem in their separation procedure and difficulty in reusability. To overcome the drawbacks of a homogeneous catalyst, the concept of PdNPs immobilized on a solid support has attracted much interest to merge all the advantages of homogeneous and heterogeneous catalysts. PdNPs immobilized nanostructured catalysts having high surface to volume ratio, low cost of processibility, good mechanical and thermal stability, and high reusability, that's why they have been used in long-lasting, cost-effective cross-coupling reaction.

II.A.5. References

References are given in Bibliography under Chapter II, Section A