CHAPTER I

A review on heterogeneous catalysis, metal nanocomposites and catalytic applications

I.1. Catalysis

Catalysis represents a new way to meet the challenges of energy and sustainability which are becoming the main concerns of the universal vision on societal challenges and world economy. Catalysis occupies an important place in chemistry; it lies at the heart of numerous chemical protocols, from research laboratories to the chemical industry. A variety of products, such as medicines, fine chemicals, polymers, fibers, fuels, paints, lubricants, and many other value-added products, would not be feasible in the absence of catalysts. Catalysis can be broadly divided into two branches, homogeneous and heterogeneous.

I.1.1. Homogeneous Catalysis

In a homogeneous catalysis, the catalyst is in the same phase as the reactants.[1] Homogeneous catalysts have several advantages such as high selectivity, better yield, and easy optimization of catalytic systems by modification of ligand and metals. In spite of their several advantages and applications, many homogeneous catalytic systems have not been commercialized because of the difficulty encountered in extrication the catalyst from the ultimate reaction product. Even when it is possible to separate the catalyst from the reaction mixture, trace amounts of catalyst are likely to remain in the final product.

I.1.2. Heterogeneous Catalysis

To overcome the problems of isolation and separation in homogeneous catalysis, chemists and engineers have investigated a wide range of strategies and the use of heterogeneous catalyst systems appears to be the superlative logical solution.[2] A vast majority of the industrial heterogeneous catalysts are high-surface area solids onto which an active component is dispersed or attached. Grafting can be achieved by covalent binding or by simple adsorption of the active catalytic molecules. The performance of heterogeneous catalysts is determined by exposed surface area.

I.1.3. Nanocatalysis

Most of heterogeneous catalytic processes take place at the active surface sites of the bulk catalyst. Therefore, it is apparent that the smaller the size the higher the surface area and activity. Since the end of the 1990s, and with the development of nanosciences, nanocatalysis has clearly emerged as a domain at the interface between homogeneous and heterogeneous catalysis, which offer unique solutions to answer the demanding conditions for catalyst improvement.[3]

Nanoparticles refer to materials with their extensions in all three dimensions smaller than 100 nm. Metal nanoparticles display unique properties on optical, electronic and chemical behavior which is quite different from bulk metal materials due to quantum size effect, surface effect and others effects.[4]

Transition metal nanoparticles as good catalysts for organic synthesis have attracted much attention over the past decade.[5] Metal nanoparticles (M-NPs) considered for catalytic process can be generated by (i) chemical reduction of a metal salt, (ii) thermal, photochemical, or sonochemical decomposition of a metal(0) complex, (iii) hydrogenation of a coordinating olefinic moiety, and (iv) vapour phase deposition.

Metal NPs without any solid support has rarely been applied in cross–coupling reactions. In such cases NPs becomes much larger in size because of aggregation and precipitation of the catalysts was observed.[6] The separation of the products and the recycling of the catalyst are not straightforward. Therefore to prevent nanocatalysts from aggregating, NPs are widely supported on some supporting materials and recycled by simple filtration. Transition metal nanoparticles can be either adsorbed on inorganic support or chemically bonded to polymeric support.

I.2. Heterogeneous Supports, Metal Nanocomposites and Catalytic Applications

The support usually has an impact on the activity of the catalytic system. Particle size, surface area, pore structure, and acid-base properties are important parameters of the support. The use of the appropriate support is therefore critical to obtain NPs of a suitable size to form highly active catalysts but also to stabilise the surface, so leaching is minimized. Popular supporting materials include mesoporous silica, alumina, zeolite, metal oxides, metal hydroxides, poly-ionic resins, carbon nanotube, graphene oxide and organic polymers.[7]

According to IUPAC notation, porous materials can be classified into microporous materials, mesoporous materials and macroporous materials according to their size. Microporous materials have pore diameters less than 2 nm; the mesoporous materials have pore diameters within the range of 2 – 50 nm and the macroporous materials have pore diameter greater than 50 nm.

I.2.1 Ordered Mesoporous Silica

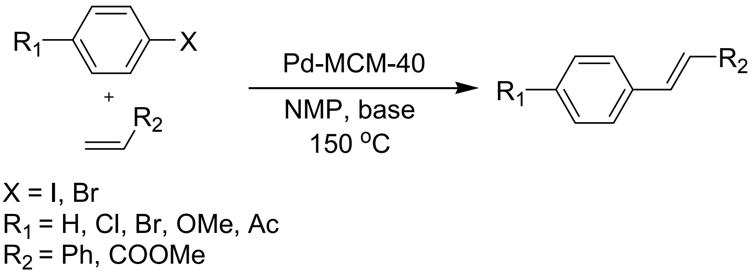
MCM-41 and SBA-15 are two most representative example of ordered mesoporous material, extensively used in heterogeneous catalysis.

MCM-41

MCM-41, the simplest mesoporous molecular sieve, has been extensively studied.[8] Hexagonally packed mesoporous molecular sieves (designated MCM-41) are of great interest to catalysis because their large and uniform pore sizes (20-100 Å) allow sterically hindered molecules facile diffusion to their internal active sites. Direct amidation of fatty acids with long-chain amines was successfully performed by using MCM-41.[9]

Since palladium-grafted mesoporous MCM-41 material designated as Pd-TMS11 was synthesized by Ying et al. in 1998.[10a] This heterogeneous material exequtes excellent activity for Heck reaction.

In 2005 Molnar et. al. have synthesized Pd–MCM–41 composite material by doing slight modification over MCM-41.[10b] The as synthesized catalyst was used in ligand-free Heck coupling reaction and also be recycled for 20 times without any activation treatment (Scheme I.1).



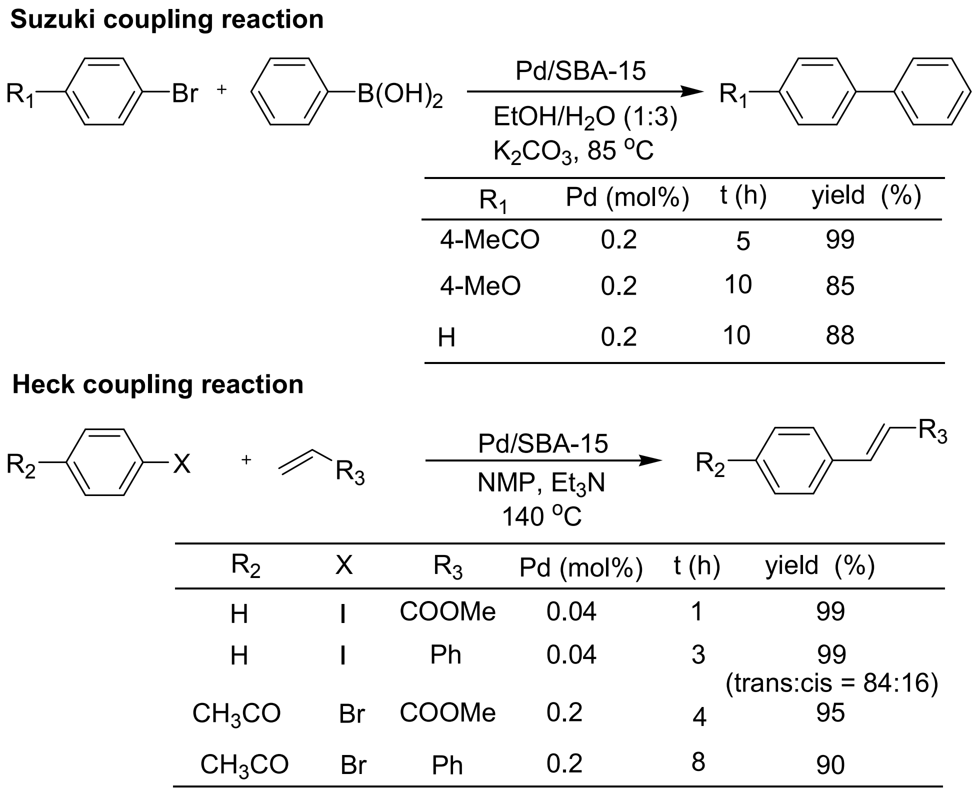
Scheme I.1. Heck coupling using Pd-MCM-40.

SBA-15

SBA-15 is the most important hexagonal mesoporous material after MCM-41, which was first reported by Zhao et. al. at the university of California, Santa Barbara.[11]

Mesoporous SBA-15 was used as the heterogeneous support since its well-defined, large pore opening provided easy access for large substrate molecules. Shi and co-workers reported the use of a thin Pd NP layer on the pore channel surface of a mesoporous silica SBA-15, obtained through impregnation with a solution of [$Pd(OAc)_2$] in THF followed by ''in situ'' reduction. The heterogeneous material was highly efficient for Heck coupling.[12]

After that in 2007 Gao and co-workers have reported a simple one-step method to synthesise palladium nanoparticles in highly ordered mesoporous channels of SBA-15, which has a pore size in the range of 5–10 nm with a large specific surface area and a highly ordered pore structure.[13] The authors have indicated that the loading amount of palladium nanoparticles in SBA-15 can be adjusted using different amounts of palladium salts and can also be controlled easily. The resulting nanocomposites exhibit a highly catalytic activity and reused ability at least after five recycles without ligand for both the Suzuki and Heck coupling reactions (Scheme I.2).



Suzuki coupling reaction

R_1	Pd (mol%)	t (h)	yield (%)
4-MeCO	0.2	5	99
4-MeO	0.2	10	85
H	0.2	10	88

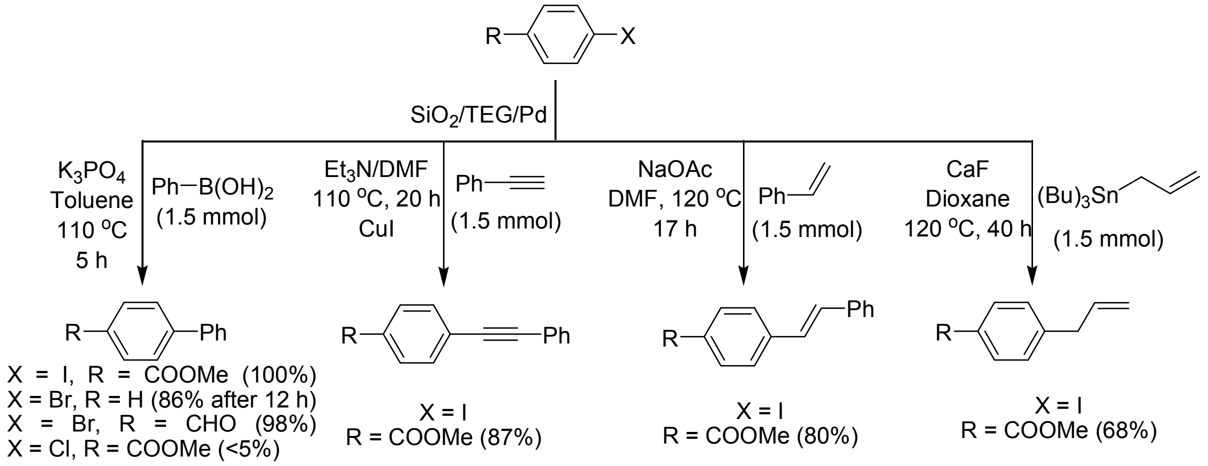
Heck coupling reaction

R_2	X	R_3	Pd (mol%)	t (h)	yield (%)
H	I	COOMe	0.04	1	99
H	I	Ph	0.04	3	99 (trans:cis = 84:16)
CH_3CO	Br	COOMe	0.2	4	95
CH_3CO	Br	Ph	0.2	8	90

Scheme I.2. Suzuki cross–coupling reactions catalysed by Pd/SBA-15 nanoparticles.

Amorphous Silica

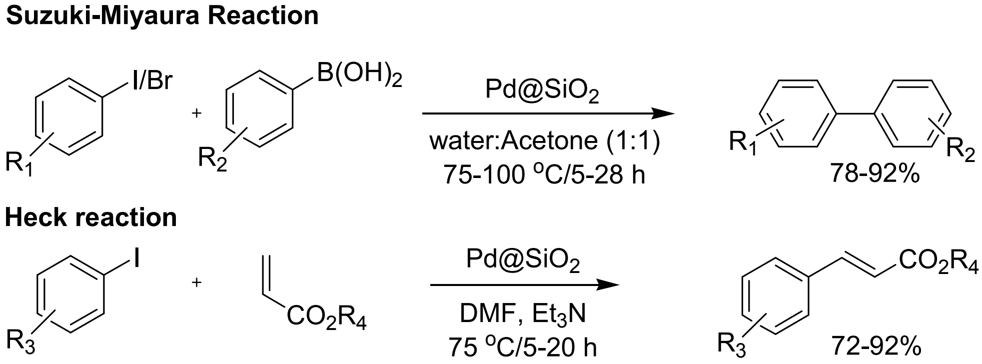
In 2004, silica-stabilised Pd nanoclusters (2–5 nm) were prepared by Park and co-workers from a mixture of [$Pd(PPh_3)_4$] in tetraethylene glycol and tetramethoxysilane through hydrolysis.[14] The resulting material exhibited good activity in the Heck, Suzuki, Sonogashira and Stille reactions at 0.75 mol% catalyst loading (Scheme I.3).



Scheme I.3. Silica supported Pd catalyst in Suzuki, Sonogashira, Heck, and Stille reaction.

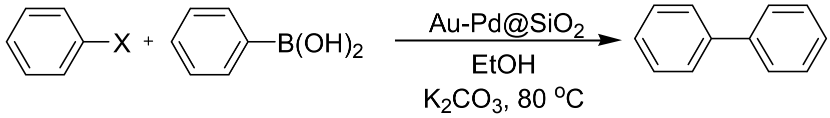
In past years an improved and eco-friendly procedure has been developed to generate meso-porous silica (particle size 325 mesh) supported palladium nanoparticles (Pd@SiO_2) from our laboratory.[15] This sustainable heterogeneous Pd catalyst was used for phosphine-free Suzuki–

Miyaura and Heck coupling reactions with excellent turnover number and turnover frequency (Scheme I.4). Pd@SiO_2 was recyclable for four consecutive run in Suzuki–Miyaura cross–coupling reaction between 4-iodotoluene and phenylboronic acid.



Scheme I.4. Pd@SiO_2 catalyzed Suzuki–Miyaura and Heck reaction.

Bimetallic nanoparticles also been investigated in many fields of science. Very recently Tang group was synthesized Au-Pd bimetallic nanocrystals in silica nanorattles.[16] Suzuki cross–coupling reactions are chosen as model reactions to evaluate the catalytic ability of these nanocatalysts (Scheme I.5). Notably, the alloy Au–Pd@SiO_2 with the lowest Pd content shows the highest catalytic activity and selectivity both for iodobenzene and bromobenzene.



Scheme I.5. Scheme illustrating the Suzuki cross–coupling reaction using Au–Pd@SiO_2 as a catalyst.

I.2.2. Zeolites

Zeolites have a crystal structure which is constructed from TO_4 tetrahedra, where T is either Si or Al. Each structure type is given a unique framework code as shown in Table I.1.

Zeolites are well-defined porous materials can be used as supports for Pd as such or in a modified manner. Pd(II) on basic zeolites was reported in the Suzuki–Miyaura coupling of bromobenzene with phenylboronic acid in toluene.[17a] No leaching was observed, and the solid catalyst could be reused after washing with water. Only a minor decrease in the catalytic activity was observed. Pd(II)-NaY zeolite or Pd(0)-NaY zeolite performed very well in Suzuki reactions of aryl bromides without the addition of a ligand.[17b,c] The catalysts exhibited excellent activity with K_2CO_3 or Na_2CO_3 as base at room temperature allowing high yields to be achieved after short reaction times. However, they were less useful for aryl chlorides.

I.2.3. Metal Oxides

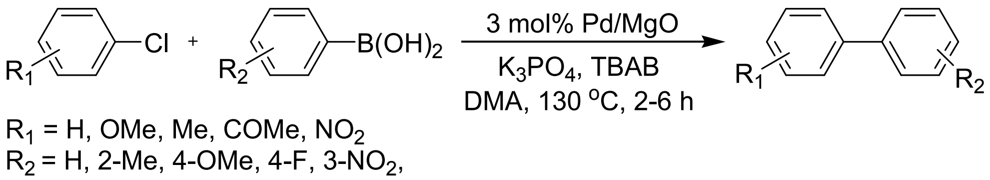
Different metal oxides have been used in nanocatalysis.

Table I.1. Zeolite ring sizes and codes.

Zeolite	Number of tetrahedral in ring	Framework Code
Sodalite	4	SOD
Zeolite-A	8	LTA
Erionite-A	8	ERI
ZSM-5	10	MFI
Fauzasite	12	FAU
Mordenite	12 and 8	MOR
Zeolite-L	12	LTL

I.2.3.1. MgO

Highly basic nanocrystalline magnesium oxide (MgO)-stabilised palladium NPs were prepared by counter ion stabilisation of $PdCl_4^{2-}$ with nanocrystalline MgO followed by reduction.[18] This catalyst was found to be very active in the Suzuki cross–coupling of aryl bromides and iodides with several arylboronic acids in pure water at room temperature (Scheme I.6).



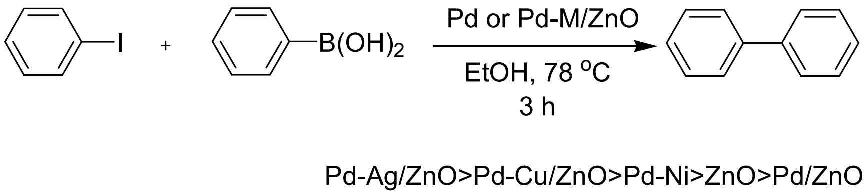
Scheme I.6. Suzuki cross–coupling reactions catalysed by PdNPs/MgO.

I.2.3.2. ZnO

ZnO-supported Pd, Pd-Ag, Pd-Cu, and Pd-Ni catalysts (Pd-M/ZnO) were prepared in $MeOH/H_2O$ mixture (4/1, v/v-%) by γ- irradiation at room temperature.[19] The catalytic efficiency of Pd and Pd-M/ZnO species was studied in Suzuki reaction (Scheme I.7). The catalytic activity was decreased in the order Pd-Ag/ZnO > Pd-Cu/ZnO > Pd-Ni/ZnO > Pd/ZnO. The Pd-Ag/ZnO was recycled successfully up to five consecutives but gradual decrease in catalytic activity was monitored.

I.2.3.3. CeO_2

Recently, cerium oxide (CeO_2) has been extensively used as heterogeneous catalysts for organic reactions.[20] One recent publication has exhibits Pd/CeO_2 system behaves as an effici-



Scheme I.7. ZnO supported bimetallic catalyst in Suzuki reaction.

ent percatalyst for Suzuki–Miyaura reaction at room temperature. Author has demonstrated that a homo generous mechanism takes place most probably through a release/re-deposition process.

I.2.3.4. TiO_2

Zhong and their group have described a novel route to load palladium NPs on the surface of hydroxyl-group-rich titania precursor. Pd nanoparticles are formed by in-situ reduction of Pd(II) by Sn(II); the latter is linked to the surface of TiO_2 precursors through inorganic grafting (Figure I.1).[21] TiO_2 precursor-Pd exhibits high catalytic activity for Suzuki cross–coupling reaction (Scheme I.8).

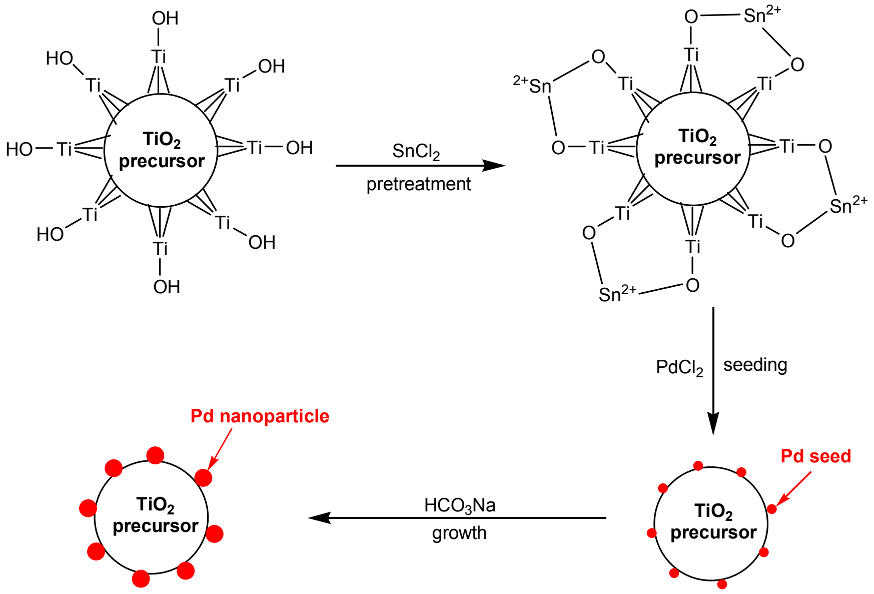
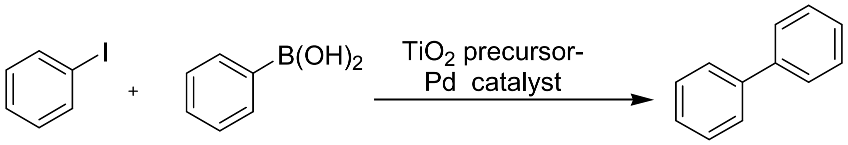


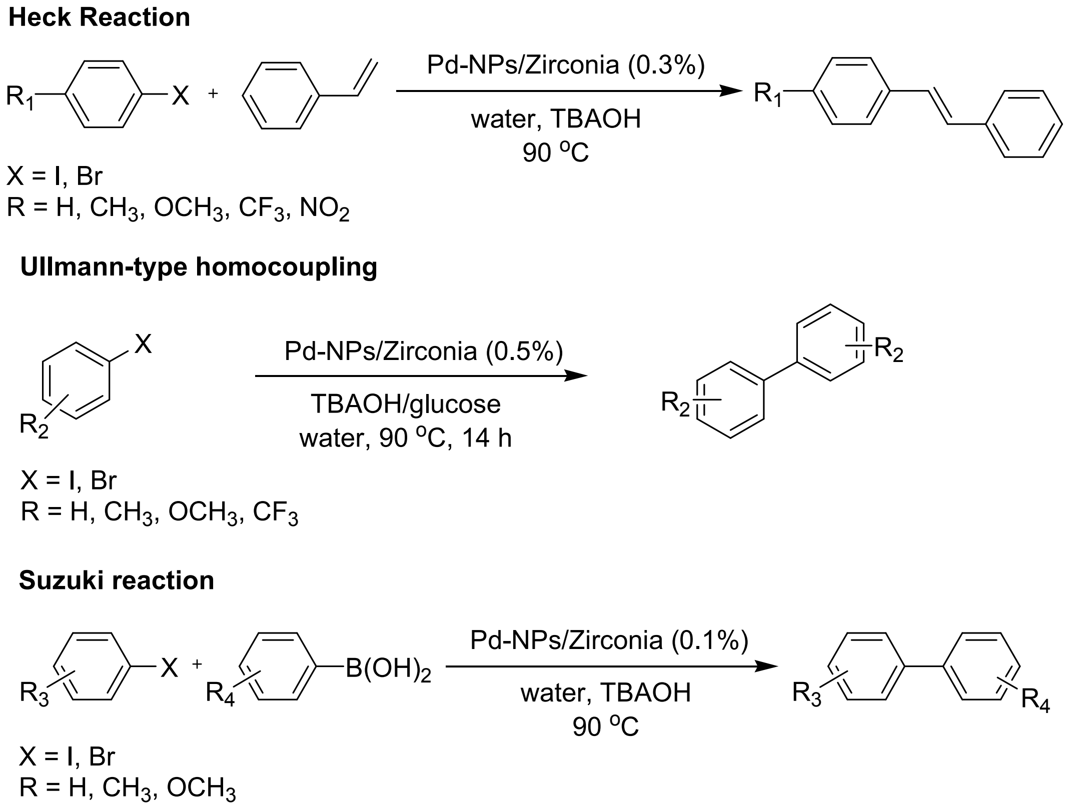
Figure I.1. Schematic process for loading Pd nanoparticles onto the surface of TiO_2 precursor.



Scheme I.8. Suzuki reaction catalyzed by TiO_2 precursor-Pd catalyst.

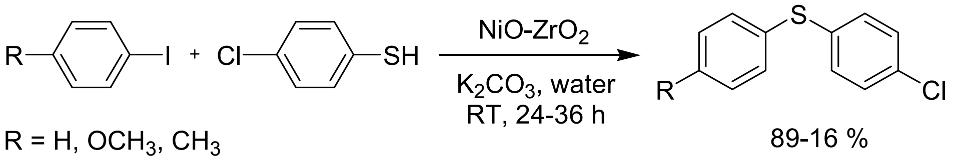
I.2.3.5. ZrO_2

Cioffi and co-workers have been used Nanostructured zirconium oxide (ZrO_2) for supporting palladium NPs by an electrochemical technique.[22] The Pd/ZrO_2 nanocatalyst was very efficient in C−C coupling reactions such as Heck, Ullmann and Suzuki cross–coupling (Scheme I.9).



Scheme I.9. Pd/ZrO_2 nanocatalyst in Heck, Ullmann and Suzuki reaction.

Bhaumik and their group have synthesized self-assembled NiO-ZrO_2 nanocatalyst *via* evaporation induced self-assembly method.[23] The calcined material was highly crystalline with a cubic crystal structure. This nanocatalyst exhibits good catalytic activity in the C−S cross–coupling reaction in aqueous medium under aerobic conditions (Scheme I.10). Since this methodology was limited for certain diaryl sulphides.



Scheme I.10. NiO-ZrO_2 catalyzed C−S cross–coupling reaction.

I.2.3.6. Al_2O_3

Alumina is probably the most common inorganic oxide that is used as the solid surface to catalyze or mediate a large variety of organic reactions. Alumina can act as a base, as an acid, or as a polar medium to cause molecular reorganizations in many types of organic compounds. Recently different composite materials were synthesized using alumina e.g. Cu/alumina,[24a] Ni-alumina,[24b] Pd/alumina[24c] and successively applied in C−S, C−N, C−O and C–C cross–coupling reaction.

I.2.3.7. KF/Al_2O_3

Alumina doped with potassium fluoride (KF/alumina) has been extensively used as solid basic surface in vast range of organic transformation,[25] since it was introduced by Ando and Clark.[26]

Palladium-doped KF/Al_2O_3 was used in solvent–free Suzuki couplings under microwave irradiation (Scheme I.11).[27]

$$\mathrm{Ar{-}X} + \mathrm{Ar'{-}B(OH)_2} \xrightarrow[\text{MW-irradiation, neat}]{\text{Pd on } KF/Al_2O_3} \mathrm{Ar{-}Ar'}$$

Ar−X	Ar'	condition	yield (%)
PhI	4-Me-Ph	2 min, 100 W	82
PhBr	4-Me-Ph	2 min, 100 W	52
PhCl	4-Me-Ph	2 min, 100 W	4

Scheme I.11. Palladium on KF/Al_2O_3, a heterogeneous catalyst for solvent-free Suzuki coupling.

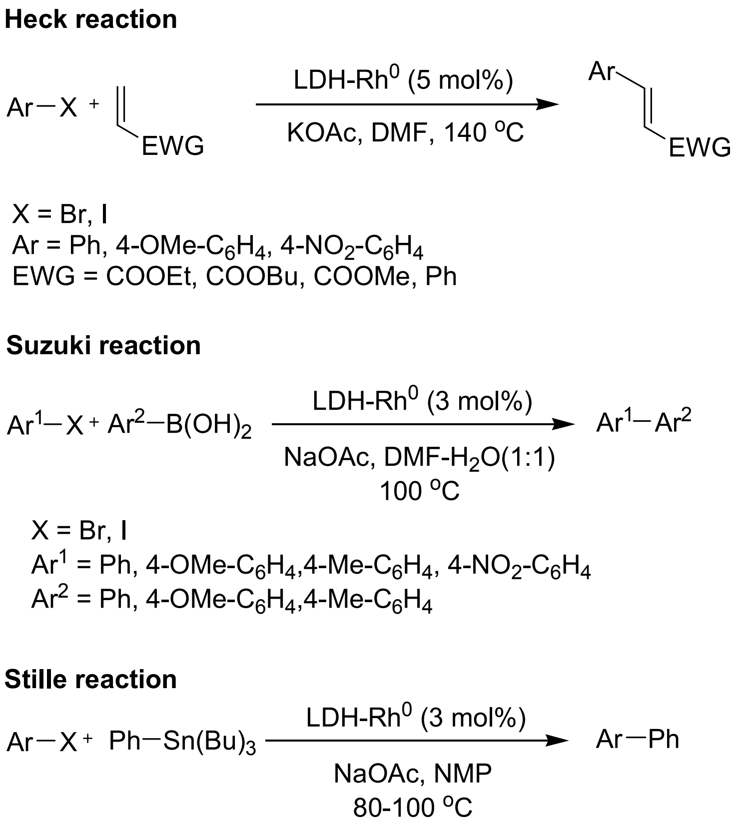
I.2.4. Layered double hydroxide

In recent years layered double hydroxides of Mg and Al (LDHs) has been receiving considerable attention due to its cation exchange capacity of the brucite layer, anion exchange by inter layer, adjustable surface basicity and adsorption capacity.[28] In addition the ability to hold metal particles in the defect sites make LDHs good support in heterogeneous catalysis and by exploiting these properties of LDHs nanorhodium was incorporated and applies in Heck, Suzuki and Stille cross–coupling of haloarenes (Scheme I.12).[29]

I.2.5. Magnetic-materials

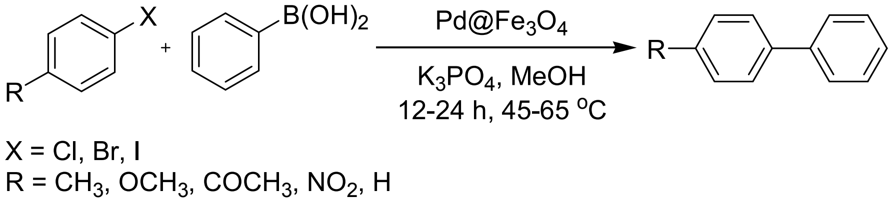
Catalyst recovery is a crucial feature of most of these processes. However, the use of magnetic nanoparticles as a support seems to be a promising option to overcome this separation problem. Because of the paramagnetic character of this support, the synthesised catalysts could also be recovered simply by using an external magnet without a filtration or centrifugation step. Recently, there has been an increasing trend towards the use of magnetically recoverable nanomaterials to develop more efficient and green chemical synthetic processes.[30]

Rana and co-workers have described a new methodology to immobilize metallic Pd on surface-functionalized ferrite nanoparticles leading to a magnetically separable catalyst,[31] which exhibits efficient catalytic activity in Suzuki–Miyaura coupling reactions (Scheme I.13).



Scheme I.12. LDH-Rh^0 in Heck, Suzuki and Stille coupling.

The amine groups of branched polyethylenimine on the ferrite surface allow entrapping Pd nanoparticles and prevent metal leaching during the reaction. In addition, the environment provided by these groups leads to a structurally stable catalytic site, which makes them recyclable without any loss in activity.



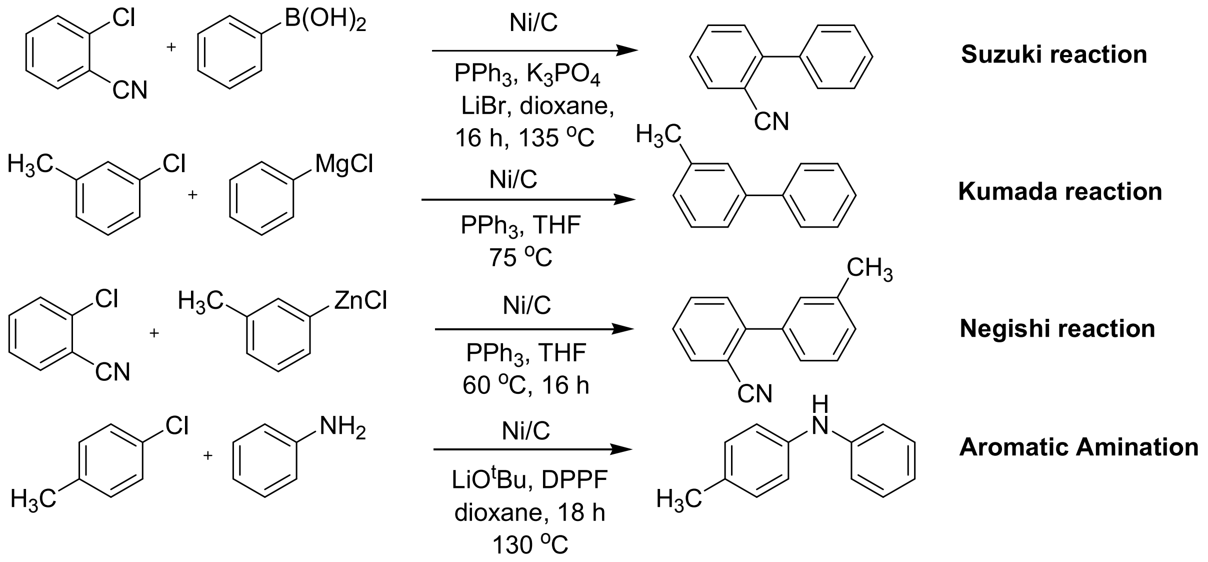
Scheme I.13. Magnetically separable catalyst (Pd@Fe_3O_4), for Suzuki–Miyaura cross–coupling reaction.

I.2.6. Charcoal

Palladium on charcoal (activated carbon) (Pd/C) is the most frequently used catalyst in heterogeneous Pd-catalyzed cross-coupling reactions. It can be purchased from various laboratory suppliers, such as Acros, Aldrich, or from the manufacturers Degussa or Johnson Matthey in various qualities with a Pd content ranging from 1% to 20%. The materials can contain water up to 50%. Different procedures for the preparation of Pd/C were reported.[32]

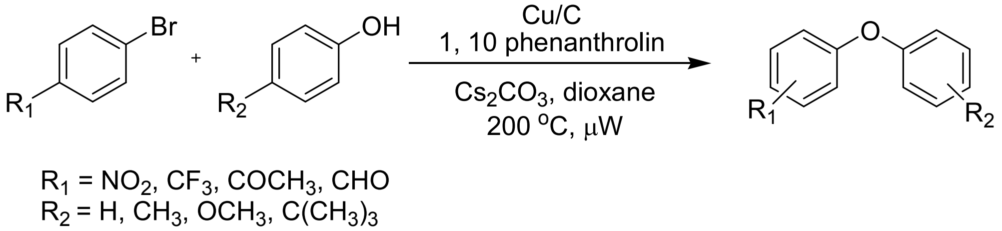
The first example of Pd/C catalyzed Suzuki reaction was reported by Marck and co-workers in 1994.[33] After that several methodologies have been invented using Pd/C catalyst for aryl bromide, chloride, iodide, or triflate. Pd/C was used with or without additional phosphine ligands, and often the application of aqueous solvents is advantageous.[34]

Lipshutz and their group synthesized Ni/C by different techniques and applying that catalyst for several cross-coupling reactions like Suzuki-, Kumada and aromatic aminations in presence suitable ligand (Scheme I.14).[35]



Scheme I.14. Ni/C catalyzed Suzuki, Kumada, Negishi and Aromatic amination reaction.

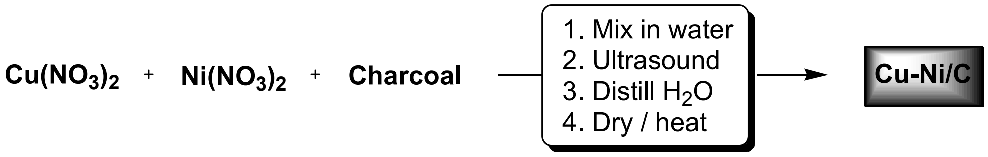
Impregnation of activated wood charcoal with $Cu(NO_3)_2$ in water using an ultrasonic bath leads to nanoparticle-sized Cu/C.[36] This heterogeneous material was an active catalyst for C−O cross coupling reaction (Scheme I.15).[37]

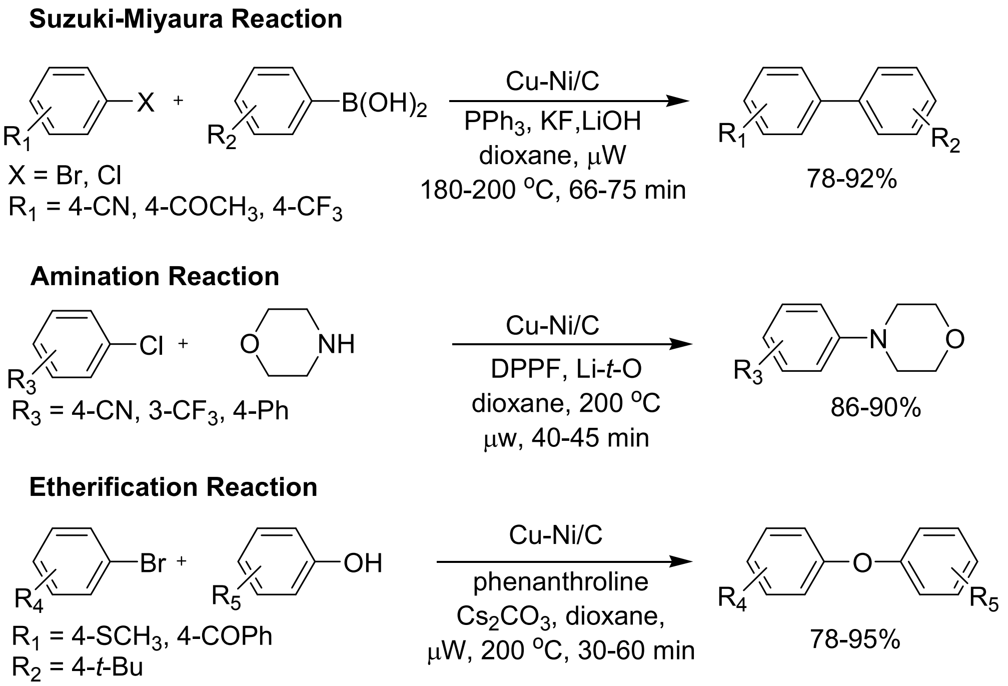


R_1 = NO_2, CF_3, $COCH_3$, CHO
R_2 = H, CH_3, OCH_3, $C(CH_3)_3$

Scheme I.15. C−O cross–coupling using Cu/C.

A new heterogeneous catalyst composed of copper and nickel oxide particles supported with charcoal has been developed. It catalyzes cross–couplings that traditionally use palladium, nickel, or copper, including Suzuki–Miyaura reactions, Buchwald-Hartwig aminations, vinylalane alkylations, etherifications of aryl halides (Scheme I.16).[38]



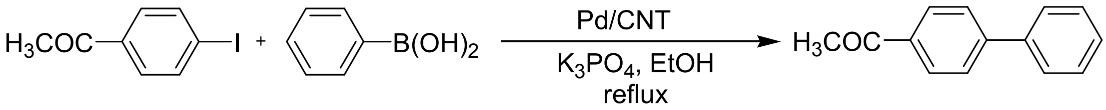


Scheme I.16. Use of Cu-Ni/C bimetallic catalyst in Suzuki–Miyaura, aromatic amination and etherification reaction.

I.2.7. Carbon nanotubes

Carbon nanotubes provide a new type of support for catalytic nanoparticles. Because of their small size, carbon nanotubes can be uniformly dispersed in solution, thus increasing contact between the reactants and the catalyst.[39]

Preparation of Pd and carbon nanotubes composites (Pd/CNTP) involves reduction of sodium tetrachloropalladate to Pd(0) on the surface of CNTs in presence SDS and ethylene glycol.[40] Ethylene glycol acts as a solvent as well as reducing agent. SDS self-assembled onto the surface of carbon nanotubes by the hydrophobic interaction between alkyl chains and graphitic surface. During the reduction process, the interaction between SDS and Pd nanoparticles resulted in the attachment of Pd nanoparticles onto the surface of carbon nanotubes. Thus, these well-dispersed spherical Pd nanoparticles were anchored tightly onto the external walls of MWNTs by the interaction between Pd nanoparitcles and SDS. The catalytic activities of these Pd/CNTP composites for Suzuki coupling reactions were investigated (Scheme I.17).



Scheme I.17. Pd/CNT catalyzed Suzuki reaction.

I.2.8. Graphene oxide

Graphene belongs to a new class of carbon nanomaterials – 2-D materials made up entirely of conjugated sp^2 carbons arranged in a honeycomb structure. The main reason behind the fast paced enlargement of graphene research is due to the unique properties of graphene. Several experimentally measured properties have already surpassed those observed in other types of materials. With enhanced electrical conductivity, high mechanical strength, high thermal conductivity, high impermeability to gases and optical transparency, graphene holds great promise as the next wonder material.[41]

Graphene oxide was discovered much earlier than graphene. The most widely accepted structural model of GO is the Lerf–Klinowski model (Figure I.2) and is defined by two distinct regions in the GO structure: one of lightly functionalized, predominately sp^2-hybridized carbon (graphene-like) atoms and a second of highly oxygenated predominately sp^3-hybridized carbon atoms. In this model, hydroxyl and epoxide functional groups are proposed to decorate the basal plane which are segregated into islands among the lightly oxidized, graphene-like regions, while carboxylic acids or carboxylates, depending on the pH of the solution, are present on the edges of the sheets.[42]

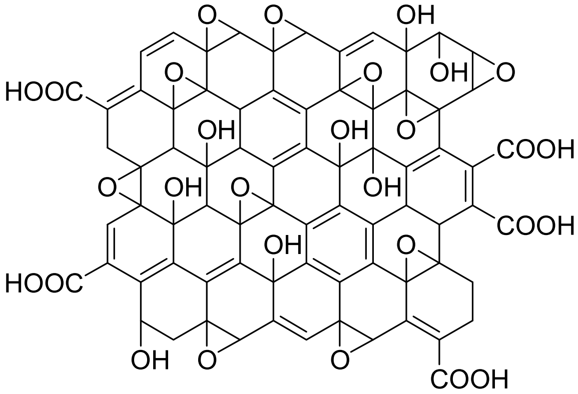


Figure I.2. Graphene oxide.

I.2.8.1. Chemical reactivity of GO

The catalytic efficiency of graphene oxide (GO) and other chemically modified graphenes (CMGs) as the carbocatalysts has raised enormous interest since the seminal papers from Bielawski and co-workers.[43] In current years GO was included in diverse organic reactions (Figure I.3).[44]

I.2.8.2. Metal on graphene

Graphene oxides (GO) and other chemically modified GOs have attracted much attention as potential carbonaceous materials to embed various metal/metal oxide resulting new nanocomposite materials.[45]

Immobilization of Pd^{2+} on graphite oxide (GO) via cation exchange and successive chemical reduction afforded Pd^0 nanoparticles and chemically derived graphenes (CDG).[46] The (GO)-

Pd and the (CDG)-Pd catalysts were effectively applied to the Suzuki–Miyaura coupling reaction (Scheme I.18). These novel heterogeneous catalysts were readily available and easy to handle as they are stable in air. Extraordinary high activities with turnover frequencies (TOF) of up to 39 000 h^{-1} and very low leaching make them an attractive alternative to commercially available Pd catalysts such as Pd on charcoal. However, recovery of the noble metal is possible because of very low leaching.

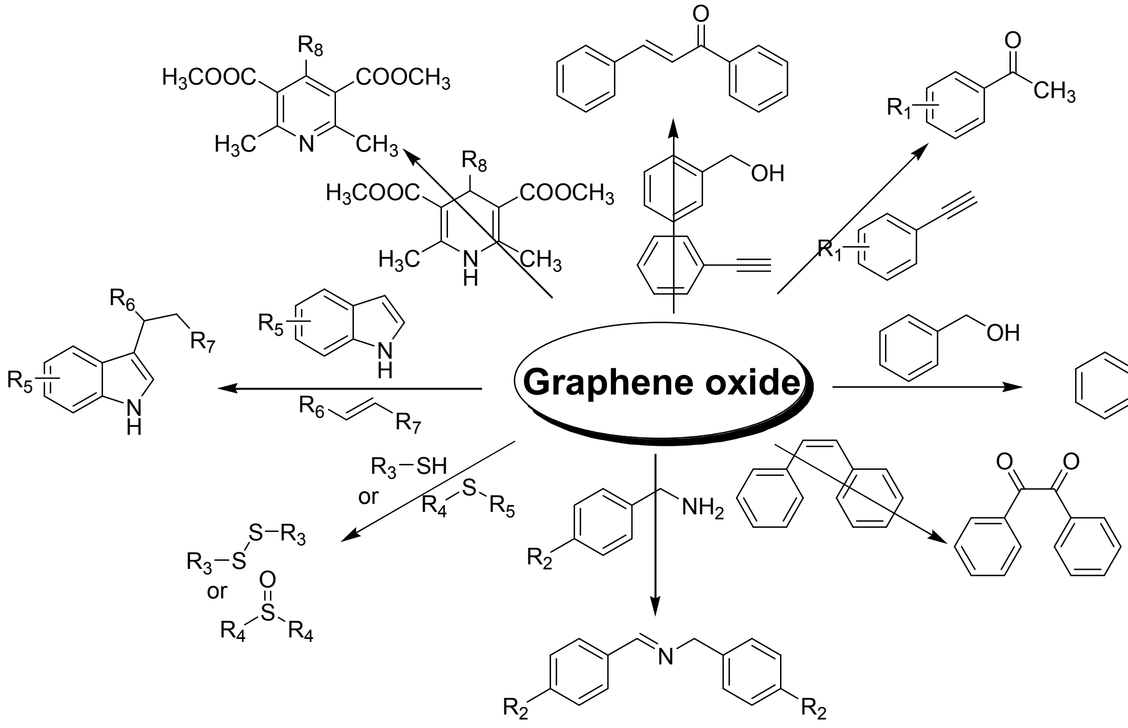
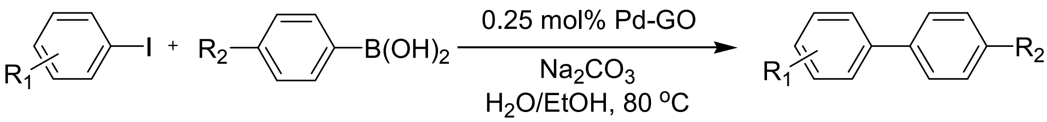


Figure I.3. Graphene oxide catalyzed organic transformations.

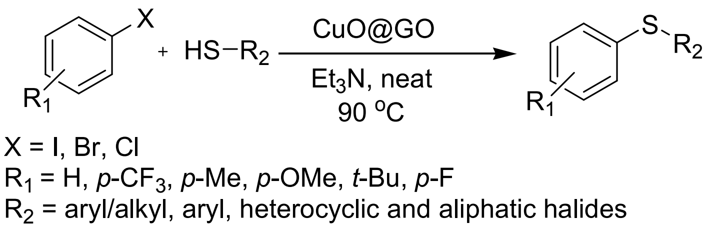


R_1 = OH, OCH_3, COOH, COOEt
R_2 = OCH_3, H

Scheme I.18. Pd-GO in Suzuki–Miyaura cross–coupling.

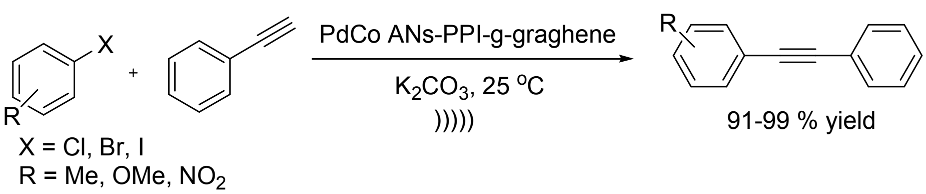
There are several routes available in literature for the synthesis of CuO NPs supported on graphene oxide but not for cross–coupling reactions.[47] One recent publication showed the preparation of copper oxide nanoparticles that are supported on graphene oxide be an active catalyst for ligand-free and solvent-free C–S cross-coupling reactions with weak bases such as triethylamine (Scheme I.19).[48] This nanocomposite was true heterogeneous and recycled up to six consecutive runs.

In 2013 Shaabani and their group designed a simple protocol to synthesized third generation



Scheme I.19. CuO@GO catalyzed C−S cross–coupling reaction.

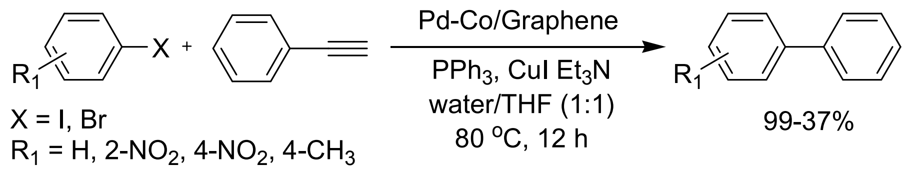
polypropylenimine (PPI) dendrimers were grown on the surface of functionalized graphene. The PPI-grafed graphene hybrid material was effectively employed as substrate for in situ generation of palladium cobalt alloy nanoparticles.[49] The as synthesized heterogeneous catalyst used for Sonogashira cross-coupling reactions under environmentally benign, aerobic and solvent free conditions at room temperature (Scheme I.20). The new hybrid material, under optimal reaction conditions, was used as an efficient heterogeneous catalyst for couplings between a wide range of terminal alkynes and aryl halides in high yield.



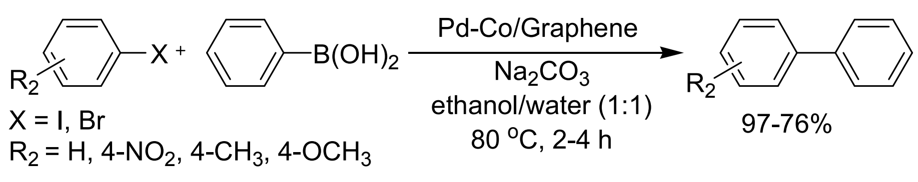
Scheme I.20. Sonogashira cross–coupling with PdCo ANP–PPI-g-graphene hybrid material.

Graphene (G) supported Pd-Co bimetallic nanoparticles (NPs) as a highly active catalyst was prepared by a chemical reduction method and used for Sonogashira and Suzuki–Miyaura cross–coupling reactions (Scheme I.21).[50] With the characterization of X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and Raman spectrum, the composition of resulting Pd-Co material was identified to be alloy structural. The recyclability also checked for Suzuki–Miyaura cross–coupling.

Sonogashira reaction



Suzuki-Miyaura reaction



Scheme I.21. Pd-Co/G catalyzed Sonogashira and Suzuki–Miyaura coupling reactions.

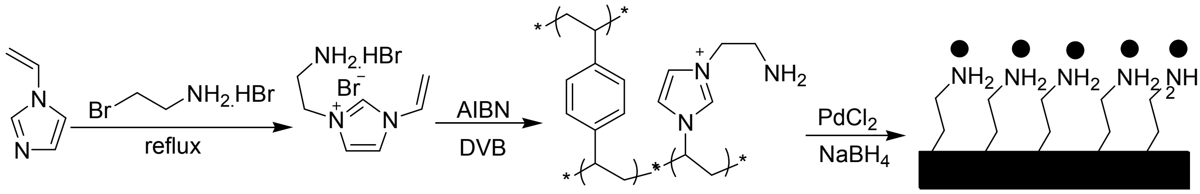
I.2.9. Organic polymers and related molecules

Over the last few decades, palladium nanoparticles have been mostly supported on inorganic materials, such as silica, other oxide-hydroxides and carbon nanotubes.[51] More recently, functionalised polymers have been used as supports in coupling reactions, and a variety of, polymers have proven to be versatile supports due to their potential to combine the easy reu se of heterogeneous catalysts and the high efficiency of homogeneous catalysts.[52]

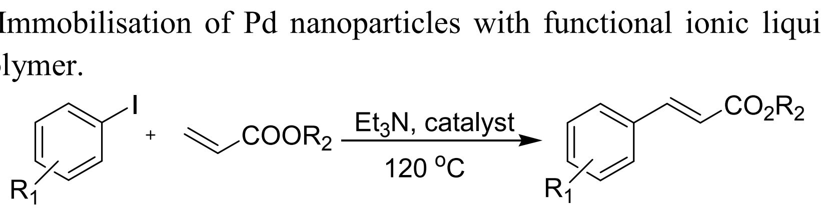
I.2.9.1. PVP

A study by Sayed et al., detailing Suzuki cross-couplings using polymer supports, reported a series of PVP stabilised Pd nanoparticles with different Pd particle sizes, prepared using the stepwise growth technique reported by Teranishi et al.[53] Using this method, the authors succeeded in preparing different PVP-Pd composites with a narrow particle size distribution and average particle sizes of 3.0, 3.9, 5.2 and 6.6 nm. Most of the Pd nanoparticles prepared by this method showed a roughly spherical morphology. The turnover frequency (TOF) for the Suzuki reaction between phenylboronic acid and iodobenzene in aqueous solutions was found to depend on the Pd particle size and to exhibit a maximum size of ca. 3.9 nm.[54]

The immobilisation of Pd nanoparticles with functional ionic liquid grafted onto cross-linked polymer was also reported by Han and their group (Scheme I.22).[55] The nanocatalysts immobilized on the copolymers showed high catalytic activity in the Heck reaction for various substrates (Scheme I.23). The catalyst was very stable and could be easily separated from the products and reused because of the insoluble nature of the cross-linked copolymer and the coordination force between the amine group and the palladium nanoparticles.



Scheme I.22. Immobilisation of Pd nanoparticles with functional ionic liquid grafted onto cross-linked polymer.



R_1 = H, 4-F, 4-Cl, 4-OH, 4-Me, 4-OMe
R_2 = Me, Et, Bu

Scheme I.23. Polymer supported Pd NPs in Heck reaction.

In recent years Kobayashi developed Copolymer-Incarcerated Nickel Nanoparticles with N-Heterocyclic Carbene Precursors.[56] These NHCs embedded in the polymer matrix were characterized by FGSR-MAS NMR analysis. This heterogeneous catalyst was successfully applied to Corriu− Kumada−Tamao (CKT) reactions with quite wide substrate generality in high yields including functional group tolerance (Scheme I.24).

$$R_1{-}X + R_2{-}MgX \xrightarrow[\text{THF, RT-100 }^{\circ}\text{C under } N_2]{\text{Ni(0) catalyst (0.25-2.5 mol\%)}} R_1{-}R_2$$

X = I, Br, Cl, F
R_1 = Aryl, alkyl, heteroaryl
R_2 = Aryl, Alkyl

Scheme I.24. Nickel nanoparticles with N-heterocyclic carbene precursors as heterogeneous composite in CKT reaction.

I.2.9.2. Polystyrene Resin

The polymeric supports used by Merrifield for his early work in solid-phase peptide synthesis were based on 2% divinylbenzene (DVB) cross- linked polystyrenes (PS). Polytyrenes has been found to be one of the most accepted polymeric material used in various synthesis because it is inexpensive, readily available, mechanically robust, chemically inert, and smoothly functionalizable.[57] Cross-linking imparts mechanical stability, improved diffusion and swelling properties to the resin. Various percentages and types of cross- linking agents have been incorporated into the PS resins, the most common being DVB, but other examples include ethylene glycol dimethylacrylate (EGDMA) and tetraethylene glycol diacrylate (TEGDA) to give different solvation properties.[58] A schematic representation of polymerization of styrene with functionalized monomers is shown in Figure I.4.

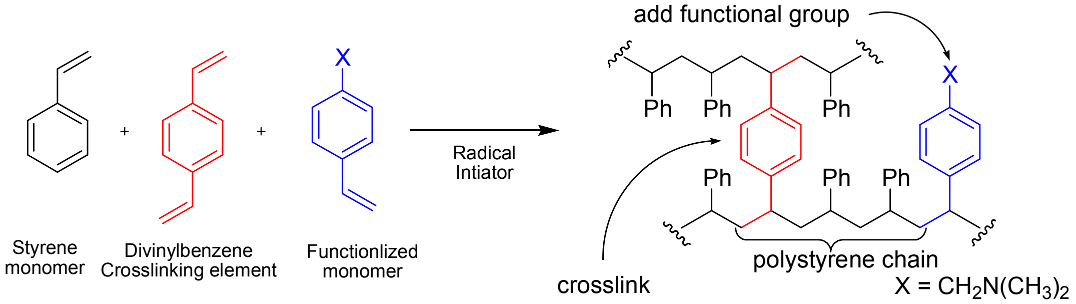
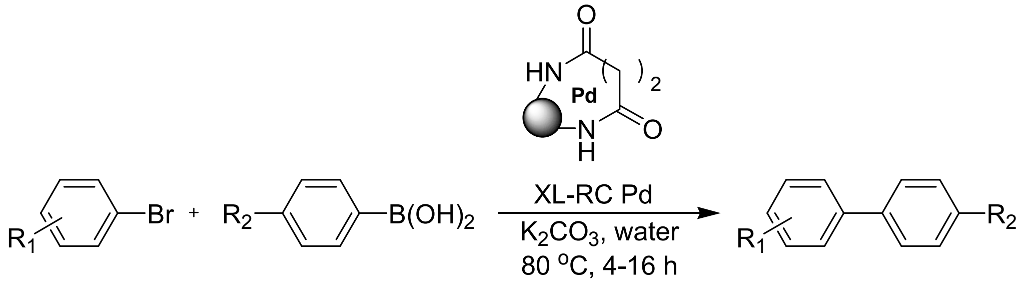


Figure I.4. Polystyrene resin formation.

TentaGel[59] and ArgoGel[60] are two commercially available examples, where the incorporation of the PEG chains dramatically increases resin compatibility with polar solvents.

Bradley and their group showed that soluble $Pd(OAc)_2$ can enter swollen resins and that amino groups on the resin can be “tied and tangled” by cross-linking, allowing permanent capture of the palladium on the resin without the assistance of any resin-bound ligand or stabilizer prior to conversion to stable palladium “nanoparticles”.[61] The prepared catalyst designated as XL-RC Pd. Aminomethylated TentaGel resin was used for this immobilization process. The as prepared catalyst has been used in Suzuki reaction (Scheme I.25). These supported catalysts are predominantly heterogeneous in nature and could be recycled without loss of activity.



X = Br, Cl
R_1 = 4-CH_3CO, 4-CH_3, 2-NO_2, 2-CH_3, 4-OCH_3
R_2 = H, OCH_3

Scheme I.25. Aminomethylated TentaGel resin supported Pd NPs in Suzuki reaction.

I.2.9.3. Ion-Exchange resins

Ion-exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them and normally obtained as beads of 1-2 mm diameter. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers). Synthetic ion exchange materials based on coal and phenolic resins were first introduced for industrial use during the 1930s. A few years' later resins consisting of polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchangers were developed. The most typical ion exchange resins are based on cross linked polystyrene and the required active groups can be introduced after polymerization, or substituted monomers can be used. For example, the cross linking is often achieved by adding 0.5-25% of divinylbenzene to polystyrene at the polymerization process. Non-cross linked polymers are used only rarely because they are less stable.

Types Ion-Exchange resin

There are four types of ion exchange resins:

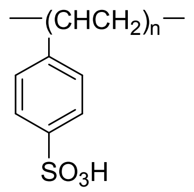
- Strong cation-exchange resins, containing sulphonic acid group or the corresponding salts.
- Weak cation-exchange resins, containing carboxylic acid groups or the corresponding salts.
- Strong anion-exchange resins, containing quaternary ammonium groups.

- Weak anion-exchange resins, containing primary, secondary, and/or ternary amino groups, e.g. polyethyelene amine.

Ion exchange resins are widely used in different separation, purification and decontamination process examples are: Water softening, Water purification, Uranium recoveries from seawater, inversion of sucrose.

Catalytic activity of ion-exchange resin in organic reactions:

Amberlyst-15 is routinely used in organic synthesis as heterogeneous reusable acid catalysts for various selective transformations of simple and complex molecules (Figure I.5).[62]



Amberlyst-15

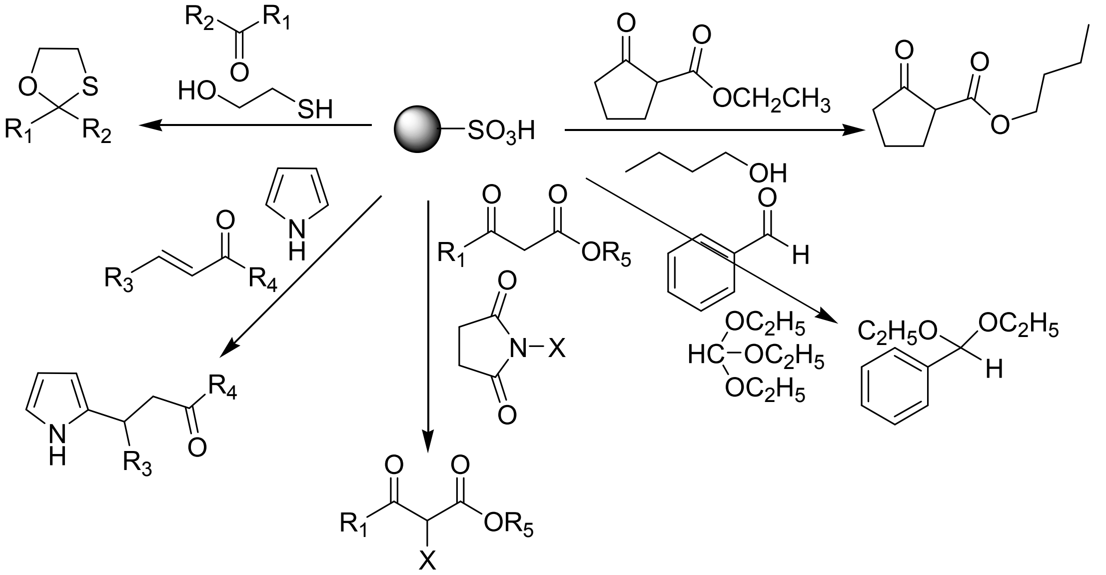
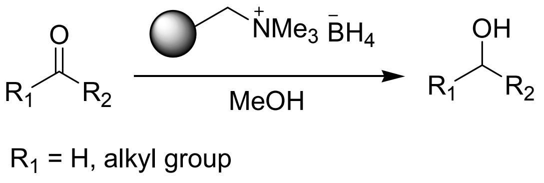


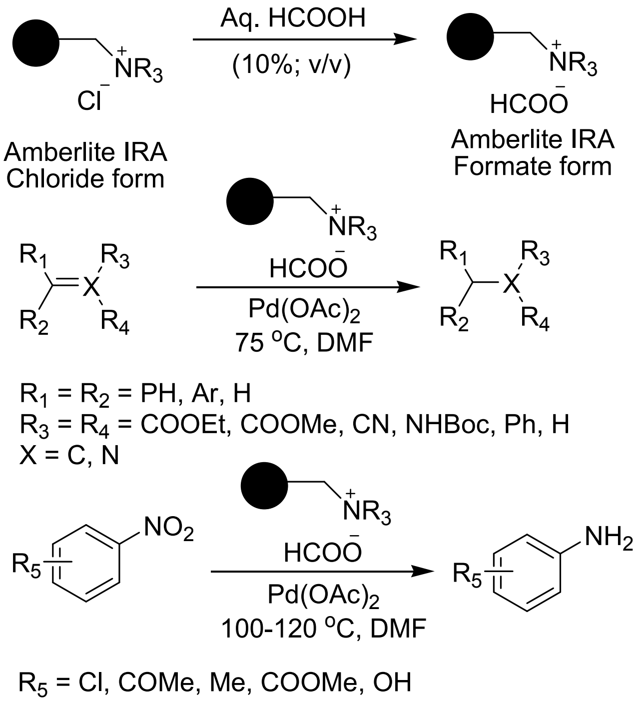
Figure I.5. Amberlyst-15 catalyzed organic transformation.

The selective reduction of functional groups is a common need in organic synthesis. Borohydride exchange resin,[63] (BER) was introduced in the 1970s and has since proven to be of considerable value in the reduction of organic compounds. This reagent reduces both ketones and aldehydes readily to corresponding alcohol (Scheme I.26)



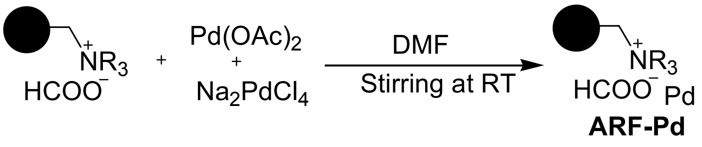
Scheme I.26. Reduction of carbonyl compounds using Borohydride Borohydride exchange resin.

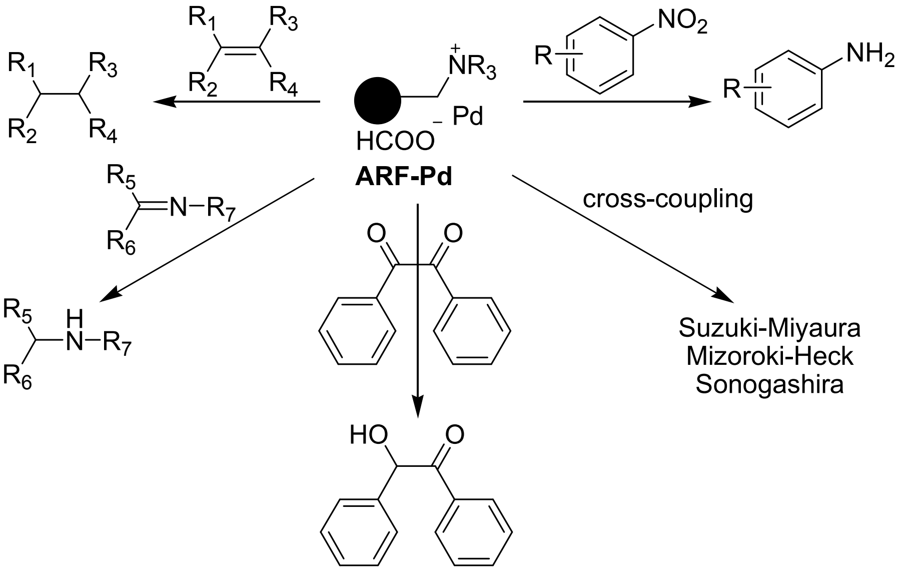
It was observed that Amberlite IRA-420 anion (chloride form) exchange resins, commercially available and inexpensive poly- ionic resin, could exchange the anion with formate anion (HCOO^{-}) easily and quantitatively. The resulting Amberlite Resin Formate (anion), designated as ARF, could be utilized as a solid-phase version of the H-donor in Pd-catalyzed catalytic transfer hydrogenation. The ARF was air stable, can be stored for several weeks and also can be recovered from a reaction and reused. Several alkenes, imine and nitroarenes were thus hydrogenated using the ARF and catalytic amount of palladium acetate under mild conditions (Scheme I.27).[64]



Scheme I.27. Amberlite resin formate in catalytic hydrogenation reactions.

The combination of formic acid and palladium acetate is known to undergo anionic ligand exchange to form a palladium diformate complex, eventually producing Pd(0) through decroxylation and loss of molecular hydrogen.[65] By applying this technique a new catalyst was invented from our laboratory. This heterogeneous catalyst was successfully applied in catalytic reduction and C–C cross–coupling reactions (Scheme I.28).[66]





Scheme I.28. ARF supported Pd in catalytic reduction and C−C cross–coupling.

I.3. References

References are given in BIBLIOGRAPHY under Chapter I (pp. 141−145).