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On the Technology of Heterogenization of Transition Metal Catalysts towards the Synthetic Applications in Ionic Liquid Matrix

Alwar Ramani, Suresh Iyer and Murugesan Muthu

Abstract

With the invention of ionic liquids, synthetic chemistry reached a new arena towards the transition metal catalyzed reactions in the syntheses of fine, specialty, agricultural, commodity, fragrant chemicals and building blocks. Inside the ionic liquid matrix, the transition metal catalysts, when immobilized, offer a valuable solution in terms of heterogenization. This technology offers high level of recyclability without loss of activity and improves the turnover number with high selectivity. Synthetic chemists, chemical engineers and technologists continue their efforts to recover and recycle the transition metal catalysts through various methodologies to convert the processes cost effective. The processes that are reported in the literature reveals that the ionic liquids by virtue of their inertness coupled with ability to retain the catalytic materials provide an excellent solution in terms of high levels of recovery and recyclability. This chapter presents a short account on the recent development in the transition metal catalyzed reactions in ionic liquid systems where both the solvent and the catalyst were recycled and reused without any emission of volatile materials.

Keywords: immobilization, heterogenized ionic liquid, transition metal catalysts, synthetic organic chemistry, recyclability

1. Introduction

Transition metal catalysis plays a pivotal role in the production of bulk chemicals, active pharmaceutical ingredients, synthetic scaffolds and aesthetically interesting petrochemical-derived materials towards the interior decoration of our built environment; consequently, manufacturers globally started employing transition metals [1]. Transition metal catalysis is ever expanding in the field of organic synthesis owing to the way to achieve higher molecular complexity by limiting the catalyst and process cost, while the potentiality and efficiency of such methodologies cannot be attained by conventional organic synthetic pathways [2]. The process of catalysis is being exploited in the manufacture of 85% of

all chemical products. Apart from the design and invention of new reactions in this field, process development is also a motivating factor since it renders highly selective organic functional group transformations in attaining structurally complex organic compounds with biological and pharmaceutical importance. Transition metals being situated at the middle part of the periodic table, either in their ionic or neutral form in solution, or *in situ*, are capable of accommodating up to nine valence shell orbitals accounting for the variable oxidation states and forms various transition states to generate hybrid molecular orbitals yielding the desired product with high chemo-, regio- and stereo-selectivity with high turnover number and turnover frequency [3]. With the advancement in the analytical techniques to understand the mechanistic pathway, transition states, and kinetics, chemists and technologists in this epoch were able to tune (through the selection of appropriate ligands and/or external additives) the catalyst according to the needs. However, the major disadvantage of the homogeneous catalytic system is that the catalyst cannot be separated easily and recycled, and also separation of product from the reaction mixture besides, in some cases, poses plethora of potential problems. In the process development of pharmaceutical drugs employing homogenous systems, the separation of the transition metallic species is very important, since if it remains in the drug molecules (product) even in the ppm level, inside our biological system, it can create undesirable side effects owing to its multivalence ability and can interfere in the biological and enzymatic process [4] and attack the immune system. Eventually, separation of the catalytic material, recovering it without losing it in the work up procedure, and subsequent reuse are the major challenges arising from the transition metal catalysis. In most of the cases, the transition metal catalyst loses its original form while quenching the reaction mixture with the treatment of water; eventually, the metal ion should be treated with new chemical procedure to acquire the original catalyst; in practice, the challenges are multifold as far as the catalyst's reuse and recyclability are concerned. On the other hand, though the heterogeneous catalytic system, separation of the catalytic material/s through a simple filtration technique is allowed, thereby the recovery and reuse are solved with ease; heterogeneous system does not offer most of the benefits that arise from that of homogeneous system; thus, the rich chemistry of transition metal catalysis remains at the top rank which is admired by academicians, chemists, technologists and entrepreneurs [5]. In the industrial processes, though the heterogeneous processes get precedence over homogeneous processes for the process of fine chemicals, in many of such processes, the undesirable side reactions give rise to unwanted products and impurities in varying proportions, and process development chemists instruct the graduate chemists to purify the products through various separation processes for instance distillation and recrystallization. Ultimately, an idea emerged in the minds of academicians to invent processes by combining the advantages of homogeneous and heterogeneous catalysis, which is the 'immobilization or heterogenization,' employing tailor-made transition metal catalytic materials. The concept of heterogenization technology has been attempted since the late 1960s [6], and it is continuously growing towards the success; now, there are many commercial processes that are operative with this technology for the production of fine chemicals to pharmaceutically important compounds. Among all the possible ways available, here in this chapter, the discussion will focus its attention on the exploitation of ionic liquids [7] as support for transition metal catalysts.

Ionic liquids are the modern technological materials made up of molten organic and inorganic salts with a melting point below 100°C, and they are

loosely bound; therefore, they are liquid under conventional ambient conditions, and they can be tailor-made according to the needs and demands, so they are also known as 'Designer Solvents' and/or 'Solvents of the future'. The design of room temperature ionic liquids has been achieved through appropriate selection of weakly coordinating cations and anions; theoretically, as per the principles of crystallography, the lattice energy has to be brought down as low as possible, and hence, the design lies on the *antithesis* of assembling pure crystal/s, and/or also symmetry in the ions should be destroyed by all means. Chemists around the globe realised the importance of ionic liquids in technology; in synthetic organic chemistry, they designed innumerable classes of ionic liquids, and mathematically through various permutations and combinations, millions of ionic liquids can be synthesized. Unlike other field of research, the field and phenomenon of ionic liquids progressed in stages, and during its progress, more and more technological applications were realized. In the year 1914, the salts of alkylammonium nitrates were identified as liquid in nature, and then chloroaluminates were identified as ionic liquids. In the 1990s, aluminates were replaced with other anions such as tetrafluoroborate $[\text{BF}_4]^-$ or hexafluorophosphate $[\text{PF}_6]^-$, and then the field of ionic liquids started gaining familiarity and popularity because of convenient recyclability. After 1990, numerous ionic liquids with variety of unique anions and cations were reported in the literature, and this field received recognition in developing neoteric technologies, very importantly, synthetic organic chemists found that the ionic liquids were useful as recyclable solvent; with this discovery, this field became appealing and convincing to synthetic organic chemists. Almost all name reactions were carried out in the ionic liquids, and the bench chemist has meticulously screened and succeeded through *trial and error* or *hit and miss* methodologies. In relevance to the title of the chapter, the discussion will revolve around the use of transition metal catalysis in ionic liquids towards organic functional group transformations. As the catalytic materials derived from d-block and rare earths remain expensive and yield unwarranted side effects when consumed by human, the chemists and technologists invented a variety of techniques to immobilize the metallic catalytic systems in various ways through high levels of creativity. Among them, ionic liquids proved to be an excellent matrix to retain the charged, neutral or polar transition metal complexes; consequently, the catalyst was recycled and reused without the loss of catalytic activity and selectivity; moreover, the separation of the product seems to be easy from the reaction mixture, the product reaches the extracting solvent, and the catalyst was held through electrostatic forces in the ionic liquid matrix. Consequently, from the last decade, ionic liquids (ILs) have been employed and found to be effective for the immobilization of homogeneous catalytic materials, and new technology has emerged, which is known as supported ionic liquids phase (SILP). In SILP, mostly an IL film is immobilized on a high-surface area porous solid through either physisorption or chemisorption, and the homogeneous catalyst is immersed in an IL matrix. This unique concept has been employed for the immobilization of homogeneous catalytic materials, absorbents, and other functional materials; consequently, this concept is expected to benefit the scientific community to simplify the lives of people at large. With the added advantages, SILP in this era is much exploited in the immobilization of homogeneous catalytic systems; ultimately, it will be surely impossible to picturize the complete overview of this area. In this chapter, we decided to limit our discussion to the most important contributions for brevity and conclude with recommendations, future perspectives, and outlook.

2. Supported ionic liquid phase (SILP)

In view of recycling and reusing the transition metal catalytic materials, the technology of immobilization or heterogenization was exploited, and the notable methodologies include polymer supports, macrocellular silica-based foams, magnetic Fe_3O_4 , carbon nanotubes (CNT), multiwalled carbon nanotubes (MWCNT), mesoporous solids, functionalized magnetic Fe_3O_4 , metal organic framework (MOF), monolithic ionogels, and SILP. Among them, the SILP technology is the most recent one; there are debates that the use of ILs is not cost-effective; however, the whole SILP system is reusable and recyclable and hence the cost can be abruptly reduced; the technology ranks to be green in nature since there is no escape of volatile organic compounds (VOCs). Metal in the form of oxides, ions, metal complexes coordinated to the cation or anion, or as nanoparticles was supported in an IL matrix through a thin film. In the SILP system, IL is a part of the support material; accordingly, the bulk properties of IL such as solvation strength, conductivity, viscosity and density are altered. ILs with hydrophobic in nature can offer excellent surface support. ILs can also act as nanoparticles stabilizers. Even though the stabilization mechanism has not been proved, ILs seem to create an electrostatic and steric barrier between nanoparticles; a stabilization type Derjaguin-Landau-Verwey-Overbeek (DLVO) has been proposed due to their polymeric structure.

2.1 SILP in macrocellular silica

The preparation of macrocellular silica is quite simple; the transition metal compounds of interest is suspended in a solution employing an ionic liquid in an volatile organic solvent. Upon stripping the volatile organic compound, the free-flowing immobilized catalytic material can be obtained where the transition metals are trapped within the SILP system. The materials thus trapped within the SILPs were found to be useful in promoting the organic functional group transformations catalyzed by transition and/or noble metals. Mainly the aryl-X activation (Mizoroki-Heck reaction) was carried out using palladium containing SILPs (in imidazolium ILs). With low palladium loading, the Heck-type coupling reaction was performed, and the reaction of iodobenzene with cyclohexyl acrylate yielded the corresponding cinnamates with high turnover numbers (TON) and turnover frequency (TOF) [8]. Palladium acetate $\text{Pd}(\text{OAc})_2$ supported on amorphous silica immobilized in [bmim] PF_6 (1-butyl-3-methylimidazolium hexafluorophosphate) was reported to be highly efficient towards the promotion of the Heck-type coupling reaction without any additional ligands, gave the trans-cinnamates in preparative yields [9], and the TON and TOF reached 68,400 and 8000 h^{-1} , respectively.

2.2 Heterogeneous ionic liquid (HIL)-encapsulated IL on silica

A variation for the synthesis of heterogeneous IL-based palladium-containing catalytic system was developed by Shi et al. [10], through a one pot synthesis of heterogeneous ionic liquid encapsulated on silica involving sol-gel method. These catalysts provided excellent activity for the carbonylation of aniline and nitrobenzene to synthesize diphenyl urea in (Pd or Rh)-EMImBF₄/silica gel (1-ethyl-3-methylimidazolium tetrafluoroborate) or (Pd or Rh)-DMImBF₄/silica gel (0.1 g, 50–60 mesh), (1-decyl-3-methylimidazolium tetrafluoroborate), or DMImBF₄ ionic liquid (2.5 g) containing Rh complex (1 mg) or 0.11 wt%Rh 35 wt% DMImBF₄/SiO₂ (0.1 g, for the purpose of comparison). The selectivity, yield, and turnover number (TON) were excellent. In the same publication, the identical catalytic system was

proved to be excellent for the carbonylation of aniline to synthesize carbamates and also oxime transfer between cyclohexanone oxime and acetone.

Yokoyama et al. [11] reported that the Mizoroki-Heck reaction of iodobenzene and 4-methyl-iodobenzene with olefins using silica-supported palladium complex catalysts was fruitful in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆), exhibiting higher activities than in DMF (N,N-dimethylformamide) in addition to easy product isolation and catalyst recycling. Silica-supported Pd catalysts were synthesized in 1-butylimidazolium hexafluorophosphate with low palladium loadings (0.35 and 0.08%); fascinatingly, both samples thus synthesized proved to be effective catalytic system for Heck-type coupling reactions between bromo- and chloroarenes with ethylacrylate. They also reported that the presence of electron withdrawing groups attached to the aromatic moiety increases the conversion and selectivity towards trans-selectivity. They could recycle the catalyst but pointed out that there is some loss of activity of the catalytic material upon recycling; the hot filtration measurements proved the leaching of Palladium [12]. A multiple-layered SILP system was developed for a hydroformylation process and found to be effective in the hydroformylation reactions [13].

2.3 Palladacycles on macroporous aluminosilicate

In a variation, oxime Pd cycle was derivatized to increase its ionophilicity by a tethered imidazolium group; the resulting IL forms an imidazolium complex which is supported on high surface area Al/MCM-41, aluminosilicate (1-butyl-3-methylimidazolium bromide is tethered onto oxime Pd cycle which is then heterogenized on Al/MCM-41). This is a solid active catalyst for the Mizoroki-Heck and Suzuki coupling. Results are moderate to good yields. Ionophilicity of the oxime Pd cycle can be significantly increased, limited by the need for basic conditions. Catalytic reuse showed increase in homocoupling [14].

2.3.1 Palladium on clay composite carrying phosphinite-functionalized ionic liquid moieties (CCPIL)

A clay composite comprising of phosphinite-functionalized ionic liquid moieties was synthesized, in which palladium nanoparticles were uniformly ligated, and this system is called as clay carrying phosphinite-functionalized ionic liquid (CCPIL) moieties or systems. The preparation involves the synthesis of an epoxy functionalized clay, which is reacted with 1-methyl imidazole and chlorodiphenyl phosphine yielding the required CCPIL. The CCPIL material thus obtained was separated by simple filtration to which later palladium was complexed. This novel catalytic material combines the advantages of homogeneous IL phase, phosphorylated ligands, and a new heterogeneous clay support for Pd catalyzed C-C bond formation in green media. The catalytic material is pictorially represented as **Figure 1**.

The heterogeneous catalyst was successfully exploited for the Suzuki coupling of aryl iodides in aqueous media to give biaryls in high yields. Bromide and chloride substrates too gave the biaryls but required longer reaction times. Recycling was repeated for five runs with little leaching observed where each run required the same reaction times. These catalysts were also used for solvent-free MH reaction. Further, copper-free Sonogashira-Hagihara reaction of aryl iodides, bromides, and chlorides with phenylacetylene was also catalyzed by these Pd on CCPIL. Recycling was also possible with little depletion, and the added advantage is that the catalyst was air and moisture stable [15].

2.4 SILP on magnetic nanoparticles

Creativity is often exploited by scientists; interestingly, iron-containing catalytic materials were developed in order to separate the catalytic material through magnetic separation techniques from the reaction mixture. In this context, few magnetically separable catalytic materials were reported in SILP, which enabled the

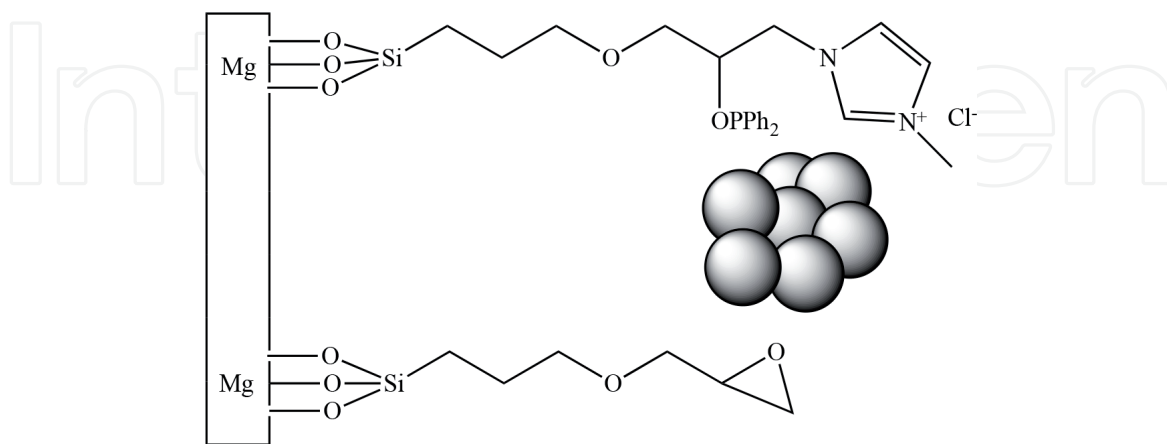


Figure 1.
Clay carrying phosphinite-functionalized ionic liquid [15].

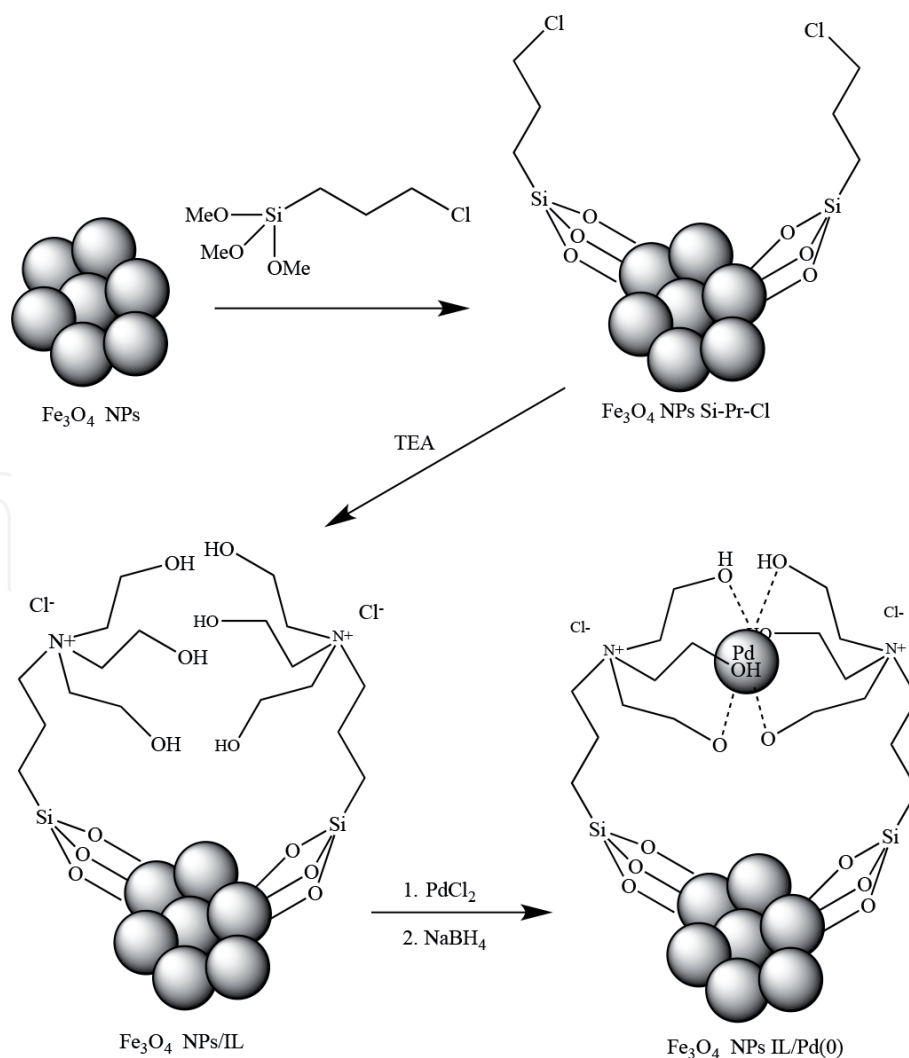


Figure 2.
SILP on magnetic nanoparticles [16].

recovery of the catalytic materials. A hybrid magnetic nanocomposite synthesis was reported with ionic nature, and the methodology was depicted as in **Figure 2**.

2.4.1 Palladium supported on Fe_3O_4

Magnetic Fe_3O_4 was functionalized with 3-chloropropyltriethoxysilane to obtain chloropropyl functionalized magnetic nanoparticles {MNP ($\text{Fe}_3\text{O}_4/\text{Si-Pr-Cl}$)}. The reaction of the MNPs with triethanolamine, triethylammonium chloride made their surfaces ionic in nature. The Fe_3O_4 nanoparticles (NPs) bonded on triethylammonium chloride (IL) was then impregnated with PdCl_2 followed by reduction with NaBH_4 to give reduced Pd NP supported on the magnetic NPs ($\text{Fe}_3\text{O}_4/\text{IL}/\text{Pd}$). Thus, it is a multistep synthetic procedure where palladium containing NPs were immobilized on the functionalized magnetic Fe_3O_4 compound. Catalytic activity was tested for the Suzuki coupling, and high yields were obtained in the reaction between bromobenzene and phenyl boronic acid to yield the corresponding biphenyl derivatives. Reactions were carried out in ethanol water solvent system. The catalyst was separated, dried, and could be reused for eight cycles with no loss of activity [16]; the methodology is depicted in **Figure 3**.

2.4.2 Functionalized magnetic nanoparticles

Gamma (γ) Fe_2O_3 MNPs immobilized with Pd-DABCO (1,4-diazabicyclo[2.2.2]octane) complex were prepared where the nitrogen atoms coordinates with

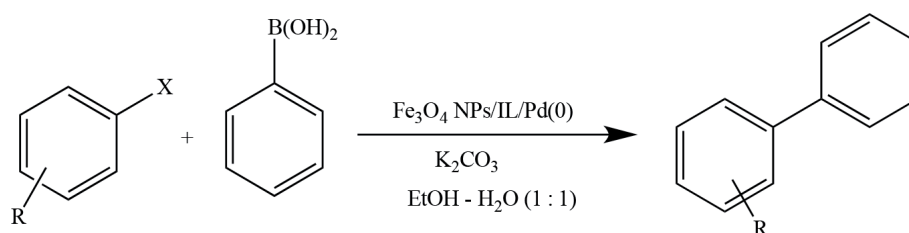


Figure 3.
Pd supported on MNPs—Suzuki coupling [16].

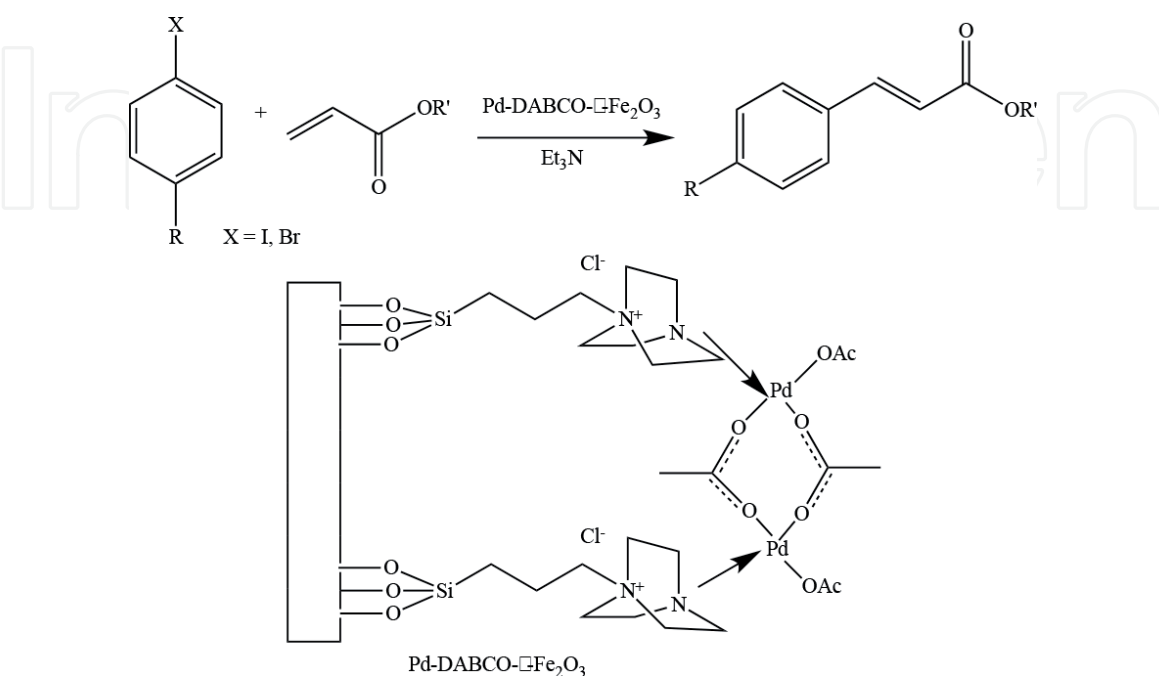


Figure 4.
Pd-DABCO supported on magnetic nanoparticles, Mizoroki-Heck reaction [17].

Palladium, forming complex (**Figure 4**). Chloro-functionalized $\gamma\text{-Fe}_2\text{O}_3$ was prepared by reacting Fe_2O_3 with chloropropyltrimethoxysilane. Treatment with DABCO gave the DABCO- $\gamma\text{-Fe}_2\text{O}_3$. Further reaction with $\text{Pd}(\text{OAc})_2$ gave the desired Pd-DABCO- $\gamma\text{-Fe}_2\text{O}_3$. This catalyst was proven to be a recyclable catalyst for Heck-type coupling reactions.

Heck reactions were carried out with aryl iodobenzene to give high yields of the products in 30 min. Aryl bromide and chlorides also underwent the Heck-type coupling reactions but requiring longer reaction times of 12–24 h. The average isolated yield of 90% was retained for five consecutive runs [17]. An external magnet was used to separate the catalyst from the reaction mixture and reused at least five times without significant degradation in its catalytic activity. The pictorial representation of the catalytic preparation and the reaction is depicted in **Figure 4**.

2.4.3 Palladium supported on amine-functionalized magnetic nanoparticles

The issue of leaching could not be fully resolved in the SILP systems too; as a result, a convenient protocol was developed to recover the palladium catalyst magnetically. Magnetic nanoparticles (NPs) were functionalized to impart stronger bonding to the metal. Towards this end amine functionalized ILs were synthesized. Fe_3O_4 was coated with silica. This was then functionalized with (3-chloropropyl)triethoxysilane. The ionic liquid moiety was then easily anchored onto the surface of the $\text{SiO}_2/\text{Fe}_3\text{O}_4$ to obtain amine-functionalized ionic liquid-modified magnetic NPs (IL- $\text{NH}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$). Excellent results were achieved with this catalyst for the Suzuki coupling of various aryl iodides and bromides (**Figure 5**). The authors claimed that the catalyst was well dispersed in the reaction medium, magnetically recovered from reaction mixture, and reused for several times without significant loss of activity. All these advantages make the protocol to be a green and convenient process for other metal catalyzed important reactions [18].

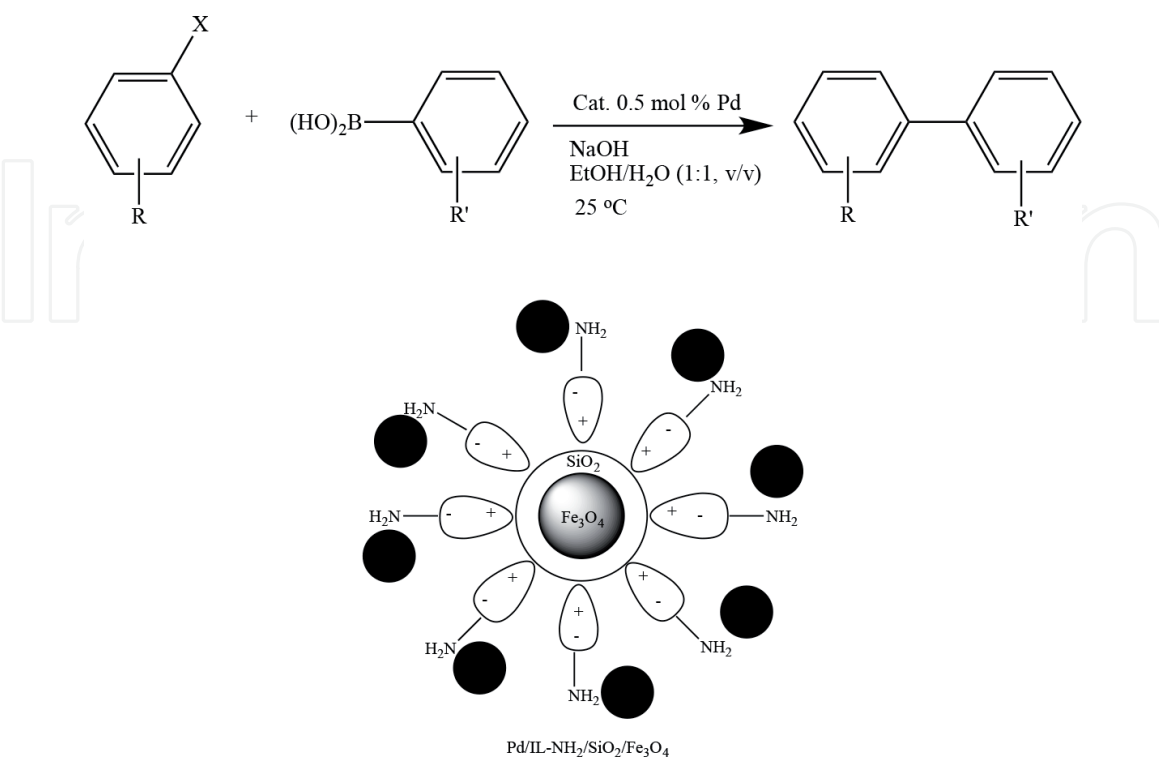


Figure 5.
Pd supported on amine-functionalized magnetic nanoparticles—Suzuki coupling [18].

2.4.4 Phosphinite-functionalized magnetic nanoparticles (MNPs)

In continuation of research on magnetite-supported palladium catalysts, the synthesis and characterization of phosphinite-functionalized magnetic nanoparticles containing imidazolium ionic liquid moiety for stabilization of palladium nanoparticles and its application as a catalyst in Suzuki-Miyaura coupling reactions were examined.

Fe_3O_4 NPs were coated with a thin layer of silica using tetraethyl orthosilicate to provide core shell Fe_3O_4 NP ($\text{SiO}_2@\text{Fe}_3\text{O}_4$ NP). These NPs were then treated with glycidoxypopyltrimethoxysilane to afford epoxy functionalized $\text{SiO}_2@\text{Fe}_3\text{O}_4$. Further reaction with 1-methyl imidazole and chlorodiphenyl phosphine gave the Im-Phos- $\text{SiO}_2-@\text{Fe}_3\text{O}_4$. The catalyst was then prepared by treating with PdCl_2 (**Figure 6**). The catalyst was characterized by various methods. The obtained compound was characterized by SEM, TEM, EDX, solid UV, VSM, XRD, XPS, FT-IR and N_2 adsorption-desorption analyses. Aryl bromides gave high yields in EtOH:water solvent. For aryl chlorides, the solvent was changed to DMF and, at 120°C , it gave high yields. Hot filtration test was carried out and showed that the catalyst was mostly heterogeneous. The catalyst was recyclable for at least eight times with little depletion of activity [19]. The scheme route of the catalyst is presented in **Figure 6**.

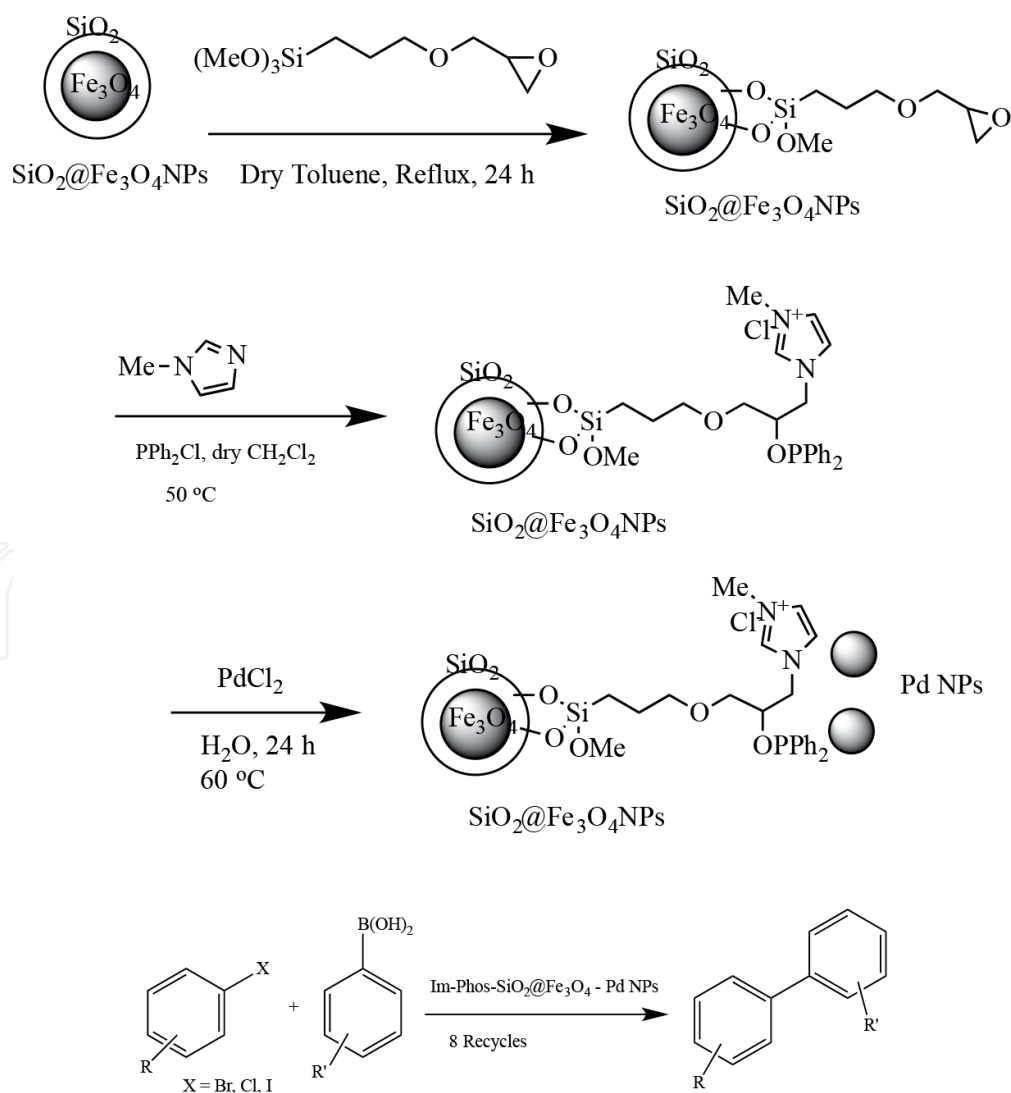


Figure 6.
Phosphinite-functionalized magnetic nanoparticles-Suzuki coupling [19].

2.4.5 Ni supported on magnetic nanoparticles (MNPs)

Ni^{2+} ion containing 1-methyl-3-(trimethoxysilylpropyl)imidazolium chloride IL was impregnated on magnetic Fe_3O_4 NP. Heck reaction was conducted at 100°C (**Figure 7**). IL catalyst separated by magnet can be reused several times after washing without loss of activity. IL immobilized on magnetic particles is an excellent technology for catalytic reactions and separation technologies with substantive progress. The combination of MNPs and ILS gives a magnetic supported IL, which exhibits the dual properties of IL as well as facile separation by magnetic external field [20].

2.5 Polymer-supported HIL

A polymer-supported catalyst was prepared, which exhibited high catalytic activity. Copolymerization of 1-vinyl-3-butylimidazolium with styrene gave polymer supports to immobilize $\text{Pd}(\text{OAc})_2$ using a method of alcohol reduction. The Pd existed as NP of less than 6 nm in these copolymers. This copolymer-supported Pd was efficient and a reusable catalyst for the Heck reaction in aqueous media in the absence of any phase transfer catalysts (PTCs) or ligands (**Figure 8**). The catalyst could be reused for three cycles without depletion of yield [21].

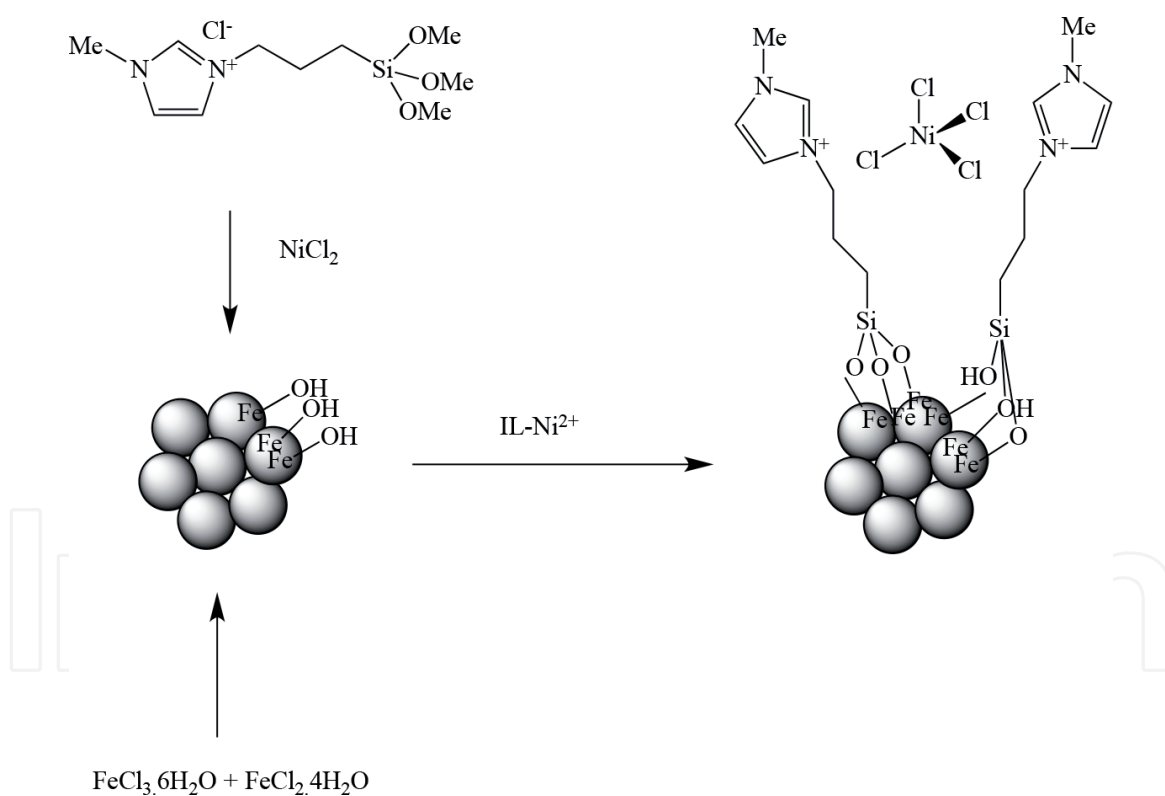


Figure 7.
Ni supported on magnetic nanoparticles [20].

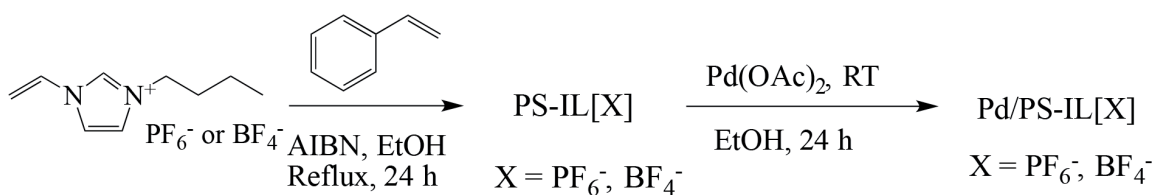


Figure 8.
Polymer-supported HIL [21].

2.6 Heterogenous ionic liquids (HILs) on carbon nanotubes (CNT) and multiwalled carbon nanotubes (MWCNT)

Ionic liquid hybrid materials comprising of either CNT or MWCNT were developed, where the CNT or MWCNT were covalently anchored with the imidazolium-based ILs. The material thus obtained as per this methodology allows specific interactions between the IL thin film and the chemical composition of the MWCNT or CNT surfaces. Typically, the catalytic material was immobilized on the IL thin film. Lee et al. [22] have functionalized MWCNTs with ionic liquid moieties. Interestingly, the change of the ionic liquid anion modulates the solubility of the nanotubes in different solvents. This property makes the modified MWCNTs soluble in ionic liquid and created an IL-based catalytic system when Pd nanoparticles are immobilized on them.

2.6.1 HIL on mesoporous solids

Palladium-containing nanoparticles were immobilized to attain heterogeneity on the mesoporous nanoparticles, namely SBA-15 using an ionic liquid, namely 1.1.3.3-tetramethylguanidinium lactate. Very interestingly, this immobilized Pd catalyst was exploited for solvent-free Heck-type coupling reactions and showed excellent activity and reusability. No deactivation was observed even after six recycles. High yields were achieved even with very low catalyst loading 0.001% of Pd, which is remarkable. Leaching occurs during the reaction, but the Pd gets redeposited on the surface at the end of the reaction with the help of TMG (1,1,3,3-tetramethylguanidine) moiety, excellent stabilizer for metallic NPs [23]. Pd acetate was immobilized on amorphous silica with the aid of an IL, namely [bmim]PF₆. This immobilized catalyst was highly efficient for the Mizoroki-Heck reaction of various aryl halides with cyclohexyl acrylate in dodecane as solvent. A TON of 68,400 and TOF of 8000 h⁻¹ were achieved in the reaction of iodobenzene with cyclohexyl acrylate. The recyclability of the catalyst was lost after three cycles. Leaching studies showed loss of less than 0.24% Pd [9]. This methodology is presented in **Figure 9**.

2.6.2 Encapsulated heterogenous ionic liquids

Pd(OAc)₂ was immobilized on amorphous silica or alumina with the aid of an ionic liquid (Pd-SILC—Pd supported ionic liquid catalyst). The catalytic materials immobilized on N,N-diethylamino propylated (NDEAP) alumina or silica with or without bmimPF₆ gave the best results for the Suzuki-Miyaura coupling of aryl halides with arylboronic to yield the respective biphenyls. The synthesis of the encapsulated heterogeneous ionic liquid and the reaction were represented below (**Figure 10**). It was found out that the immobilization with the aid of an IL, bmimPF₆ was essential for inhibiting leaching of Pd(OAc)₂. The catalyst gave 95%

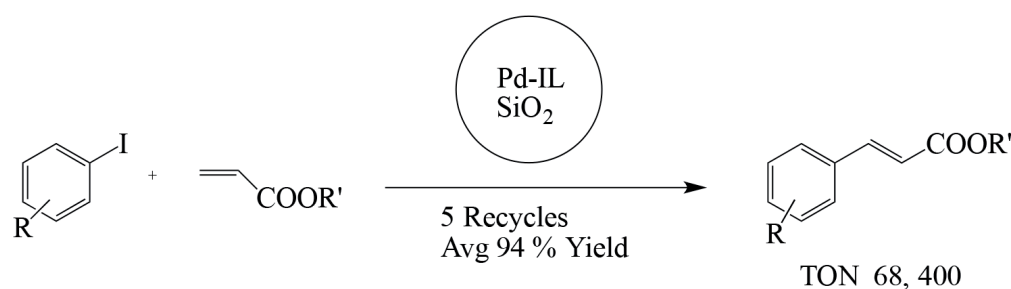
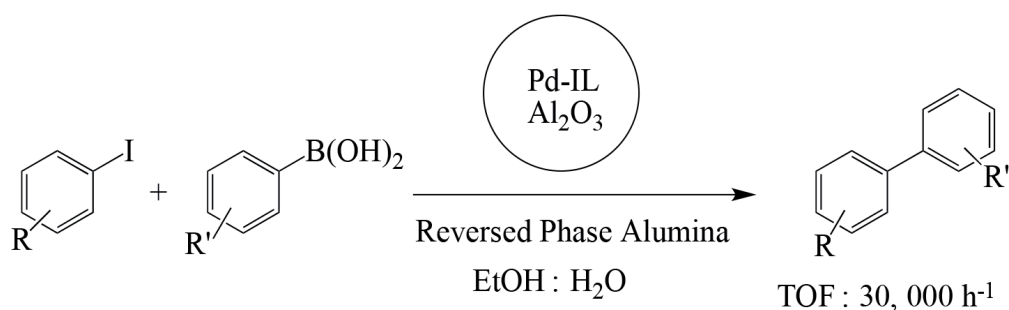


Figure 9.
 HIL on mesoporous solids—Mizoroki-Heck reaction.

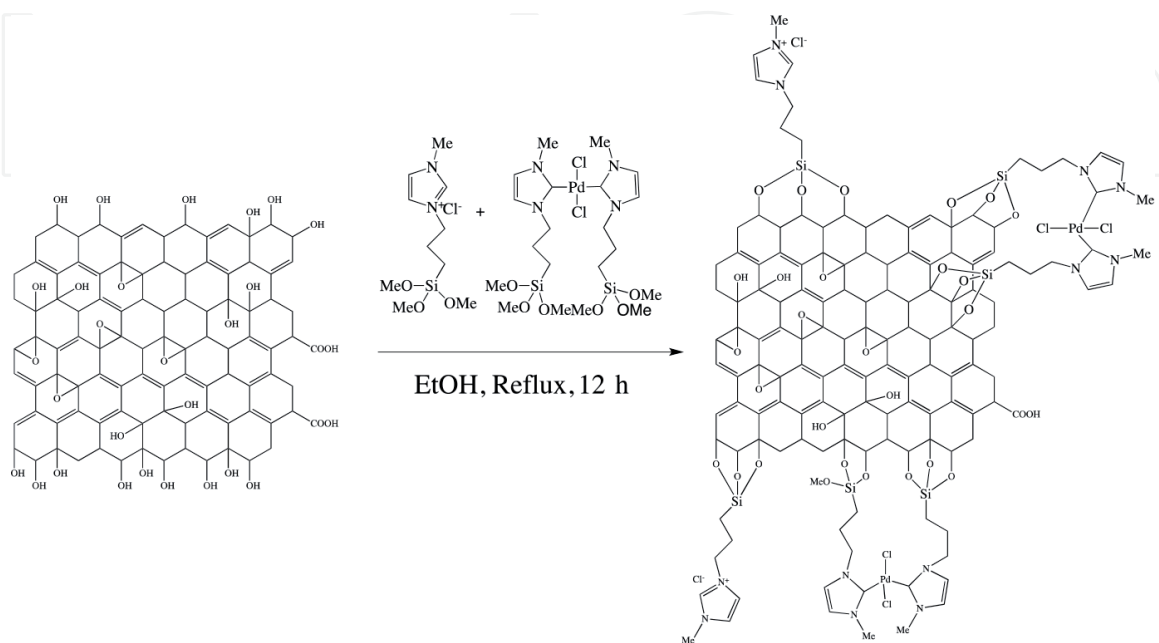
**Figure 10.**

Suzuki-Miyaura reaction catalyzed by immobilized Pd catalyst on reversed phase alumina [24].

average yield in reuse studies up to five times though catalyst activity was gradually lost. High efficiency of the catalyst was exhibited by a TON of 2 million and TOF of 30,000 h⁻¹ in the reaction of 4-bromo acetophenone and phenyl boronic acid [24].

2.6.3 Graphene oxide-based heterogeneous ionic liquid

From the structural point of view, graphene is a single layer of sp² C atoms bonded in a hexagonal lattice. They have extremely large surface area, fast charge mobility, remarkably high mechanical strength, Young's modulus and chemical stability; they are inexpensive and thus are excellent candidate to disperse or immobilize catalytically active species. Silylation modification technique on graphene oxide provides graphene nanocomposites with catalytic activities. To prepare the catalyst, first, a sub-stoichiometric amount of Pd(OAc)₂ was reacted with an excess of 1-methyl-3-(3-(trimethoxysilyl)propyl)-1H-imidazol-3-ium chloride to afford the (NHC) N-heterocyclic carbene Pd IL. This NHC-Pd was grafted on the surface of the graphene oxide (GO) in refluxing ethanol (**Figure 11**). The catalyst was characterized by FT-IR, SEM, TEM, Raman, XPS, TGA, and EDS measurements. The catalyst provided high yields with aryl iodide and bromides but required the addition of tetrabutylammonium bromide (TBABr) for chloride substrates. The

**Figure 11.**

HIL on graphene oxide [25].

catalyst could be recycled five times. The hot filtration test was conducted showing very little loss of Pd [25].

2.7 Silica-supported N-heterocyclic carbene-Pd

N-heterocyclic carbenes (NHCs) have been found to be excellent ligands for several aryl-X activation reactions due to the high dissociation energies of NHC-metal complexes and making them good ligands for heterogeneous systems. Polymers, silica, or NPs have been used as supports. Immobilization of Pd complexed with NHCs is a much wanted technology for the recycling of the catalyst. The immobilization was carried out by the reaction of appropriately functionalized imidazolium chlorides, triethoxysilylpropylimidazolium chloride with silica gel, or variations. The catalyst $\text{Pd}(\text{OAc})_2$ was then anchored on this silica-supported ionic liquid. Other catalysts were supported on polymers like polystyrene, surface-grafted polystyrene resins (**Figure 12**). These could be recycled for over 10 successive runs with very high TONs exceeding 50,000 and TOFs of 5200 (**Figure 13**). Heterogeneous silica NHC-Au (I) gave good results for the Suzuki coupling of aryl iodides [26]. Pd-NHCs were immobilized on the surface of polymer or silica-coated

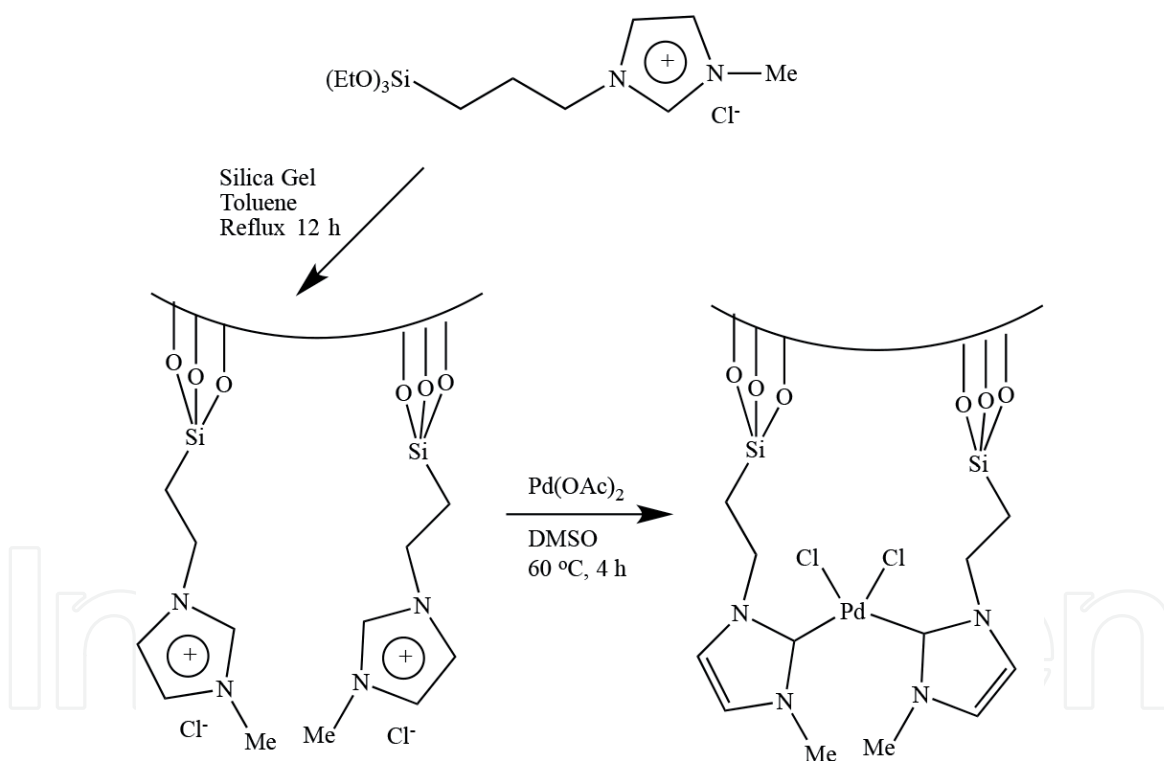


Figure 12.
 Silica-supported NHC Pd complex [27].

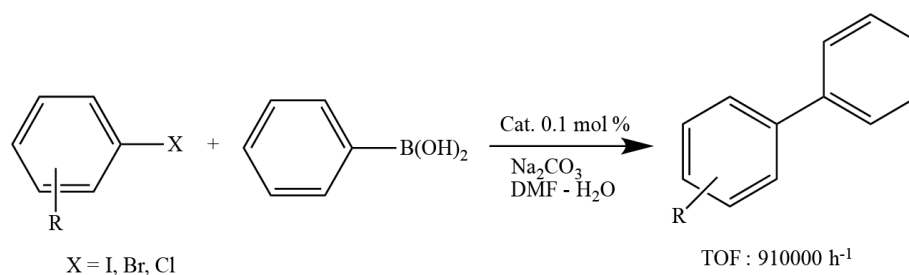


Figure 13.
 Silica-supported N-heterocyclic carbene-Pd-Suzuki coupling [27].

MNPs to generate MNP-Pd-NHC complexes. Catalysts could be easily separated by external magnets [27].

The Suzuki coupling of aryl iodides was catalyzed by this heterogenized ionic liquid transition metal catalysts (HIL-TMCs), and reactions were complete in 0.5 h. Bromides were equally active while substituted aryl chlorides gave lower yields and required longer reaction times mixed with some homocoupling of the aryl boronic acids as byproduct. The catalyst could be reused for six times without significant loss of activity. Atomic absorption spectroscopy (AAS) showed no leaching of Pd [28].

3. Conclusion and recommendations

The bird's eye view on the immobilization technologies in IL matrix shows an amazing picture; using SILP technologies, a rich chemistry of organic functional transformations has been tremendously developed over the recent decades. From the point of view of recyclability and reusability, these novel technologies represent that the metallic species can be as much as possibly retained in the IL matrix. Though the success was achieved in many of the reported research articles, theoretically, academically and technically, many queries need to be addressed, and they are recommended as below:

1. The cohesive force that is operative in retaining the metallic species in IL matrix needs to be understood in detail using the principle of physical organic chemistry.
2. The nature of the catalytic material/s that is undergoing reaction in the IL matrix is not yet understood, and studies need to be carried out in this regard.
3. Not much is known about the role of IL matrix during the reaction, more answer is needed whether the IL is acting in only dissolving the reactants or alters the oxidation states of the catalytic material.
4. The ILs can be broadly classified as hydrophobic (phosphonium ILS—ionic liquid supported) and hydrophilic (nitrogen-based ILs), and hence, we need to identify whether the hydrophilic ILs can deactivate or slower the kinetics in the consecutive runs.
5. The main advantage of IL matrix is that we can carry out the reaction at elevated temperatures depending on the thermal stability of ILs but not much literature reports are known on kinetic measurements at elevated temperatures.
6. More exploration is needed to estimate the nature of side products and impurities in the recycle experiments, if any.

This multidisciplinary research has united many professionals and entrepreneurs to work together; though this chapter has highlighted on the transition metal catalysis, this surface coating of solid materials in thin film and using them in IL matrix does not limit to organic synthesis alone. The summary of the recent research article findings show tremendous advantages of the individual homogeneous and heterogeneous catalytic systems reported in IL matrix. This area of research will soon end up in chemical processes for the manufacture of fine chemicals and so on with the fundamental understanding of various physicochemical properties of SILP systems with improved activity, selectivity and recyclability.

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