Applied Organometallic Chemistry

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MINIREVIEW

Recent Updates on Pd-Incorporated Ionic Liquids Catalyzed Suzuki Cross-Coupling Reaction: A Mini-Review

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Received: 14 July 2024 | **Revised:** 13 September 2024 | **Accepted:** 24 September 2024

Keywords: coupling reaction | carbon–carbon bond | ionic liquids | palladium | Suzuki reaction

ABSTRACT

Ionic liquids (ILs) have been recognized for their potential as environmentally friendly solvents when compared to traditional organic solvents. Additionally, their function goes beyond that of solvents, and cocatalysts, as they frequently act as stabilizing agents and ligands for the metal-active species and intermediates in catalytic systems. This comprehensive review primarily focuses on the application of Pd-incorporated ILs in catalyzing cross-coupling Suzuki reactions. The responses play a vital role in creating a wide range of structurally diverse and highly functionalized organic compounds, focusing specifically on nucleopalladation Suzuki coupling reactions. The review provides a detailed summary of the reaction conditions, stereoselectivity and regioselectivity, and the underlying mechanisms. Furthermore, it underscores crucial and characteristic illustrations, displaying the practical implementations of these coupling reactions. The aim of this review is to stimulate further research efforts, with the ultimate goal of expanding our understanding and utilization of ILs in various fields in the future.

1 | Introduction

Over the past three decades, ionic liquids (ILs) have emerged as a highly intriguing and rapidly advancing domain within the realm of technologies, engineering, and modern physical chemistry. These ILs possess the remarkable ability to be tailored and utilized for a wide range of applications across various fields [1]. They find utility in diverse areas such as sensors [2], fuel cells [3], batteries [4], plasticizers [5], extractants [6], lubricants [7], synthesis, and catalysis [1a, 8]. The modular nature of their physicochemical properties, encompassing characteristics like viscosity, density, hydrophobicity, ionic mobility, and miscibility with molecular solvents, coupled with their advantageous traits of negligible vapor pressure and nonflammability, have prompted chemists to explore the potential of ILs as environmentally friendly media for synthesis, catalysis, and extraction processes. ILs provide additional benefits beyond serving as an eco-friendly alternative reaction medium. ILs stand out from molecular solvents due to their unique ionic properties and specific arrangement. ILs are typically defined as compounds that consist entirely of ions and have a melting point lower than 100°C. Ethylammonium nitrate, the first IL, was identified by Paul Walden in 1914. At that time, he could not have anticipated that ILs would evolve into a significant field of scientific research nearly a century later. With the expansion of their chemical diversity, ILs have been categorized into several distinct types, such as room-temperature ILs (RTILs) [9], task-specific ILs (TSILs) [10], polyionic liquids (PILs) [11], and supported IL membranes (SILMs) [12], which consist of IL composites integrated with metal–organic frameworks (MOFs) [13]. The combination of organic and ionic characteristics in ILs, along with the resulting intermolecular interactions, leads to a diverse array of phenomena, making this field of study both intriguing and demanding. For instance, ILs involving the 1,3-dialkylimidazolium cation display an impressive three-dimensional structural organization because of the rigid and planar ring, along with a complex network of dispersive forces, and hydrogen bonds that cover both polar and nonpolar nanodomains. Various nanoscale structures have been effectively created using the specific structural arrangement, including the production of highly dispersed transition metal nanoparticles (NPs), which can be considered as soluble forms of heterogeneous catalysts. Hence, the involvement of ILs in homogeneous catalysis primarily revolves around improving catalytic performances such as activity and selectivity, as well as enabling recycling and/or catalyst separation. Environmental considerations, on the other hand, are now only seen as a matter of historical significance. ILs have the ability to act as gentle solvents, although they are more commonly utilized as cocatalysts, ligands, and stabilizing agents for the active species and intermediates present in the catalytic process. Figure 1 illustrates a significant surge in the investigation of utilizing ILs as catalysts in organic reactions from 2000 to September 4, 2024.

The domain of catalysis that shows the most potential for ILs as an alternative to conventional solvents is the formation of C–C bonds through transition–metal catalysis. In the last four decades, this area of organometallic chemistry has emerged as a potent tool for organic synthesis, greatly augmenting the capacity of synthetic organic chemists to construct intricate molecular structures and revolutionizing our perception of synthesis [14]. The C–C cross-coupling reactions catalyzed by Pd have gained significant attention due to their theoretical, mechanistic, historical, and practical significance. These processes have been extensively discussed and studied. Palladium exhibits a remarkable ability to insert into various carbon–LG bonds, where LG represents a leaving group such as triflate, halogen, or diazonium. Additionally, palladium demonstrates a propensity for transmetallation with commonly used organometallic reagents and displays tolerance towards a wide range of functional groups. These unique properties make palladium the only metal capable of facilitating such a diverse array of reactions. Palladium possesses a remarkable capability to form novel C–C bonds using a diverse range of unsaturated starting materials such as aryls, vinyls, heteroaryls, and acetylides. This unique ability allows for the creation of a vast array of organic compounds with various molecular architectures and intricate skeletons. These compounds are often challenging to construct using alternative synthetic methods. The introduction of this newfound capacity to shape carbon–carbon bonds has opened up exciting prospects, particularly in the realm of total synthesis. It has also expanded the scope of industrial applications, encompassing fields such as medicinal chemistry, agriculture, polymer sciences, and material chemical biology, nano-technology, and opto-electronics.

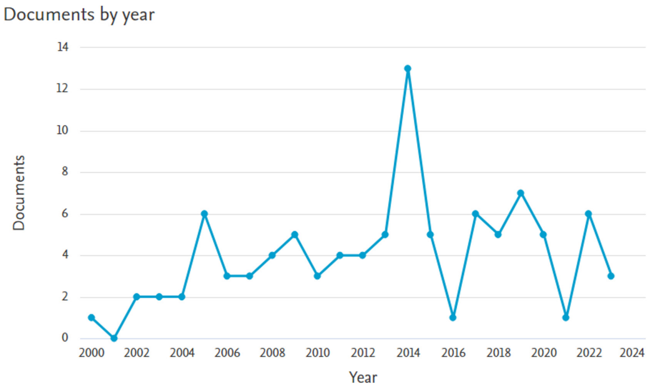


FIGURE 1 | The number of documents regarding the application of ILs as catalysts/solvents in Suzuki–Miyaura coupling reaction between 2000 to 4-September (Scopus search engine) (The curve exported from keywords "Ionic Liquid" and "Suzuki reaction" in the article title).

The formation of the biphenyl structure using the Suzuki–Miyaura reaction with aryl halides and organoboronic acid is commonly acknowledged as the most efficient technique. The biaryl scaffold has garnered increasing attention in recent years, being recognized as a privileged structure by the pharmaceutical industries and agrochemicals [15]. This structural motif is found in various advanced materials, natural products, sensors, polymers, and ligands for asymmetric catalysis. Therefore, it is crucial to prioritize the advancement of novel and effective synthetic techniques for these compounds within the realm of organic chemistry. Historically, Suzuki cross-coupling reactions have been catalyzed by soluble phosphine palladium complexes in organic solvents, utilizing iodo and bromoarenes as the typical reagents. Nevertheless, this procedure encounters difficulties when it comes to the reuse and recovery of costly homogeneous catalysts. To address these limitations, extensive research has been dedicated to the development of palladium-recyclable catalytic systems in ILs. Numerous studies have been published in the literature, with over a hundred papers focusing on the Suzuki coupling in IL media. Moreover, some review papers on the application of ILs in carbon–carbon coupling reactions have recently been published including (i) a micro-review by Jiang and coworkers [16], (ii) a review by Sing and coworkers [17], (iii) a comprehensive review by Varma and coworkers [18], and (iv) role of ILs as solvent and catalysts for Heck and Suzuki reaction by Tomar and coworkers [19]. The pointed reviews have focused on the application of ILs as cocatalyst and medium in the presence of Pd elements for reviewing carbon–carbon Suzuki–Miyaura cross-coupling reaction. This approach aims to enhance the sustainability and cost-effectiveness of the Suzuki cross-coupling reactions by utilizing ILs as reaction media and facilitating the recovery and reuse of the catalysts.

The characterization of catalysts plays a crucial role in their development [20]. Understanding the structure, composition, and chemical characteristics of the solids employed in heterogeneous catalysis, as well as the adsorbates and intermediates on the catalyst surfaces during reactions, is essential for gaining insights into the correlation between catalyst properties and their catalytic effectiveness. Understanding this information is crucial for the advancement of more efficient, targeted, and long-lasting catalysts, as well as for the enhancement of reaction conditions. Electron microscopy techniques, including transmission electron microscopy (TEM) and scanning electron microscopy (SEM), have been employed to characterize heterogeneous catalysts, focusing on their shape, size, and morphology. Additionally, X-ray diffraction (XRD) has been utilized to analyze the elemental composition, while gas adsorption methods have been applied to assess the surface area of the materials. Nevertheless, defining the functional groups attached to the supports can be quite difficult, primarily because there is insufficient information regarding the accessibility and chemical reactivity of the materials involved. Fourier transform infrared spectroscopy (FT-IR) appears to be the most effective method for characterizing functionalized catalysts. Other characterization techniques including thermal analysis such as TGA and DSC could assist in the identification of heterogeneous catalysis.

In this review article, we have undertaken a comprehensive examination of the Suzuki cross-coupling reaction, focusing specifically on its catalysis by palladium-incorporated ILs. Figure 2 depicts a number of important compounds that have been created through the Suzuki–Miyaura cross-coupling reaction for pharmaceutical applications.

1.1 | Suzuki Cross-Coupling Reaction Catalyzed by Pd-Incorporated ILs

An effective heterogeneous nanocatalyst was developed through the immobilization of a palladium complex onto the surface of imidazolium-based IL-functionalized Fe_3O_4 nanoparticles (Pd-imidazolium@Fe_3O_4 NPs) (Catalyst 1), as reported by Nouri and colleagues in 2023 (Scheme 1) [21]. The characterization of this nanocatalyst, referred to as catalyst 1, was conducted using various techniques including Raman spectroscopy, XRD), TGA, TEM, SEM, EDX, FT-IR, ICP, and VSM. The catalytic efficiency of catalyst 1 was tested in the Suzuki–Miyaura cross-coupling reaction under mild conditions, utilizing PEG-400 as an environmentally friendly and biodegradable solvent. Catalyst 1 demonstrated significant catalytic activity in this reaction. Additionally, this robust nanocatalyst can be conveniently separated and recovered from the reaction mixture, allowing for reuse in at least eight consecutive cycles without any noticeable loss in catalytic performance. The recovered catalyst 1 was further characterized using FT-IR, XRD, SEM, EDX, and atomic absorption spectroscopy.

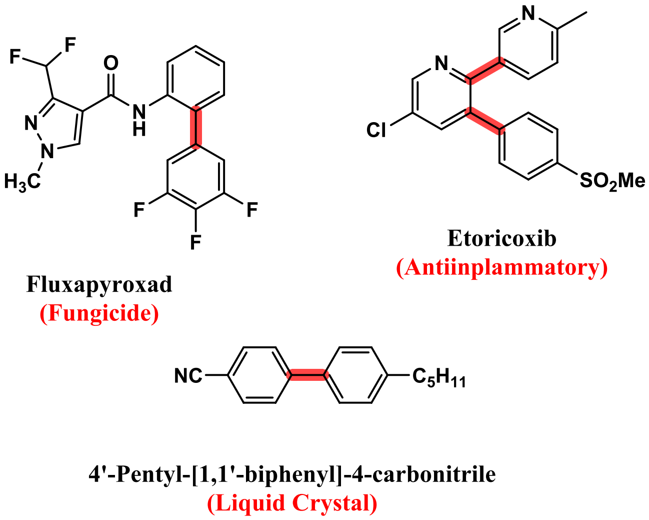
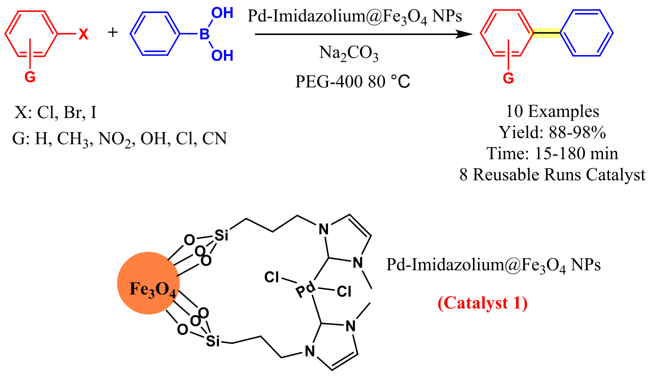


FIGURE 2 | Some of the important compounds synthesized via the Suzuki–Miyura cross-coupling reaction.

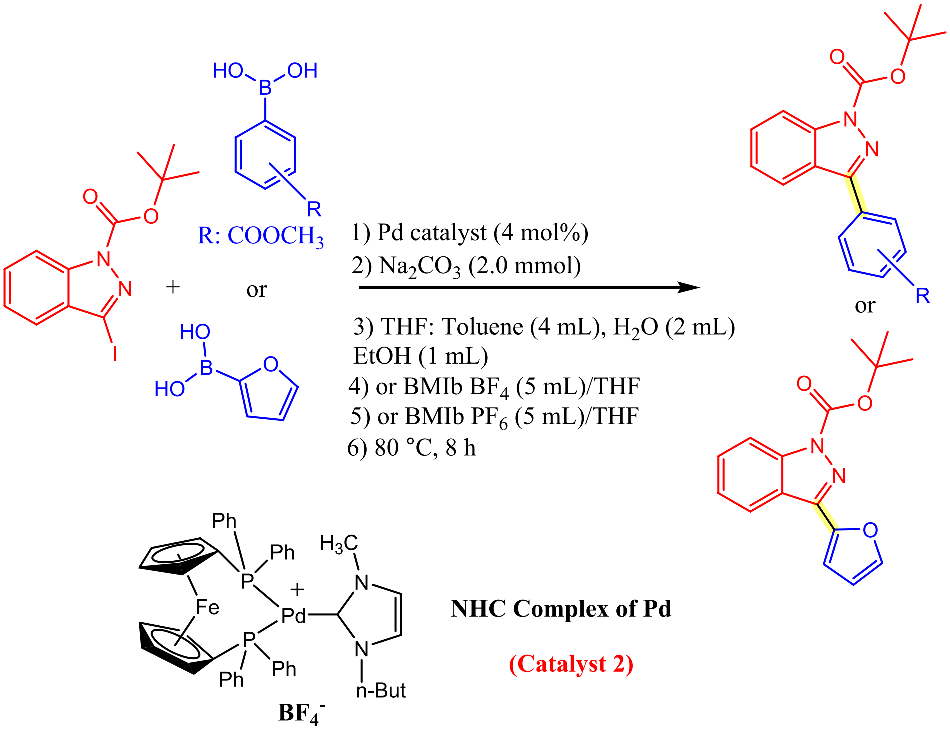


SCHEME 1 | The cross-coupling Suzuki–Miyaura reaction catalyzed by Pd-imidazolium@Fe_3O_4 NPs.

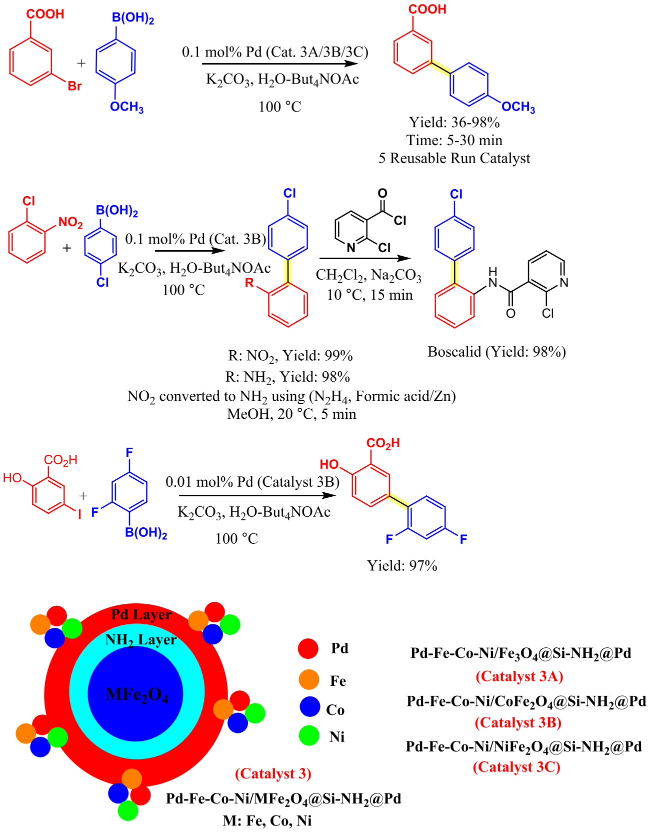
The C-3 functionalization of 1H-indazole has the potential to yield numerous valuable pharmaceutical intermediates, which can be utilized in the treatment of cancer and various inflammatory conditions. In 2023, Yu and colleagues concentrated on the C-3 functionalization of 1H-indazole via Suzuki–Miyaura cross-coupling, employing 3-iodo-1H-indazole and PhB $(OH)_2$, with various palladium catalysts supported on imidazolium ILs while exploring catalyst recycling (Scheme 2) [22]. A comprehensive examination of several reaction parameters, including substrate, catalyst, and IL, was conducted. It is noteworthy that the yields from the Suzuki–Miyaura cross-coupling were primarily influenced by the choice of catalyst and solvent rather than the substrate's chemical structure. Additionally, ferrocene-based divalent palladium complexes demonstrated superior catalytic performance compared to conventional palladium salts. The use of two imidazolium ILs, BMImX (where $BMIm^+$ represents 1-n-butyl-3-methylimidazolium and X^- denotes BF_4^- or PF_6^-), not only enhanced the yields of the cross-coupled products but also mitigated the formation of Pd (0) black, in contrast to reactions without ILs, thereby facilitating more efficient catalyst recycling. On average, they found that $BMImBF_4$ outperformed $BMImPF_6$. Interestingly, computational studies indicated that the 1,10-bis (diphenylphosphino)ferrocene-palladium (II)dichloride dichloromethane complex ($PdCl_2$(dppf)) exhibited a lower energy barrier for intermediate formation compared to [1,10-bis (di-tert-butylphosphino)ferrocene]dichloropalladium (II) ($PdCl_2$(dtbpf)), resulting in enhanced catalytic efficiency. This research may pave the way for the development of novel pharmaceuticals derived from 1H-indazole.

In 2023, Bumagin synthesized hybrid materials based on magnetic ferrites of Fe (magnetite), Co, and Ni, which were modified with 3-aminopropyltriethoxysilane (APTES). These materials, designated as Pd–Fe–Co–Ni/MFe_2O_4@Si–NH_2@Pd (Catalyst 3) (where M represents Fe, Co, or Ni), feature a protective palladium coating (Scheme 3) [23]. The resulting Pd-polymetallic composites demonstrate significant catalytic activity in the Suzuki reaction when conducted in an aqueous IL solution, attributed to their synergistic effects. Furthermore, these catalysts can be easily separated from the reaction mixture through magnetic decantation and are capable of being reused multiple times without a decline in catalytic performance.

In 2022, Shaikh et al. developed a catalytic system consisting of mixed metallic Ag–Pd NPs supported on sugarcane bagasse ash silica (Scheme 4) [24]. This was achieved through the immobilization of 1-[3-(dimethylamino)



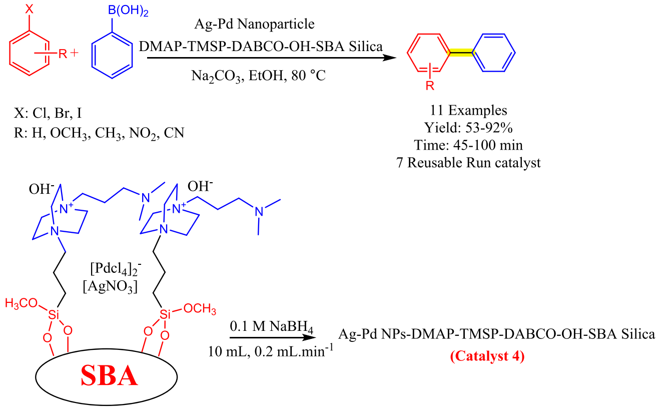
SCHEME 2 | Suzuki cross-coupling reaction catalyzed by NHC Pd complex.



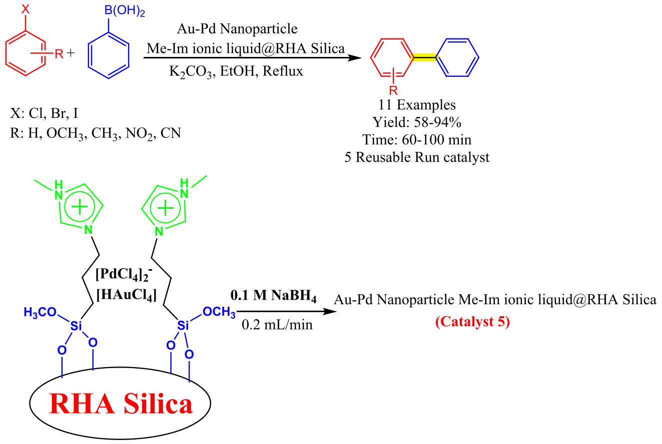
SCHEME 3 | Different reaction conditions for Suzuki–Miyaura coupling reaction using catalyst 3.

propyl]-3-(3-trimethoxysilylpropyl)-1,4-diazabicyclo [2.2.2] octan-1-ium hydroxide]ionic liquid. The catalytic system of Catalyst 4 was synthesized by employing $NaBH_4$ as a reducing agent with precise control over the feed rate. The resulting catalytic system was found to be highly effective in ligand-free Suzuki coupling reactions in an EtOH solvent system at 80°C. Characterization of the synthesized catalytic system was performed using TGA-DSC, FT-IR, XRD, and SEM-EDS analysis. The catalytic activity of the mixed metallic Ag–Pd NP system surpassed that of the monometallic NPs. Additionally, the hybrid system of IL and mixed metallic NPs immobilized on natural waste rice husk ash silica demonstrated high efficiency, enhanced stability, and improved physicochemical properties through intermolecular interactions. Additionally, the catalytic system demonstrated superb reusability for a maximum of seven cycles with no decrease in catalytic performance.

In 2022, Shaikh and colleagues effectively created a catalytic system comprising a combination of gold–palladium nanoparticles immobilized on silica derived from rice husk ash (Scheme 5) [25]. This was achieved by supporting imidazolium chloride ILs. Catalyst 5 was prepared using a controlled feed rate and $NaBH_4$ as the reducing agent. This catalytic system proved to be highly effective for ligand-free Suzuki coupling reactions in EtOH at 80°C. To characterize the synthesized catalytic system, various analytical techniques such as XRD, NMR, FT-IR, TGA-DSC, and SEM-EDS analysis were employed. The results confirmed the presence of mixed metallic Au–Pd NPs and demonstrated that this catalytic system exhibited superior activity compared to monometallic NPs. Furthermore, the hybrid system of ILs and mixed metallic NPs supported on rice husk ash silica showed high efficiency, enhanced stability, and improved physicochemical properties through intermolecular interactions. As a result, this system allowed for easy recyclability for up to seven cycles without any decrease in catalytic efficiency.

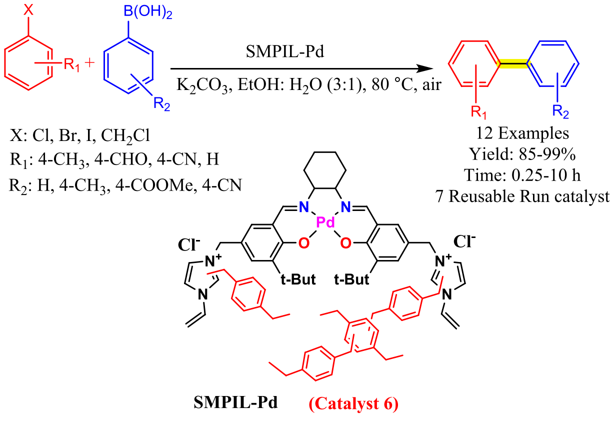


SCHEME 4 | Suzuki coupling reaction using Ag–Pd NP–(DMAP–DABCO)OH–SBAsilica (Catalyst 4)



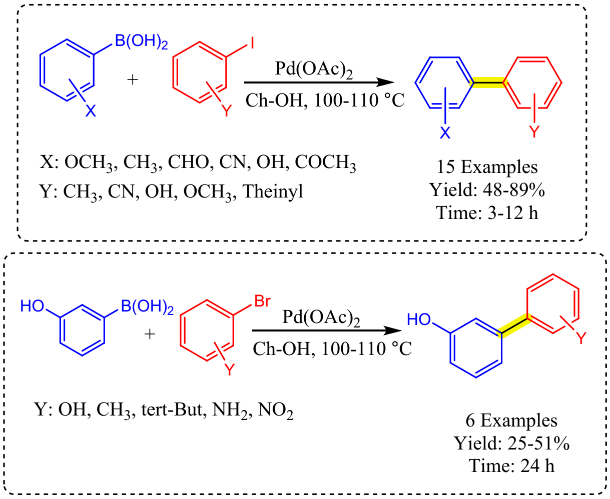
SCHEME 5 | Suzuki cross-coupling reaction catalyzed by Au–PdNP–Me–IM IL (Catalyst 5).

Extensive focus has been dedicated to Pd-catalyzed Suzuki–Miyaura cross-coupling reactions. To address the limitations of homogeneous reactions, researchers have turned to porous organic polymers (POPs) as potential heterogeneous catalysts. Nevertheless, the majority of POPs are microporous, leading to a hindrance in the mass transfer process during catalytic reactions. In 2022, Tian and colleagues recently presented a new study where they unveiled a mesoporous poly (ionic liquid) (SMPIL–Pd) with a highly cross-linked structure, incorporating Pd as a heterogeneous catalyst to facilitate Suzuki–Miyaura coupling reactions (Scheme 6) [26]. The catalyst was formed by extensively crosslinking a mesoporous poly (ionic liquid) containing salen through a basic Friedel–Crafts alkylation process, then coordinating Pd (II) with the tetradentate salen structure. Characterization studies revealed that Catalyst 6 possesses rigid networks, mesoporous structures, significant porosity, large specific surface areas, and well-dispersed catalytic active sites. The catalyst exhibited outstanding catalytic performance in Suzuki–Miyaura coupling reactions under ambient conditions using 50% aqueous ethanol. Furthermore, Catalyst 6 exhibited recyclability, and remarkable stability maintaining its activity for up to seven cycles without significant loss. Notably, considering the diverse nature of green catalysis, the turnover number (TON) and turnover frequency (TOF, h^{-1}) for Catalyst 6 were recorded at values ranging from 1063 to 1233 and 119 to 2475, respectively.



SCHEME 6 | SMPIL–Pd (Catalyst 6) catalyzed Suzuki cross-coupling reaction.

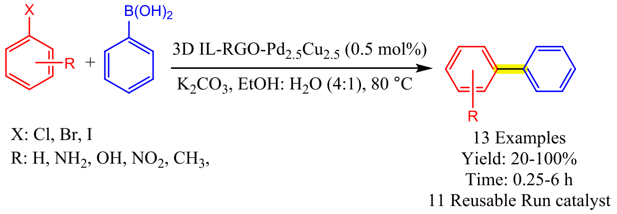
In 2020, Joo and his team introduced an innovative approach to creating carbon–carbon bonds by utilizing arylboronic acids and aryl halides in their recent study (Scheme 7) [27]. The reaction conditions are versatile, and mild allowing for the formation of unsymmetrical and/or symmetrical biaryl products in satisfactory yields. The key components of this system are the readily available choline hydroxide (ChOH), biodegradable room-temperature ILs, and a ligand-free Pd (OAc)$_2$ catalyst.



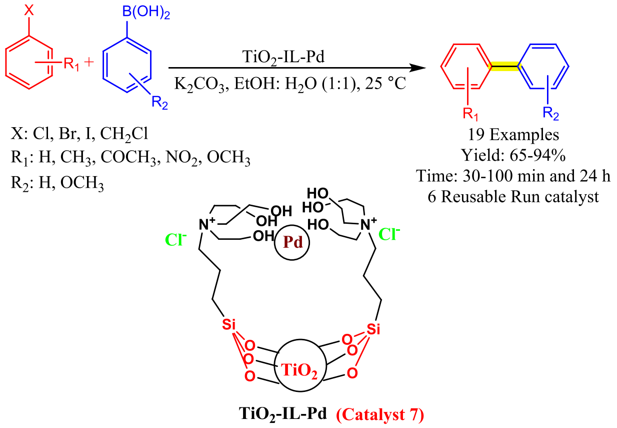
SCHEME 7 | Suzuki coupling reaction catalyzed by palladium acetate under ligand and base-free conditions.

Surprisingly, the cross-coupling reactions can be completed without the requirement of any external base or ligand. Furthermore, the reaction solvent demonstrates excellent reusability, a key factor in promoting sustainable practices in chemistry. Nevertheless, a recently created Pd–catalyst system, Pd $(OAc)_2$/ChOH, has proven to be efficient in facilitating the Suzuki–Miyaura cross-coupling reaction. This coupling reaction was notably conducted in an aerobic environment without requiring ligands or bases. The Pd $(OAc)_2$/ChOH system is readily retrievable through straightforward handling, and tests for reusability have demonstrated its favorable recyclability. This innovative approach offers an efficient and versatile protocol for coupling reactions between boronic acids and suitable substrates. Furthermore, the utility of this catalytic system is being expanded to encompass other coupling reactions and functional group transformations of organic compounds in laboratory settings.

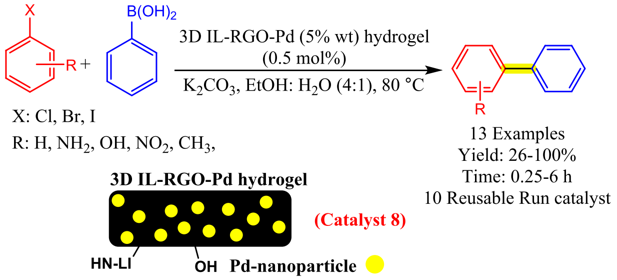
In 2019, a team led by Ru successfully synthesized bimetallic alloy NPs consisting of Pd and Cu, which were evenly distributed on NH_2-terminated IL functional 3D graphene (3D IL-rGO/Pd-Cu) (Scheme 8) [28]. This catalyst proved to be highly efficient for Suzuki cross-coupling reactions and was prepared using a simple synthetic method. The addition of IL–NH_2 cations to the graphene sheets' surface successfully inhibited the re-deposition of graphene, enabling the catalyst to be utilized for multiple cycles, up to 10 times. The addition of Cu not only reduced costs but also ensured a high catalytic efficiency. Notably, the catalyst 3D IL-rGO/$Pd_{2.5}Cu_{2.5}$ exhibited an impressive yield of 100% in just 0.25 h for the Suzuki cross-coupling reaction, which was nearly double the yield achieved by the pristine IL-rGO/$Pd_{2.5}$ catalyst (52%). The presence and distribution of Pd and Cu in the bimetallic NPs were confirmed through XRD and EDS mapping. TEM revealed that the NPs had an average diameter of 3.0 ± 0.5 nm. XPS analysis demonstrated the electron transfer from Cu to Pd upon alloying. This alloying-induced electronic modification, along with the large specific surface area of the 3D ILs functional graphene, contributed to the enhanced catalytic performance.



SCHEME 8 | The 3D IL–rGO/Pd–Cu-catalyzed Suzuki cross-coupling reaction.



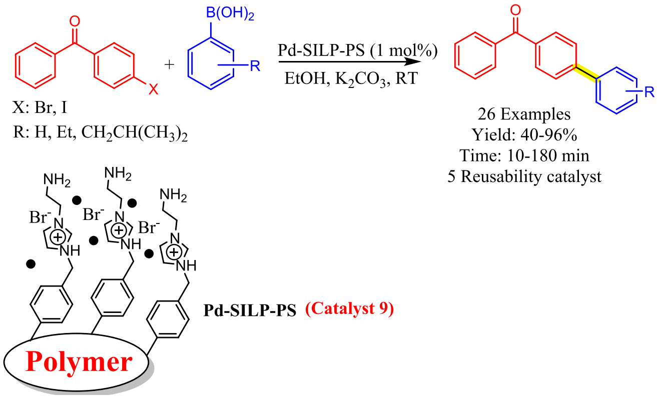
SCHEME 9 | Suzuki cross-coupling reaction catalyzed by TiO_2-IL-Pd (Catalyst 7).



SCHEME 10 | Suzuki cross-coupling reaction catalyzed by 3D IL–rGO/Pd (Catalyst 8).

In 2019, Veisi et al. successfully implemented a readily available procedure to prepare innovative palladium NPs decorated on triethanolammonium chloride IL–functionalized TiO_2 NPs [TiO_2/IL–Pd] (Scheme 9) [29]. The synthesized nanocatalyst underwent various characterization methods including HR-TEM, XRD, XPS, EDX, FE-SEM, FT-IR, and ICP. Catalyst 7 demonstrated outstanding catalytic performance in facilitating the Suzuki–Miyaura cross-coupling reaction between various aryl halides and arylboronic acid in water at ambient temperature. The ICP analysis of the recycled catalyst after six cycles showed a slight decrease in the amount of Pd leaching, confirming the nanocatalyst's sustainability for C–C Suzuki–Miyaura coupling reactions. The catalyst is capable of being separated through filtration with ease and can be reused for up to six cycles without any notable decrease in activity, offering an eco-friendlier option compared to current methods for the Suzuki–Miyaura reaction.

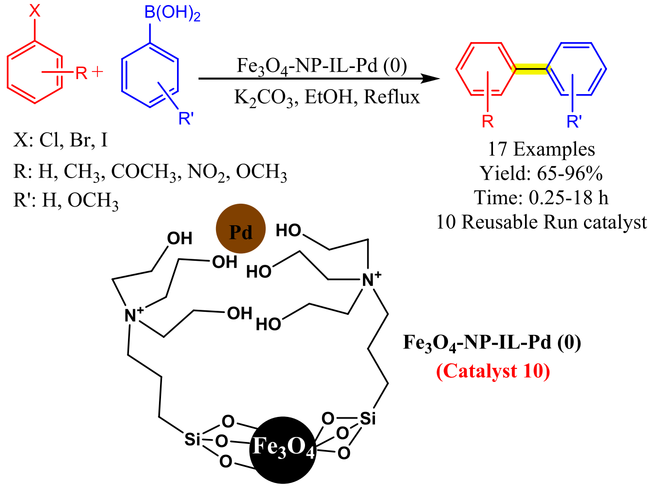
In 2018, Huang and colleagues successfully developed a novel method to fabricate (3D) NH_2-terminated ILs covalently functionalized Pd/graphene composite aerogels (Scheme 10) [30].



SCHEME 11 | Suzuki cross-coupling reaction catalyzed by Pd@SILP-PS (Catalyst 9).

This method involves a green reduction-inducing self-assembly process. The morphology and composition of Catalyst 8 were thoroughly analyzed using different analyses such as SEM, TEM, FTIR, XRD, BET, XPS, and Raman spectroscopy. The introduction of NH_2–IL cations onto the surface of graphene sheets in these composites prevents restacking and increases the specific surface area. This, in turn, facilitates efficient transport pathways and enhances the catalytic performance. The positively charged imidazolium ring moiety of NH_2–IL effectively binds to the negatively charged Pd precursors ($PdCl_4^{2-}$), leading to the creation of evenly dispersed Pd NPs with diminutive particle sizes on the graphene sheets. This maximizes the active surface area of the catalysts and improves their catalytic activity. The catalytic experiments show that Catalyst 8 displays outstanding efficiency as a catalyst for Suzuki cross-coupling reactions in gentle environments. These composite aerogels are not only efficient but also easily separable, recyclable, and stable. Even after 10 repeated cycles, there is no significant loss in catalytic efficiency. Catalyst 8 demonstrated superior catalytic efficiency, achieving a TOF (h^{-1}) of 800 when compared to findings in other published studies.

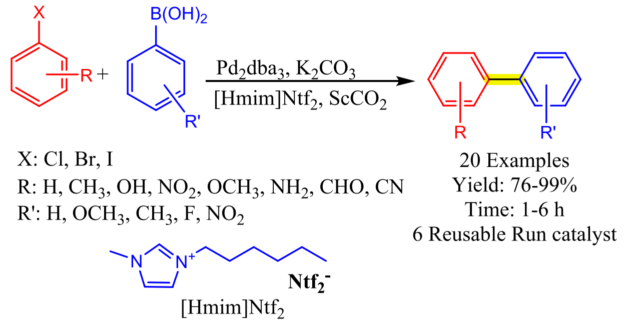
In 2017, a new Pd–SILP (Pd@SILP–PS) (Catalyst 9) has been synthesized by More et al., which is based on amino-functionalized imidazolium ILs immobilized on Merrifield resin (Scheme 11) [31]. The characterization of the catalyst was conducted using different analyses such as TEM, SEM-EDS, FT-IR, XPS, and TGA-DTA. The catalyst displayed significant activity during the Suzuki–Miyaura cross-coupling reaction between various aryl boronic acids and aryl halides in EtOH at ambient temperature. The solvent type and the substituents on the aryl halides significantly influenced the catalyst's activity and the nature of the product. When ethanol, a protic polar solvent, was used, the desired cross-coupling product was obtained in good to excellent yields at room temperature. Conversely, THF (aprotic polar solvent) led to the formation of a homocoupling product. Remarkably, the catalyst demonstrated recyclability for at least five cycles without any decrease in product yield.



SCHEME 12 | Suzuki cross-coupling reaction catalyzed by Fe_3O_4/IL/Pd (Catalyst 10).

In 2017, Veisi et al. conducted a study where they successfully synthesized novel Pd NPs immobilized on triethanolamine-functionalized magnetic NPs [Fe_3O_4/IL/Pd] (catalyst 10) (Scheme 12) [32]. To understand the characteristics of these NPs, various characterizations such as FT-IR, XRD, HR-TEM, TGA, EDX, FE-SEM, ICP, XPS, and VSM were performed. The findings indicated that catalyst 10 demonstrated significant catalytic efficiency in facilitating Suzuki–Miyaura cross-coupling reactions in water at ambient temperature. Catalyst 10 was discovered to function as a zwitterionic IL-type heterogeneous catalyst, allowing for simple separation from the reaction mixture. Additionally, it demonstrated excellent recyclability, maintaining its activity for at least eight cycles without significant loss.

In 2016, Wang and his colleagues have effectively created a catalytic system that is highly efficient for $Pd_2(dba)_3$-catalyzed ligand-free Suzuki cross-coupling reactions in a green medium of [Hmim]NTf_2/supercritical CO_2 biphasic system (Scheme 13) [33]. A broad variety of aryl halides can be cross-coupled with different arylboronic acids using this system, all under gentle conditions. The use of the environmentally friendly [Hmim] NTf_2/supercritical CO_2 biphasic system, with K_2CO_3 as a base, enables the synthesis of the desired products in good to high yields. One of the notable advantages of this catalytic system is its recyclability without any significant loss of catalytic activity. The researchers also provide a possible mechanism for the Suzuki cross-coupling reaction in their paper. Overall, this new catalytic system, comprising [Hmim]NTf_2 and $Pd_2(dba)_3$ under supercritical carbon dioxide conditions, offers a straightforward

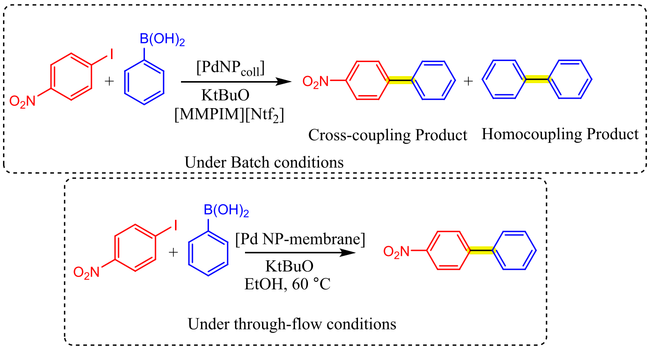


SCHEME 13 | Suzuki cross-coupling reaction catalyzed by $Pd_2(dba)_3$ under supercritical carbon dioxide conditions.

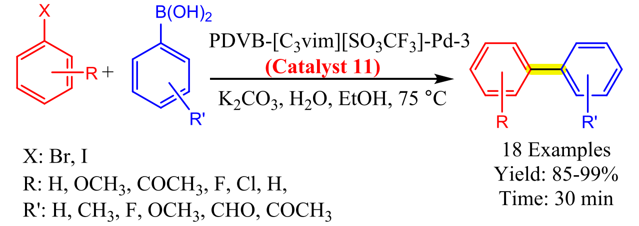
and efficient approach for the Suzuki–Miyaura coupling reaction between aryl boronic acids and different aryl halides. The methodology boasts attractive features such as high yields, simplicity of operation, excellent recyclability, and easy product isolation. Currently, their laboratory is further investigating the scope, mechanism, and synthetic applications of this reaction.

In 2015, a polymeric catalytic membrane containing palladium NPs was developed using a photo-grafting process with imidazolium-based IL monomers as modifying agents and microPESs as the support membrane (Scheme 14) [34]. The ILs functioned as a stabilizer and immobilizer for the Pd nanoparticles, enabling the Suzuki–Miyaura cross-coupling reaction to take place on the catalytic membrane in a flow-through setup. Remarkably, complete conversion was obtained in just 10 s with a single filtration, without any byproduct formation. The reaction rate constant on the catalytic membrane was three orders of magnitude higher than in a batch reactor, and no leaching of the catalyst was detected. The catalytic membrane provides the benefit of uninterrupted production, eliminating the requirement for a distinct catalyst separation process. The catalytic membrane greatly enhanced the Suzuki–Miyaura cross-coupling reaction in comparison to colloidal Pd NPs in batch conditions, showing potential as a catalyst for a wide range of applications.

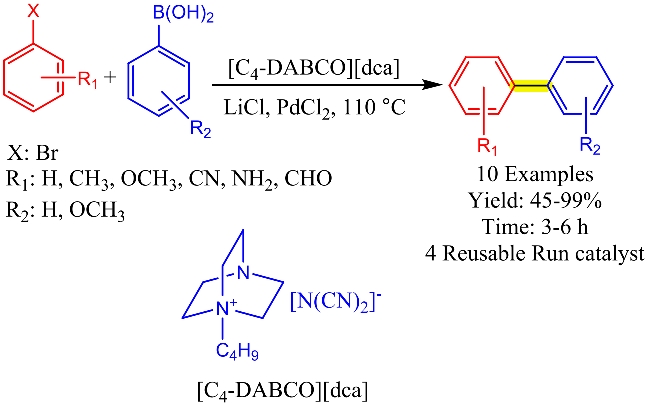
In 2014, Liu et al. successfully synthesized superoleophilic, nanoporous polymeric ILs supported Pd $(OAc)_2$ (PDVB–[C_3vim][SO_3CF_3]–Pd–xs) (Catalyst 11) as robust heterogeneous catalysts in the Suzuki–Miyaura cross-coupling reaction (Scheme 15) [35]. The PDVB–[C3vim][SO_3CF_3] support was prepared via solvothermal copolymerization of vinylimidazole and divinylbenzene without the need for templates, followed by functionalization with IL groups. Catalyst 11 exhibited good stability, homogeneous dispersion of Pd active species, large BET surface areas, and super wettability toward different aromatic reactants. These characteristics led to significantly improved reactant enrichment properties. Compared to Pd $(OAc)_2$ immobilized onto activated carbon and ordered mesoporous silica of SBA-15, Catalyst 11 demonstrated enhanced catalytic activity and recyclability in the Suzuki–Miyaura reaction. The interesting activity of Catalyst 11 can be related to the synergistic effects between its large surface areas and unique enrichment properties for different aromatic reactants, which enhance the exposure of Pd active sites to the reactants.



SCHEME 14 | The Suzuki cross-coupling reaction catalyzed by Pd NPs/membrane under batch and flow conditions.



SCHEME 15 | Suzuki cross-coupling reaction catalyzed by PDVB–[C_3vim][SO_3CF_3]–Pd–xs (Catalyst 11).

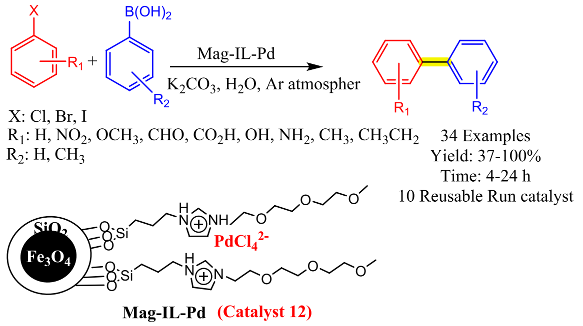


SCHEME 16 | Suzuki cross-coupling reaction catalyzed by [C_4–DaBCO][dca].

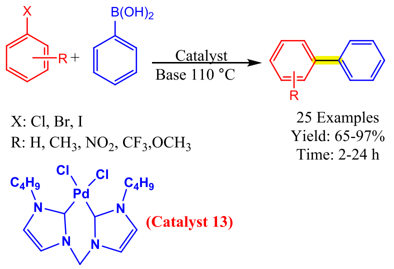
In 2014, Boruah and his colleagues successfully conducted Suzuki–Miyaura cross-coupling reactions between $ArB(OH)_2$ and Ar–X using basic ILs and lithium chloride as a promoter (Scheme 16) [36]. These coupling reactions yielded excellent results without the need for a base or ligand, allowing for easy product isolation and catalyst recycling. This innovative approach presents a green protocol for Suzuki–Miyaura cross-coupling reactions, eliminating the need for a base and ligand while introducing basic ILs as environmentally friendly solvents and LiCl as a promoter. Notably, aryl bromides exhibited efficient reactivity with $ArB(OH)_2$ under this new catalytic system. Additionally, the catalytic system showcased the capability to be reused and recycled with minimal reduction in catalytic performance.

In 2014, Karimi and his colleagues developed a unique magnetic NPs that is functionalized with ILs. These NPs, which are coated with silica and contain imidazolium ILs with triethylene glycol moieties, serve as an excellent host for immobilizing a Pd catalyst. The process involves a simple ion exchange method, resulting in a Pd catalyst (Mag–IL–Pd) (Catalyst 12) that is highly dispersible in water and can be easily recovered using a magnet. Catalyst 12 displayed exceptional activity in the Suzuki–Miyaura coupling reaction carried out in water, demonstrating effectiveness even with difficult substrates like ortho-substituted aryl halides, heteroaryl halides, and aryl chlorides (Scheme 17) [37]. What is impressive is that this high activity was achieved with a very low loading of Pd, leading to excellent yields and high TONs. In this research, the range of TON and TOF (h^{-1}) for catalyst 12 were (174–4000) and (7.8–666.7), respectively. One of the key advantages of this catalyst is its extremely low solubility in organic solvents. This means that the aqueous phase containing the catalyst can be reused for up to 10 consecutive runs without a significant decrease in activity. Upon completion of the process, the catalyst can be effortlessly isolated from the aqueous phase using an external magnetic field. The environmentally friendly and cost-effective catalyst 12 is made possible by an innovative double-separation strategy that minimizes leaching, making it ideal for this transformation.

In 2013, Zhang et al. successfully synthesized room-temperature ILs containing pincer bisimidazole cationic nuclei. The phase transition of this compound occurs at −51°C, whereas its thermal decomposition temperature is 412°C. In their study, Suzuki reactions were investigated using different catalysts, namely, $PdCl_2$, Pd $(OAc)_2$, and Pd–N–heterocyclic carbene complex (Catalyst 13), in the same room-temperature ILs (Scheme 18) [38]. The results indicate that aryl bromide has the ability to react with phenylboronic acid, producing a yield of more than 85% in the presence of sodium acetate and 0.5 mol% of catalyst 13. Furthermore, it was observed that the loading capability of catalyst 13 in the room temperature ILs is the most optimal. Catalyst 13 demonstrates high efficiency, environmental friendliness, recoverability, and easy separation of products.



SCHEME 17 | Suzuki cross-coupling reaction catalyzed by Mag–IL–Pd (Catalyst 12).

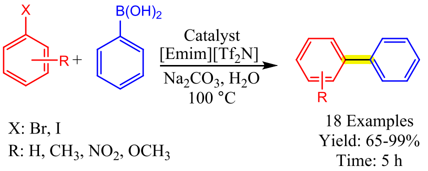


SCHEME 18 | Suzuki cross-coupling reaction catalyzed by Pd-NHC complex (Catalyst 13) in room-temperature ionic liquids.

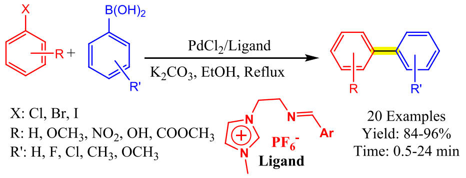
In 2012, imidazolium salts containing aromatic groups, namely, 1,3-bis(9-anthracenylmethyl)imidazolium chloride ([Bamim]Cl), 1,3-bis(1-naphthalenylmethyl)imidazolium chloride ([Bnmim]Cl), and 1,3-bis (benzylmethyl)imidazolium chloride ([Bbmim]Cl), were subjected to a reaction with $PdCl_2$, resulting in the preparation of corresponding tetrachloropalladate salts (Scheme 19) [39]. These newly formed palladium-containing salts were then assessed as precatalysts in Suzuki cross-coupling reactions conducted in ILs. The outcomes of these evaluations demonstrated high conversion rates. Additionally, the formation of palladium NPs was observed during the reactions, prompting a discussion on their role within the overall catalytic mechanism.

In 2010, Li and colleagues documented the production of a new category of IL-supported Schiff bases. The synthesis involved the condensation of aromatic aldehydes with 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate ILs, as outlined in Scheme 20 [40]. The salicylaldehyde Schiff base supported by ILs was chosen for additional investigation as a ligand in the Pd-catalyzed Suzuki–Miyaura coupling reaction. Further examination was conducted on the IL-supported salicylaldehyde Schiff base as a ligand in the Pd-catalyzed Suzuki–Miyaura coupling reaction. This reaction, conducted in an ethanol solution under air, resulted in the formation of biaryls with high yields. Remarkably, the $PdCl_2$/ligand catalytic system exhibited excellent recyclability, maintaining its activity for at least five consecutive cycles.

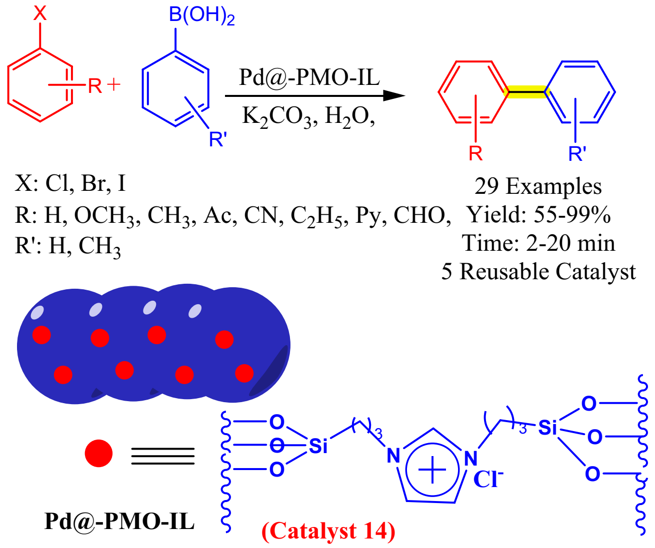
In 2010, Karimi et al. provided a detailed account of their work on the synthesis of a new type of palladium-supported periodic mesoporous organosilica (Pd@PMO–IL) (Catalyst 14) using alkylimidazolium ILs (Scheme 21) [41]. This innovative material exhibits a uniform distribution of imidazoilium ILs within the silica mesoporous framework. The researchers conducted various characterization techniques including N_2 adsorption–desorption, TEM, DRIFTS, and solid-state NMR spectroscopy to analyze both the parent PMO–IL and Catalyst 14. Their findings demonstrate that Catalyst 14 serves as a reusable and efficient



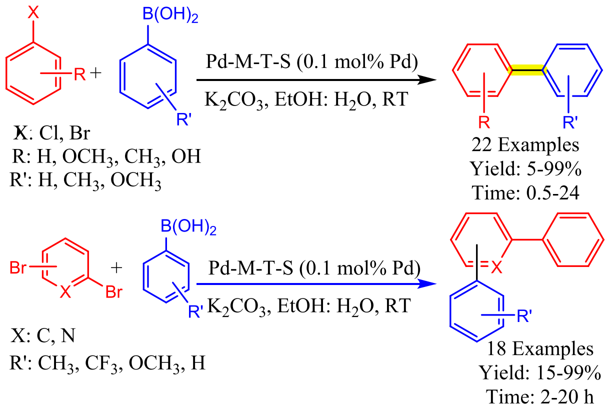
SCHEME 19 | Suzuki cross-coupling reaction catalyzed by Pd-based catalyst in ionic liquid [Emim][Tf_2N].



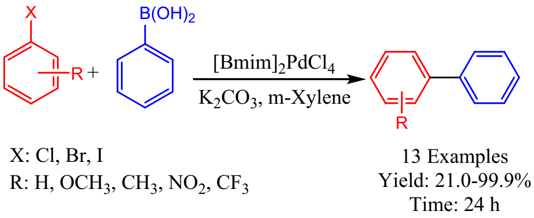
SCHEME 20 | $PdCl_2$/ligand-catalyzed Suzuki cross-coupling reaction.



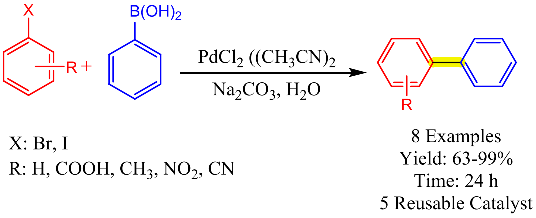
SCHEME 21 | Suzuki cross-coupling reaction catalyzed by Pd@PMO–IL (Catalyst 14) in water.



SCHEME 22 | Suzuki cross-coupling reaction catalyzed by Pd–M–T–S at room temperature.



SCHEME 23 | Suzuki coupling reaction catalyzed by $[Bmim]_2PdCl_4$.



SCHEME 24 | Suzuki cross-coupling reaction catalyzed by $PdCl_2(CH_3CN)_2$.

catalyst for the Suzuki–Miyaura coupling reaction involving different types of bromo-, iodo-, and even deactivated aryl chlorides in an aqueous environment. Interestingly, the PMO-IL nanostructure not only acts as a reservoir for soluble Pd species but also functions as a nanoscaffold, preventing the extensive agglomeration of Pd NPs by recapturing them into the mesochannels. The reason behind this behavior is the existence of separate IL units, which play a crucial role in regulating the reaction mechanism by preventing Pd agglomeration and aiding in the dispersion and recapture of Pd NPs throughout the reaction. Additionally, the catalyst shows outstanding recyclability, being capable of being retrieved and utilized for a minimum of four reaction cycles with no notable decrease in effectiveness.

In 2008, Han et al. conducted a study in which they modified the pore walls of mesoporous silica SBA-15 with chlorotrimethylsilane (Scheme 22) [42]. Imidazolium salts were subsequently integrated covalently into the inner pore walls of mesoporous silica SBA-15, this time without relying on a template. Subsequently, Pd salts were introduced into the pore channels of the previously modified mesoporous silica through electrostatic interaction. The obtaining Pd catalysts exhibited remarkable activity for the Suzuki coupling reaction at room temperature in mixed solvents of water and organic compounds. These catalysts also demonstrated good recycling ability for a minimum of four to six cycles. The turnover frequency of the catalysts reached an impressive value of 84,000 h^{-1} at 50°C. The researchers employed various analytical techniques such as solid-state NMR, TEM, FT-IR, XPS, nitrogen adsorption–desorption isotherms, and XRD to analyze the corresponding samples. Additionally, the imidazolium salt and the mesoporous walls played a crucial role in regulating the palladium catalyst agglomeration in the Suzuki coupling reaction.

In 2008, Sasaki and his colleagues conducted a study in which they prepared and characterized immobilized metal ion-containing ILs (ImmM IL) on silica surfaces (Scheme 23) [43]. The characterization involved the use of techniques such as UV–Vis, TGA, EXAFS, and elemental analysis. The researchers found that the prepared ImmCu^{2+} IL exhibited higher activity compared to the unsupported $[Bmim]_2CuCl_4$ ILs. Furthermore, it was discovered to be recyclable for the Kharasch addition reaction involving CCl_4 and styrene. Similarly, the prepared Imm-Pd^{2+} IL showed activity and reusability for the Suzuki cross-coupling reaction between phenylboronic acid and aryl-halide. The study confirmed that the catalysts prepared using the present method were efficient and could be reused.

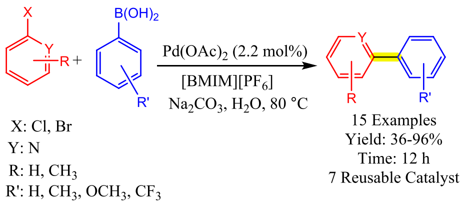
In 2008, Yang and colleagues reported on the assessment of imidazolium- and pyridinium-based ILs containing polyether/ether substituents as solvents for Pd-catalyzed Suzuki C–C coupling reactions (Scheme 24) [44]. These solvents have shown higher efficiency in facilitating the reactions compared to other ILs. This improved efficiency is attributed to the enhanced stabilization of the palladium catalyst, which involves weak interactions with the ether groups. The outcome of the coupling reactions in the imidazolium-based ILs is strongly influenced by the number and position of oxygen atoms in the ether side chain. However, no significant influence is observed for the pyridinium-based liquids. Carbene derivatives, which are believed to be formed from the imidazolium-based ILs, are thought to contribute to the termination of the catalytic cycle. Representative species of these carbene derivatives have been isolated and characterized through stoichiometric reactions.

In 2008, the utilization of palladium acetate as a catalyst in the Suzuki reaction between arylboronic acids and halopyridines has been examined in ILs at room temperature, without the presence of a phosphine ligand (Scheme 25) [45]. The influence of the Suzuki reaction in ILs was significantly affected by the presence of H_2O. The combination of the ILs and H_2O notably increased the rate of the coupling reaction. The resulting product could be easily separated through extraction with Et_2O, and the Pd $(OAc)_2$–[bmim][PF_6] (1-butyl-3-methylimidazolium hexafluorophosphate) catalyst could be reused up to six times with minimal loss of reactivity. Furthermore, the [bmim][PF_6]–H_2O solvent system demonstrated its usefulness as an alternative reaction medium for the cross-coupling of bromopyridines with ArB $(OH)_2$, utilizing palladium acetate as the catalyst without the need for a phosphine ligand. H_2O was found to have a remarkable accelerating effect on the Suzuki reaction in ILs. The Pd $(OAc)_2$–[bmim][PF_6] catalyst could be reused up to six times with only a slight loss in reactivity. This method outlines an eco-friendly strategy for producing heterobiaryl compounds.

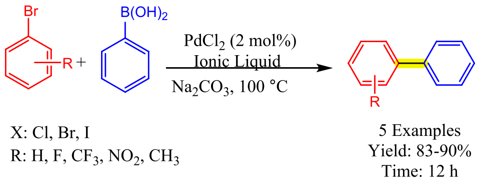
In 2005, the diquaternary salts were obtained in high yields when 2,2′-biimidazole reacted with an excess of polyfluoroalkyl or alkyl iodides at 140°C, followed by anion exchange using LiN $(SO_2CF_3)_2$ or KPF_6 (Scheme 26) [46]. By modifying the reaction stoichiometry, 2,2′-biimidazole can also undergo monoquaternization with identical electrophiles at 100°C using comparable parameters. The resulting monoquaternary salts underwent metathesis reactions with KPF_6 or LiN $(SO_2CF_3)_2$, leading to the formation of ILs with high yields. The thermal properties of these compounds were analyzed using TGA-DSC. Most of the monoquaternary salts exhibited characteristics of room-temperature ILs. Among them, 1,3,1′-tributyl-2,2′-biimidazolium hexafluorophosphate demonstrated excellent ligand and solvent properties for Pd-catalyzed Suzuki cross-coupling reactions. The catalytic ILs system showed recyclability for at least 14 cycles without loss in activity. Different monoquaternized and diquaternized 2,2′-biimidazolium-based ILs, including polyfluoroalkylated ones, were synthesized and characterized. Their thermal stabilities and physical were investigated, with the majority of the monoquaternary products exhibiting room-temperature IL properties. Notably, 1,3,1′-tributyl-2,2′-biimidazolium hexafluorophosphate, a monoquaternary room-temperature IL, proved to be an efficient and recyclable solvent for palladium-catalyzed Suzuki cross-coupling reactions. The coordination ability of the monoquaternary ILs effectively prevented Pd leaching during recycling tests.

In 2004, Mathews et al. conducted a study on substituted imidazoles in combination with palladium (II) sources in ILs and found that this system provides a stable platform for Suzuki reactions (Scheme 27) [47]. In order to achieve a successful reaction, it was necessary to initiate the catalytic system in the ILs prior to the reaction. This was accomplished by heating the palladium source with the imidazole in the ILs, resulting in a completely colorless catalytic solution. Without this initiation step, the catalytic decomposition led to low yields. The effectiveness and stability of the catalytic system in the ILs were strongly influenced by the specific imidazole ligands used, as well as the anion and cation of the ILs. The $(CH_3CN)_2PdCl_2$ 4mim catalytic system exhibited high activity in [$C_4C_1C_1$im][BF_4], [C_4C1py][N $(SO_2CF_3)_2$] and molecular solvents, although significant catalyst decomposition occurred. The reactivity of the different solutions varied depending on the cation and anion of the ILs, with [C_4C_1im][PF_6] and [C_4C_1im][OSO_2CF_3] being the most active among those tested. Furthermore, the study demonstrated that the choice of imidazole ligand can enhance reactivity, with 1-methylbenzimidazole and 1-phenylimidazole proving to be the most effective catalysts in [C_4C_1im][BF_4]. Therefore, there is significant potential for further exploration and development of this new catalyst system, offering a wide range of synthetic possibilities.

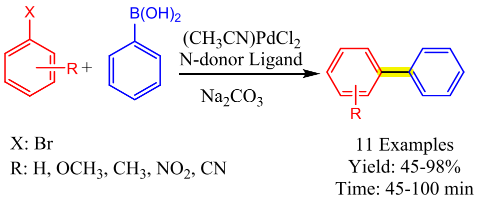
In 2003, Mclachlan and colleagues conducted research on utilizing palladium-catalyzed Suzuki cross-coupling reactions in ILs at room temperature, as outlined in Scheme 28 [48]. The researchers found that these ILs exhibit high reactivity toward bromoarenes and facilitate easy isolation of the desired products. The study also investigates the optimal reaction conditions and explores



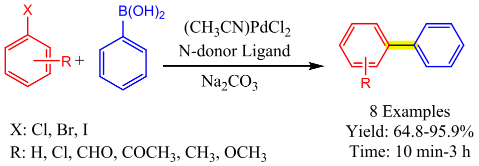
SCHEME 25 | Suzuki coupling reaction catalyzed by Pd $(OAc)_2$ in [BMIM][PF_6] ionic liquid.



SCHEME 26 | Suzuki cross-coupling reaction catalyzed by $PdCl_2$ in ionic liquid.



SCHEME 27 | Suzuki cross-coupling reaction catalyzed by $(CH_3CN)_2PdCl_2$.



SCHEME 28 | Suzuki cross-coupling reaction catalyzed by N-donor ligand incorporated Pd.

the impact of different components in the ILs. Additionally, the scientists illustrate the in-situ creation of mixed imidazolylidene/phosphine Pd complexes in all catalytically effective solutions, whereas these complexes are not present in inactive solutions. The synthesis of 1,3-dialkyl-2-arylimidazolium salts is also detected, indicating that these salts can act as a supplier of arene in the reaction. Put simply, both oxidative addition and reductive elimination are taking place with 1,3-dialkyl-2-arylimidazolium salts on palladium. The study thoroughly examines the implications of these findings for the application of ILs as solvents in Suzuki reactions.

To facilitate a quick and straightforward examination of the data related to the cited paper in this review, we have included Table 1 for reference.

TABLE 1 | A brief survey of Pd-ILs for application in Suzuki–Miyaura cross-coupling reaction.

Entry	Authors	Year	Catalyst	Base	*T* (°C)	Yield (%)	Time	Ref.
1	Nouri et al.	2023	Pd-imidazolium@Fe_3O_4 NPs	Na_2CO_3	80	88–98	15–180 min	[21]
2	Yu et al.	2023	NHC Pd complex	Na_2CO_3	80	68–99	8 h	[22]
3	Bumagin et al.	2023	Pd–Fe–Co–Ni/MFe_2O_4@Si–NH_2@Pd	K_2CO_3	100	36–98	5–30 min	[23]
4	Shaikh et al.	2022	Ag–Pd NP–(DMAP–DABCO)OH–SBAsilica	Na_2CO_3	80	53–92	45–100 min	[24]
5	Shaikh et al.	2022	Au–Pd NP–Me–IM ionic liquid	K_2CO_3	EtOH/reflux	58–94	60–100 min	[25]
6	Tian et al.	2022	SMPIL–Pd	K_2CO_3	80	85–99	0.25–10 h	[26]
7	Joo et al.	2020	Pd $(OAC)_2$	—	100–110	25–89	3–24 h	[27]
8	Ru et al.	2019	3D IL–rGO/Pd–Cu	K_2CO_3	80	20–100	0.25–6 h	[28]
9	Veisi et al.	2019	TiO_2–IL–Pd	K_2CO_3	25	65–94	30–100 min	[29]
10	Huang et al.	2018	3D IL–rGO/Pd	K_2CO_3	80	26–100	0.25–6 h	[30]
11	More et al.	2017	Pd@SILP–PS	K_2CO_3	Room temperature	40–96	10–180 min	[31]
12	Veisi et al.	2017	Fe_3O_4/IL/Pd	K_2CO_3	EtOH/Reflux	65–96	0.25–18 h	[32]
13	Wang et al.	2016	$Pd_2(dba)_3$	K_2CO_3	—	76–99	1–6 h	[33]
14	Gu et al.	2015	Pd NPs/membrane	Kt-ButO	60	—	—	[34]
15	Liu et al.	2014	PDVB–[C_3vim][SO_3CF_3]–Pd–xs	K_2CO_3	75	85–99	30 min	[35]
16	Boruah et al.	2014	[C_4–DaBCO][dca], $PdCl_2$	LiCl	110	45–99	3–6 h	[36]
17	Karimi et al.	2014	Mag–IL–Pd	K_2CO_3	—	37–100	4–24 h	[37]
18	Zhang et al.	2013	Pd–NHC complex	Base	110	65–97	2–24 h	[38]
19	Song et al.	2012	Pd catalyst in [Emim][Tf_2N]	Na_2CO_3	100	65–99	5 h	[39]
20	Li et al.	2010	$PdCl_2$/ligand	K_2CO_3	EtOH/Reflux	84–96	0.5–24 min	[40]
21	Karimi et al.	2010	Pd@PMO–IL	K_2CO_3	—	55–99	2–20 min	[41]
22	Han et al.	2008	Pd–M–T–S	K_2CO_3	Room Temperature	5–99	0.5–24 h	[42]
23	Sasaki et al.	2008	$[Bmim]_2PdCl_4$	K_2CO_3	—	21–99.9	24 h	[43]
24	Yang et al.	2008	$PdCl_2(CH_3CN)_2$	Na_2CO_3	—	63–99	24 h	[44]
25	Xin	2008	Pd $(OAc)_2$ in [BMIM][PF_6]	Na_2CO_3	80	36–96	12 h	[45]
26	Xiao et al.	2005	$PdCl_2$ in IL	Na_2CO_3	100	83–90	12 h	[46]
27	Mathews et al.	2004	$(CH_3CN)_2PdCl_2$	Na_2CO_3	—	45–98	45–100 min	[47]
28	Mclachlan et al.	2003	N-donor ligand incorporated Pd	Na_2CO_3	—	64.8–95.9	10 min-3 h	[48]

2 | Conclusion and Future Outlook

ILs have become widely used in different fields due to their unique properties, including no volatility, nonflammability, a wide liquid range, strong solubility capacity, high thermal stability, and the ability to tune their structure and properties. These characteristics make ILs an interesting and promising medium that cannot be replaced. IL chemistry has made significant contributions to both industrial and academic research applications. In the realm of organic chemistry, transition metal-catalyzed cross-coupling reactions in ILs, particularly Pd-catalyzed coupling reactions, have emerged as a captivating and vibrant branch. These reactions have proven to be economically and environmentally friendly synthetic methods, as they enable the production of structurally diverse and more complex organic molecules. In most cases, ILs were initially regarded as nonparticipative or cosolvents or inert green solvents. Nevertheless, it has been demonstrated to improve the overall reaction rates in these chemical conversions. Notably, ILs also serve as ligands, cocatalysts, and stabilizing agents for both the intermediates and catalytically active species of the catalytic cycle. Therefore, ILs play a crucial role in green chemistry and organic synthetic chemistry as green solvents. Nevertheless, researchers have raised several questionable issues regarding ILs. Despite numerous studies on the physicochemical, toxicological, and biodegradability aspects of ILs, the environmental and toxicity impacts of these compounds remain uncertain. The incorporation of palladium into ILs as solvents and catalysts in synthetic organic chemistry, particularly in carbon–carbon coupling reactions, has attracted significant interest from both researchers and industry professionals. This interest stems from the superior efficiency of ILs compared to conventional solvents and metal-based catalysts in facilitating these reactions. This advancement represents a promising development in synthetic organic chemistry, with considerable opportunities for further investigation.

Author Contributions

Ali Thoulfikar A.Imeer: investigation, conceptualization, methodology, software, data curation. **Abdul Amir H. Kadhum:** conceptualization, methodology, validation, investigation, software, data curation. **Suzan Duraid Ahmed:** conceptualization, methodology, validation, investigation, software. **Hussein Ali Al-Bahrani:** software, methodology. **Raed Muslim Mhaibes:** software, methodology, writing – review and editing, writing – original draft, supervision, conceptualization. **Guang Shu:** writing – original draft, writing – review and editing, supervision, software, conceptualization, project administration.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. (a) S. K. Singh and A. W. Savoy, "Ionic Liquids Synthesis and Applications: An Overview," *Journal of Molecular Liquids* 297 (2020): 112038. (b) F. Ren, J. Wang, F. Xie, K. Zan, S. Wang, and S. Wang, "Applications of Ionic Liquids in Starch Chemistry: A Review," *Green Chemistry* 22 (2020): 2162–2183. (c) G. Kaur, H. Kumar, and M. Singla, "Diverse Applications of Ionic Liquids: A Comprehensive Review," *Journal of Molecular Liquids* 351 (2022): 118556. (d) M. Mirzaei-Saatlo, E. Asghari, H. Shekaari, B. G. Pollet, and R. Vinodh, "Performance of Ethanolamine-Based Ionic Liquids as Novel Green Electrolytes for the Electrochemical Energy Storage Applications," *Electrochimica Acta* 474 (2024): 143499. (e) W. Zhang, I. D. Boateng, and J. Xu, "How Does Ultrasound-Assisted Ionic Liquid Treatment Affect Protein? A Comprehensive Review of Their Potential Mechanisms, Safety Evaluation, and Physicochemical and Functional Properties," *Comprehensive Reviews in Food Science and Food Safety* 23 (2024): 1–24. (f) F. Hu, B. Dong, R. Zhao, et al., "Lignosulfonate Sodium and Ionic Liquid Synergistically Promote Tough Hydrogels for Intelligent Wearable Human–Machine Interaction," *International Journal of Biological Macromolecules* 254 (2024): 127958. (g) I. Mubeen, S. Shah, E. Pervaiz, and W. Miran, "The Promising Frontier for Next-Generation Energy Storage and Clean Energy Production: A Review on Synthesis and Applications of MXenes," *Materials Science for Energy Technologies* 7 (2024): 180–194. (h) N. Lei, H. Wang, L. Fan, and X. Chen, "Highly Luminescent Soft Aggregates and Films Assembled by Amphiphilic Polyoxometalate Complex in a Polymerizable Aprotic Ionic Liquid," *Journal of Photochemistry and Photobiology A: Chemistry* 448 (2024): 115290. (i) L. Zhang, Y. Li, and J. Gao, "Selectively Extraction of Astaxanthin From *Haematococcus Pluvialis* by Aqueous Biphasic Systems Composed of Ionic Liquids and Deep Eutectic Solutions," *Food Chemistry* 434 (2024): 137399. (j) Y. Ding, G. Ai, J. Du, et al., "Synthesis and Demulsification Performance of a Gemini Ionic Liquid With Dual Cationic Active Centers," *Separation and Purification Technology* 330 (2024): 125242.

2. R. Ghanbari, D. Khorsandi, A. Zarepour, et al., "Ionic Liquid-Based Sensors," *Materials Chemistry Horizons* 1 (2022): 123–135.

3. (a) M. F. Hassan, A. Al-Othman, M. Tawalbeh, A. Ka'ki, and S. Mohamad, "Novel Chitosan–Ionic Liquid Immobilized Membranes for PEM Fuel Cells Operating Above the Boiling Point of Water," *International Journal of Hydrogen Energy* 53 (2024): 592–601. (b) H. A. Elwan, M. Mamlouk, and K. Scott, "A Review of Proton Exchange Membranes Based on Protic Ionic Liquid/Polymer Blends for Polymer Electrolyte Membrane Fuel Cells," *Journal of Power Sources* 484 (2021): 229197.

4. (a) K. Liu, Z. Wang, L. Shi, S. Jungsuttiwong, and S. Yuan, "Ionic Liquids for High Performance Lithium Metal Batteries," *Journal of Energy Chemistry* 59 (2021): 320–333. (b) W. Zhou, M. Zhang, X. Kong, W. Huang, and Q. Zhang, "Recent Advance in Ionic-Liquid-Based Electrolytes for Rechargeable Metal–Ion Batteries," *Advanced Science* 8 (2021): 2004490. (c) C. F. J. Francis, I. L. Kyratzis, and A. S. Best, "Lithium–Ion Battery Separators for Ionic-Liquid Electrolytes: A Review," *Advanced Materials* 32 (2020): 1904205.

5. (a) J. Wang, Y. Liang, Z. Zhang, et al., "Thermoplastic Starch Plasticized by Polymeric Ionic Liquid," *European Polymer Journal* 148 (2021): 110367. (b) A. S. F. M. Asnawi, M. H. Hamsan, S. B. Aziz, M. F. Z. Kadir, J. Matmin, and Y. M. Yusof, "Impregnation of [Emim] Br Ionic Liquid as Plasticizer in Biopolymer Electrolytes for EDLC Application," *Electrochimica Acta* 375 (2021): 137923.

6. (a) M. Cai, Q. Yu, W. Liu, and F. Zhou, "Ionic Liquid Lubricants: When Chemistry Meets Tribology," *Chemical Society Reviews* 49 (2020): 7753–7818. (b) J. Song, "Research Progress of Ionic Liquids as Lubricants," *ACS Omega* 2021, no. 6: 29345–29349.

7. (a) T. Wongsawa, N. Traiwongsa, U. Pancharoen, and K. Nootong, "A Review of the Recovery of Precious Metals Using Ionic Liquid Extractants in Hydrometallurgical Processes," *Hydrometallurgy* 198 (2020): 105488. (b) M. Atanassova, "Solvent Extraction Chemistry in Ionic Liquids: An Overview of f-Ions," *Journal of Molecular Liquids* 343 (2021): 117530.

8. (a) M. M. Seitkalieva, D. E. Samoylenko, K. A. Lotsman, K. S. Rodygin, and V. P. Ananikov, "Metal Nanoparticles in Ionic Liquids: Synthesis and Catalytic Applications," *Coordination Chemistry Reviews* 445 (2021): 213982. (b) M. Hejazifar, O. Lanaridi, and K. Bica-Schröder, "Ionic Liquid Based Microemulsions: A Review," *Journal of Molecular Liquids* 303 (2020): 112264. (c) T. Zhang, T. Doert, H. Wang, S. Zhang, and M. Ruck, "Inorganic Synthesis Based on Reactions of Ionic Liquids and Deep Eutectic Solvents," *Angewandte Chemie International Edition* 60 (2021):

22148–22165. (d) A. J. Greer, J. Jacquemin, and C. Hardacre, "Industrial Applications of Ionic Liquids," *Molecules* 25 (2020): 5207. (e) S. Sadjadi, "Magnetic (Poly) Ionic Liquids: A Promising Platform for Green Chemistry," *Journal of Molecular Liquids* 323 (2021): 114994. (f) F. Liu, J. Yu, A. B. Qazi, L. Zhang, and X. Liu, "Metal-Based Ionic Liquids in Oxidative Desulfurization: A Critical Review," *Environmental Science & Technology* 55 (2021): 1419–1435. (g) H. C. Ong, Y. W. Tiong, B. H. H. Goh, et al., "Recent Advances in Biodiesel Production From Agricultural Products and Microalgae Using Ionic Liquids: Opportunities and Challenges," *Energy Conversion and Management* 228 (2021): 113647. (h) J. N. Appaturi, R. Ratti, B. L. Phoon, et al., "A Review of the Recent Progress on Heterogeneous Catalysts for Knoevenagel Condensation," *Dalton Transactions* 50 (2021): 4445–4469. (i) C. S. Buettner, A. Cognigni, C. Schröder, and K. Bica-Schröder, "Surface-Active Ionic Liquids: A Review," *Journal of Molecular Liquids* 347 (2022): 118160. (j) N. Nasirpour, M. Mohammadpourfard, and S. Zeinali Heris, "Ionic Liquids: Promising Compounds for Sustainable Chemical Processes and Applications," *Chemical Engineering Research and Design* 160 (2020): 264–300. (k) J. Płotka-Wasylka, M. de la Guardia, V. Andruch, and M. Vilková, "Deep Eutectic Solvents vs Ionic Liquids: Similarities and Differences," *Microchemical Journal* 159 (2020): 105539. (l) Y. Wu, J. Xu, K. Mumford, G. W. Stevens, W. Fei, and Y. Wang, "Recent Advances in Carbon Dioxide Capture and Utilization With Amines and Ionic Liquids," *Green Chemical Engineering* 1 (2020): 16–32. (m) S.-Y. Zhang, Q. Zhuang, M. Zhang, et al., "Poly (Ionic Liquid) Composites," *Chemical Society Reviews* 49 (2020): 1726–1755.

9. (a) J. P. Hallett and T. Welton, "Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2," *Chemical Reviews* 111 (2011): 3508–3576. (b) J. E. Bara, T. K. Carlisle, C. J. Gabriel, et al., "Guide to CO_2 Separations in Imidazolium-Based Room-Temperature Ionic Liquids," *Industrial & Engineering Chemistry Research* 48 (2009): 2739–2751. (c) Z. Lei, C. Dai, and B. Chen, "Gas Solubility in Ionic Liquids," *Chemical Reviews* 114 (2014): 1289–1326. (d) G. Chatel and D. R. MacFarlane, "Ionic Liquids and Ultrasound in Combination: Synergies and Challenges," *Chemical Society Reviews* 43 (2014): 8132–8149. (e) N. L. Mai and Y.-M. Koo, "Computer-Aided Design of Ionic Liquids for High Cellulose Dissolution," *ACS Sustainable Chemistry & Engineering* 4 (2016): 541–547. f) *Chemical Reviews* 2017, no. 117: 6633–6635.

10. (a) B. E. Gurkan, J. C. de la Fuente, E. M. Mindrup, et al., "Equimolar CO_2 Absorption by Anion-Functionalized Ionic Liquids," *Journal of the American Chemical Society* 132 (2010): 2116–2117. (b) K. N. Ruckart, R. A. O'Brien, S. M. Woodard, K. N. West, and T. G. Glover, "Equimolar CO_2 Absorption by Anion-Functionalized Ionic Liquids," *The Journal of Physical Chemistry C* 119 (2015): 20681–20697.

11. (a) M. F. Rojas, F. L. Bernard, A. Aquino, et al., "Poly (Ionic Liquid)s as Efficient Catalyst in Transformation of CO_2 to Cyclic Carbonate," *Journal of Molecular Catalysis A: Chemical* 392 (2014): 83–88. (b) W. Qian, J. Texter, and F. Yan, "Frontiers in Poly (Ionic Liquid)s: Syntheses and Applications," *Chemical Society Reviews* 46 (2017): 1124–1159.

12. (a) S. Wickramanayake, D. Hopkinson, C. Myers, et al., "Mechanically Robust Hollow Fiber Supported Ionic Liquid Membranes for CO_2 Separation Applications," *Journal of Membrane Science* 470 (2014): 52–59. (b) P. Scovazzo, D. Havard, M. McShea, S. Mixon, and D. Morgan, "Long-Term, Continuous Mixed-Gas dry fed CO_2/CH_4 and CO_2/N_2 Separation Performance and Selectivities for Room Temperature Ionic Liquid Membranes," *Journal of Membrane Science* 327 (2009): 41–48.

13. Y. Pan, W. Huang, Z. H. Liu, Z. Z. Yang, J. J. Tan, and B. M. Xu, "Recent Progress of Metal–Organic Frameworks for Liquid Fuels Desulfurization," *Separation & Purification Reviews*: 21–21.

14. (a) I. S. Hamza, W. A. Mahmmoud, A. A. Al-Hamdani, S. D. Ahmed, A. W. Allaf, and W. Al Zoubi, "Synthesis, Characterization, and Bioactivity of Several Metal Complexes of (4-Amino-N-(5 -Methyl-Isaxazol-3-Yl)-Benzenesulfonamide)," *Inorganic Chemistry Communications* 144 (2022): 109776. (b) V. T. Suleman, A. A. S. Al-Hamdani, S. D. Ahmed, et al., "Phosphorus Schiff Base Ligand and Its Complexes: Experimental and Theoretical Investigations," *Applied Organometallic Chemistry* 34 (2020): e5546. (c) V. Y. Jirjees, V. T. Suleman, A. A. Salih Al-Hamdani, and S. D. Ahmed, "AJ Csian OURNALOF HEMISTRY AJ Csian OURNALOF HEMISTRY," *Asian Journal of Chemistry* 31 (2019): 2430–2438. (d) W. Al Zoubi, A. A. S. Al-Hamdani, S. Duraid Ahmed, et al., "Synthesis, Characterization, and Antioxidant Activities of Imine Compounds," *Journal of Physical Organic Chemistry* 32 (2019): e3916. (e) W. Al Zoubi, V. Jirjees, V. Suleman, et al., "Synthesis and Bioactivity Studies of Novel Schiff Bases and Their Complexes," *Journal of Physical Organic Chemistry* 32 (2019): e4004. (f) R. K. H. Al-Daffay and A. A. S. Al-Hamdani, "Characterization, and Thermal Analysis of a New Acidicazo Ligand's Metal Complexes," *Baghdad Science Journal* 20 (2023): 0121.

15. (a) R. Fareghi-Alamdari, M. Golestanzadeh, and O. Bagheri, "Meso-Tetrakis [4-(Methoxycarbonyl) Phenyl] Porphyrinatopalladium (II) Supported on Graphene Oxide Nanosheets (Pd (II)–TMCPP–GO): Synthesis and Catalytic Activity," *RSC Advances* 6 (2016): 108755–108767. (b) M. Golestanzadeh and H. Naeimi, "Palladium Decorated on a new Dendritic Complex With Nitrogen Ligation Grafted to Graphene Oxide: Fabrication, Characterization, and Catalytic Application," *RSC Advances.* 9 (2019): 27560–27573. (c) R. Fareghi-Alamdari, M. Golestanzadeh, and O. Bagheri, "An Efficient and Recoverable Palladium Organocatalyst for Suzuki Reaction in Aqueous Media," *Applied Organometallic Chemistry* 31 (2017): e3698. (d) R. Pourkaveh and H. Karimi, "An air Stable and Efficient Palladium Catalyst for Suzuki–Miyaura Cross Coupling Reaction at Room Temperature," *Iranian Journal of Catalysis* 6 (2016): 489–495. (e) A. Hajipour, F. Abrishami, and F. Rafiei, *Iranian Journal of Catalysis* 4 (2014): 181–187. (f) R. Nagarajan, P. S. Rajeswari, and L. Emmanuvel, "Synthesis of Novel Tridentate Ligand-Based Palladium Catalyst and Investigation of Its Reactivity Towards Suzuki, Sonogashira and Heck Coupling Reactions," *Iranian Journal of Catalysis* 10 (2020): 259–265. (g) M. Mohammadi Rasooll, *Iranian Journal of Catalysis* 13 (2023): 229–234.

16. J. Li, S. Yang, W. Wu, and H. Jiang, "Recent Advances in Pd-Catalyzed Cross-Coupling Reaction in Ionic Liquids," *European Journal of Organic Chemistry* 2018 (2018): 1284–1306.

17. R. Singh, M. Sharma, R. Mamgain, and D. S. Rawat, "Ionic Liquids: A Versatile Medium for Palladium-Catalyzed Reactions," *Journal of the Brazilian Chemical Society* 19 (2008): 357–379.

18. S. E. Hooshmand, B. Heidari, R. Sedghi, and R. S. Varma, "Recent Advances in the Suzuki–Miyaura Cross-Coupling Reaction Using Efficient Catalysts in Eco-Friendly Media," *Green Chemistry* 21 (2019): 381–405.

19. R. Tomar, P. Kundra, J. Sharma, "Sangeeta, *Catalysis Surveys from Asia*," (2024), https://doi.org/10.1007/s10563-10024-09430-10565.

20. (a) H. Topsøe, "Developments in Operando Studies and In Situ Characterization of Heterogeneous Catalysts," *Journal of Catalysis* 216 (2003): 155–164. (b) J. C. Védrine, "Acid–Base Characterization of Heterogeneous Catalysts: An Up-To-Date Overview," *Research on Chemical Intermediates* 41 (2015): 9387–9423.

21. K. Nouri, M. Ghassemzadeh, F. Mohsenzadeh, and M. Afsharpour, "Imidazolium Organometallic Complex of Palladium on Fe_3O_4 Nanoparticles as Selective and Magnetically Recoverable Nanocatalyst for C-C Cross-Coupling Reactions," *Applied Organometallic Chemistry* 37 (2023): e7031.

22. J. Yu, A. Zheng, L. Jin, et al., "The C-3 Functionalization of 1H-Indazole Through Suzuki–Miyaura Cross-Coupling Catalyzed by a Ferrocene-Based Divalent Palladium Complex Immobilized Over Ionic Liquid, as Well as Theoretical Insights Into the Reaction Mechanism," *Applied Sciences* 13 (2023): 4095.

23. R. S. Keri, V. Adimule, P. Kendrekar, and B. S. Sasidhar, *Topics in Catalysis* (2022), https://doi.org/10.1007/s11244-11022-01562-11240.

24. N. M. Shaikh, V. Adimule, G. B. Bagihalli, and R. S. Keri, "A Novel Mixed Ag–Pd Nanoparticles Supported on SBA Silica Through [DMAP-TMSP-DABCO] OH Basic Ionic Liquid for Suzuki Coupling Reaction," *Topics in Catalysis* (2022): 1–10.

25. N. M. Shaikh, A. D. Sawant, G. B. Bagihalli, M. Challa, and V. M. Adimule, “Highly Active Mixed Au–Pd Nanoparticles Supported on RHA Silica Through Immobilised Ionic Liquid for Suzuki Coupling Reaction,” *Topics in Catalysis* (2022): 1–10.

26. Y. Tian, C. Xing, W. Wang, S. Zhang, and Y. Zhang, “A Highly Crosslinked, Mesoporous Poly(Ionic Liquid) Containing Salen–Pd for Efficient, Eco-Friendly Suzuki–Miyaura Coupling Reactions,” *New Journal of Chemistry* 46 (2022): 8855–8862.

27. S. R. Joo, G. T. Kwon, and S. H. Kim, “A Combination of Biocompatible Room Temperature Ionic Liquid and Palladium Catalyst for Base- and Ligand-Free Suzuki Coupling Reactions,” *Asian the Journal of Organic Chemistry* 9 (2020): 584–587.

28. Y. Ru, Y. Huang, Y. Wang, and L. Dai, “Pd–Cu Alloy Nanoparticle Supported on Amine-Terminated Ionic Liquid Functional 3D Graphene and Its Application on Suzuki Cross-Coupling Reaction,” *Applied Organometallic Chemistry* 33 (2019): e5198.

29. H. Veisi, S. A. Kamangar, P. Mohammadi, and S. Hemmati, “Palladium Nanoparticles-Decorated Triethanolammonium Chloride Ionic Liquid-Modified TiO_2 nanoparticles (TiO_2/IL-Pd): A Highly Active and Recoverable Catalyst for Suzuki–Miyaura Cross-Coupling Reaction in Aqueous Medium,” *Applied Organometallic Chemistry* 33 (2019): e4909.

30. Y. Huang, Q. Wei, Y. Wang, and L. Dai, “Three-Dimensional Amine-Terminated Ionic Liquid Functionalized Graphene/Pd Composite Aerogel as Highly Efficient and Recyclable Catalyst for the Suzuki Cross-Coupling Reactions,” *Carbon* 136 (2018): 150–159.

31. S. More, S. Jadhav, R. Salunkhe, and A. Kumbhar, “Palladium Supported Ionic Liquid Phase Catalyst (Pd@SILP–PS) for Room Temperature Suzuki–Miyaura Cross-Coupling Reaction,” *Molecular Catalysis* 442 (2017): 126–132.

32. H. Veisi, M. Pirhayati, and A. Kakanejadifard, “Immobilization of Palladium Nanoparticles on Ionic Liquid–Triethylammonium Chloride Functionalized Magnetic Nanoparticles: As a Magnetically Separable, Stable and Recyclable Catalyst for Suzuki–Miyaura Cross-Coupling Reactions,” *Tetrahedron Letters* 58 (2017): 4269–4276.

33. H. B. Wang, Y.-L. Hu, and D.-J. Li, “Facile and Efficient Suzuki–Miyaura Coupling Reaction of Aryl Halides Catalyzed by $Pd_2(dba)_3$ in Ionic Liquid/Supercritical Carbon Dioxide Biphasic System,” *Journal of Molecular Liquids* 218 (2016): 429–433.

34. Y. Gu, I. Favier, C. Pradel, et al., “High Catalytic Efficiency of Palladium Nanoparticles Immobilized in a Polymer Membrane Containing Poly(Ionic Liquid) in Suzuki–Miyaura Cross-Coupling Reaction,” *Journal of Membrane Science* 492 (2015): 331–339.

35. F. Liu, G. Feng, M. Lin, C. Wang, B. Hu, and C. Qi, “Superoleophilic Nanoporous Polymeric Ionic Liquids Loaded With Palladium Acetate: Reactants Enrichment and Efficient Heterogeneous Catalysts for Suzuki–Miyaura Coupling Reaction,” *Journal of Colloid and Interface Science* 435 (2014): 83–90.

36. P. R. Boruah, M. J. Koiri, U. Bora, and D. Sarma, “A new Recyclable/Reusable Ionic Liquid/LiCl System for Suzuki–Miyaura Cross Coupling Reactions,” *Tetrahedron Letters* 55 (2014): 2423–2425.

37. B. Karimi, F. Mansouri, and H. Vali, “A Highly Water-Dispersible/Magnetically Separable Palladium Catalyst Based on a Fe_3O_4@SiO_2 Anchored TEG–Imidazolium Ionic Liquid for the Suzuki–Miyaura Coupling Reaction in Water,” *Green Chemistry* 16 (2014): 2587–2596.

38. C. Zhang, R. Shi, C. Chen, and C. Jin, “Suzuki Cross-Coupling Reactions in Dicationic Room Temperature Ionic Liquid,” *Chinese Journal of Organic Chemistry* 33 (2013): 611.

39. H. Song, N. Yan, Z. Fei, et al., “Evaluation of Ionic Liquid Soluble Imidazolium Tetrachloropalladate Pre-Catalysts in Suzuki Coupling Reactions,” *Catalysis Today* 183 (2012): 172–177.

40. Y.-Q. Li, B. Li, and J. Zheng, “A Novel Ionic Liquid-Supported Schiff Base Ligand Applied in the Pd-Catalyzed Suzuki–Miyaura Coupling Reaction,” *ARKIVOC* 2010 (2010).

41. B. Karimi, D. Elhamifar, J. H. Clark, and A. J. Hunt, “Ordered Mesoporous Organosilica With Ionic-Liquid Framework: An Efficient and Reusable Support for the Palladium-Catalyzed Suzuki–Miyaura Coupling Reaction in Water,” *Chemistry–A European Journal* 16 (2010): 8047–8053.

42. P. Han, H. Zhang, X. Qiu, X. Ji, and L. Gao, “Palladium Within Ionic Liquid Functionalized Mesoporous Silica SBA-15 and Its Catalytic Application in Room-Temperature Suzuki Coupling Reaction,” *Journal of Molecular Catalysis A: Chemical* 295 (2008): 57–67.

43. T. Sasaki, M. Tada, C. Zhong, T. Kume, and Y. Iwasawa, “Immobilized Metal Ion-Containing Ionic Liquids: Preparation, Structure and Catalytic Performances in Kharasch Addition Reaction and Suzuki Cross-Coupling Reactions,” *Journal of Molecular Catalysis A: Chemical* 279 (2008): 200–209.

44. X. Yang, Z. Fei, T. J. Geldbach, et al., “Suzuki Coupling Reactions in Ether-Functionalized Ionic Liquids: The Importance of Weakly Interacting Cations,” *Organometallics* 27 (2008): 3971–3977.

45. B. Xin, “Phosphine-Free Cross-Coupling Reaction of Halopyridines With Arylboronic Acids in an Ionic Liquid: Water Mixture,” *Journal of Chemical Research* 2008 (2008): 412–415.

46. J.-C. Xiao and J. N. M. Shreeve, “Synthesis of 2,2′-Biimidazolium-Based Ionic Liquids: Use as a New Reaction Medium and Ligand for Palladium-Catalyzed Suzuki Cross-Coupling Reactions,” *Journal of Organic Chemistry* 70 (2005): 3072–3078.

47. C. J. Mathews, P. J. Smith, and T. Welton, “N-Donor Complexes of Palladium as Catalysts for Suzuki Cross-Coupling Reactions in Ionic Liquids,” *Journal of Molecular Catalysis A: Chemical* 214 (2004): 27–32.

48. F. McLachlan, C. J. Mathews, P. J. Smith, and T. Welton, “Palladium-Catalyzed Suzuki Cross-Coupling Reactions in Ambient Temperature Ionic Liquids: Evidence for the Importance of Palladium Imidazolylidene Complexes,” *Organometallics* 22 (2003): 5350–5357.