catalysts

Review

Emerging Trends in Palladium Nanoparticles: Sustainable Approaches for Enhanced Cross-Coupling Catalysis

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Abstract: Palladium nanoparticles (PdNPs) are transforming the landscape of modern catalysis and offer sustainable and efficient alternatives to traditional catalysts for cross-coupling reactions. Owing to their exceptional surface area-to-volume ratio, PdNPs exhibit superior catalytic activity, selectivity, and recyclability, making them ideal for greener chemical processes. Recent innovations have focused on improving the stability and reusability of PdNPs through environmentally benign approaches, such as water-based reactions, renewable stabilizers, and magnetic nanoparticle supports. Advances in catalyst design, including PdNP immobilization on magnetic nanosilica for enhanced recyclability in Suzuki–Miyaura reactions, nitrogen-doped carbon nanosheets achieving up to ninefold improvements in turnover frequencies, and biodegradable biopolymer matrices that reduce environmental impact, have effectively addressed key challenges such as catalyst leaching, support degradation, and agglomeration. The shift from conventional catalysis to these cutting-edge nanocatalytic techniques signifies a critical movement toward sustainable chemistry, positioning PdNPs at the forefront of industrial applications and the future of eco-friendly chemical synthesis.

Keywords: palladium nanoparticles; heterogeneous catalysis; cross-coupling; green synthesis; sustainability; biocatalysts; catalytic mechanisms

1. Introduction

The increasing demand for environmentally friendly and efficient chemical processes has established sustainable catalysis at the forefront of modern chemical syntheses. Globally, industries are focusing on catalytic systems that achieve high efficiency while minimizing environmental impacts, including waste generation, energy consumption, and the use of hazardous materials. Such processes enable the production of chemical compounds with a reduced ecological footprint, thereby aligning industrial practices with sustainability goals [1–6].

By leveraging their high surface area-to-volume ratio, palladium nanoparticles (PdNPs) exhibit remarkable catalytic activity and selectivity, enabling efficient cross-coupling reactions and other key processes in pharmaceutical and fine chemical syntheses. This property reduces the catalyst quantities required and minimizes environmental impact, solidifying the transformative role of PdNPs in advancing sustainable and industrially scalable catalysis. Various forms of nanocatalysts have been developed, including

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supported, Schiff-based, graphene-based, thin-film, mixed metal oxide, magnetic, and core-shell nanocatalysts [7]. Among these, palladium-based nanocatalysts have garnered extensive attention in both academia and industry because of their versatility in carbon–carbon and carbon-heteroatom cross-coupling reactions, as well as other catalytic processes such as hydrogenation, oxidation, reduction, and esterification [8–12]. The exceptional catalytic activity, selectivity, and reusability of palladium-based nanocatalysts render them invaluable for applications ranging from fine chemical synthesis to large-scale industrial processes, where they are used in the production of various valuable compounds, such as natural products, biologically active molecules, and pharmaceuticals [13–27]. For instance, several drugs and intermediates such as naproxen (an anti-inflammatory agent) [28,29], prosulfuron (herbicide) [30], Singulair (antiasthma) [31,32], Eletriptan [31,33–35], BVDU (antiviral), [36] axitinib (antitumor) [37], 2-ethylhexyl-*p*-methoxycinnamate (UV sunscreen B agent) [38], and co-monomers of styrene polymers [39], have been prepared by Heck reactions.

Palladium nanoparticles (PdNPs) have attracted significant attention in organic synthesis owing to their remarkable advantages over traditional catalysts. The significantly enhanced surface area-to-volume ratio of PdNPs facilitates more efficient active site utilization, which is critical for optimizing the reaction rates in complex processes such as pharmaceutical syntheses and fine chemical production. This characteristic also supports better dispersion on the supports, further improving the catalytic efficiency and durability under industrial conditions [40–45]. Additionally, PdNPs demonstrate exceptional recyclability and reusability, which are critical factors in sustainable chemistry. Their ability to maintain catalytic performance over multiple cycles makes them ideal for large-scale industrial applications by reducing the need for frequent replacement and minimizing waste [45].

Recent studies have highlighted the efficiency of PdNPs in cross-coupling reactions by using sustainable approaches. Pd nanocatalysts are often immobilized on supports, such as inorganic carbonaceous materials, silica, metal oxide-based hybrids, biopolymers, organic polymeric hybrids, and magnetic nanostructures [46–49]. These supports enhance the catalytic environment and create synergy between the support and the nanocatalyst [41,46,50,51]. For instance, PdNPs supported on fibrous nanosilica (KCC-1) or stabilized by heteroatom-donor-modified polystyrene-based polymer ionic liquids have demonstrated high catalytic efficiency and recyclability in Suzuki–Miyaura cross-coupling reactions under mild conditions, achieving significantly higher turnover numbers (TONs) than conventional Pd catalysts [52,53]. Another innovative approach utilizes iron to reduce the quantity of palladium required, thereby enhancing sustainability and cost-effectiveness [54].

The selectivity of PdNPs for catalytic reactions is another distinguishing feature. This selectivity allows for precise control over the reaction pathways, resulting in higher yields of the desired products, with fewer by-products [55]. Advanced designs, such as water-soluble dendrimer-encapsulated PdNPs, offer remarkable stability and efficiency in various cross-coupling reactions under mild conditions, thus supporting the principles of green chemistry [56,57]. These dendrimer-encapsulated nanoparticles, with their small size distributions, enable better characterization in kinetic studies of carbon–carbon coupling reactions [56,57].

Recent innovations include the development of Pd-loaded cucurbit[7]uril-modified iron oxide nanoparticles for green solvents, as well as nitrogen-doped carbon nanosheets, which have achieved ninefold increases in turnover frequencies for Suzuki reactions compared to conventional Pd/C catalysts [58,59].

Biomass-derived boron carbon nitride has achieved high yields and recyclability in Suzuki–Miyaura and CN arylation reactions [60]. These systems demonstrate the integration of biodegradable and renewable materials and the potential for eco-friendly support. Bio-based supports, such as kenaf-cellulose modified with poly(amidoxime) ligands, and bacterial supports, such as *Paracoccus yeei*, highlight the potential of biodegradable materials to reduce the environmental impact while maintaining excellent catalytic efficiency [61,62].

These advances, coupled with the rational design of nanostructured supports that enhance substrate selectivity and reduce catalyst deactivation [46], underscore the potential of sustainable methods for optimizing catalytic performance while addressing environmental concerns. This review provides a comprehensive overview of recent innovations in PdNP synthesis and catalytic applications, with a focus on strategies to enhance efficiency, selectivity, and sustainability. By critically analyzing these developments and identifying gaps in current methodologies, this review highlights key areas for future research to overcome these limitations and guide the design of next-generation PdNP catalysts for widespread industrial adoption.

2. Palladium Nanoparticles Supported on Biopolymers for Cross-Coupling Reactions

Biopolymers and biomass-derived polymers, such as cellulose, starch, pectin, agarose, chitosan, proteins, and enzymes, have gained attention as promising supports for metal nanoparticles because of their low toxicity, cost efficiency, high biocompatibility, and abundance. These materials provide sustainable alternatives to traditional supports, particularly in catalytic applications such as cross-coupling reactions [47,63–65].

However, the application of biopolymer-supported nanoparticles under extreme conditions poses significant challenges. High temperatures, strongly acidic or basic environments, and prolonged reaction times can lead to the degradation of biopolymer supports, reducing the overall stability and efficiency of catalytic systems. Zhao et al. demonstrated that such extreme conditions significantly affect the structural integrity of biopolymers, thereby limiting their long-term applicability in catalytic processes [66]. Additionally, achieving homogeneous functionalization of biopolymers can be challenging because of their inherent structural variability and complex surface chemistry, which can impact the reproducibility and efficiency of the catalytic processes [67].

Inorganic supports such as silica and metal oxides offer superior thermal stability and mechanical strength, making them more suitable for harsh reaction conditions. However, biopolymers lack biodegradability and renewability, presenting a trade-off between robustness and sustainability [68,69]. This contrast underscores the importance of tailoring support materials to specific applications, while balancing environmental considerations with performance requirements.

Innovative approaches have been developed to address these issues. Hybrid systems that combine biopolymers with inorganic supports, such as magnetic nanoparticles embedded in biopolymer fibers, provide enhanced thermal behavior and additional functionalities [69]. Structural modifications, including cross-linking or blending with other polymers, have also shown promise in improving the thermal and chemical stabilities of biopolymer-supported catalysts, extending their applicability under extreme conditions [70].

Despite these challenges, the unique properties of biopolymers, particularly their environmental benefits, render them highly attractive for catalytic applications. The limitations of biopolymer-supported nanoparticles can be mitigated by leveraging advanced design strategies and hybrid systems, thus paving the way for their broader use in sustainable catalysis.

2.1. Palladium Nanoparticles Supported on Chitosan

Among the various biopolymers explored for Pd nanoparticle (PdNP) stabilization, chitosan (CS) has gained prominence owing to its unique structural and functional properties. Unlike cellulose, starch, or pectin, chitosan possesses abundant amine (-NH_2) and hydroxyl (-OH) groups, which provide strong coordination sites for metal nanoparticles, significantly enhancing their stability, dispersion, and catalytic efficiency [71–73]. These chelating groups enable the effective immobilization of PdNPs, preventing aggregation while facilitating highly active catalytic sites for cross-coupling reactions [74–77]. Additionally, chitosan exhibits intrinsic biocompatibility, biodegradability, and hydrophilicity, making it an environmentally friendly support for heterogeneous catalysis.

Beyond its molecular interactions, the ability of chitosan to form composites, beads, and hybrid materials further enhances its mechanical robustness and ensures stability under reaction conditions [78–81]. This structural versatility allows for tunable porosity and functionalization, making it an ideal platform for engineering advanced Pd-based catalysts. Recent studies have demonstrated that Pd-chitosan nanocatalysts exhibit high turnover frequencies (TONs), excellent recyclability, and thermal stability, maintaining their catalytic activity across multiple reaction cycles. By incorporating strategic functionalization approaches, such as ligand modification and hybridization with inorganic nanoparticles, researchers have significantly expanded the catalytic potential of chitosan-based Pd catalysts.

These modifications enhance stability, recyclability, and catalytic efficiency, addressing challenges such as metal leaching and deactivation under reaction conditions.

Building on these properties, Dohenduo et al. developed a novel supramolecular Pd(II) catalyst grafted on chitosan with L-asparagine and an EDTA linker, named Pd@ASP–EDTA–CS (Figure 1) [82].

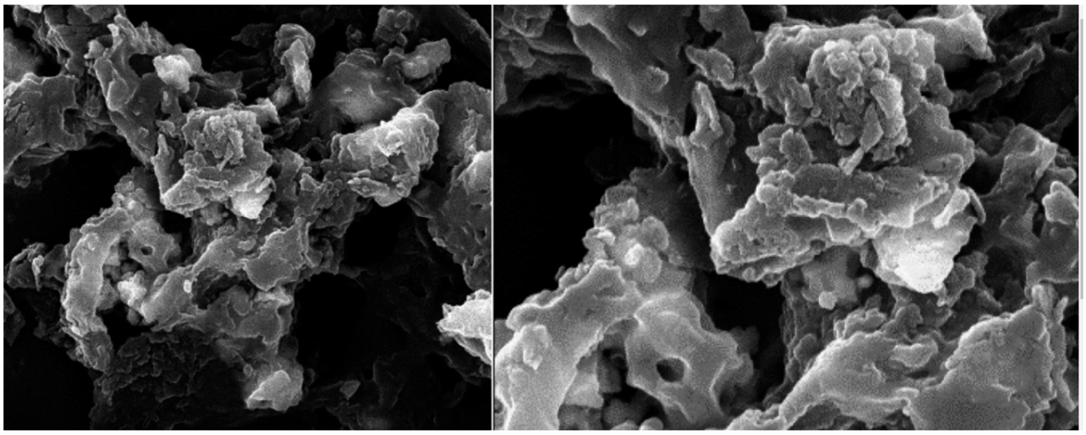
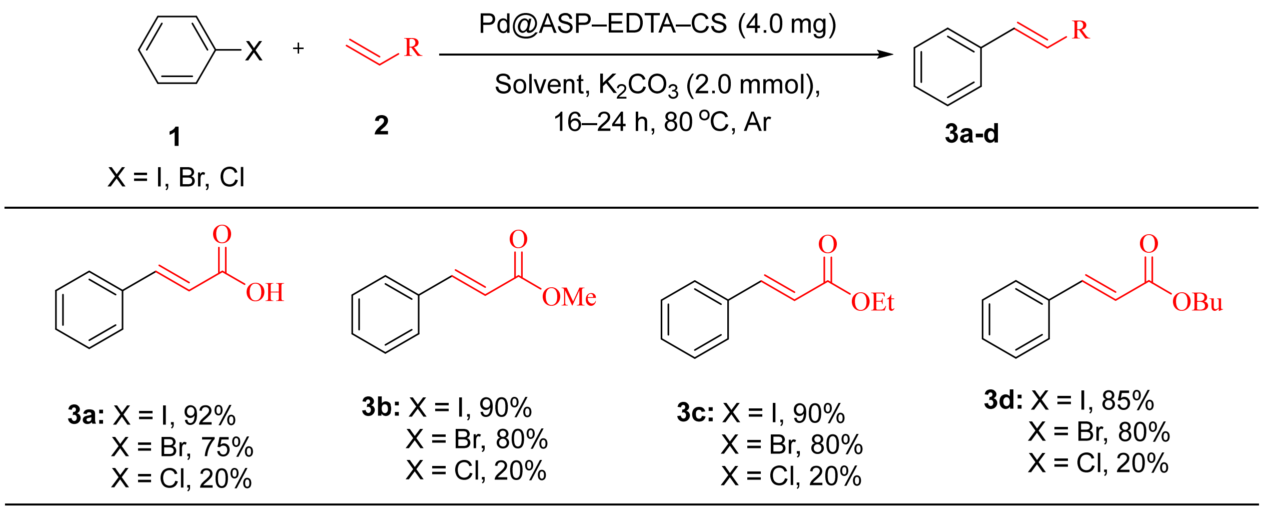


Figure 1. FESEM images of the Pd@ASP–EDTA–CS nanocatalyst adapted from Dohendou et al. [82].

This catalyst was successfully employed in the Heck cross-coupling reaction of aryl halides (**1**) with alkenes (**2**) to produce biologically active cinnamic acid derivatives (**3**) in good-to-excellent yields (Scheme 1). The catalyst demonstrated more than five cycles of reusability with no significant loss in efficiency and no detectable leaching of Pd into the reaction medium or final products [82].

The reaction conditions were optimized using iodobenzene and methyl acrylate, achieving the best yields under 4.0 mg catalyst loading (4.46% palladium loading), DMF or acetonitrile solvents, and a reaction temperature of 80 °C. Under these conditions, methyl acrylate afforded the highest yield (90%), whereas ethyl and butyl acrylates furnished slightly lower yields (85% each). However, substrates with electron-withdrawing groups (EWGs) on aryl halides afforded trace yields, highlighting the limitations of this system [82]. This study highlights the potential of Pd@ASP–EDTA–CS as a sustainable and effective catalytic system for cross-coupling reactions, offering significant advancements in green chemistry.



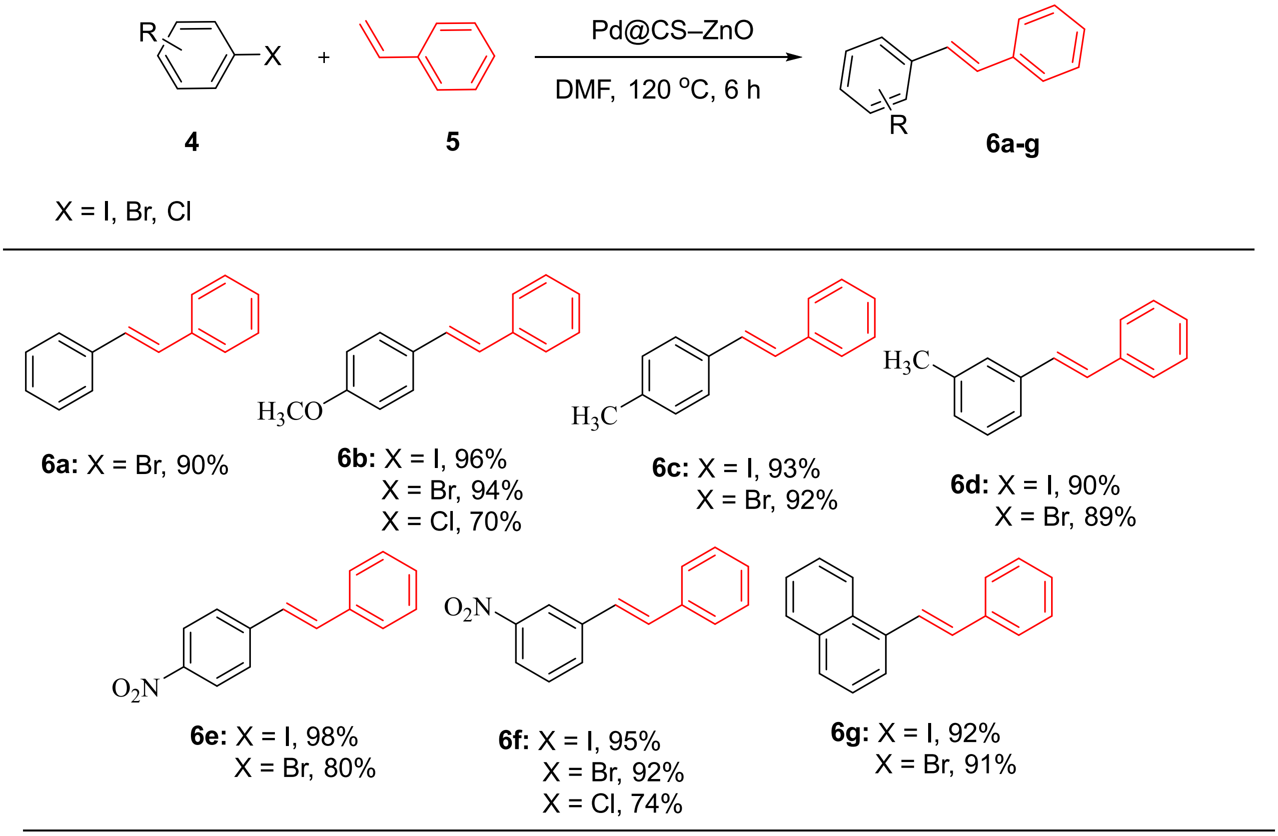
Scheme 1. Heck reaction of alkenes (**1**) with halobenzenes (**2**) catalyzed by PdNPs@EDTA-CS [82].

In a related study, Calistan et al. developed a novel palladium nanocatalyst (Pd@CS–ZnO) supported on chitosan and ZnO nanoparticles to enhance the efficiency and reusability of the Heck coupling reactions [83]. The study used 1-bromo-4-nitrobenzene as the substrate to determine optimal reaction conditions, reacting with styrene to optimize reaction parameters such as solvent choice, base system, reaction time, and catalyst amount. The optimal conditions identified were DMF as the solvent, K_2CO_3 as the base, a catalyst dosage of 30 mg of Pd@CS-ZnO, and a reaction time of 6 h. The catalyst was applied to the coupling reactions of various aryl halides (**4**) with styrene (**5**), achieving yields of 70–98% with high chemical stability, cost efficiency, and eco-friendliness (Scheme 2). Notably, the catalyst maintained a 91% yield after six cycles, highlighting its reusability. These findings suggest that Pd@CS-ZnO is a competitive candidate for enhanced cross-coupling catalysis, addressing the limitations of traditional homogeneous Pd catalysts, such as cost, toxicity, and separation difficulties, by being phosphine-free and supported on a solid matrix, thus making it more environmentally friendly and economically viable [83].

2.2. Palladium Nanoparticles Supported on Kenaf-Cellulose Modified with Poly(amidoxime) Ligands

Islam et al. developed a functionalized biopolymer palladium nanocatalyst (PdNc@PA) by embedding Pd nanoparticles in biodegradable kenaf-cellulose modified with poly(amidoxime) ligands [61]. This catalyst exhibited high efficiency in diverse cross-coupling reactions, including Mizoroki–Heck, Suzuki–Miyaura, and Hiyama reactions, consistently yielding excellent product conversion. Its structural integrity and well-distributed active sites contributed to prolonged catalytic activity over multiple cycles without significant performance deterioration. Moreover, leveraging biodegradable materials in catalyst design represents an environmentally conscious approach to Pd nanoparticle catalysis, aligning with green chemistry principles, while maintaining excellent reactivity.

A deeper exploration of the Suzuki–Miyaura reaction involving various arylboronic acids and aryl/heteroaryl chlorides revealed the efficacy of this catalyst for the synthesis of biaryl products **9a–r** (Scheme 3). Aryl and heteroaryl chlorides with phenylboronic acid yielded products **9a–d** in excellent yields. 4-Methoxyphenylboronic acid coupled with both activated and deactivated aryl chlorides yielding products **9e–j** (85–93%). Sterically hindered naphthylboronic acid yielded products **9k–o** in up to 92% yield. Notably, (*E*)-styrylboronic acid coupled with 4-chlorotoluene to furnish (*E*)-1-methyl-4-styrylbenzene **9p** in 84% yield. Mesitylboronic acid produced 2,5-dimesitylthiophene **9q** in 85% and dibenzo[b,d]furan-3-ylboronic acid with chlorobenzene yielded **9r** in 84% [61].



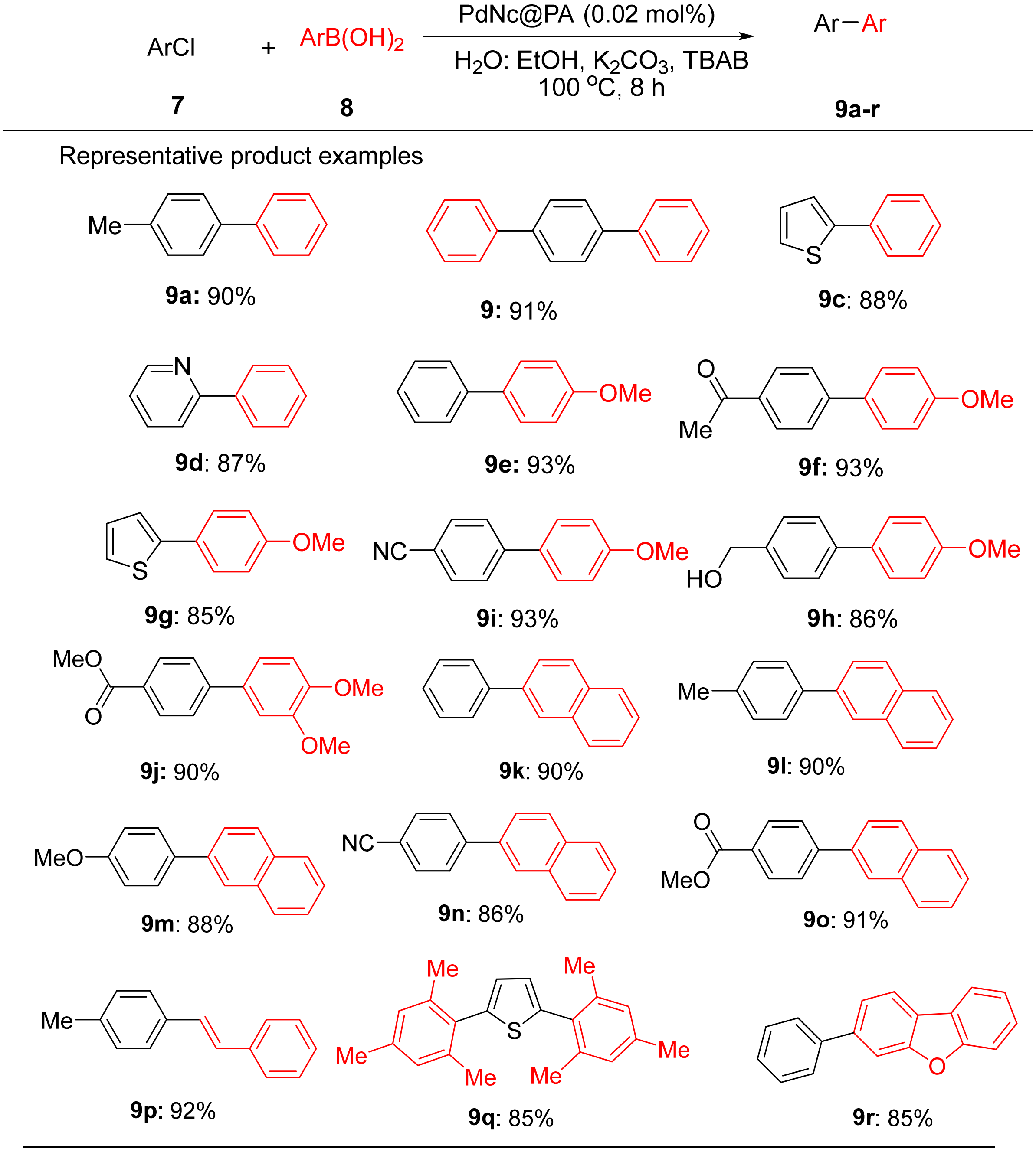
Scheme 2. Heck reaction of styrene and aryl halides catalyzed by Pd@CS–ZnO [83].

PdNc@PA was compared with other catalysts for Suzuki reactions. While catalysts such as Pd/MIL-101 (0.9 mol%, 97% yield) and Pd/WA30 (10 mol%, 100% yield) were effective, PdNc@PA achieved up to a 93% yield with a significantly lower loading (0.6–0.5 mol%), demonstrating superior catalytic efficiency [61]. PdNc@PA is a highly efficient catalyst for bond formation with minimal loading. Diagnostics, including hot filtration tests and ICP-AES analysis, confirmed that the reaction proceeded via a heterogeneous mechanism with no detectable leaching of the Pd species, ensuring the stability and reusability of the catalyst.

Similarly, the PdNc@PA catalyst demonstrated outstanding efficiency in the Heck–Matsuda reaction of chlorobenzene (**10**) with styrene and methyl acrylate (**11**) (Schemes 4 and 5). This system outperformed conventional catalysts, affording higher yields even at low catalytic loadings, further demonstrating its versatility.

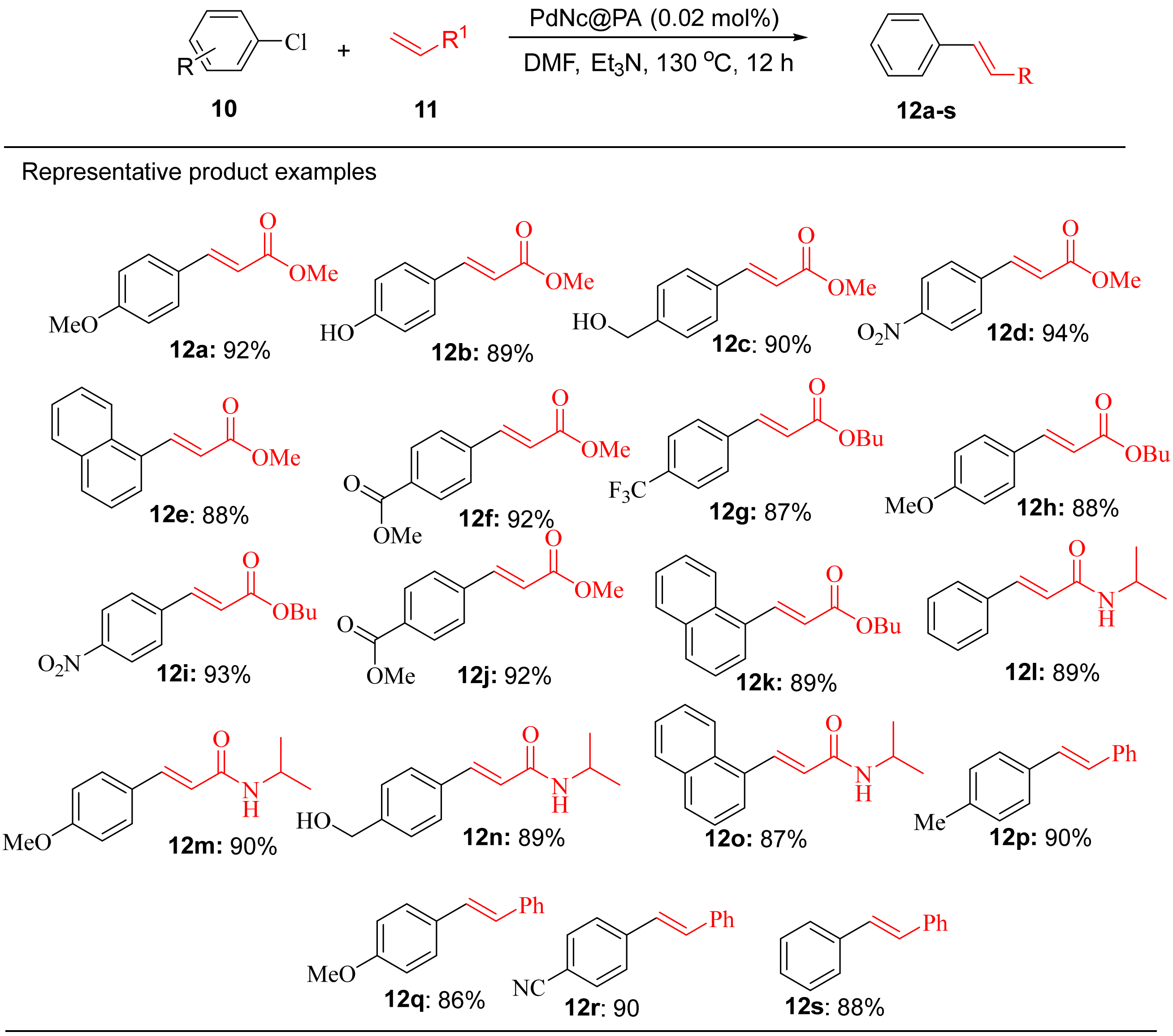
Recyclability studies of PdNc@PA in the Mizoroki–Heck and Suzuki–Miyaura reactions showed remarkable durability, with consistent catalytic performance over multiple cycles. Only a slight decline in efficiency was observed, primarily because of the minor losses during the decantation process [61].

The PdNc@PA catalyst also exhibited the Hiyama coupling of various aryl chlorides with organosilane reagents (Scheme 6). The organosilicon reagent triethoxy(4-methoxyphenyl)silane (**15**) was reacted with a variety of aryl chlorides (**10**) to give their respective biaryl derivatives (**16**) in yields of up to 91%. Interestingly, a heteroaryl chloride, 2-chlorothiophene, provided the cross-coupling product **9g** in 82% yield and readily coupled with triethoxy(phenyl)silane to afford the corresponding biaryl products **16a–h** in excellent yields. This operational simplicity and functional group tolerance broaden the scope of its application and further support its environmental and practical advantages.

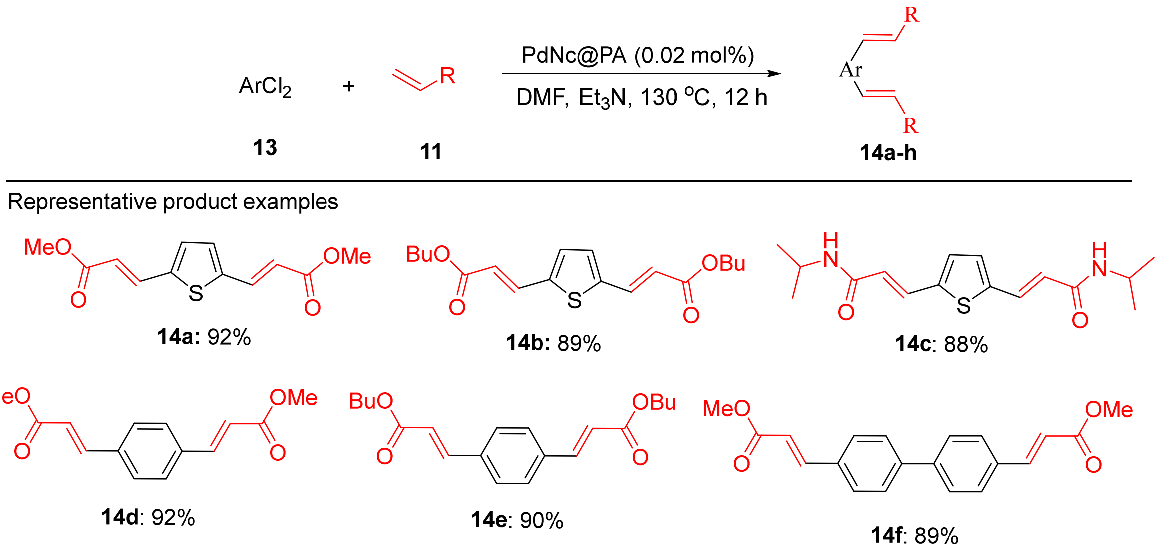


Scheme 3. Suzuki–Miyaura coupling of aryl chlorides with boronic acids catalyzed by PdNc@PA catalyst [61].

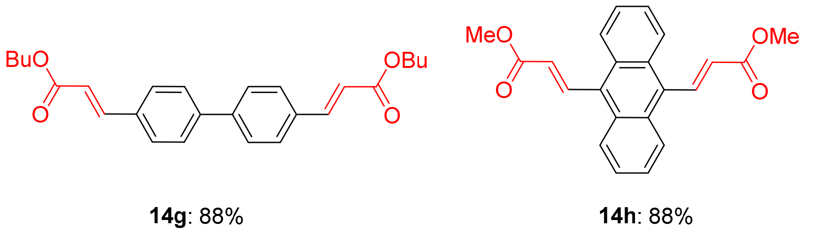
These results indicated that PdNc@PA is a powerful and sustainable catalyst for cross-coupling reactions that combines efficiency, reusability, and environmental benefits. Its versatility across a diverse range of substrates, along with its minimal environmental impact, makes it a promising tool for advancing green chemistry. Other catalysts using Pd supported on biopolymers have been reported in the literature [15,44,84].



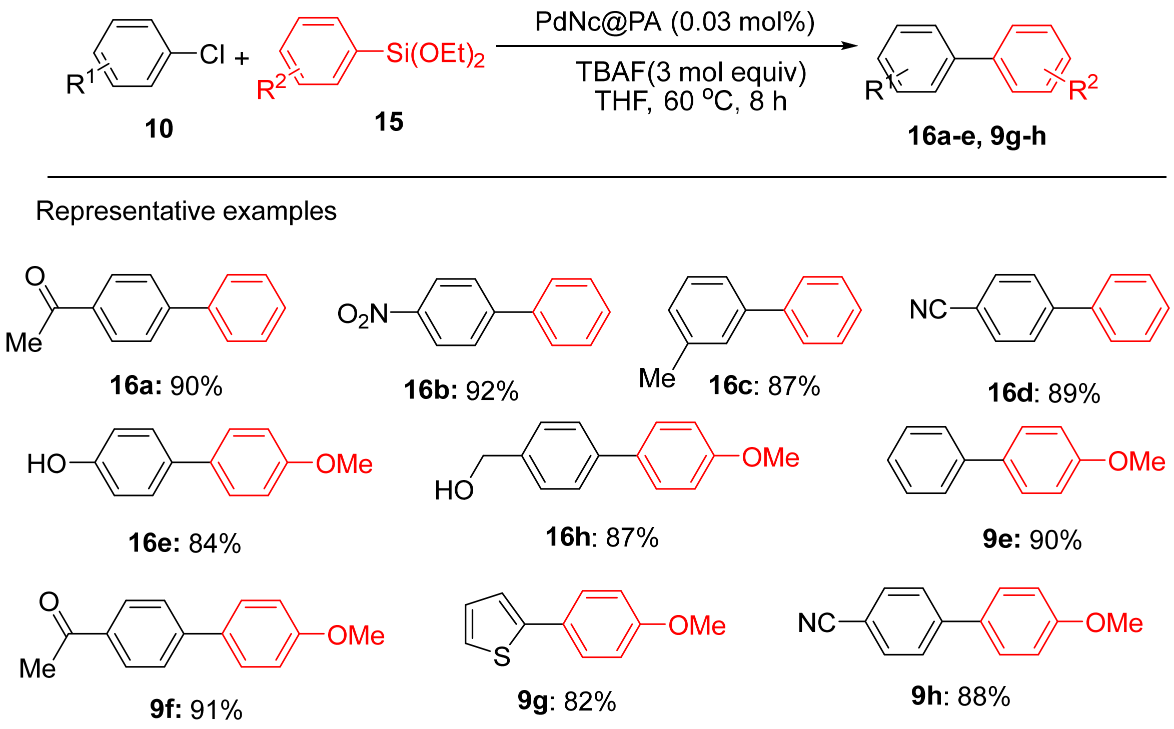
Scheme 4. Heck reaction of aryl halides with alkenes catalyzed by PdNc@PA catalyst [61].



Scheme 5. *Cont.*



Scheme 5. Heck coupling of disubstituted aryl chlorides with alkenes using PdNc@PA as a catalyst [61].



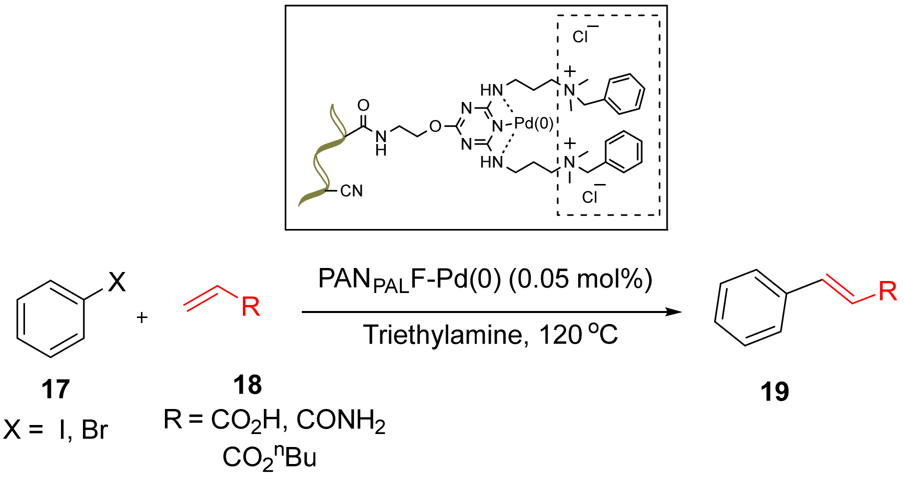
Scheme 6. Hiyama coupling of various aryl chlorides with organosilane reagents [61].

3. Palladium Nanoparticles Supported on Polymers

Polymers have emerged as versatile supports for nanoparticles owing to their tunable chemical structures, high surface areas, and ability to enhance nanoparticle dispersion and stability. Their functional groups facilitate strong metal coordination, reduce agglomeration, and improve catalytic efficiency [85,86]. Polymers provide a stabilizing environment that prevents metal nanoparticle aggregation and sintering, thereby extending the catalyst lifespan and improving reaction efficiency. Recently, using novel engineered polymers such as polyorganophosphazenes with an inorganic backbone [87], polyvinyl pyridines [86,88], fibers [86], and dendrimers [86,89,90] as supports has become increasingly popular. Several of these have been implicated in various cross-coupling reactions for chemical synthesis and industrial applications, and many have been reviewed previously [44]. Herein, we report on the most recent studies.

Palladium Nanoparticles Supported on Functionalized Polyacrylonitrile Fiber

Wu et al. [91] developed a cutting-edge aza-ligand-functionalized polyacrylonitrile fiber (PANPALF) as a support for Pd(0) nanoparticles. Functionalization of the fiber introduced amino groups and quaternary ammonium salt moieties, which facilitated strong chelation, effectively anchoring the Pd(0) nanoparticles to the polymer matrix. The in situ reduction process ensured uniform nanoparticle dispersion, preventing aggregation and enhancing catalytic accessibility, thereby improving the reaction efficiency. This innovative PANPALF-Pd(0) catalyst demonstrated exceptional performance in solvent-free Heck coupling reactions of terminal olefins, achieving yields of 43–99% (Scheme 7). The wide variation in yield can be attributed to the differences in substrate reactivity, steric hindrance, and catalytic efficiency under solvent-free conditions. Specifically, acrylic acid displayed slightly higher reactivity than acrylamide and *n*-butanol acrylate, suggesting that although no strong correlation was observed between olefin polarity and Heck reaction efficiency in this study, subtle solvent and catalyst interactions may still play an indirect role in modulating reactivity [91]. Similarly, the catalyst displayed a significantly higher turnover number (TON) of 89,000 for iodinated aromatics over brominated aromatics, which was attributed to the ease of C-I bond cleavage. Both the electron-donating and electron-withdrawing groups on the halogenated aromatics facilitated smooth reactions, highlighting the broad applicability of the catalyst.



Scheme 7. The Heck reaction of different substrates catalyzed by PANPALF-Pd(0) [91].

The PANPALFPd(0) system offers substantial advantages such as excellent catalytic activity, solvent-free operation, and extensive substrate compatibility. Remarkably, the catalyst retained a high yield of 93% even after 11 cycles of reuse, with minimal Pd leaching (0.075%), highlighting its stability and sustainable potential for industrial applications [91]. These findings highlight the effectiveness of synthetic polymer-supported palladium nanoparticles in enhancing the catalytic performance of cross-coupling reactions.

4. Palladium Nanoparticles Supported on Nitrogen-Doped Materials

The development of novel and efficient catalysts remains a cornerstone of research in heterogeneous catalysis, addressing the challenges in both fundamental science and industrial applications. Historically, carbon materials have been widely used as supports for catalysts because of their high surface areas, tunable porosities, and functional versatility [92]. Recently, nitrogen-doped carbon materials have emerged as revolutionary supports for palladium nanoparticles (PdNPs), offering enhanced catalytic performance through tailored electronic properties and robust metal-support interactions.

Nitrogen doping, in its essence, involves the incorporation of nitrogen atoms into the carbon backbone, whereas nitrogen functionalization typically refers to nitrogen atoms attached to the material's surface. In situ methods, such as the pyrolysis of nitrogen- and carbon-rich precursors, yield materials with nitrogen distributed both in the bulk and on the surface [93,94]. In contrast, post-treatment methods, such as ammonia pyrolysis, primarily result in surface nitrogen functionalities [95]. These variations in nitrogen placement influence the electronic properties and catalytic behavior of the material, tailoring its performance for specific reactions.

Nitrogen functionalities, including pyridinic, graphitic, and amine groups, significantly enhance PdNP stabilization, electron transfer, and metal-support interactions. This synergy not only improves the stability and efficiency of PdNPs but also broadens their applicability in catalytic processes [7,46,96]. Furthermore, N-doped supports address traditional challenges such as nanoparticle agglomeration, leaching, and low turnover frequencies, which are pivotal in the development of high-performance and sustainable catalytic systems [46,59].

Although nitrogen-doped materials have emerged as highly efficient supports for Pd nanoparticles (PdNPs), their synthesis and scalability remain significant challenges. Achieving uniform nitrogen doping requires precise control over the reaction conditions, as demonstrated in the synthesis of N-doped MXenes and graphene films, where parameters such as temperature, precursor selection, and reaction time critically influence nitrogen incorporation and catalytic performance [97,98]. Additionally, the introduction of excess nitrogen functionalities, such as pyridinic and graphitic nitrogen, can alter electronic properties, leading to unintended variations in catalytic behavior [99].

The cost and complexity of nitrogen-doped material synthesis also present limitations. Traditional high-temperature pyrolysis and prolonged reaction times contribute to increased production costs [100]. To counter this, low-temperature alternatives such as atmospheric-pressure plasma synthesis have been explored, offering a more energy-efficient and scalable solution [100]. However, ensuring the reproducibility and uniformity of nitrogen dispersion remains a concern in large-scale applications.

From a catalytic standpoint, while nitrogen doping enhances metal dispersion, electron transfer, and catalyst stability, balancing the nitrogen functionalities is important. A high concentration of pyridinic nitrogen is beneficial for active site formation, but an excess of graphitic nitrogen may reduce the surface availability of the reactants, affecting the reaction kinetics [101,102].

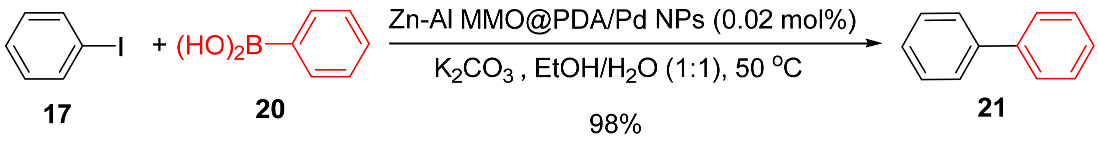
For industrial applications, nitrogen-doped materials have been explored for energy storage, CO_2 capture, and heterogeneous catalysis [97,103]. Although these materials enhance Pd nanoparticle dispersion and longevity, concerns such as catalyst leaching and deactivation over multiple reaction cycles remain [104].

To address these challenges, researchers are investigating alternative synthetic routes involving renewable precursors and low-energy fabrication techniques [100,101]. Furthermore, understanding the interplay between nitrogen configuration and catalytic efficiency is essential for designing next-generation cost-effective, high-performance nitrogen-doped supports. Balancing material stability, cost efficiency, and performance optimization is key to unlocking their full potential in sustainable catalysis.

These advancements highlight the transformative potential of N-doped materials in catalysis, bridging the gap between innovation and sustainability. In the following sections, we explore their role in addressing longstanding limitations and enabling new frontiers in PdNP-based catalysis.

4.1. Palladium Nanoparticles Supported on Polydopamine-Functionalized–Zn-Al Mixed Metal Oxides (Zn-Al MMO)

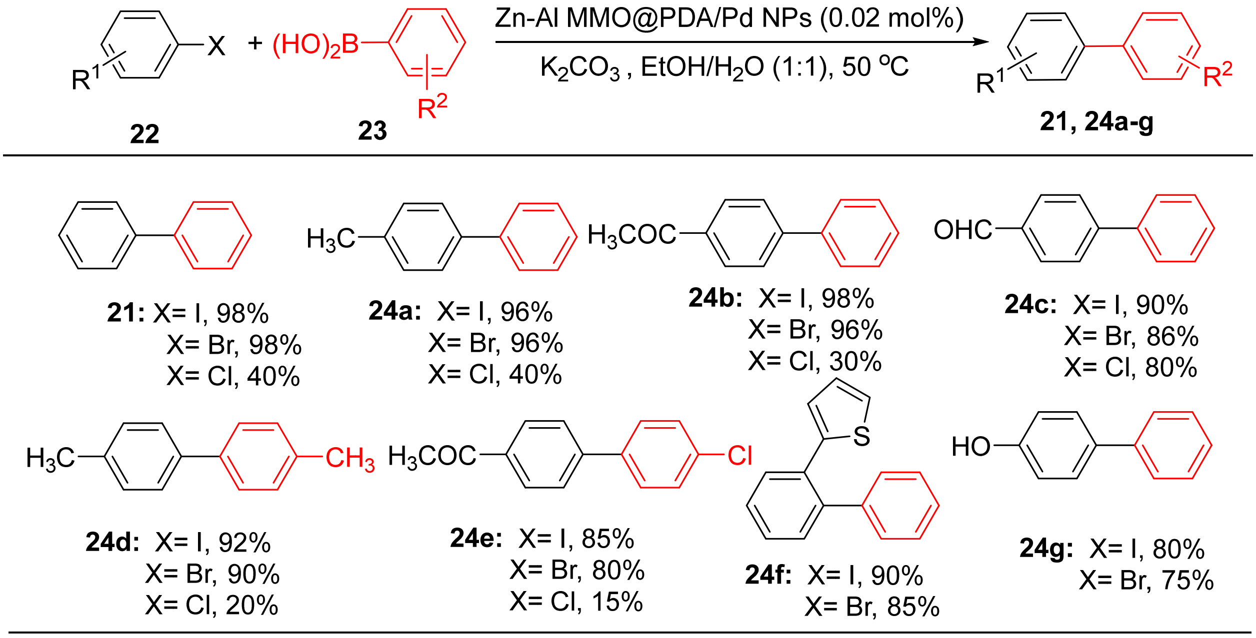
Joshani et al. synthesized a PdNP catalyst supported on polydopamine-functionalized Zn-Al MMO, demonstrating the use of polydopamine as a green stabilizing biotemplate [105]. This system afforded exceptional yields in the Suzuki–Miyaura coupling of a variety of substrates (Scheme 8). The reaction was optimized by screening different solvents such as H_2O, EtOH, DMF, toluene, and solvent mixtures, an additive base such as K_2CO_3, Et_3N, and Na_2CO_3, and the catalyst at a loading of 0.1–0.03 mol% Pd at a temperature of 50 °C. Interestingly, the probe reaction afforded the best conversion with an EtOH/H_2O (1:1) mixture as the solvent with 98% yield in just 1 h of reaction time at 0.02 mol% Pd catalyst loading, and with K_2CO_3 as the base (Scheme 8).



Scheme 8. Suzuki–Miyaura reaction of aryl halide with boronic acid catalyzed by palladium nanoparticles (PdNPs) immobilized on Zn-Al mixed metal oxides (Zn-Al MMO@PDA/PdNPs) [105].

The optimized reaction conditions were used to demonstrate the applicability and versatility of the catalysts across a wide variety of substrates. As seen with other systems, chloro was less reactive than bromo or iodo analogs because of the poor leaving capacity of Cl. Otherwise, all the reactions proceeded within 1–3 h, producing excellent yields, regardless of the nature of the organic substituents [105].

However, the electronic properties of the substituents played a notable role in modulating the reaction efficiency. Electron-donating groups, such as methyl (-CH_3), methoxy (-OCH_3), and hydroxyl (-OH), typically enhance the reactivity by increasing the electron density on the aromatic ring, facilitating oxidative addition. Conversely, electron-withdrawing groups such as acetyl (-$COCH_3$) and nitro (-NO_2) stabilize the transition state and reduce the reaction rate. This effect is particularly pronounced in Suzuki–Miyaura cross-coupling, where electronic effects significantly influence the oxidative addition efficiency and overall catalytic performance (Scheme 9) [105].



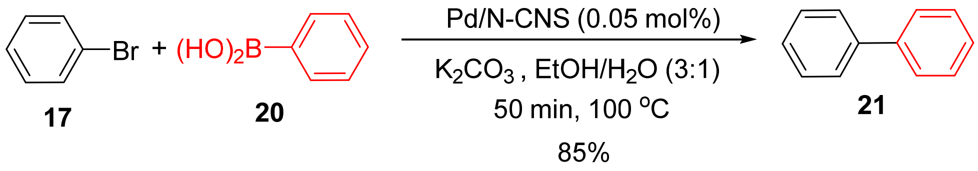
Scheme 9. Suzuki–Miyaura reaction of phenylbromide with phenylboronic acid catalyzed by palladium nanoparticles (PdNPs) immobilized on Zn-Al mixed metal oxides (Zn-Al MMO@PDA/PdNPs) [105].

This catalyst displayed remarkable durability and maintained its activity over eight cycles without any significant loss. Compared to Pd/N-CNS, the Zn-Al MMO system offered similar recyclability while accommodating sterically hindered substrates [105]. The developed Zn-Al MMO@PDA/PdNPs nanocatalyst was also investigated and found to outperform the previously published technique in terms of yield and reaction time when the optimized reaction conditions were used for the Suzuki–Miyaura coupling of 4-bromoanisole and phenyl boronic acid. Therefore, they concluded that the catalyst had remarkable reusability, maintaining activity over eight consecutive cycles, highlighting emerging trends in sustainable Pd nanoparticle applications for cross-coupling catalysis [105].

4.2. Palladium Nanoparticles Supported on 3D-Printed Silicon Oxycarbide (SiOC) Monoliths

Building on these advancements, Dory et al. developed a novel 3D-printed silicon oxycarbide monolith functionalized with PdNPs to further enhance catalytic performance using atomic layer deposition (ALD) [106]. This innovative methodology represents a significant advancement in heterogeneous catalysis, particularly for Suzuki–Miyaura reactions conducted in aqueous media. ALD enables precise control over Pd deposition, ensuring a uniform and well-distributed layer of PdNPs across the monolithic surface, which is important for achieving consistent and high catalytic activity.

The 3D-printed architecture of the SiOC monoliths provided a highly optimized catalytic environment, characterized by enhanced mass transfer and improved substrate accessibility. These structural features facilitate efficient interactions between the reactants and the active sites on the PdNPs, significantly improving their catalytic performance. This was demonstrated by achieving yields of up to 83% in the Suzuki–Miyaura coupling of iodobenzene with phenylboronic acid under aqueous conditions (Scheme 10).



Scheme 10. Suzuki–Miyaura cross-coupling of the bromobenzene with phenylboronic acid [106].

The monoliths also exhibited remarkable robustness and reusability, thereby addressing key challenges in sustainable catalysis. The precise and uniform deposition of PdNPs via ALD minimizes deactivation and leaching, ensuring a consistent catalytic efficiency over multiple reaction cycles. The Suzuki–Miyaura cross-coupling reaction, illustrated in Scheme 10, further highlights the efficacy of this system in promoting efficient organic transformations [106].

4.3. Palladium Nanoparticles Supported on Nitrogen-Doped Carbon Nanosheets (N-CNS)

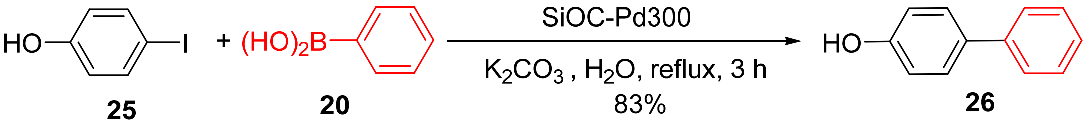
Palladium nanoparticles supported on nitrogen-rich carbon nanosheets (Pd/N-CNS) represent a significant advancement in heterogeneous catalysis, particularly in Suzuki cross-coupling reactions. Using an intercalation templating strategy, Cui et al. synthesized two-dimensional nitrogen-rich carbon nanosheets (N-CNSs) derived from petroleum asphalt [59]. These carbon nanosheets were enriched with pyridinic nitrogen species and served as robust supports for palladium nanoparticles by enhancing metal-support interactions and stabilizing the nanoparticles [59]. This nitrogen-rich environment also improves the dispersibility of palladium, which is necessary for achieving high catalytic performance.

The Pd/N-CNS catalyst achieved an impressive turnover frequency (TOF) of 2390 h^6 under mild conditions for Suzuki cross-coupling reactions, representing a nearly ninefold increase in activity compared to commercial Pd/C catalysts. It also maintained high activity over five consecutive reaction cycles, with a TOF of 2294 h^{-1}, demonstrating exceptional stability and reusability [59]. Theoretical insights have attributed the enhanced performance to efficient electron transfer facilitated by the high density of the pyridinic nitrogen species.

The presence of pyridinic nitrogen species plays an important role in enhancing the dispersion of Pd nanoparticles and the catalytic efficiency. Pyridinic nitrogen atoms coordinate with palladium, stabilizing the nanoparticles and preventing agglomeration, which ensures a uniform distribution essential for maximizing the catalytic activity [59]. Furthermore, the high density of pyridinic nitrogen species facilitates efficient electron transfer between the Pd nanoparticles and the support, strengthening the metal-support bonding and promoting the reactant conversion [59]. The presence of these nitrogen species also modifies the electronic environment around Pd, making it more reactive in catalytic cycles, such as oxidative addition and reductive elimination.

The remarkable performance of Pd/N-CNS is attributed to the high nitrogen doping, which stabilizes palladium nanoparticles and enhances electron density, thereby improving catalytic efficiency. The unique two-dimensional structure of carbon nanosheets facilitates better mass transfer, ensuring that reactants can access active sites more efficiently than conventional porous carbon materials [59]. Additionally, the strong metal anchoring effect of pyridinic nitrogen prevents palladium leaching and maintains catalyst integrity over multiple reaction cycles.

In practical applications, the Pd/N-CNS catalyst maintained a high TOF of 2294 h^6 even after five consecutive reaction cycles, demonstrating exceptional stability and reusability [59]. The catalyst's effectiveness was further validated in the Suzuki cross-coupling reaction between bromobenzene and phenylboronic acid (Scheme 11), where it achieved a significantly higher conversion rate of 85% compared to the other support systems [59].



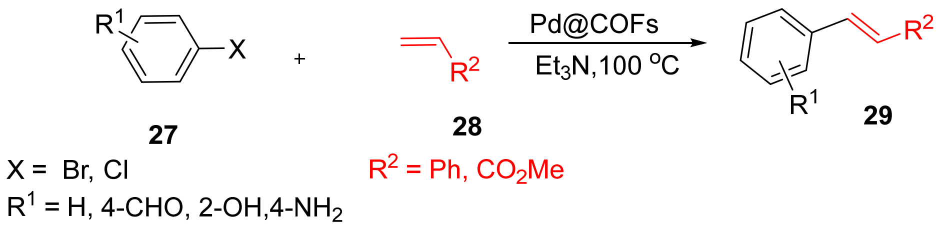
Scheme 11. Suzuki–Miyaura cross-coupling of the iodobenzene with phenylboronic acid [59].

These findings highlight the synergistic effect of pyridinic nitrogen species and nanostructured supports, positioning Pd/N-CNS as a leading catalyst for sustainable and high-efficiency cross-coupling reactions.

4.4. Palladium Nanocrystals-Embedded Covalent Organic Framework (Pd@COF)

Abdulah et al. demonstrated the potential of palladium nanocrystals (Pd NCs) embedded in covalent organic frameworks (COFs) as highly efficient heterogeneous catalysts for carbon–carbon (C–C) cross-coupling reactions, particularly Heck reactions [107]. The versatility of Pd NCs@COFs for sustainable catalysis has been highlighted in recent studies [108–111]. Pd NCs were synthesized in situ within COFs via a solvothermal method using tricarboxylic acids such as 2,4,6-tri-p-carboxyphenylpyridine (H_3L2), 4,4′,4′-tri carboxyl triphenylamine (H_3L1), 1,3,5-benzenetricarboxylic acid (H_3BTC), and 1,3,5-triazine-2,4,6-triamine moieties. This approach yielded Pd NCs@COFs with particle sizes ranging from 1 nm to 5 nm, ensuring excellent catalytic performance [107].

The catalytic efficacy of the Pd NCs@COFs was demonstrated by the Heck reaction (Scheme 12), where vinyl derivatives reacted with aryl halides in the presence of trimethylamine as a base. Using only 5 mol.% of Pd NCs@COFs, complete conversion (100%) was achieved under mild reaction conditions. Various substrates, including chloro- and bromobenzene derivatives, were successfully employed both with and without functional groups, such as formyl (CHO), hydroxyl (O–H), and amine (NH_2). Vinyl derivatives such as styrene and methyl acrylate also exhibited excellent conversions, highlighting the versatility of the catalyst.



Scheme 12. Heck reaction of aryl halides with vinyl derivatives catalyzed by Pd NCs@COFs [107].

A notable advantage of Pd NCs@COFs is their exceptional recyclability, which was investigated under identical reaction conditions over multiple catalytic cycles. Even after the fourth cycle, the catalyst retained over 95% conversion, with no observable palladium leaching, as confirmed by ^{1}H NMR spectroscopy [107]. The solid catalyst can be easily separated via filtration or centrifugation, washed with ethanol, and reused without significant loss of performance. This stability is attributed to the nitrogen-rich framework of the COFs, which enhances the stabilization of the Pd nanocrystals and prevents their agglomeration [109].

The straightforward synthesis of the Pd NCs@COFs further underscores their practical applicability. The addition of Pd salts to COFs facilitated the coordination of Pd^{2+} ions, followed by in situ reduction to Pd^0, resulting in a robust and efficient catalyst. The high stability and consistent performance of the Pd NCs@COFs make them excellent candidates for sustainable catalysis, in alignment with green chemistry principles [112].

The innovative design and synthesis of Pd NCs@COFs represent a significant advancement in cross-coupling catalysis. By combining exceptional catalytic performance, recyclability, and environmental compatibility, Pd NCs@COFs provide a powerful platform for eco-friendly chemical processes, underscoring their potential as next-generation catalysts for organic synthesis [107].

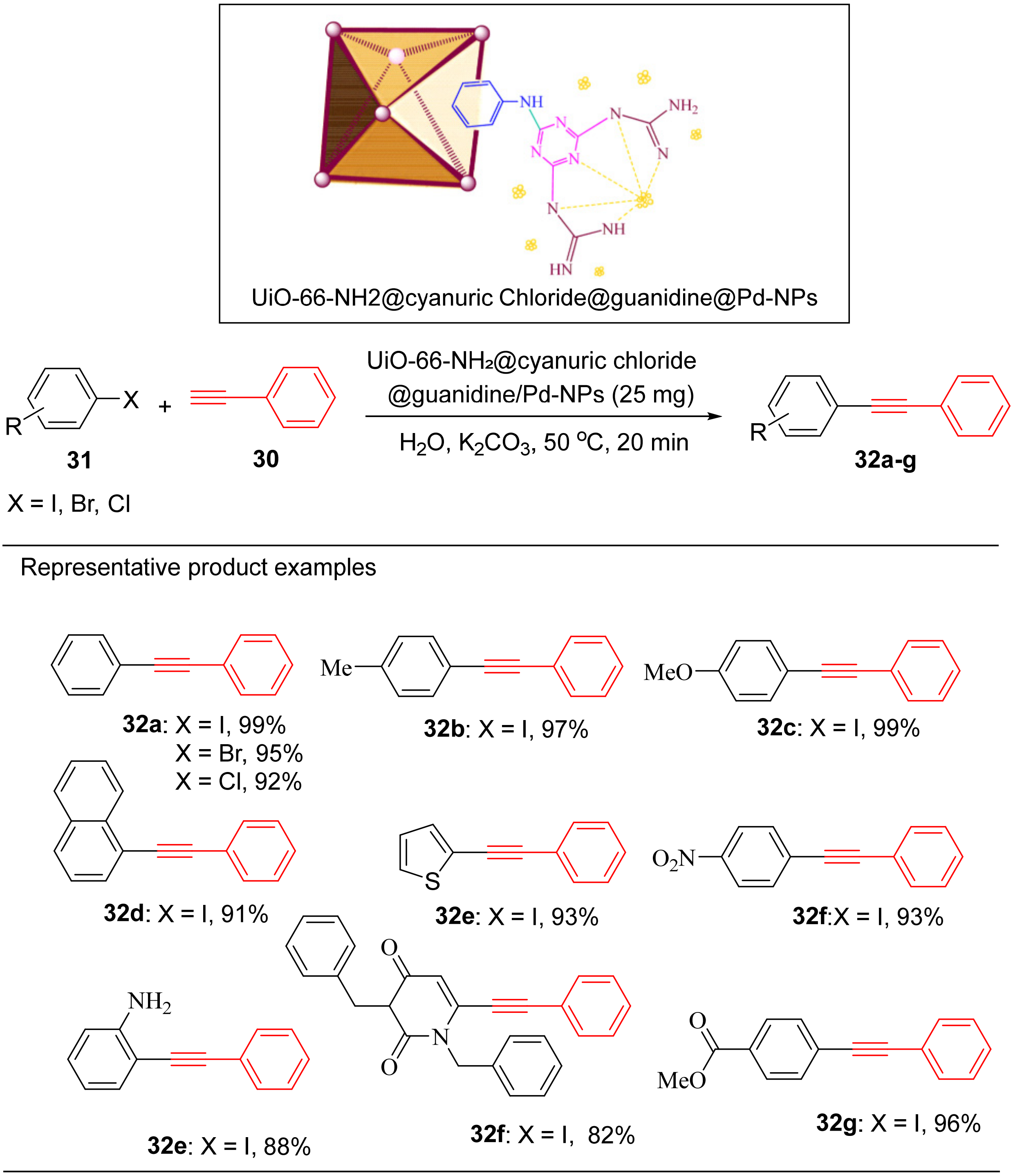
4.5. Palladium Nanoparticle-Decorated Porous Metal–Organic-Framework (Zr)@Guanidine

Metal–organic frameworks (MOFs) have emerged as exceptional supports for immobilizing palladium nanoparticles (PdNPs) in recent decades, significantly enhancing their catalytic activity and stability [113,114]. MOFs have garnered considerable attention for catalytic C–C coupling reactions owing to their unique properties, including their extensive surface area, highly ordered structures, adjustable pore sizes, uniformly distributed metal nodes, and excellent chemical modifiability [10,92]. Among these, UiO-66-NH_2, a zirconium-terephthalate MOF is particularly noteworthy because of its remarkable chemical, thermal, and mechanical stability, intrinsic open metal sites, large surface area, and amino group functionalities, making it an excellent candidate for post-synthetic functionalization [115,116].

Mohammadi and Vaezi developed UiO-66-NH_2 functionalized with cyanuric chloride and guanidine, nitrogen-rich organic ligands, via a post-synthetic modification (PSM) approach [117]. The guanidine moiety, with its amino functionalities, acted as a robust binding center, modifying the electronic structure of UiO-66-NH_2 and effectively immobilizing Pd^{2+} ions. These ions were subsequently reduced to Pd^0, resulting in the uniform dispersion of PdNPs across the MOF. This innovative design enhanced the catalyst's stability and efficiency, particularly in aqueous environments, due to the strong coordination between the Zr_6 cluster secondary building units (SBUs) and the nitrogen-rich linker [118–124].

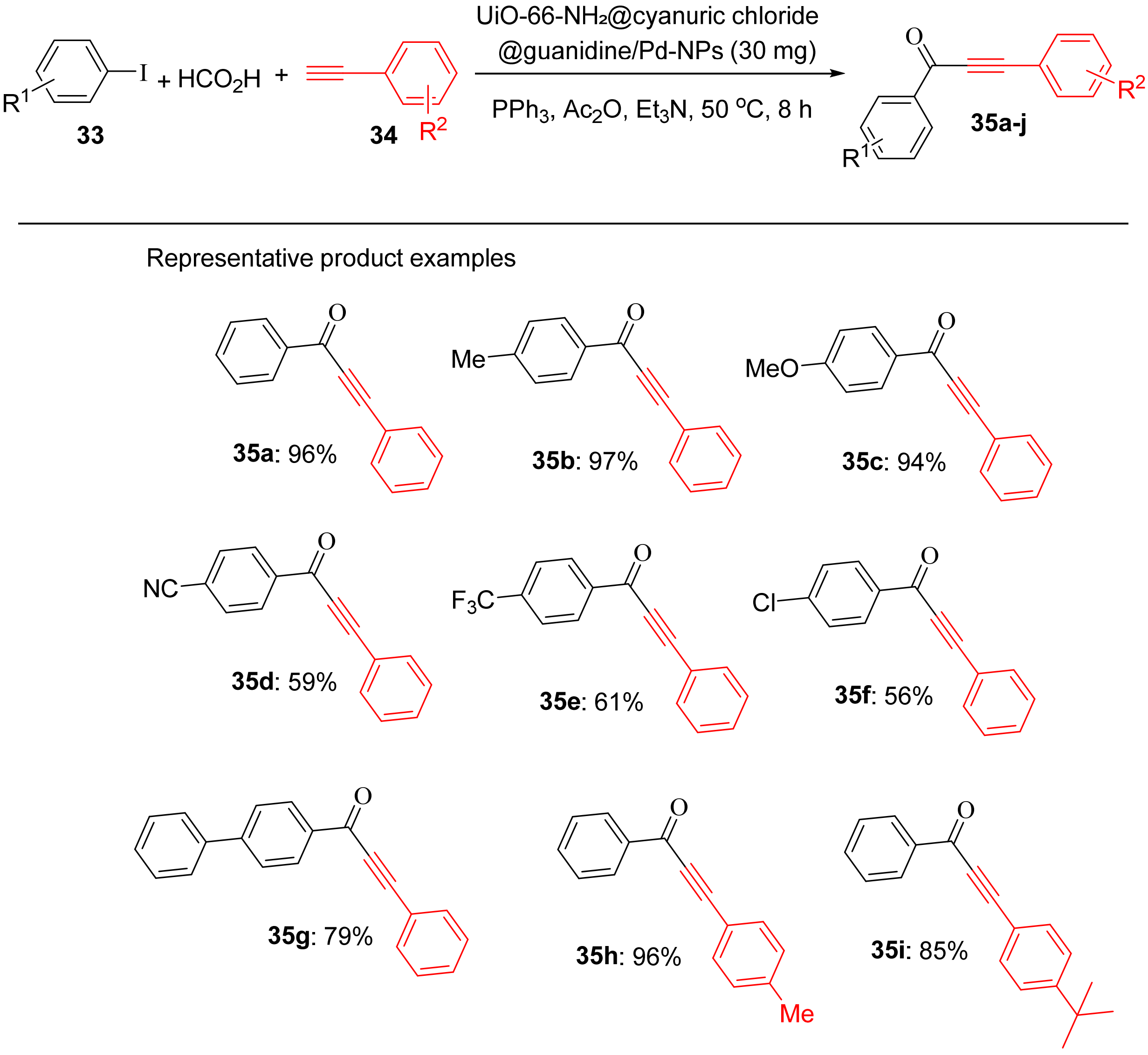
The catalytic efficacy of UiO-66-NH_2@cyanuric chloride@guanidine/Pd-NPs was thoroughly investigated in the Suzuki, Heck, and Sonogashira cross-coupling reactions [117].

The reaction conditions were optimized via the reaction of iodobenzene and phenylacetylene with UiO-66-NH2@cyanuric chloride/guanidine/Pd-NPs (Scheme 13). The optimal reaction conditions were then applied to Sonogashira reactions of diverse aryl halides and terminal alkynes to afford diverse organic compounds in high yields (Scheme 13).



Scheme 13. Sonogashira reaction of iodobenzene with phenylacetylene catalyzed by UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs [117].

The synthesized catalyst was highly efficient and widely applicable, as demonstrated by its ability to catalyze Sonogashira coupling in the presence of iodine, bromine, and chlorine derivatives of aromatic compounds. Moreover, the catalyst was efficient for the Sonogashira carbonylative reaction (Scheme 14).

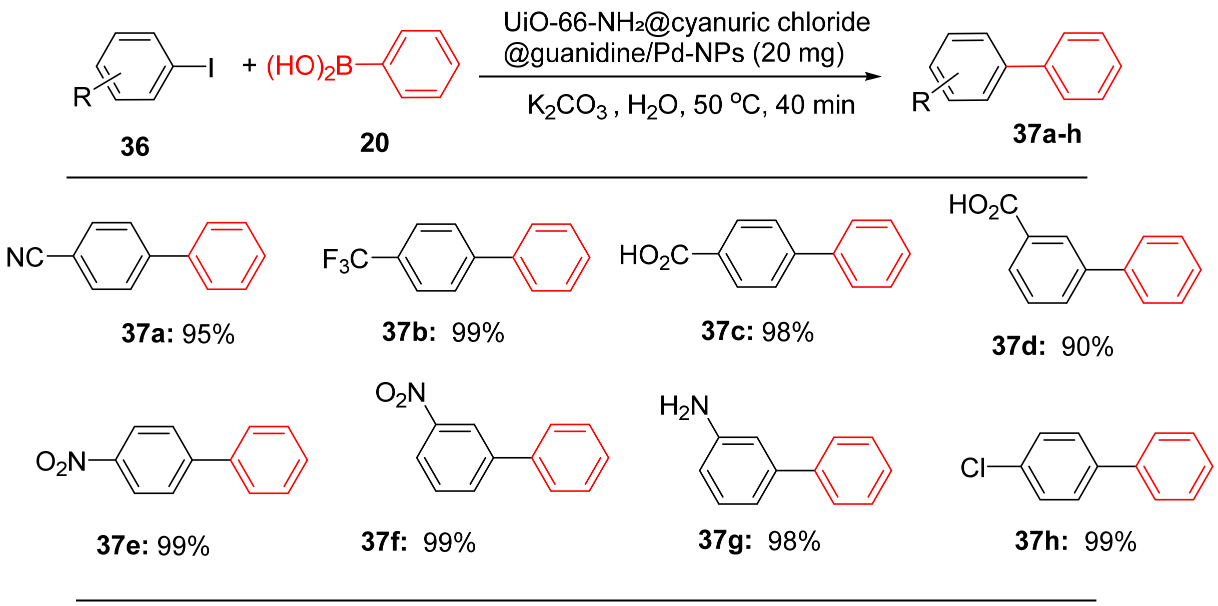


Scheme 14. Sonogashira carbonylation reaction of iodobenzene with phenylacetylene using UiO-66-NH_2@cyanuric chloride@guanidine/Pd-NPs catalyst [117].

For the Suzuki reaction, iodobenzene was reacted with boronic acids efficiently in water, and the optimum conditions (20 mg of catalyst in the presence of K_2CO_3 at 50 °C and a reaction time of 40 min) were applied to afford some of these representative compounds (Scheme 15).

Similarly, the catalyst was also efficient in the Heck reaction involving halobenzene and various alkenes under the same conditions, affording high product yields within 2 h using 30 mg of the catalyst (7.28%wt palladium loading) [117]. These results demonstrate the broad substrate compatibility, high selectivity, and exceptional efficiency of this catalyst for diverse C–C coupling reactions. In addition, the catalyst exhibits outstanding performance in carbonylative Sonogashira reactions under mild conditions, further demonstrating its versatility.

A significant feature of UiO-66-NH_2@cyanuric chloride@guanidine/Pd-NPs was their exceptional recyclability and stability. The catalyst retained over 85% of its initial activity after nine consecutive cycles, with no significant loss in efficiency or Pd leaching observed during the reactions. This durability is attributed to the robust nitrogen-rich framework provided by guanidine and the structural integrity of UiO-66-NH_2. The straightforward synthesis and functionalization of the catalyst further enhanced its scalability and practicality for industrial applications.



Scheme 15. Suzuki–Miyaura reaction of phenyliodides with phenylboronic acid catalyzed by using UiO-66-NH_2@cyanuric chloride@guanidine/Pd-NPs catalyst [117].

The UiO-66-NH_2@cyanuric chloride@guanidine/Pd-NP catalyst represents a significant advancement in heterogeneous catalysis owing to its excellent catalytic performance, sustainability, and recyclability. Its ability to operate in water as a green solvent and its compatibility with various substrates underscore its potential for eco-friendly organic synthesis. With the continued advancements in the synthesis, stability, and catalytic applications of MOF-supported PdNPs, this study highlights a promising platform for green and sustainable chemistry.

5. Palladium Nanoparticles Supported on Functionalized Synthetic Material

The immobilization of palladium nanoparticles (PdNPs) on non-polymeric synthetic materials offers an innovative approach to catalysis that combines enhanced stability, reusability, and efficiency with green chemistry principles. Synthetic supports, such as boehmite nanoparticles, polydimethylsiloxane (PDMS) films, amphiphilic frameworks, and surfactant-based systems, provide robust platforms for stabilizing PdNPs, preventing leaching, and optimizing catalytic performance in demanding applications [125–127]. Similarly, boehmite-supported PdNPs provide excellent porosity and thermal stability, contributing to catalyst longevity in industrial applications [125]. The high surface area and porosity of boehmite facilitate enhanced PdNP dispersion by providing abundant anchoring sites that prevent nanoparticle aggregation [125]. Additionally, its strong chemical affinity with PdNPs arises from the surface hydroxyl groups, which stabilize the nanoparticles and promote efficient catalytic activity in cross-coupling and hydrogenation reactions [125]. These materials create precisely tuned environments for PdNPs, facilitating superior activity and selectivity in key transformations such as Suzuki–Miyaura, Heck, and Sonogashira couplings, while ensuring recyclability and minimal environmental impact [10,46].

Each type of synthetic support has unique advantages in catalytic systems. For example, functionalized boehmite nanoparticles enhance the catalytic stability in environmentally friendly solvents, such as PEG-400, while minimizing palladium leaching [125]. PDMS films improve the dispersion and durability of PdNPs, enabling efficient C–C coupling and pollutant reduction under mild conditions [126]. Additionally, PdNPs supported on micellar structures provide a versatile platform for advanced cross-coupling reactions [128], whereas chiral surfactants offer novel opportunities for asymmetric catalysis, with a reduced reliance on toxic ligands and solvents [127]. Together, these systems illustrate the transformative potential of functionalized synthetic materials for advanced PdNP-based catalysis.

The use of functionalized PDMS and boehmite as PdNP catalysts has drawn significant attention owing to their stability and reusability, making them highly valuable for industrial applications, particularly in the pharmaceutical and petrochemical sectors [61,129]. However, these materials also pose challenges related to synthesis complexity, scalability, and cost. Functionalized PdNP-based catalysts are widely employed in C-C coupling reactions for the synthesis of active pharmaceutical ingredients (APIs) and hydrocarbon transformations, such as hydrocracking and selective hydrogenation.

Despite the complexity of their synthesis, PDMS-supported PdNPs offer hydrophilicity and strong anchoring sites for the catalytic processes. The intrinsic hydrophobicity of PDMS films influences substrate interactions by enhancing their compatibility with organic reactants in cross-coupling reactions. This property facilitates the selective adsorption of non-polar molecules while repelling aqueous contaminants, thereby improving the catalyst efficiency in organic phase reactions [130]. Modified PDMS surfaces, such as those treated with atmospheric-pressure atomic layer deposition (AP-ALD), can maintain their hydrophilicity over time, providing stable and strong anchoring sites for catalytic nanoparticles such as PdNPs, which is crucial for long-term catalytic efficiency [131]. Despite these modifications, the hydrophobic recovery of PDMS remains a challenge, requiring ongoing research on more durable and effective modification techniques [132].

However, the synthesis of PDMS-supported PdNPs often requires complex surface modifications, including atmospheric pressure atomic layer deposition (AP-ALD), to enhance solvent resistance and nanoparticle stability, significantly increasing production costs and processing time [131]. Nevertheless, PDMS-supported PdNPs remain a preferred choice for biosensing and high-performance catalytic applications because of their ability to immobilize nanoparticles effectively, improving the reaction efficiency and recyclability [131].

Similarly, boehmite-supported PdNPs provide excellent porosity and thermal stability, which contribute to the longevity of the catalyst in industrial applications. However, achieving optimal porosity requires precise thermal treatment, making large-scale synthesis challenging [125]. Boehmite-supported PdNP catalysts have demonstrated high efficiency in cross-coupling reactions, as observed for Pd-adenine@boehmite, which maintained catalytic activity after multiple reaction cycles [133]. Functionalization strategies, such as the use of tannic acid, have further enhanced the hydrogenation efficiency of PdNPs, demonstrating superior catalytic activity compared with non-functionalized boehmite supports [134].

In the pharmaceutical industry, PdNP-based catalysts play a critical role in C-C coupling reactions, contributing to the efficient synthesis of APIs used for antiviral and anticancer drugs. Their stability and recyclability significantly improve the sustainability of the process by reducing metal leaching and waste generation [61]. In the petrochemical industry, functionalized PdNPs are employed in hydrocarbon transformations because of their resistance to harsh reaction conditions and high durability, which lowers operational costs by extending catalyst lifetimes [129].

Despite the clear advantages of functionalized PDMS and boehmite supports, their scalability remains a challenge owing to the complexity of their synthesis and cost constraints. Advancements in functionalization techniques and the integration of bio-derived heterogeneous Pd nanocatalysts provide promising cost-effective and sustainable alternatives, enhancing the applicability of PdNP-based catalysts in large-scale industrial settings [61].

This section explores the latest advancements in these synthetic supports, highlighting their contribution to enhancing the stability, sustainability, and efficiency of PdNPs across diverse applications.

5.1. Palladium Nanoparticles Supported on Boehmite Nanoparticles (Pd(0)-SMTU-Boehmite)

Palladium nanoparticles (PdNPs) supported on boehmite, a hydrated aluminum oxide, have gained prominence because of their remarkable thermal stability and their ability to enhance nanoparticle dispersion [135,136]. These attributes make it an excellent candidate for various catalytic applications, particularly in C–C coupling reactions and other industrial processes. The high surface area and mesoporous structure of boehmite provide an optimal environment for catalytic activity, as has been demonstrated in numerous studies [134,137].

In a notable study, Hajighasemi et al. synthesized palladium complex-supported boehmite nanoparticles (Pd(0)-SMTU-boehmite) and successfully applied them to Mizoroki–Heck and Suzuki–Miyaura C–C coupling reactions. The coupling of iodobenzene with butyl acrylate under optimized conditions of temperature, catalyst loading, base, and solvent demonstrated the versatility and efficiency of Pd(0)-SMTU-boehmite for carbon–carbon bond formation [125]. Iodobenzene was first coupled with butyl acrylate under different operating conditions, including temperature, amount of catalyst, base, and solvent, and the optimum conditions were applied to the coupling of different aryl halides **38** (Scheme 16). This catalyst exhibited broad applicability to various aryl halides and maintained excellent activity under mild reaction conditions.

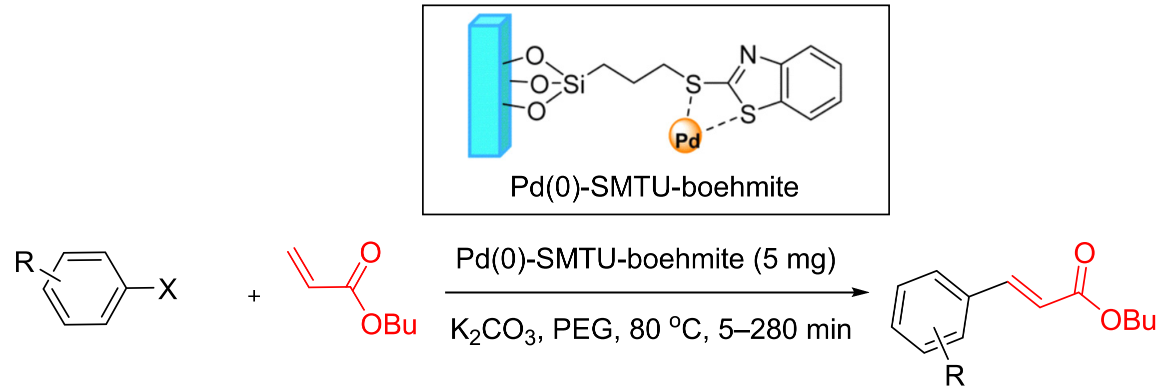
The authors also explored the reactivity of the catalyst in the Suzuki–Miyaura cross-coupling reaction to expand the application of the catalyst in biaryl synthesis through the reaction of various types of aryl halides **38** under the optimum reaction conditions (Scheme 17).

These reactions were conducted under environmentally benign conditions, highlighting the role of this catalyst in advancing green chemistry. Importantly, the catalyst demonstrated excellent recyclability, retaining its activity over multiple cycles with negligible Pd leaching, as verified through ICP-OES and hot filtration tests [125,138].

The robustness of boehmite-supported palladium catalysts also extends to high-temperature applications such as selective oxidation and hydrogenation reactions, where they provide stable and efficient platforms for catalytic transformations [134,135]. Despite these advantages, challenges in preparing and modifying boehmite surfaces remain, necessitating further research to maximize their catalytic potential. Nevertheless, the outstanding performance of Pd(0)-SMTU-boehmite in cross-coupling reactions underscores its critical role in the development of sustainable catalytic technologies.

5.2. Palladium Nanoparticles Supported on Micellular Structures

Palladium nanoparticles (PdNPs) supported on micellar structures represent a significant advancement in catalytic technologies, particularly for cross-coupling reactions such as the Suzuki–Miyaura reaction. The amphiphilic architecture of micelles provides a unique aqueous environment that enhances the catalytic efficiency, stability, and recyclability of the PdNPs. This approach aligns with green chemistry principles, leveraging water as a solvent while reducing reliance on hazardous organic reagents. Among these systems, poly(2-(dimethylamino)ethyl methacrylate)-*b*-poly(lauryl methacrylate) (PDMAEMA-*b*-PLMA) micelles have demonstrated exceptional performance, achieving yields of 73–98% at room temperature with as little as 0.05 mol% Pd loading without requiring additional ligands [128,139]. This stability is further enhanced by the micellar framework, which prevents the agglomeration of PdNPs and enables multiple catalyst reuse cycles with minimal activity loss [128,139].

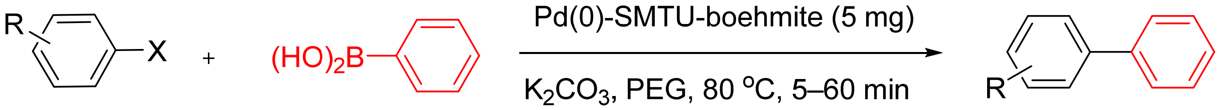


38 **39**

X = I, Br, Cl
R = H, CH_3, OCH_3, Cl, CN, NO_2

40a: R = H, X = I, >99%
40b: R = 2-CH_3, X = I, 95%
40a: R = 4-CH_3, X = I, 95%
40c: R = 2-OCH_3, X = I, 95%
40d: R = 4-OCH_3, X = I, 97%
40e: R = H, X = Br, 15%
40f: R = 4-CH_3, X = Br, 70%
40g: R = H, X = Cl, 15%
40h: R = 4-Cl, X = I, 90%
40i: R = 4-CN, X = Br, 94%
40j: R = 4-NO_2, X = I, 92%

Scheme 16. Heck reaction catalyzed by Pd(0)-SMTU-boehmite [125].



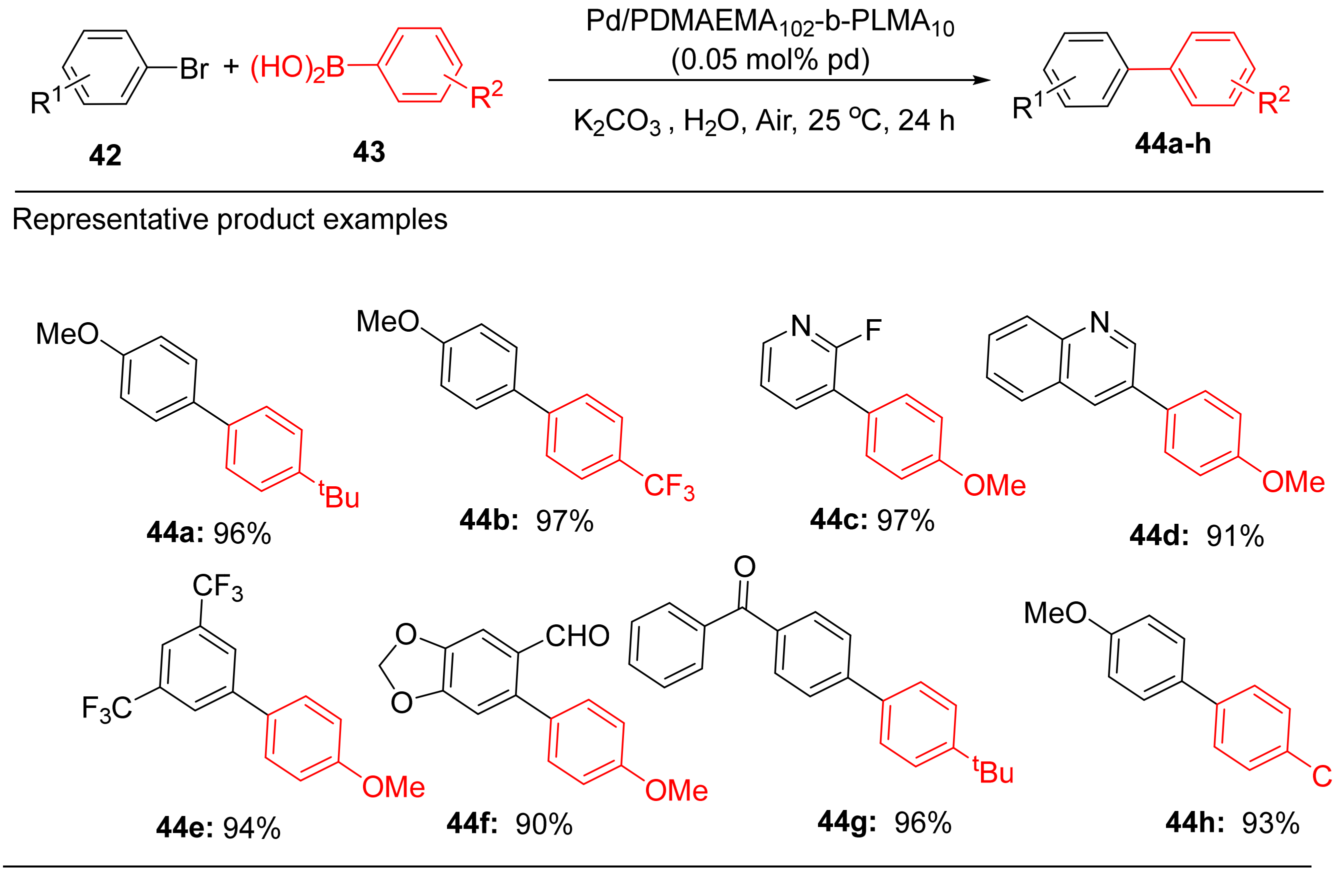
38 **20**

X = I, Br, Cl
R = H, CH_3, OCH_3, Cl, CN

41a: R = H, X = I, >99%
41b: R = H, X = I, >99%
41c: R = H, X = Cl, 30%
41d: R = 4-CH_3, X = I, >99%
41e: R = 4-CH_3, X = Br, >99%
41f: R = 2-CH_3, X = I, 92%
41g: R = 2-OCH_3, X = I, 90%
41h: R = 4-Cl, X = I, 90%
41i: R = 4-CN, X = Br, 94%

Scheme 17. Suzuki–Miyaura coupling reaction catalyzed by Pd(0)-SMTU-boehmite [125].

The structural properties of the micelles are critical for determining their catalytic performance. Increasing the hydrophilic PDMAEMA segment significantly improved the efficiency, whereas increasing the hydrophobic PLMA content diminished the activity. Pd/PDMAEMA102-*b*-PLMA10, with an optimized Pd:N ratio of 1:10, consistently demonstrated greater than 99% yield in Suzuki–Miyaura cross-coupling reactions [91]. Conversely, lower Pd:N ratios, such as 1:30, led to reduced catalytic activity, which was attributed to insufficient stabilization of PdNPs, resulting in larger, less reactive particles. These micellar systems also exhibited broad substrate compatibility, efficiently coupling electron-rich and electron-poor aryl bromides, including challenging ortho-substituted derivatives. Functionalized arylboronic acids, bulky substituents, and pharmaceutically relevant scaffolds such as pyridyl and quinolinyl derivatives were successfully transformed, highlighting the versatility of these catalysts (Scheme 18) [91].

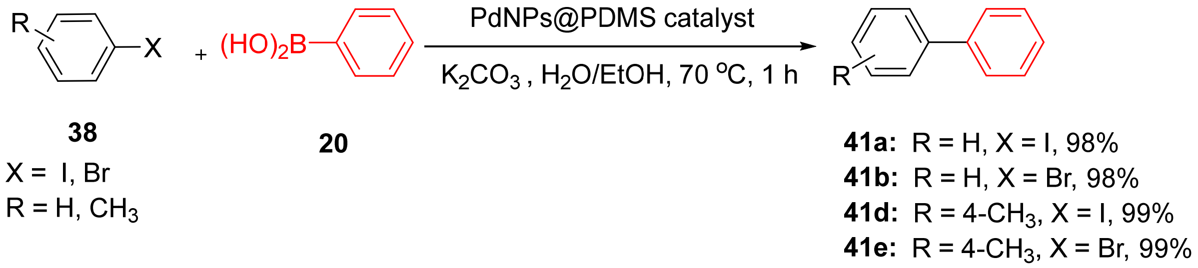


Scheme 18. Suzuki–Miyaura cross-coupling reactions in water catalyzed by Pd/PDMAEMA-*b*-PLMA [91].

Mechanistically, micelles act as nanoreactors, providing a confined space that enhances solubilization and electron transfer between the PdNPs and reactants, thereby optimizing the reaction rates and selectivity. The synergistic interactions between the PdNPs and the micellar framework create a favorable microenvironment for efficient catalytic transformations [139,140]. Despite these promising attributes, challenges remain in scaling these systems for industrial applications. Micelle degradation over extended use and substrate compatibility with aqueous systems require further research. Nonetheless, the continued development of robust micellar designs and innovative surfactants offers the potential to overcome these limitations and expand the applications of micellar-supported PdNPs in sustainable catalysis [139,140].

5.3. Palladium Nanoparticles Supported on Polydimethylsiloxane Film

Polydimethylsiloxane (PDMS) films have emerged as innovative supports for palladium nanoparticles (PdNPs), offering enhanced stability and catalytic performance for diverse applications. Majhi et al. [126] developed a novel method for immobilizing PdNPs on PDMS films, demonstrating their efficacy in Suzuki–Miyaura cross-coupling (Scheme 19).



Scheme 19. Suzuki–Miyaura cross-coupling reaction catalyzed by PdNP@PDMS [126].

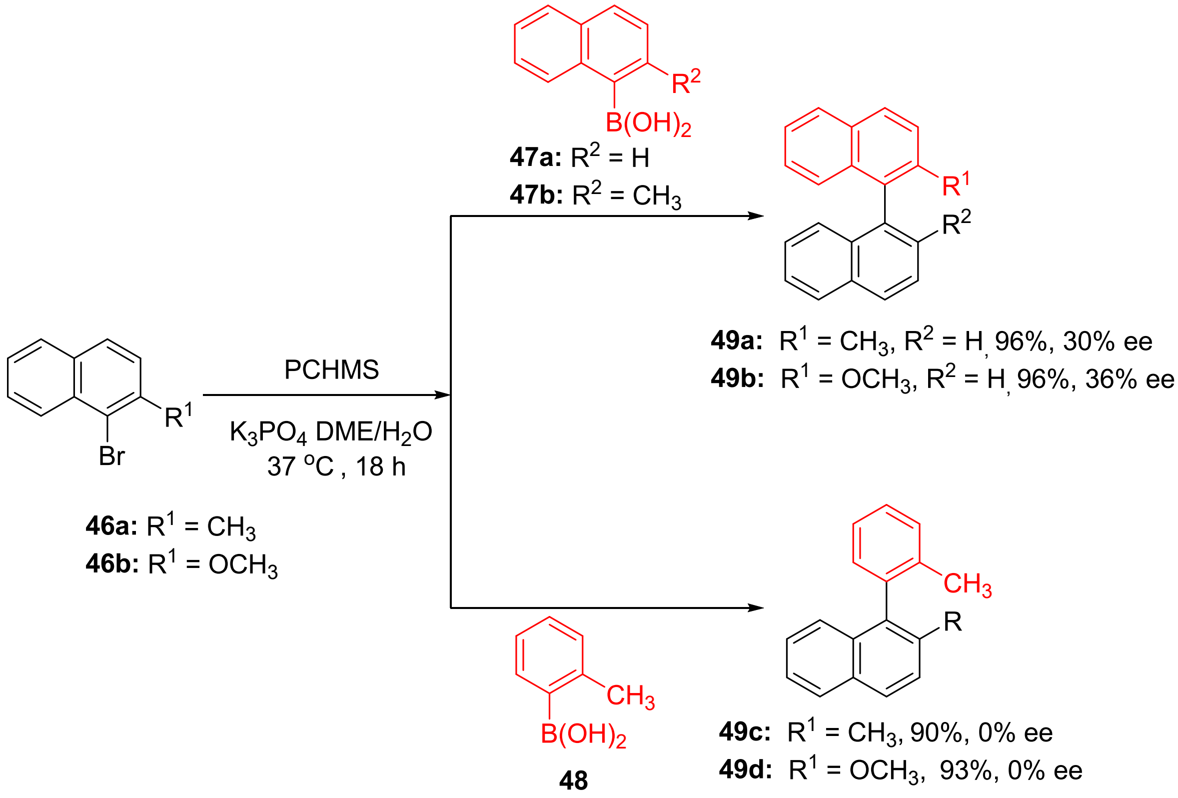
The catalyst was also effective in Sonogashira reactions, as well as in the reduction of organic pollutants. The PDMS matrix provided a durable and flexible platform for PdNPs, ensuring stability under the reaction conditions while maintaining excellent catalytic efficiency. This approach is particularly significant in the context of sustainable catalysis because PDMS-based systems eliminate the need for high-energy reaction conditions and hazardous solvents. Moreover, the hydrophobic nature of the PDMS films facilitates the dispersion of PdNPs and enhances substrate interactions, contributing to an improved turnover frequency and selectivity. The use of PDMS as a functionalized support aligns with emerging trends in green chemistry, providing a robust, reusable, and environmentally friendly platform for Pd-based catalysis.

5.4. Palladium Nanoparticles Supported on Chiral Surfactants

Chiral surfactants offer a unique platform for stabilizing Pd nanoparticles, enabling asymmetric catalysis with enhanced selectivity and efficiency. Ranganath et al. demonstrated the efficacy of chiral surfactants in stabilizing PdNPs in asymmetric Suzuki cross-coupling reactions [127]. They evaluated various substrates under optimized reaction conditions (Scheme 20), revealing significant enantioselectivity. The reaction between 1-bromo-2-methyl-naphthalene (**46a**) and naphthalene-1-boronic acid (**47a**) catalyzed by PCHMS afforded the cross-coupling product **49a** in a high 96% and 30% enantiomeric excess (ee). Similarly, 1-bromo-2-methoxy-naphthalene (**46b**) reacted with **47a** to yield **49b** in 96% yield with a slightly improved enantiomeric excess (ee) of 36%. However, reactions involving 2-methyl-phenyl-1-boronic acid (**48**) resulted in excellent yields (90–93%) but without ee, likely because of low axial rotation energy and increased entropy in products **49c** and **49d** relative to **49a** and **49b** [141].

Further studies revealed that using a bulkier catalyst, PCDXGS, in the coupling of **46a** and **47b** afforded **49a** at a slightly lower 90% yield but retained an ee of 30%, suggesting that steric factors influence enantioselectivity.

These findings highlight the important role of chiral surfactants in tuning the catalytic behavior of PdNPs, demonstrating their ability to promote enantioselective transformations while reducing the need for traditional ligands and harsh solvents. The chiral microenvironment provided by these surfactants not only enhances product selectivity but also aligns with green chemistry principles by minimizing waste and incorporating sustainable methodologies into catalytic systems. Moreover, their stabilizing effect on PdNPs ensures consistent activity and selectivity under mild reaction conditions, thereby facilitating the synthesis of enantioenriched compounds. These advances illustrate the growing importance of integrating catalyst efficiency with sustainability, positioning PdNP-supported chiral surfactants as a promising avenue for asymmetric cross-coupling, and broadening the scope of enantioselective catalysis.



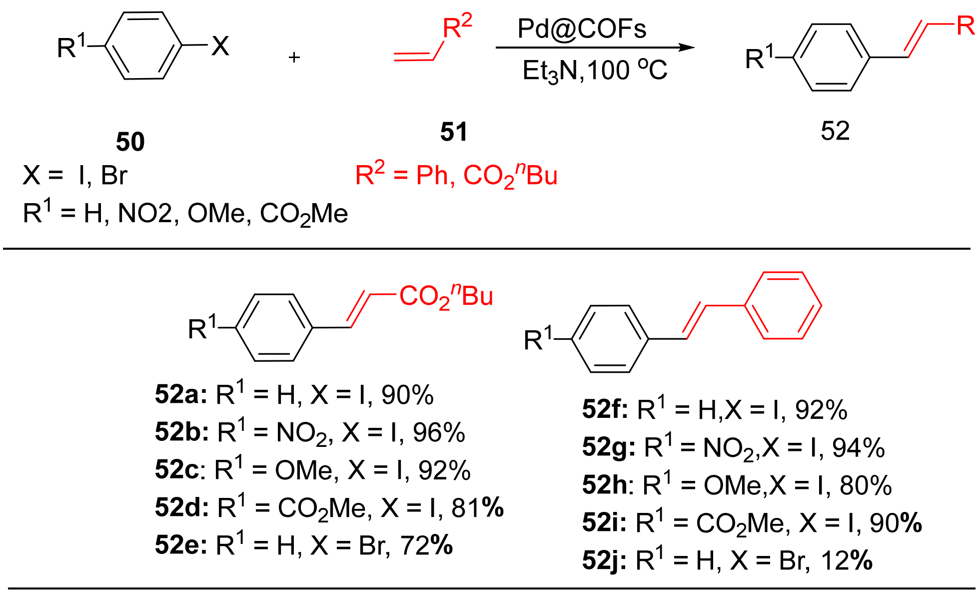
Scheme 20. Asymmetric Suzuki coupling reaction of naphthalenes catalyzed by PdNPs [127].

6. Palladium Nanoparticles Supported on Aerobic Bacterial Cells (*Paracoccus yeei*)

The innovative use of aerobic bacterial cells, specifically *Paracoccus yeei*, as a sustainable support for palladium nanoparticles (PdNPs) represents a breakthrough in green catalytic technologies. Rybochkin et al. explored this biohybrid system using *Paracoccus yeei* VKM B-3302 as the supporting matrix, addressing the high energy consumption and wastage associated with traditional Pd catalysts [62]. The resulting biohybrid catalyst exhibited exceptional efficiency in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions, achieving catalytic performances comparable to those of the commercial Pd/C catalysts (Scheme 21) [62].

A notable advantage of this system is its recyclability, which maintains consistent activity over five reuse cycles without significant performance degradation. This recyclability not only underscores its economic viability, but also its alignment with sustainability goals. The integration of biological supports into catalytic systems highlights the potential of biohybrid catalysts to reduce environmental impact while maintaining high efficiency. By leveraging the metabolic and structural properties of aerobic bacteria, this approach opens up new avenues for designing eco-friendly and cost-effective catalytic systems for industrial applications.

The selection of *Paracoccus yeei* as a support for palladium nanoparticles (PdNPs) in catalytic applications is driven by its unique metabolic and structural properties, which facilitate efficient nanoparticle formation and stabilization. This bacterium provides a sustainable and effective platform for PdNP immobilization, thereby advancing green catalytic technologies. By leveraging its adaptability and biochemical composition, Paracoccus yeei enhances the catalytic performance in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions while aligning with sustainability goals by reducing waste and energy consumption [62].



Scheme 21. Heck reaction of various substituted phenylhalids with styrene/butylacrylate catalyzed by Pd/*P. yeei* [62].

The metabolic versatility of *Paracoccus yeei* enables it to thrive in diverse environments, making it particularly suitable for PdNP synthesis and stabilization. Its ability to manage oxidative stress and metal-ion interactions facilitates the formation of highly dispersed PdNPs, thereby optimizing their catalytic performance [62]. Additionally, its cell surface provides an ideal biotemplate for PdNP deposition, ensuring uniform nanoparticle distribution and strong interactions between the nanoparticles and biological support. This structural compatibility is crucial for maintaining the catalyst's durability and activity over multiple reaction cycles. A major advantage of using *Paracoccus yeei* in PdNP immobilization is its exceptional recyclability. The biohybrid catalyst retained consistent catalytic activity over five reuse cycles with minimal leaching and negligible performance loss, demonstrating its economic viability and alignment with green chemistry principles [62].

The selection of microorganisms for PdNP synthesis depends on their biochemical composition and reducing capabilities. Microorganisms with cell wall proteins and carbohydrates rich in amine, thiol, and hydroxyl groups promote PdNP nucleation and growth, thereby ensuring a uniform size distribution. Species such as *Shewanella* and *Bacillus* have been widely explored because of their strong bioreduction ability and high metabolic adaptability [142]. However, *Paracoccus yeei* presents additional advantages owing to its structural compatibility, metabolic resilience, and recyclability, making it a superior choice for catalytic applications [62].

When compared to other microbial supports, *Paracoccus yeei* exhibits superior PdNP stabilization efficiency. *Geobacter sulfurreducens*, an electroactive bacterium capable of reducing metal ions and synthesizing PdNPs via electrode respiration, presents a sustainable approach but is limited by its reliance on electrochemical systems, making it less versatile than *Paracoccus yeei* [143], Similarly, *Escherichia coli* has been utilized to recover Pd from spent catalysts, demonstrating high electron transfer efficiency. However, its primary function is Pd recycling rather than direct Pd NP synthesis, which distinguishes its role from that of *Paracoccus yeei* [142]. Furthermore, non-biological supports, such as carbon nanosheets and metal oxides, often require complex preparation methods and lack the recyclability of biological systems, making *Paracoccus yeei* a more environmentally friendly and scalable alternative [59,105].

While *Paracoccus yeei* represents a promising approach to sustainable PdNP immobilization, research on alternative microbial and non-biological supports continues to evolve. For example, *Geobacter sulfurreducens* provides an innovative electroactive method that could be advantageous for electrode-based catalytic systems [143]. Additionally, hybrid bioinorganic systems that integrate biological and synthetic supports offer new opportunities to enhance the efficiency and sustainability of industrial catalytic applications. As microbial and material science advances, exploring the synergy between biological and synthetic supports may lead to more effective and scalable catalytic solutions for next-generation green catalysis.

7. Palladium Nanoparticles Supported on Porous Silica Materials

Porous silica materials have emerged as versatile supports for palladium nanoparticles (PdNPs), offering exceptional stability, recyclability, and efficiency for heterogeneous catalysis [46,144]. Recent advancements in the synthesis and application of PdNPs immobilized on zeolites and mesoporous silica-based materials have underscored their significant potential for sustainable cross-coupling reactions, including the Suzuki–Miyaura, Heck, Stille, and Sonogashira reactions [49,144–146]. By immobilizing PdNPs on porous silica structures, these systems mitigate critical issues, such as nanoparticle aggregation and leaching, ensuring consistent catalytic activity across multiple cycles [44,144].

Despite their advantages, porous silica supports are fragile under extreme reaction conditions. Their susceptibility to structural collapse at high temperatures can significantly reduce their long-term stability. This fragility is particularly concerning for high-loading single-atom catalysts, where the integrity of the support is important for maintaining the catalytic activity [147]. Additionally, the thermal degradation of silica at elevated temperatures can lead to the sintering of PdNPs, diminishing the catalytic efficiency, a limitation that must be addressed for industrial applications requiring sustained high-temperature reactions [148].

Another key challenge is Pd leaching, particularly in functionalized silica systems utilized for liquid-phase reactions. PdNP leaching not only leads to catalyst deactivation but also contaminates the reaction products, thereby reducing the overall process efficiency [46]. This issue further affects catalyst reusability, as repeated catalytic cycles can result in a progressive decline in Pd concentration and activity [144].

To mitigate these limitations, several functionalization and stabilization strategies have been explored. The incorporation of organic ligands and stabilizing agents into porous silica matrices enhances the Pd NP binding affinity, thereby reducing leaching and improving long-term stability [149]. Additionally, the development of hybrid materials, such as magnetic silica supports, has demonstrated promising results in improving catalyst recyclability by facilitating the separation and recovery of PdNPs post-reaction [150].

Studies have demonstrated that PdNPs supported on mesoporous silica exhibit remarkable catalytic efficiency and can be reused several times without significant loss of activity, making them particularly attractive for industrial-scale applications [144,146]. The porous structure of silica not only enhances substrate accessibility, but also ensures uniform dispersion of active catalytic sites, significantly improving the reaction rates and selectivity. Moreover, functionalized porous silica materials allow precise tuning of catalytic properties, paving the way for advanced and sustainable catalytic systems [144].

As highlighted in the recent literature, the versatility of porous silica supports continues to drive innovation in Pd NP-based catalysis [49,144–146]. These systems address the dual challenges of efficiency and sustainability, reinforcing their role as essential tools for greener chemical syntheses in cross-coupling reactions.

The unique attributes of porous silica materials, as detailed in this section, contribute to the broader discussion of the solid matrices presented in Section 9. This interconnected perspective emphasizes the major role of silica-based supports in advancing Pd NP catalysis across diverse applications.

8. Palladium Nanoparticle Immobilized on Coconut Coir Extract Coated Boron Carbon Nitride

Boron carbon nitride (BCN) materials have garnered significant interest in catalysis owing to their unique laminar structures and well-distributed active sites, which facilitate strong metal-support interactions. These materials provide an ideal scaffold for Pd nanoparticle (PdNP) immobilization, enhancing their stability, dispersion, and electron transfer properties, which are key factors in catalytic efficiency. The functionalization of BCN with natural compounds, such as coconut coir extract (CCE), further enhanced PdNP anchoring and improved reusability and catalytic activity in cross-coupling reactions.

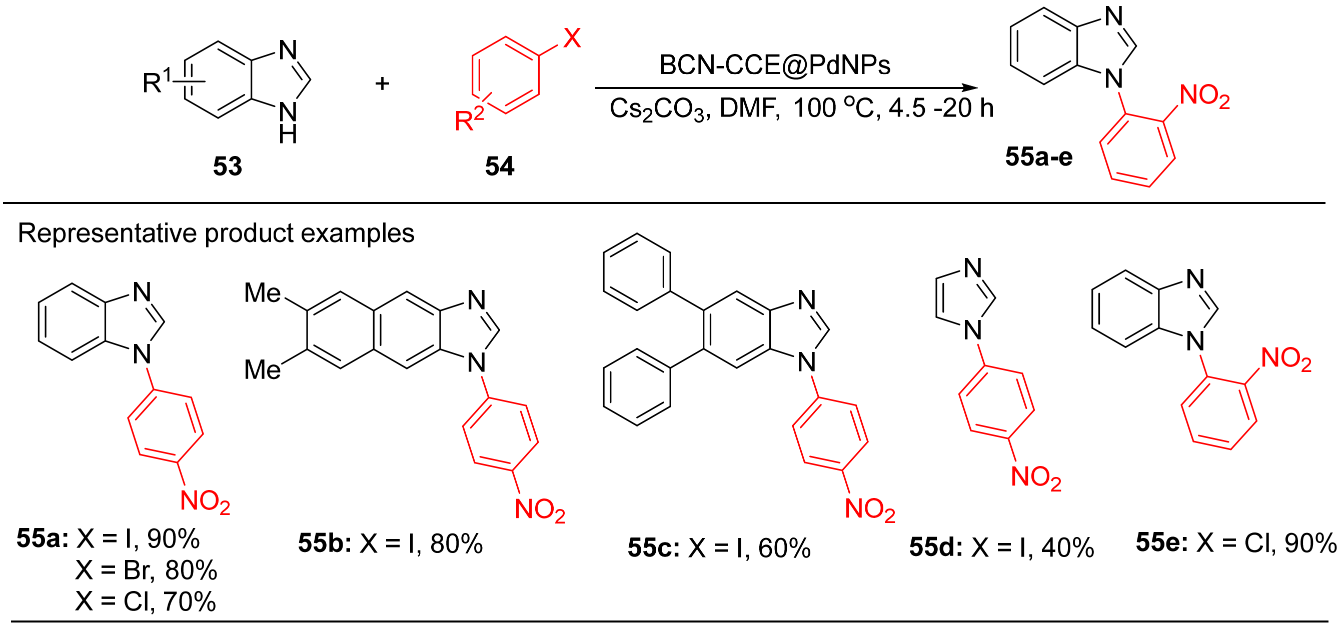
The interaction between the laminar structure of BCN and PdNPs plays a crucial role in optimizing catalytic performance. BCN materials possess adjustable active sites, where B and N species at the B–N–C sites serve as acid and base catalysts, respectively, facilitating key transformations such as Knoevenagel condensation [151]. Additionally, the laminar structure of BCN provides a high surface area for PdNP deposition, ensuring a uniform distribution and strong interaction between the nanoparticles and the support. Functionalization with amino acids or natural compounds such as tryptophan significantly alters the adsorption energy of BCN nanotubes, making them more soluble and interactive with biological molecules, thereby extending their potential applications in catalysis and drug delivery [151]. The introduction of functional groups on BCN nanosheets via chemical routes, including dibromocarbene modification, allows precise tuning of the electronic properties, further optimizing the PdNP interactions [152].

Chandrashekharan et al. presented a novel approach to sustainable catalysis through the development of a Pd nanocatalyst immobilized on boron carbon nitride coated with coconut coir extract (BCN-CCE@Pd) [60]. This eco-friendly system demonstrated remarkable catalytic efficiency in Suzuki–Miyaura cross-coupling and C–N arylation reactions under mild conditions, achieving excellent product yields (Scheme 22) [60]. The synergy between the boron carbon nitride support and coconut coir extract significantly enhanced the stability and reactivity of PdNPs, providing a highly active and reusable catalytic platform.

Despite their promising properties, porous BCN-based materials can exhibit challenges, such as structural fragility under extreme conditions and potential PdNP leaching. Their susceptibility to thermal degradation at high temperatures can lead to the collapse of the support structure, reducing the catalytic performance, which is similar to the mechanisms observed in other porous ceramic materials [153–156]. Moreover, PdNP leaching in liquid-phase reactions affects catalyst stability and reusability, necessitating functionalization strategies to enhance Pd binding affinity. Functionalization with stabilizing agents such as amino acids and organic ligands improves electron transfer and ensures long-term catalytic efficiency [149].

The catalytic efficiency of the BCN-CCE@Pd nanocatalyst over multiple reaction cycles highlights its potential for industrial applications in which sustainability and cost-effectiveness are critical. This study underscores emerging trends in the utilization of natural and renewable materials to support Pd catalysts, paving the way for greener methodologies for cross-coupling catalysis.

By integrating natural extracts into BCN-based catalytic systems, researchers can enhance the catalyst's stability and sustainability while minimizing the environmental impact. The exploration of alternative functionalization techniques, such as hybrid bioinorganic supports, offers exciting possibilities for optimizing Pd-based catalytic materials. As advancements in functionalized BCN systems continue to evolve, they represent a promising pathway toward next-generation eco-friendly and highly efficient catalytic solutions.



Scheme 22. C-N arylation reaction between aryl halides and *N*-heterocyclic compounds catalyzed by BCN-CCE@Pd nanocatalyst [60].

9. Palladium Nanoparticles Supported on Metal Oxides and Metal Oxide Hybrid Materials as Catalysts for Cross-Coupling Reactions

The strategic integration of palladium nanoparticles (PdNPs) with advanced support materials has led to transformative innovations in catalysis, particularly in the cross-coupling and oxidation reactions [105]. Among these, metal oxides provide an ideal platform for stabilizing and dispersing Pd species, enhancing their accessibility, activity, and durability [105,157]. Atomically dispersed Pd on metal oxides exemplifies this advancement, with superior catalytic efficiency and selectivity attributed to uniform active sites and enhanced turnover frequencies [144]. These catalysts not only improve energy efficiency, but also align with sustainable chemistry principles, making them indispensable for precision-driven applications.

Despite these advantages, the use of metal oxides as supports for PdNPs presents certain challenges that must be addressed to optimize catalytic performance. One of the primary concerns is Pd leaching in aqueous media, which can significantly affect catalyst recyclability. In liquid-phase reactions, PdNPs may detach from the support owing to weak metal-support interactions, leading to catalyst deactivation and contamination of the reaction mixture [157]. This phenomenon has been observed in Fe_3O_4@L-Threonine-Pd systems, where, despite high efficiency, some degree of metal leaching occurs, necessitating strategies for catalyst recovery and reuse. To mitigate leaching, surface functionalization approaches have been explored, including metal–organic frameworks (MOFs), which create a molecular fence effect, prevent PdNP detachment, and improve catalyst longevity [158].

Another significant limitation is the restricted dispersion of PdNPs on certain metal oxides, which can lead to nanoparticle aggregation, thereby reducing the number of available active sites. Poor dispersion lowers catalytic turnover and selectivity, particularly in cross-coupling reactions requiring high surface availability [59]. To address this, modifications such as polydopamine-functionalized–Zn-Al mixed metal oxides have been employed, enhancing both PdNP dispersion and stability for repeated catalytic cycles [105]. Similarly, Schiff base-modified ZnO exhibited improved Pd anchoring, thereby boosting the reaction efficiency [159].

Recent research has focused on developing innovative support materials to mitigate these limitations. For instance, pyridinic N-rich carbon nanosheets have demonstrated strong Pd-support interactions, reducing leaching while maintaining excellent catalytic activity in various organic transformations [59]. Additionally, hybrid metal-oxide nanostructures have shown promise in creating synergistic effects that enhance the stability and dispersion of PdNPs, thereby opening new avenues for robust catalytic systems.

Metal oxides remain critical in catalysis because of their thermal stability and tunable electronic properties, and addressing Pd leaching and dispersion challenges is essential for their broader industrial adoption. Surface modification, functionalization strategies, and the incorporation of hybrid materials represent viable solutions for enhancing the efficiency, durability, and recyclability of Pd-based catalysts. Continued research on next-generation metal oxide supports will be pivotal in advancing sustainable catalytic technologies for cross-coupling reactions.

This section discusses the synergistic role of PdNPs and metal oxide supports in catalytic applications, with a focus on cutting-edge systems [105,144,157,159–161]. These innovations illustrate how tailored support materials can amplify the catalytic potential of palladium while addressing key challenges in scalability, environmental impact, and mechanistic understanding. By exploring these advancements, this section highlights the critical contributions of metal oxide-supported PdNPs to modern industrial and environmental catalysis.

9.1. Immobilized Palladium Nanoparticles on Schiff Base-Modified ZnO Particles (Pd–ZnO–Scb)

Baran and co-workers employed nanoparticles immobilized on Schiff base-modified ZnO particles (Pd–ZnO–Scb) (Figure 2) as catalysts for Heck coupling reactions [159].

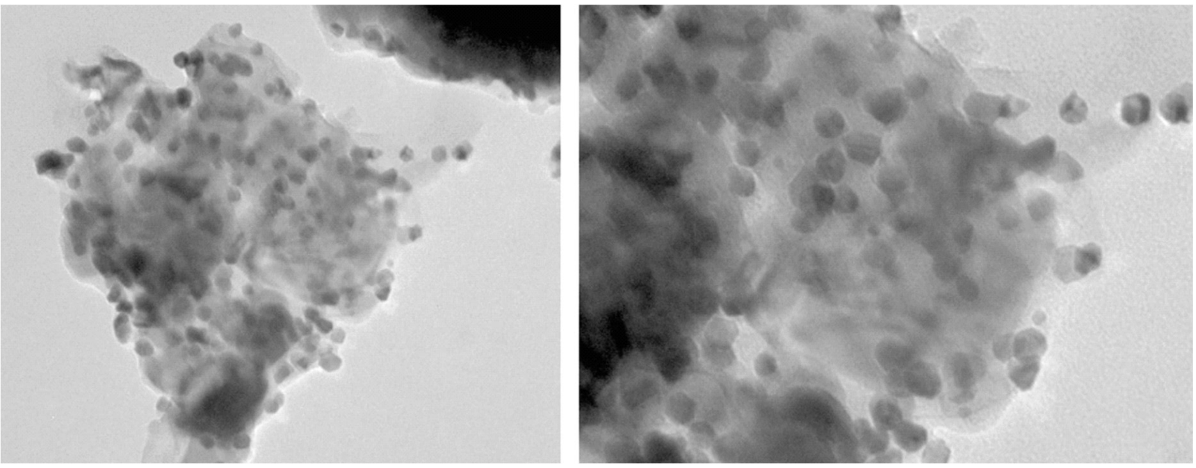
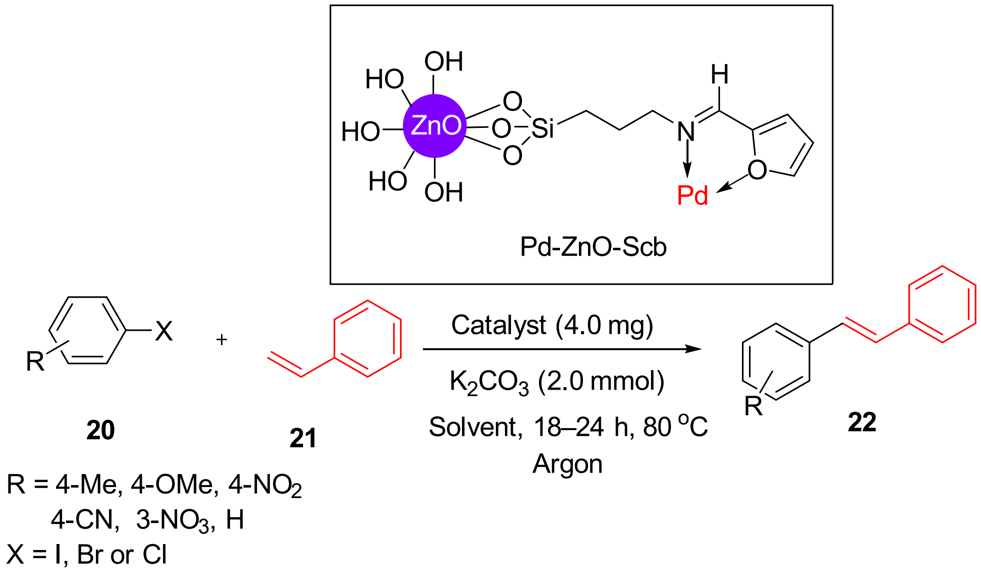


Figure 2. TEM image of Pd-ZnO-Scb nanocatalyst adapted from Baran et al. [159].

This study highlighted the effectiveness of this catalyst in the coupling of various aryl halides (**20**) with styrene (**21**), and the yield was up to 98% (Scheme 23). Compared to other methods, the authors found that the catalyst was also highly efficient in the reduction of 4-nitrophenol owing to the formation of only one product, which was achieved in 135 s at room temperature [159].



Scheme 23. Heck reaction of aryl halides with alkenes catalyzed by nanoparticles immobilized on Schiff base-modified ZnO particles (Pd–ZnO–Scb) [159].

9.2. Pd Nanoparticles Supported by Atomically Dispersed Metal Oxide

Atomically dispersed palladium (Pd) catalysts stabilized by metal oxides represent a breakthrough in cross-coupling catalysis, offering enhanced catalytic performance, stability, and sustainability. These catalysts were synthesized via oxidative fragmentation, where metallic Pd nanoparticles were converted to PdO at 400 °C and subsequently fragmented into atomically dispersed Pd cations at temperatures above 500 °C. These atomically dispersed species, stabilized by metal oxide supports, exhibit high surface accessibility and unique electronic properties that enhance their catalytic efficiency and selectivity in reactions such as Suzuki–Miyaura and Heck couplings [162].

Among metal oxides, magnesium oxide (MgO) has demonstrated exceptional efficacy in stabilizing Pd cations during these transformations. The Pd species, surface-dispersed on MgO, show superior catalytic activity because of their optimized coordination environments, which facilitate effective substrate interactions and accelerate reaction rates. The strong metal-support interactions provided by MgO prevent nanoparticle agglomeration and ensure consistent catalytic performance under diverse conditions, highlighting its critical role in enabling efficient cross-coupling reactions [162].

Eco-friendly synthetic methods are integral to the development of these catalysts. Green chemistry principles, such as the use of ethanol as a solvent, energy-efficient ultrasonic cavitation techniques, and recycling strategies to minimize Pd leaching enhance the sustainability and durability of these systems. These approaches align with the industrial demands for environmentally responsible catalysis [162]. Magnetic supports, such as Fe_3O_4 nanoparticles, further improve catalyst recovery and reusability, making them practical for repeated applications without significant loss of activity [162].

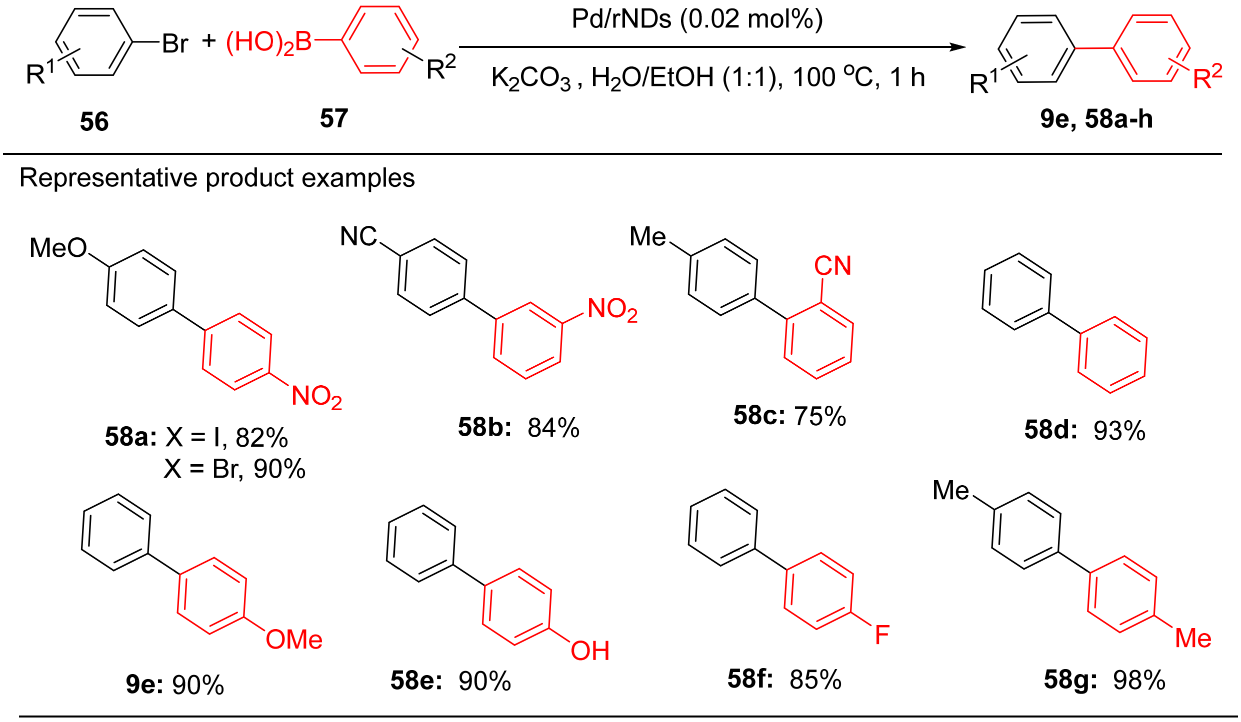
Atomically dispersed Pd catalysts excel in stabilizing intermediates and provide uniform active sites, leading to high turnover frequencies (TOFs), superior selectivity, and energy-efficient operation at lower temperatures. Alternative supports, such as Al_2O_3 and TiO_2, present opportunities to diversify catalytic properties, while computational modeling and experimental studies will deepen the mechanistic understanding. These advances will drive the rational design of next-generation catalytic systems, thereby solidifying the role of atomically dispersed Pd catalysts in sustainable industrial catalysis [162].

9.3. Palladium Nanoparticles Supported on Solid Matrices

Solid matrices play an important role in enhancing the performance of palladium nanoparticles (PdNPs) in cross-coupling reactions by addressing challenges, such as nanoparticle agglomeration, leaching, and deactivation. These matrices significantly improved the stability, dispersion, and catalytic efficiency of PdNPs, thereby extending their applicability in Suzuki–Miyaura, Heck, and Sonogashira reactions. By leveraging a wide array of support materials, from graphene-based platforms to hybrid organic–inorganic systems, researchers have established solid matrices as indispensable tools for modern catalysis [46,163].

The inclusion of functionalized organic and inorganic supports, such as dendritic organosilica (DON), aminobenzamide-modified silica-coated superparamagnetic iron oxide, and chitosan-MWCNT hybrids, has proven to be particularly effective in enhancing the recyclability and catalytic efficiency of PdNPs [164]. These support mitigated nanoparticle aggregation while promoting improved substrate interactions. Furthermore, materials such as biochar, carbon nanohorns, and mesoporous silica provide high surface areas, tailored pore structures, and functionalized surfaces, which contribute to their superior catalytic performance [46].

Graphene oxide (GO) has emerged as a widely studied support due to its high surface area, electronic conductivity, and chemical stability, which enable the effective stabilization of PdNPs [165]. Kumar et al. demonstrated the exceptional catalytic activity of PdNPs immobilized on GO in Suzuki–Miyaura and Mizoroki–Heck reactions, highlighting their environmentally friendly design with minimal reliance on toxic reagents [163]. Similarly, nanodiamond-based supports, such as Pd/rNDs, synthesized by Pocklanová et al., achieved yields of up to 98% for biaryl products in Suzuki reactions under mild solvent-free conditions. These catalysts also exhibited excellent stability and retained activity over multiple reuse cycles. (Scheme 24) [161].



Scheme 24. Suzuki reaction between aryl halides and boronic acid catalyzed by Pd/rNDs [161].

Notably, the substrate functional groups strongly influence the catalytic efficiency. In Suzuki reactions catalyzed by Pd/rNDs, electron-withdrawing groups such as nitro- and hydroxy-substituted substrates gave slightly lower yields and required longer reaction times than electron-donating groups such as methyl- and methoxy-substituted substrates. High yields were consistently obtained for all substrates bearing electron-donating or electron-withdrawing groups at the ortho and para positions. The aryl bromides also demonstrated excellent interactions with *p*-tolylboronic acid, yielding the desired products with remarkable efficiency [161].

Inorganic supports, such as mesoporous graphitic carbon nitride (mpg-CN), offer tailored pore structures and high thermal stability, enabling the efficient dispersion of PdNPs and robust catalytic activity under mild conditions [84]. Biochar, derived from renewable resources is a cost-effective and sustainable alternative. Functionalized biochars, such as Pd(0)-TBA@biochar, exhibit high turnover frequencies and recyclability, aligning well with green chemistry principles [46].

Hybrid support systems further enhance Pd NP catalysis by combining the strengths of the organic and inorganic materials [162]. Metal–organic frameworks (MOFs) with tunable porosities and functional surfaces create highly stable environments for PdNPs, optimizing their performance in cross-coupling reactions [166]. Additionally, Zn-Al mixed metal oxides modified with polydopamine have shown high recyclability and catalytic efficiency in Suzuki–Miyaura reactions [105].

Magnetic supports, such as Fe_3O_4 nanoparticles, offer an innovative approach by enabling straightforward recovery and reuse through magnetic separation. For example, phosphonated polyethylenimine-grafted Fe_3O_4 nanoparticles retain high catalytic efficiency over multiple cycles in the Heck and Suzuki–Miyaura reactions, reducing waste and promoting sustainable catalytic practices [167].

Although solid matrices have significantly enhanced the performance of Pd nanoparticles in cross-coupling reactions, ongoing efforts to optimize these supports highlight the dynamic interplay between material innovation and catalytic efficiency. Advances in hybrid systems, scalable synthesis, and sustainable practices will continue to expand the applicability of solid matrices, thereby setting the stage for broader discussions of future challenges and directions in the field.

10. Future Directions and Challenges

Catalytic applications of palladium nanoparticles (PdNPs) have made substantial advancements; however, challenges such as leaching, support degradation, and scalability persist, limiting their industrial adoption. Addressing Pd leaching is critical for ensuring catalyst recyclability and preventing the contamination of reaction products. Studies have shown that nitrogen-doped carbon materials, such as Pd/N-CNS and biochar-based supports, effectively reduce Pd leaching owing to strong metal-support interactions, enabling consistent catalytic performance over multiple cycles [46,59].

Support degradation under harsh conditions, such as elevated temperatures or prolonged reaction cycles, presents another significant challenge. Robust materials, such as mesoporous graphitic carbon nitride (mpg-CN) and biochar, have demonstrated enhanced durability, while hybrid supports, such as polydopamine-modified Zn-Al mixed metal oxides, exhibit superior thermal and chemical stabilities [84,105]. However, these systems require further optimization to achieve widespread applications under various reaction conditions.

Scalability remains a barrier, particularly for complex hybrid designs or systems that depend on expensive materials. Simplified synthetic approaches, such as the use of renewable biopolymers and natural templates, can facilitate the development of cost-effective catalytic systems. Techniques, such as 3D-printed supports and sol-gel synthesis, have shown promise for creating uniform scalable catalysts without compromising performance [46,166].

Future advancements will rely heavily on computational modeling integrated with experimental studies to predict the reaction mechanisms and optimize the catalyst design. Understanding the interplay between the heterogeneous and homogeneous catalytic pathways, particularly in atomically dispersed Pd systems, can reveal new efficiencies [162]. Additionally, eco-friendly synthesis methods, including solvent-free processes and the use of renewable starting materials, will align catalyst development with green chemistry principles and ensure sustainability and performance.

By addressing these challenges through innovations in material design, process scalability, and eco-conscious practices, PdNP catalysis continues to evolve as a cornerstone of industrial chemistry.

11. Mechanism

The mechanistic underpinnings of PdNP-catalyzed C–C cross-coupling reactions continue to be an area of significant debate, particularly regarding the interplay between the homogeneous and heterogeneous pathways (Figure 3). A key hypothesis, the dissolution-redeposition theory, suggests that PdNPs act as reservoirs, releasing active palladium species into the reaction medium, which subsequently redeposit onto the nanoparticle surface to sustain catalysis [168].

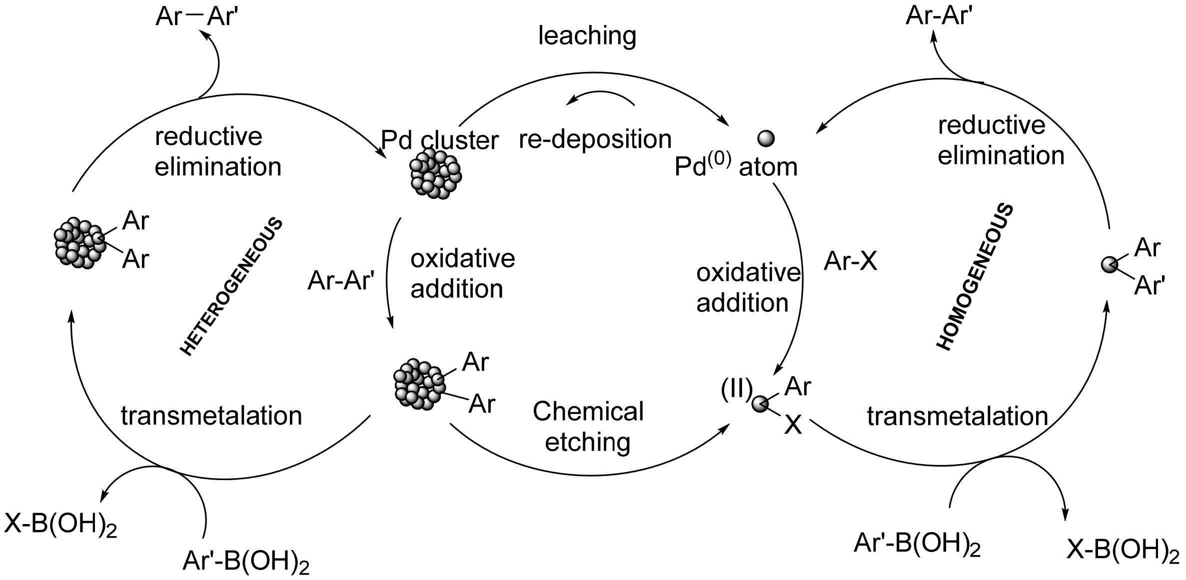


Figure 3. Proposed mechanism for nanoparticle cross-coupling reactions of aryl halides. Adapted from Perez-Lorenzo et al. [168].

Real-time fluorescence imaging by Costa et al. confirmed the migration of Pd species during the Suzuki–Miyaura reaction, indicating that catalysis primarily occurred on the surface, supporting a heterogeneous mechanism [169]. Despite these findings, some evidence suggests that homogeneous pathways can also play a role, depending on the reaction conditions and extent of Pd leaching [170]. Trzeciak and Augustyniak further demonstrated that active Pd species leached into the solution but ultimately re-adsorbed onto the solid support, highlighting a dynamic equilibrium between the heterogeneous and homogeneous mechanisms [170]. This interplay extends beyond Suzuki–Miyaura reactions and is also observed in Heck and Sonogashira cross-coupling reactions. The demand for greener catalytic approaches, such as biogenic and mild reaction conditions, has further strengthened the potential of environmentally sustainable catalytic processes [171].

The size of PdNPs significantly influences their catalytic activity, primarily due to variations in the surface area-to-volume ratio, electronic properties, and active site accessibility. Smaller nanoparticles generally exhibit enhanced catalytic performance owing to their increased surface area, which provides more active sites for the reactions. However, excessively small nanoparticles may suffer from agglomeration and instability, which can negatively impact the long-term catalytic efficiency. The increased surface area-to-volume ratio facilitates greater accessibility of catalytic sites, as seen in Suzuki–Miyaura and Heck cross-couplings, where enhanced exposure optimizes reactant–catalyst interactions [172]. However, at extremely small sizes, nanoparticle aggregation becomes a concern, reducing catalytic efficiency over extended reaction cycles [173].

The electronic properties of PdNPs are highly size-dependent, influencing the charge carrier mobility and modulating the electronic density at active sites, ultimately affecting the reaction kinetics. Density Functional Theory (DFT) studies have demonstrated that variations in the electronic structure influence adsorption energies and catalytic efficiency [173]. Smaller nanoparticles tend to lower the reaction barriers, improving the kinetics of oxidative addition and reductive elimination steps, which are key elementary reactions in Pd-mediated catalysis. The accessibility of the active sites is another crucial factor; while smaller PdNPs provide greater surface exposure, overly small particles are prone to sintering, leading to deactivation and reduced turnover [174]. Studies on Pt-based nanozymes have confirmed that maintaining an optimal PdNP size is essential for maximizing the catalytic performance while ensuring long-term stability. While smaller nanoparticles generally enhance the catalytic performance, challenges such as stability, synthesis reproducibility, and leaching must be addressed. Conversely, larger PdNPs exhibit unique electronic properties that may be beneficial in specific catalytic applications, emphasizing the necessity of optimizing the nanoparticle size based on reaction mechanisms, support materials and conditions [172,173,175,176].

Computational modeling has been instrumental in elucidating the reaction pathways involved in PdNP catalysis. The increasing availability of high-performance computing (HPC) centers and advancements in Density Functional Theory (DFT) have enabled the accurate prediction of the mechanistic pathways in organometallic reactions. However, a simplified chemical approach using Lewis structures, Valence Shell Electron Pair Repulsion (VSEPR) theory, and kinetic modeling provides experimental chemists with an intuitive method for visualizing mechanistic transformations. This conceptual approach suggests that electropositive centers react with electronegative centers to maintain the octet rule, with kinetically favored pathways being those that minimize the intermediate formation and reaction steps. This reasoning likely guided Heck's original mechanistic proposal for the Heck cross-coupling reaction, as shown in Figure 4.

In Heck's original proposal, the catalytic cycle begins with palladium (II) salt, palladium(II) acetate, which is then reduced by the ligand triphenylphosphine to generate the active Pd(0) species. The oxidative addition of the organic halide (phenyl bromide) to the active Pd(0) species occurs in Step A, forming a Pd(II)–aryl complex. The alkene then coordinates to the Pd(II) center, followed by syn addition (Step B) of the Pd–C bond into the alkene. In Step C, β-hydride elimination occurs, forming the C–C coupled product, which binds to Pd(II) via π-complexation before desorption as the final product. The catalyst is regenerated in Step D via reductive elimination, facilitated by a base, restoring the Pd(0) complex, and completing the cycle [177]. In Heck's original mechanism, one of the phosphine ligands momentarily detaches during alkene binding and rebinds upon formation of intermediate **52**, which is not explicitly illustrated in Figure 4.

Advances in spectroscopic analysis and mechanistic investigations have further refined the understanding of PdNP catalysis, particularly in heterogeneous catalysis. Wang et al. demonstrated that PdNPs immobilized on zeolites maintain high catalytic stability and recyclability with negligible palladium leaching, ensuring that the catalytic activity remains localized on the PdNP surface [176]. Enhanced electronic interactions between the PdNP surface and substrate molecules have been shown to increase the turnover frequency (TOF), providing additional evidence that the dominant catalytic activity is surface-driven [175].

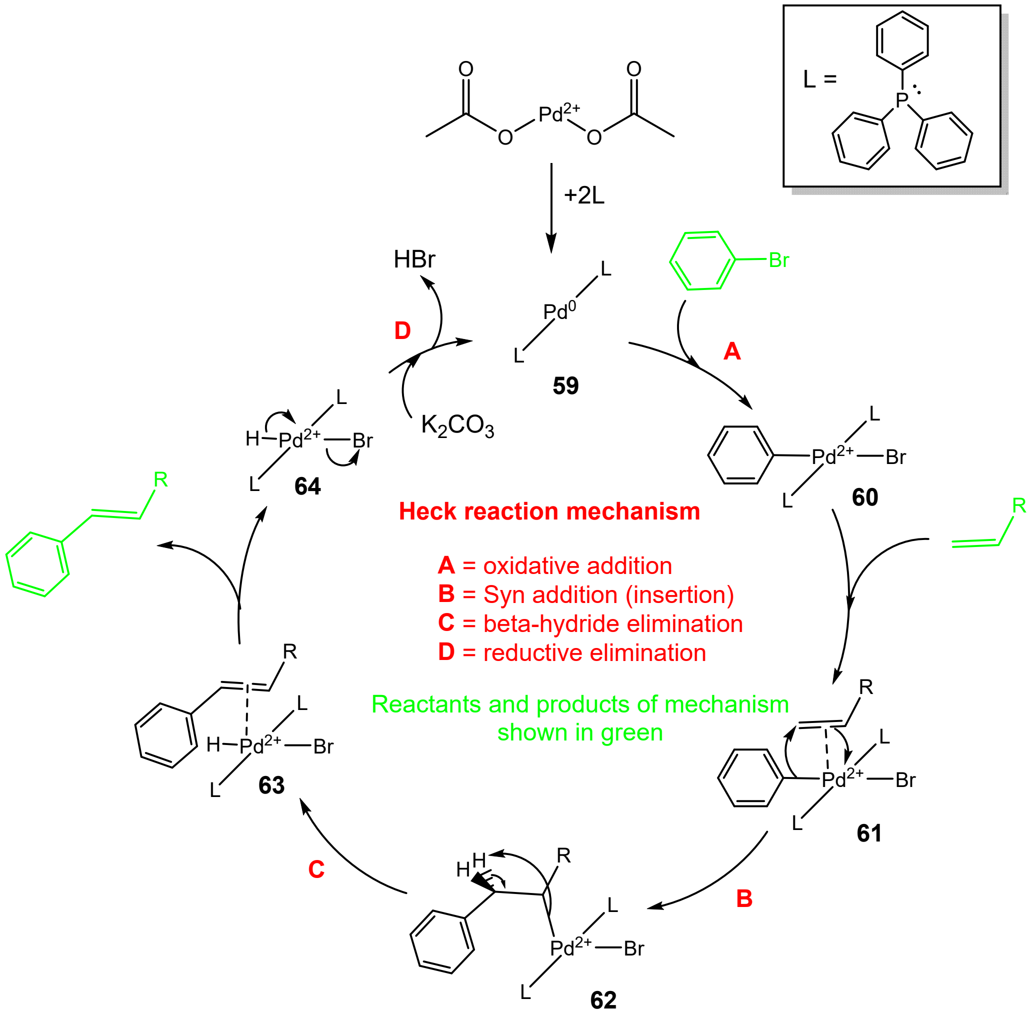


Figure 4. Mechanism of Heck reaction adapted from Dieck and Heck 1974 [177].

The consensus now favors a predominantly heterogeneous mechanism, where direct interactions between the PdNP surfaces and aryl halides drive cross-coupling reactions. However, the negligible activity of the leached Pd species under well-controlled conditions suggests that homogeneous catalysis is unlikely to be significant in well-optimized catalytic systems [169]. As research advances, the development of innovative PdNP support materials coupled with real-time mechanistic studies will be important to further resolve these mechanistic debates and optimize PdNP-based catalysis for scalable industrial applications.

12. Conclusions

The integration of Pd nanoparticles (PdNPs) into sustainable catalysis has led to a paradigm shift in modern chemical synthesis, offering exceptional catalytic efficiency, selectivity, and recyclability. Their high surface area-to-volume ratio facilitates their widespread application in cross-coupling reactions, thereby addressing critical challenges such as palladium leaching, nanoparticle aggregation, and environmental toxicity [55,178–180]. The ability to fine-tune the PdNP properties through size control, ligand engineering, and advanced support materials has positioned them at the forefront of green chemistry, enabling more efficient, scalable, and environmentally benign catalytic processes [178,179].

Recent advancements in PdNP-supported catalysis have underscored the important role of innovative support materials in enhancing catalytic performance. Functionalized nitrogen-doped carbon nanosheets optimize the electronic environment, significantly improving turnover frequency and catalytic activity [59]. Similarly, biopolymer-based supports, including kenaf-cellulose and chitosan derivatives, introduce a biodegradable dimension, ensuring sustainability while maintaining high yields and catalytic stability [61]. These developments have demonstrated that the rational design of PdNP systems can mitigate many of the challenges associated with traditional catalysts, offering unprecedented control over their stability, selectivity, and reusability.

Despite these achievements, the industrial-scale implementation of PdNP-based catalytic systems remains constrained by factors such as cost efficiency, long-term stability, and catalyst recovery [181]. Key limitations include the tendency of smaller PdNPs to aggregate, leading to a loss of the active surface area and diminished catalytic performance over extended reaction cycles. Strategies such as ligand stabilization, surface functionalization, and hybrid support architectures provide promising pathways for addressing these issues. Moreover, optimizing the PdNP size is critical, as variations in the surface area-to-volume ratio, electronic properties, and active site accessibility profoundly impact the catalytic efficiency. A balance between maximizing surface activity and preventing aggregation is necessary to unlock the full potential of PdNPs in industrial applications [173].

Looking ahead, the convergence of machine learning, high-throughput experimentation, and computational modeling will revolutionize catalyst design, enabling predictive tailoring of PdNPs for specific reactions. The development of hybrid catalytic systems that integrate biological and synthetic supports offers an exciting frontier for enhancing both stability and catalytic efficiency while maintaining environmental sustainability [176]. Furthermore, expanding PdNP catalysis to new frontiers, including asymmetric transformations, electrocatalytic processes, and pharmaceutical applications, will further establish its indispensability for fine chemical synthesis [175].

This review highlights the transformative role of PdNPs in bridging the gap between conventional and sustainable catalytic systems. By addressing current challenges and leveraging state-of-the-art innovations, PdNP-based catalysis has been poised to redefine the standards of efficiency, selectivity, and sustainability in modern chemistry. The integration of advanced support materials, real-time mechanistic studies, and scalable synthetic strategies will be instrumental in optimizing PdNP-based catalysis for widespread industrial adoption. As the field continues to evolve, PdNPs will play a pivotal role in shaping the future of green chemistry, driving progress toward more sustainable, economically viable, and environmentally friendly catalytic technologies.

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