International Journal of Chemical Science
www.chemicaljournals.com
Online ISSN: 2523-2843
Received: 14-02-2026; Accepted: 16-03-2026; Published: 31-03-2026
Volume 10, Issue 1, 2026, Page No. 66-70

Pd (0) immobilized on Montmorillonite Clay K10 as an efficient catalyst for Sonogashira Cross Coupling Reaction

Parmita Phukan[1*], Manashjyoti Konwar[2], Bidyutjyoti Dutta[3]
[1] Department of Chemistry, North Lakhimpur University, North Lakhimpur, Assam, India
[2] Department of Chemistry, Dibru College, Dibrugarh, Assam, India
[3] Department of Chemistry, Murkong Selek College, Jonai, Dhemaji, Assam, India

Abstract

In this work, we report a simple and efficient method for the synthesis of palladium nanoparticles immobilized on Montmorillonite K10 under mild and environmentally benign conditions. The synthesized catalyst demonstrated excellent efficiency in the Sonogashira cross-coupling reaction for the formation of internal alkynes. The prepared catalyst was thoroughly characterized using various techniques, including transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (TEM-EDX), scanning electron microscopy (SEM), and X-ray powder diffraction (XRD) analysis.

Keywords: Palladium Nanoparticles, Cross-Coupling Reactions, Room Temperature, Heterogeneous Catalysis

Introduction

Over the past few decades, catalysis has emerged as a strategic and rapidly advancing field of science, attracting significant interest from the scientific community due to its potential to address challenges related to sustainability and energy. The concept of sustainability, which has enhanced the innovative scope of catalysis, has become a fundamental pillar of Green Chemistry [1-3]. In homogeneous catalysis, the interaction between active catalytic sites and reactants is more efficient because all components are present in the same phase. This leads to high selectivity, high turnover numbers, and ease of optimization of catalytic activity. However, homogeneous catalysts are often difficult to isolate and recover from reaction mixtures, resulting in a high risk of metal contamination in the final products, which is particularly problematic in the pharmaceutical and drug industries. To overcome these limitations, the heterogenization of active catalytic species has been introduced. In this approach, active molecules are immobilized onto the surface or within the pores of solid supports such as alumina or silica, either through covalent bonding or physical adsorption. Nevertheless, compared to homogeneous systems, heterogeneous catalysts may exhibit reduced catalytic activity due to limited accessibility of active sites, as only sites located on the external surface of the support are readily available for reaction.

Consequently, there is a growing need for catalytic systems that bridge the gap between homogeneous and heterogeneous catalysis by retaining the advantages of both. To address this challenge, nanocatalysts have been developed that combine the ease of recovery and reusability characteristic of heterogeneous systems with the high efficiency and activity typical of homogeneous catalysts. In recent years, noble metal nanoparticles have attracted considerable attention due to their wide range of applications and notable structural stability. Nanostructured transition metal particles exhibit physicochemical properties that differ markedly from those of their bulk counterparts, which has led to significant interest from both fundamental and technological perspectives.

Metal nanoparticles are of particular interest in the field of nanocatalysis owing to their unique properties and broad potential in a wide range of organic reactions and transformations, as well as their applications across various scientific disciplines, including medicine, materials science, and sensor design. Nanoparticles can be employed as innovative materials due to their remarkable electronic, magnetic, and thermal properties [4-6]. Their large surface-to-volume ratio results in enhanced surface activity compared to bulk materials, enabling them to function as highly efficient catalysts [7]. Palladium, one of the most versatile transition metals, has been extensively utilized in nanoparticle catalysis. In recent decades, nanosized palladium crystals have attracted considerable research interest due to their exceptional catalytic properties [8-10]. They serve as strong and efficient catalysts for a wide range of important reactions, including hydrogenation reactions [11], hydrocarbon oxidation in automobile exhaust systems [12-13], carbon–carbon bond-forming reactions such as the Heck [14], Suzuki [15], and Stille [16] couplings, as well as C–N coupling reactions [17]. Numerous synthetic methodologies have been reported in recent years for the preparation of stable palladium nanoparticles suitable for catalytic applications.

Over the past three decades, the Sonogashira cross-coupling reaction has emerged as one of the most important methods for carbon–carbon bond formation and has played a crucial role in the synthesis of pharmaceuticals, agrochemicals, and functional materials [18]. Typically, this reaction is carried out in the presence of phosphine ligands using a combination of palladium and copper salts, along with a large excess of amines as the base [19]. These conditions enhance the reactivity of the reagents and enable the reaction to proceed at room temperature, making the Sonogashira cross-coupling highly valuable. However, the use of copper salts as co-catalysts often leads to undesirable homocoupling of terminal alkynes as reported earlier. In addition, phosphine ligands are sensitive to air and moisture, which restricts the reaction to inert atmospheric conditions. To address these limitations, significant efforts have been directed toward the development of copper-free systems employing palladium alone, reactions under reducing atmospheres (H_2), and palladium complexes bearing air-stable ligands [20]. Furthermore, in response to environmental concerns, Sonogashira reactions conducted in aqueous media have gained increasing attention [21-23].

Experimental

Synthesis of Nanopalladium immobilized on Montmorrilonite Clay –Imm-Pd-K10:

Immobilized heterogeneous metal catalysts play an important role in environmentally benign processes by enabling easy separation of products from the reaction mixture with minimal metal contamination. To facilitate the recovery of nanoparticles, their immobilization on insoluble supports has proven highly attractive, and numerous efforts have been devoted to the development of supported nanoparticle catalysts. Consequently, there is a strong demand for supports that enhance catalyst sustainability by allowing facile separation and reuse without obstructing the accessibility of catalytic active sites.

In our methodology, a mixture of Montmorillonite clay (1 g), 5 M LiCl (2 mL), phenylboronic acid (100 mg), and potassium carbonate (200 mg) was prepared in an isopropanol–water system and taken in a 100 mL round-bottom flask. Upon the addition of $PdCl_2$ (20 mg) to this mixture, the solution rapidly turned black within a few seconds, indicating the formation of palladium nanoparticles as reported in literature [24]. The resulting reaction mixture was then washed several times with various organic and aqueous solvents, including ether, hexane, ethyl acetate, acetone, and water, followed by centrifugation. The washed catalyst was subsequently oven-dried at 800 °C and further dried under vacuum to remove any residual moisture, yielding the catalyst in pure powdered form as shown in Figure 1.

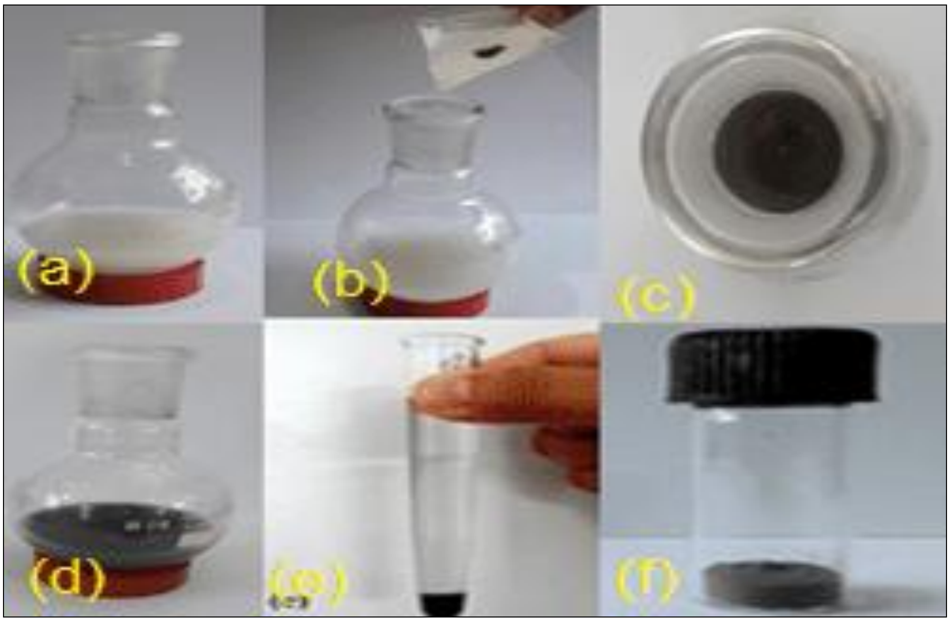

Fig 1: Pictorial representation of the experimental procedure of catalyst preparation

(a) Mixture of phenylboronic acid, K_2CO_3, Montmorillonite clay, i-PrOH and water. (b) Addition of $PdCl_2$ to (a). (c) Instant change in colour after addition of $PdCl_2$ to (a). (d) Complete black colour of the reaction mixture. (e) Purified Palladium Nanoparticles after centrifugation (f) Dried powder form of prepared catalyst.

Results and Discussion

The newly synthesized catalyst was characterized by transmission electron microscopy (TEM) to determine the particle size and morphology. The analysis revealed that the particles are distributed within the nanoscale regime. Representative TEM images showing nanoparticles with average sizes of approximately 50 nm, 10 nm, and 1 nm are presented in Figure 2 (A, B, and C) respectively.

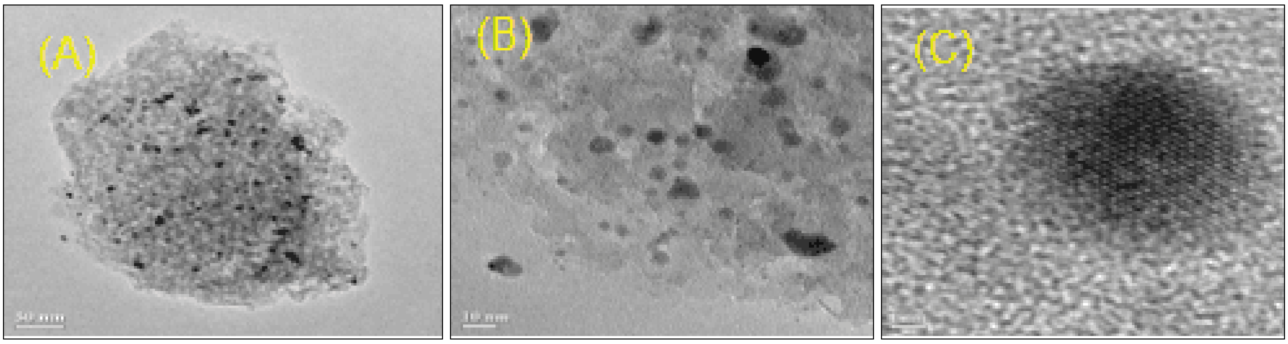

Fig 2: TEM images (A, B and C) of catalyst 2 (Imm-Pd (0)-K10)

TEM-EDX analysis was performed to evaluate the elemental composition of the newly synthesized solid-supported nano catalyst. The TEM-EDX spectrum confirmed the presence of palladium, along with the other constituent elements of Montmorillonite K10, as shown in Figure 3. The synthesized catalyst was also characterized by Scanning Electron Microscopy (SEM) as shown in Figure 4 which clearly represents the uniform distribution of Pd nanoparticles.

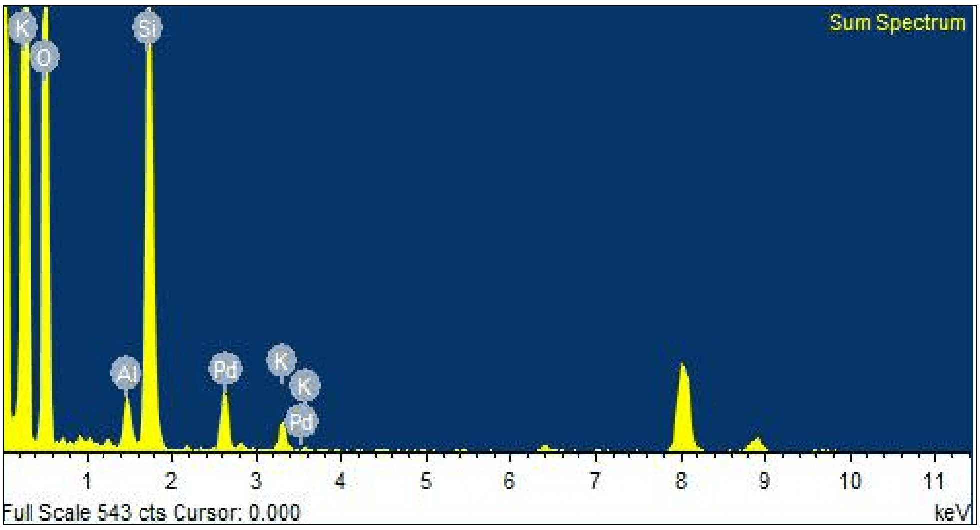

Fig 3: TEM-EDX pattern of catalyst 2 (Imm-Pd (0)-K10)

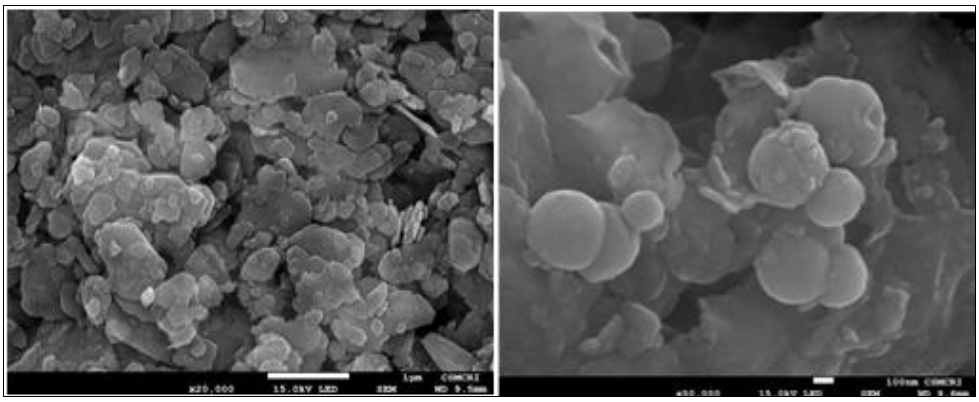

Fig 4: SEM images of the synthesized catalyst

X-ray diffraction (XRD) analysis of the Imm-Pd (0)-K10 catalyst revealed prominent Bragg reflections at 2θ values of 40.63°, 46.23°, 65.92°, and 78.85°, corresponding to the (111), (200), (220), and (311) planes of a face-centered cubic (fcc) crystalline structure, confirming the formation of palladium nanoparticles. The XRD pattern of the synthesized catalyst along with SAED pattern is presented in Figure 5 (a and b).

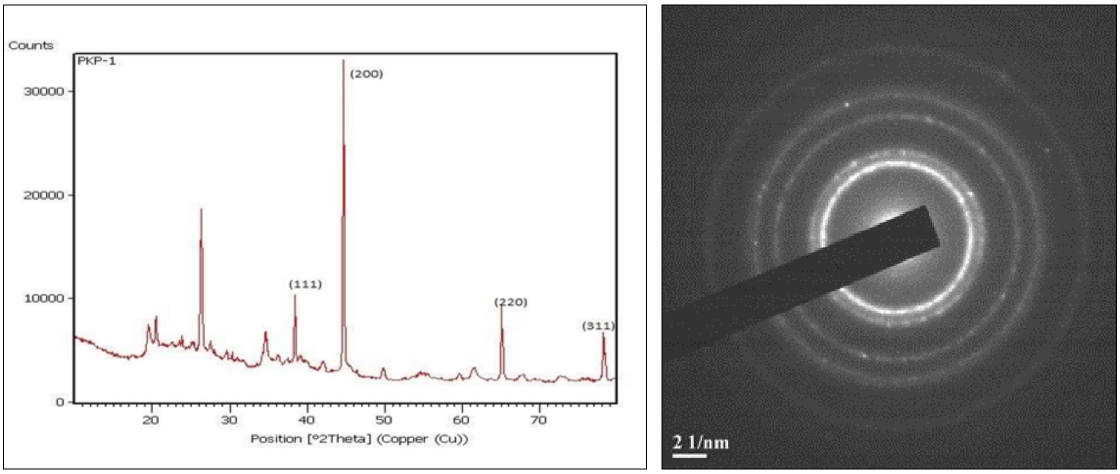

Fig 5: (a) XRD plot of catalyst 2 (Imm-Pd (0)-K10) (b) SAED pattern of the catalyst 2 (Imm-Pd (0)-K10) indicating the presence of (111), (200), (220) and (311) crystalline

The effects of solvent and base on the reaction rate were investigated by performing the Sonogashira reaction under different conditions. For this study, 4-bromotoluene and phenylacetylene were chosen as model substrates. Initial reactions were carried out using 4-bromotoluene (1 mmol), phenylacetylene (1.2 mmol), triethylamine (Et_3N, 2 mmol), and Imm-Pd (0)-K10 catalyst (3 mg) at room temperature in an i-PrOH /H_2O solvent system. The influence of different solvents on the reaction outcome is summarized in Table 1.

The reaction was carried out in a variety of solvent systems. Using water (H_2O) as the sole solvent resulted in a low product yield (Table 1, entry 6), whereas ethanol (EtOH) provided a significantly higher yield (Table 1, entry 2). The highest yield was achieved in the i-PrOH/H_2O mixed solvent system (Table 1, entry 3). The effect of different bases on the Sonogashira coupling was also investigated, and the results are summarized in Table 1. Triethylamine (Et_3N) was found to be the most effective base, affording the best yield under the optimized conditions (Table 1, entry 3).

From the above analysis of various solvents and bases, further reactions were carried out using Et_3N as base in i-PrOH/H_2O as solvent.

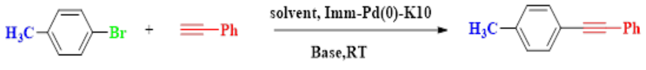

Table 1: Screening the efficiency of solvent and base for coupling of aryl bromides and phenylacetylene at room temperature. [a]

Entry	Solvent	Base	Time(h)	Yield^b (%)
1	-	Et_3N	5	65
2	EtOH	Et_3N	5	68
3	i-PrOH/H_2O (1:1)	Et_3N	2	78
4	-	K_2CO_3	5	56
5	i-PrOH	Et_3N	4	60
6	H_2O	Na_2CO_3	6	62

^{a}**Reaction Condition:** aryl halide (1 mmol), acetylene (1.2 mmol), Imm-Pd (0)-K10 (3 mg), solvent (4 ml) at room temperature. ^{b}Isolated yield

The applicability of the Imm-Pd (0)-K10 catalyst was evaluated by performing the Sonogashira reaction with a range of electron-rich and electron-deficient substrates under the optimized reaction conditions, and the results are summarized in Table 2.

Both aryl iodides and aryl bromides were successfully coupled with phenylacetylene, affording good yields of the desired products. As shown in Table 2, the reaction was effective for substrates bearing both electron-donating and electron-withdrawing groups.

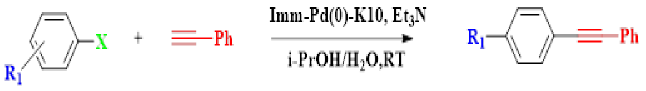

Table 2: Imm-Pd (0)-K10 catalyzed Sonogashira reactions using aryl halides and phenylacetylene at room temperature. [a]

Entry	R_1	X	Time(h)	Yield^b (%)
1	4-NO_2	I	4	65
2	2-OCH_3	I	4	68
3	4-CH_3	Br	2	78
4	4-NO_2	Br	4	68
5	2-OCH_3	Br	4	73
6	4-OCH_3	Br	4	75

^{a}**Reaction Condition:** aryl halide (1 mmol), phenylacetylene(1.2mmol), Imm-Pd (0)-K10 (3 mg), Et_3N (2 mmol), i-PrOH/H_20(1:1, 4ml) at room temperature. ^{b}Isolated yield

The reusability of the catalytic system was evaluated through consecutive Sonogashira reactions using 4-bromotoluene and phenylacetylene, with Et_3N as the base and an i-PrOH/H_2O solvent system at room temperature. After completion of each cycle, diethyl ether was added to the reaction mixture, and the organic layer was separated by centrifugation. The recovered catalyst was then washed, dried, and immediately reused in the subsequent cycle with fresh reactants. The catalyst retained its activity effectively up to the fourth cycle without significant loss of performance (Table 3, entries 1–4). In order to exclude the leaching of Palladium metal to the reaction media, hot filtration test was carried out for the model reaction. It was observed that no Pd species had leached to the reaction mixture.

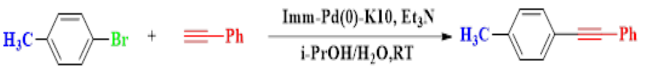

Table 3: Recyclability of the catalytic system. [a]

Entry	Run	Time (h)	Yield^b (%)
1	1st	2	78
2	2nd	2	78
3	3rd	2	78
4	4th	2.5	65

^{a}**Reaction Condition:** aryl bromide (1 mmol), phenylboronic acid (1.2 mmol), Imm-Pd (0)- K10(3 mg), Et_3N (2 mmol), i-PrOH: H2O (1:1, 4 ml) at room temperature. ^{b}Isolated yield

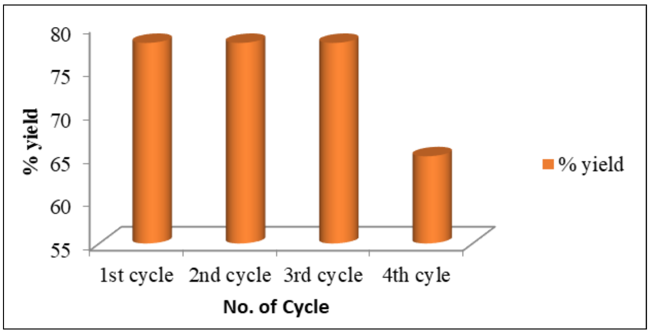

Fig 5: Bar diagram for reusability of synthesized catalyst in Sonogashira reaction

Conclusion

In summary, we have developed a rapid and efficient method for the synthesis of nanopalladium anchored on Montmorillonite K10 at room temperature. This approach stands in contrast to existing methodologies that often employ toxic reagents and harsh reaction conditions. The synthesized catalyst was characterized using several techniques, including Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray spectroscopy (TEM-EDX), Scanning Electron Microscopy (SEM), and X-Ray Powder Diffraction (XRD) analysis. The as-prepared catalyst demonstrates high efficiency in the Sonogashira cross-coupling reaction of aryl bromides with phenylacetylene, yielding the desired internal alkynes in satisfactory amounts.

Acknowledgement

The authors thank Dibrugarh University for providing all the infrastructural facility along with TEM, TEM-EDX, SEM, XRD and FTIR analysis.

References

1. Zimmerman J B, Anastas P T, Erythropel H C, Leitner W. Designing for a green chemistry future. Science,2020:367(6476):397–400.
2. Roschangar F, Sheldon R A, Senanayake C H. Overcoming barriers to green chemistry in the pharmaceutical industry–the Green Aspiration Level™ concept. Green Chemistry,2015:17(2):752–768.
3. Kar S, Sanderson H, Roy K, Benfenati E, Leszczynski J. Green chemistry in the synthesis of pharmaceuticals. Chemical Reviews,2021:122(3):3637–3710.
4. Horikoshi I, Serpone K. Introduction to nanoparticles. Microwaves in Nanoparticle Synthesis Fundamentals and Applications, 2013, 1–24.
5. Griffith D M, Li H, Werrett M V, Andrews P C, Sun H. Medicinal chemistry and biomedical applications of bismuth-based compounds and nanoparticles. Chemical Society Reviews,2021:50(21):12037–12069.
6. Pathakoti K, Goodla L, Manubolu M, Hwang H M. Nanoparticles and their potential applications in agriculture, biological therapies, food, biomedical, and pharmaceutical industry a review. Nanotechnology and Nanomaterial Applications in Food Health and Biomedical Sciences, 2019, 121–162.
7. Akbari A, Amini M, Tarassoli A, Eftekhari-Sis B, Ghasemian N, Jabbari E. Transition metal oxide nanoparticles as efficient catalysts in oxidation reactions. Nano-Structures and Nano-Objects,2018:14:19–48.
8. Favier I, Pla D, Gómez M. Palladium nanoparticles in polyols synthesis catalytic couplings and hydrogenations. Chemical Reviews,2019:120(2):1146–1183.
9. Phukan P, Boruah P R, Gehlot P S, Kumar A, Bordoloi A, Sarma D, *et al*. A quick efficient and simple protocol for synthesis of bimetallic nickel palladium nanoparticles effective catalyst for biaryl synthesis. ChemistrySelect,2017:2(35):11795–11800.
10. Phukan P, Boruah P R, Gehlot P S, Kumar A, Sarma D. A simple quick and novel protocol for biaryl synthesis using LiCl promoted in situ generated Pd nanoparticles. Applied Organometallic Chemistry, 2018, 32(2).
11. Kim S K, Kim C, Lee J H, Kim J, Lee H, Moon S H, *et al*. Performance of shape controlled Pd nanoparticles in the selective hydrogenation of acetylene. Journal of Catalysis,2013:306:146–154.
12. Marei M N, Khan H A, Badra J A, Montoya A, Farooq A, Masri A R. Comparative study of the catalytic oxidation of hydrocarbons on platinum and palladium wires and nanoparticles. Energy and Fuels,2022:36(4):2044–2057.
13. Hong K, Sajjadi M, Suh J M, Zhang K, Nasrollahzadeh M, Jang H W, *et al*. Palladium nanoparticles on assorted nanostructured supports applications for Suzuki Heck and Sonogashira cross coupling reactions. ACS Applied Nano Materials,2020:3(3):2070–2103.
14. Khalafi-Nezhad A, Panahi F. Size controlled synthesis of palladium nanoparticles on a silica cyclodextrin substrate a novel palladium catalyst system for the heck reaction in water. ACS Sustainable Chemistry and Engineering,2014:2(5):1177–1186.
15. Majhi S K, Jash S. Recent developments of nanocatalysts for Stille coupling reaction. Synthetic Communications,2023:53(24):2061–2087.
16. Pacardo D B, Knecht M R. Exploring the mechanism of Stille C C coupling via peptide capped Pd nanoparticles results in low temperature reagent selectivity. Catalysis Science and Technology,2013:3(3):745–753.
17. Konwar M, Phukan P, Chaliha A K, Buragohain A K, Damarla K, Gogoi D, *et al*. An unexplored Lewis acidic catalytic system for synthesis of pyrazole and its biaryls derivatives with antimicrobial activities through cycloaddition iodination Suzuki reaction. ChemistrySelect,2019:4(35):10236–10245.
18. Dudnik A S, Gevorgyan V. Formal inverse Sonogashira reaction direct alkynylation of arenes and heterocycles with alkynyl halides. Angewandte Chemie, 2010, 49(12).
19. Yan F, Zhang X, Li D, Zhu N, Bao H. Recent applications of the Sonogashira reaction in the synthesis of drugs and their derivatives a review. Applied Organometallic Chemistry, 2025, 39(1).
20. Sato R, Kanbara T, Kuwabara J. Air stable Pd 0 catalyst bearing dual phosphine ligands a detailed evaluation of air stability and catalytic property in cross coupling reactions. Dalton Transactions,2020:49(36):12814–12819.
21. Sheikh S, Nasseri M A, Allahresani A, Varma R S. Copper adorned magnetic nanoparticles as a heterogeneous catalyst for Sonogashira coupling reaction in aqueous media. Scientific Reports,2022:12(1):17986.
22. Li Y, Zhou P, Dai Z, Hu Z, Sun P, Bao J, *et al*. A facile synthesis of PdCo bimetallic hollow nanospheres and their application to Sonogashira reaction in aqueous media. New Journal of Chemistry,2006:30(6):832–837.
23. Jakobi M, Gallou F, Sparr C, Parmentier M. A general protocol for robust Sonogashira reactions in micellar medium. Helvetica Chimica Acta, 2019, 102(3).
24. Zhang A, Liu M, Liu M, Xiao Y, Li Z, Chen J, *et al*. Homogeneous Pd nanoparticles produced in direct reactions green synthesis formation mechanism and catalysis properties. Journal of Materials Chemistry A,2014:2(5):1369–1374.