

Advanced synthesis of Palladium nanoparticles immobilized The Schiff-base-functionalized ZSM-5 for promoting C-C Coupling Reactions under mild condition

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Abstract: A newly developed heterogeneous catalyst, ZSM-5@APTMS, has been synthesized with a focus on enhancing its efficiency and reusability. This catalyst incorporates a double Schiff-base functionalization with (*E*)-4-((pyridin-2-ylimino) methyl) benzaldehyde, which stabilizes palladium nanoparticles (Pd-NPs) to improve their performance in carbon-carbon coupling reactions under mild conditions. Palladium-based catalysts are particularly sought after for their effectiveness in facilitating the formation of carbon-carbon bonds, making them invaluable in the synthesis of various functional organic compounds. Furthermore, a direct correlation has been identified between the catalytic performance of the palladium nanoparticles and the density of acid sites present in the ZSM-5 framework during organic reactions. In this study, we developed a highly effective heterogeneous catalyst derived from ZSM-5, which was functionalized with (*E*)-4-((pyridin-2-ylimino) methyl) benzaldehyde and incorporated with palladium nanoparticles. This catalyst, referred to as ZSM-5@APTMS@(*E*)-4-((pyridin-2-ylimino) methyl) benzaldehyde@Pd-NPs, was successfully synthesized and employed to enhance cross-coupling reactions in water serving as a green solvent under mild conditions. Initially, ZSM-5 underwent immobilization using APTMS (3-aminopropyltrimethoxysilane), followed by modification with (*E*)-4-((pyridin-2-ylimino) methyl). This amine-activated Zeolite@(*E*)-4-((pyridin-2-ylimino) methyl) was subsequently utilized to enhance the stabilization of palladium as metal nanoparticles. The reduction of palladium (II) to palladium (0) was achieved through treatment with hydrazine, resulting in the formation of active metal sites. The characteristics of the Pd/ZSM-5@ structure were thoroughly analyzed using FTIR, SEM, TEM, XRD, EDS, and ICP-AES techniques. The catalyst demonstrated significant advantages, including compatibility in with aqueous environments, high thermal stability, exceptional catalytic efficiency, and reusability.

Keywords: Porousness, Nanostructures, Zeolites, Pd-NPs, Heterogeneous Catalyst, Reusability

Introduction

Cross-coupling reactions and their associated methodologies represent a category of highly effective synthetic strategies, predominantly facilitated by essential transformations catalyzed by transition metals. Notably, palladium-catalyzed processes, utilizing heterogeneous

palladium species as catalysts, serve as a robust approach for the formation of carbon-carbon bonds. This technique has gained significant traction in the synthesis of various functional organic compounds, underscoring its importance in contemporary organic chemistry [1,2]. In recent times years, there has been a significant expansion in the reactions associated with this category, primarily

driven by the critical role of catalysts that incorporate palladium (Pd) nanoparticles, specifically designed for such applications. Furthermore, the most notable catalytic reactions involving Pd metal that have undergone volatilization are presented to enhance contemporary techniques aimed at augmenting the reactivity of Pd metal [3, 4].

It is important to highlight that the field of synthetic organic chemistry has undergone significant transformation through the development of Palladium-catalyzed cross-coupling reactions. Notable examples of these reactions include Suzuki-Miyaura [2, 5], Sonogashira-Mizorogi [6], Heck [7], Negishi [8], Silence [9], Kumada [10, 11] and Sonogashira [12] all of which have advanced considerably in recent years.

The formation of a carbon-carbon bond results from a cross-coupling reaction, which is characterized by the replacement of a heteroatom nucleophile with an alkyl, aryl, or vinyl halide [13-17]. The synthesis of various aryl derivatives can be achieved simultaneously with a high degree of selectivity and yield, eliminating the necessity for the isolation of intermediate products [18, 19]. One notable example is the Heck reaction, a process that converts olefins bearing various substituents into their corresponding aryl derivatives [20, 21]. Non-symmetric biphenyl compounds can be produced through the application of the Suzuki coupling method, whereas diaryl-alkyne derivatives can be synthesized utilizing the Sonogashira coupling technique [22-26]. Heteroaryl and biaryl frameworks serve as crucial foundational elements in the synthesis of natural products and pharmaceuticals, including the antibiotic vancomycin and various anticancer agents [27, 28].

The synthesis of organic compounds utilizing environmentally friendly aquatic solvents or under solvent-free conditions has emerged as a prominent area of interest within the contemporary scientific community [29, 30]. Achievements in the domain of green chemistry have created significant opportunities for enhancing the efficiency and effectiveness of chemical processes while simultaneously minimizing their negative impacts. This advancement not only promotes safety and well-being through the adoption of milder conditions but also broadens the range of organic reactions that can be effectively conducted [19, 31-36].

ZSM-5 zeolite, classified within the pentasil zeolite family, is notably characterized by its capacity for isomorphous metal substitution within its framework, a property that is attributed to its resilience under high-temperature conditions [37, 38]. The material also proved to be highly beneficial for a range of organic transformations, particularly in its role as a support for metal catalysts [39]. Building upon our ongoing research in the field of heterogeneous catalysis, we present a novel synthetic approach for the preparation of palladium supported on modified ZSM-5 zeolite [40-42]. The role

of the newly introduced mesoporosity in zeolite was illustrated through its application in a cross-coupling reaction conducted under aerobic conditions. Notably, aluminosilicate zeolites are crystalline materials characterized by their porous structure, exhibiting remarkable stability in thermal, chemical, and mechanical aspects. These properties render them highly valuable in industrial applications, particularly as supports for metal catalysts [43,44]. ZSM-5 has the capacity to engage with the metal species that are assembled, leading to modifications in the electronic characteristics of these metals. This interaction has the potential to enhance the catalytic efficiency of the assembled metal species [45, 46]. The incorporation of mesoporous into zeolite crystals has the potential to enhance the mass transfer of both bulk substrates and products, thereby augmenting their catalytic efficiency. Consequently, by leveraging the unique structural attributes of the zeolite framework alongside the catalytic characteristics of transition metals, it is feasible to engineer and fabricate highly active and stable metal catalysts. In this design, the metal species would be strategically confined within the mesoporous zeolite framework, facilitating effective organic transformations.^{47, 48}

In this study, we present a newly developed heterogeneous catalyst, ZSM-5@ APTMS@ (*E*)-4-((pyridin-2-ylimino) methyl) @Pd-NPs, which has demonstrated remarkable efficacy in facilitating carbon-carbon coupling reactions under mild conditions. This catalyst has been successfully employed in the preparation of Suzuki, Sonogashira, and Heck coupling reactions, achieving high performance yields. A contributing factor to the catalyst's impressive regeneration capabilities may be attributed to its enhanced water resistance. The medium-pore structure of zeolites such as ZSM-5 introduces increased steric hindrance for reactant molecules within the zeolite pores, leading to improved yields of aromatic products and reduced coke formation, thereby maintaining the structural integrity of the catalyst against potential degradation by water molecules. The catalyst developed demonstrates enhanced catalytic efficiency attributed to the alteration of the microenvironment surrounding the palladium nanoparticles (Pd-NPs). The use of amino-activated ZSM-5 combined with (*E*)-4-((pyridin-2-ylimino) methyl) serves as a robust support for the catalyst, with Pd nanoparticles functioning as the anchored transition metal. The incorporation of amino groups into the ZSM-5 framework was aimed at creating a nitrogen-rich support that effectively immobilizes the Pd nanoparticles, resulting in a high loading capacity of palladium without significant leaching of the Pd-NPs. Furthermore, the catalyst exhibited remarkable recyclability, maintaining its performance over ten cycles.

Experimental:

Materials and Methods

All materials and reagents employed in this study were sourced from Merck and Sigma-Aldrich, and they were utilized without any further purification.

Synthesis of the *E*-4-((pyridin-2-ylimino) methyl) benzaldehyde

The synthesis of *E*-4-((pyridin-2-ylimino)methyl)benzaldehyde was achieved through the condensation reaction of 2-aminopyridine with terephthalaldehyde, following the methodology established in the literature by Gutha and Munagapati.⁴⁹ In a round-bottom flask, 0.2 g of 2-aminopyridine was dissolved in 25 ml of ethanol, followed by the addition of 2.81 g of terephthalaldehyde, which had been dissolved in 40 ml of methanol. Acetic acid was then added dropwise, in a quantity of 3 to 5 drops, while stirring the mixture at room temperature. The reaction was subsequently conducted at a temperature of 65°C for a duration of 2 to 4 hours. Upon completion of the reaction, the mixture was poured into crushed ice made from deionized water to facilitate cooling. This process resulted in the formation of a yellow precipitate, which was collected by filtration using a Buchner funnel under vacuum conditions. The precipitate was then crystallized using water (Figure 1).

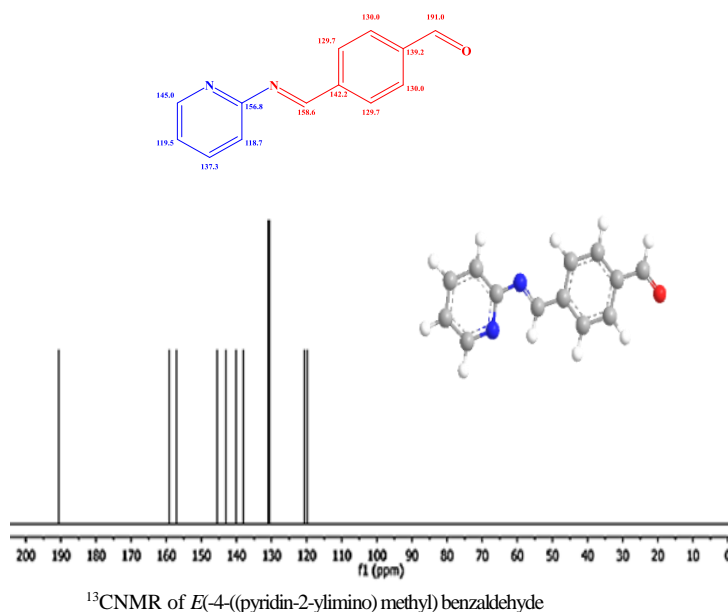
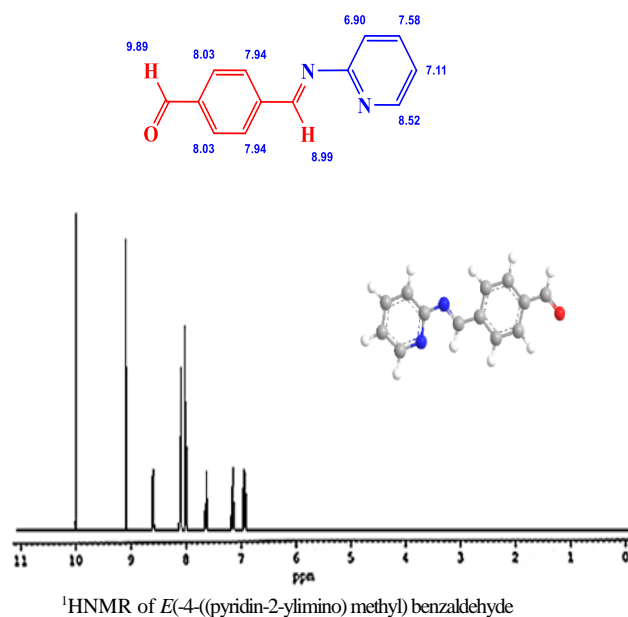


Fig. 1. Synthesis of *E*-4-((pyridin-2-ylimino) methyl) benzaldehyde

Synthesis of amine-Functionalized ZSM-5

The synthesis of ZSM-5@APTMS commenced with the transfer of 1.0 g of ZSM-5 and 60 ml of dry toluene into a dry round-bottom flask, where the mixture was subjected to ultrasonic irradiation for a duration of 30 minutes to ensure thorough dispersion. Following this initial step, the well-dispersed mixture was functionalized by the gradual addition of 1.1 ml of APTMS (3-aminopropyltrimethoxysilane), which had been previously diluted in 2-3 ml of dry toluene, at room temperature. Subsequently, the flask was fitted with a condenser and subjected to reflux at 80 °C for 24 hours. Upon completion of the reaction, the amine-functionalized ZSM-5 was isolated through filtration, washed three times with dry toluene to remove any unreacted materials, and then dried in a vacuum oven at 55 °C for 12 hours to yield the final product.

Synthesis of ZSM-5@APTMS@ *E*-4-((pyridin-2-ylimino) methyl) benzaldehyde

In the preceding step, 0.5 g of Zeolite-NH₂ was combined with 25 ml of acetonitrile (CH₃CN) and stirred at room temperature for a duration of 30 minutes. Subsequently, 0.15 g of *E*-4-((pyridin-2-ylimino(methyl)benzaldehyde) was fully dissolved in 15 ml of acetonitrile and added to the mixture, which was then stirred at room temperature for an additional 15 minutes. Following this, the reaction mixture was subjected to reflux conditions at 75°C for 24 hours. Upon completion of the reaction period, the resultant product was centrifuged, washed twice with acetonitrile, and subsequently dried in a vacuum oven at

60°C for 12 hours, yielding ZSM-5@APTMS@E(-4-((pyridin-2-ylimino) methyl) benzaldehyde).

Stabilization of Pd-NPs on ZSM-5@APTMS@ E(-4-((pyridin-2-ylimino) methyl) benzaldehyde

A total of 0.04 grams of palladium acetate ($\text{Pd}(\text{OAc})_2$) was initially dissolved in 50 milliliters of acetonitrile at ambient temperature. Subsequently, 0.2 grams of ZSM-5@APTMS@E(-4-((pyridin-2-ylimino) methyl) benzaldehyde) was introduced into the flask containing the clear amber solution of palladium acetate in acetonitrile, and the mixture was stirred at a temperature range of 40 to 45 degrees Celsius for a duration of eight hours. After this period, the temperature was reduced to room temperature, and the reaction mixture was treated with 0.3 milliliters of a freshly prepared hydrazine hydrate solution, which consisted of three drops of hydrazine hydrate diluted in three milliliters of deionized water, and stirred at room temperature for an additional 24 hours. The final step involved separating the reaction mixture using a centrifuge operating at 9000 rpm, followed by a wash with acetonitrile and subsequent drying in an oven (Figure 2).

Spectroscopic Characterization of ZSM-5@APTMS@terephthalaldehyde/2-aminopyridine @ Pd-NPs Catalyst

In this report, we present a novel and efficient palladium-based catalyst designed to facilitate C-C coupling reactions, building upon our previous efforts to establish straightforward and sustainable methodologies for various organic transformations. The process commenced with the preparation and modification of ZSM-5 using organic ligands. Subsequently, the synthesized ZSM-5@APTMS@ (E)-4-((pyridin-2-ylimino) methyl)/Pd-NPs served as a support for the heterogenization of palladium nanoparticles (as illustrated in Figure 2). Ultimately, the developed ZSM-5@APTMS@E(-4-((pyridin-2-ylimino) methyl) @Pd-NPs was utilized as a catalyst in the C-C coupling reaction. (Figure 3).

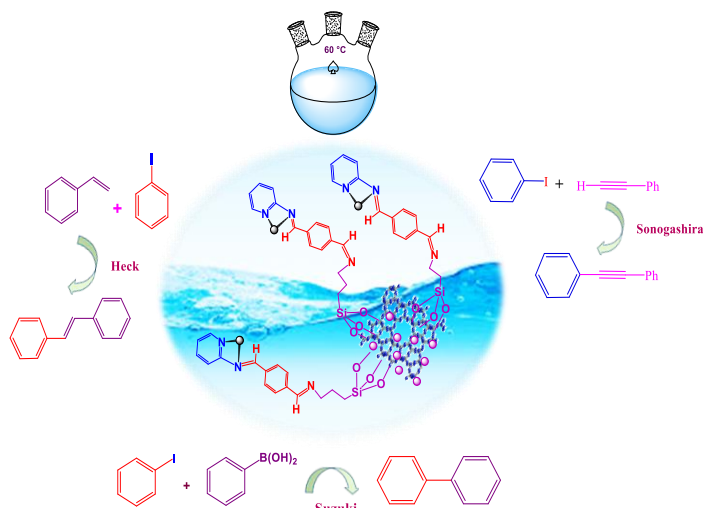


Fig. 2. Schematic of ZSM-5@APTMS@ (E)-4-((pyridin-2-ylimino) methyl) @ Pd-NPs catalyst for C-C coupling reaction

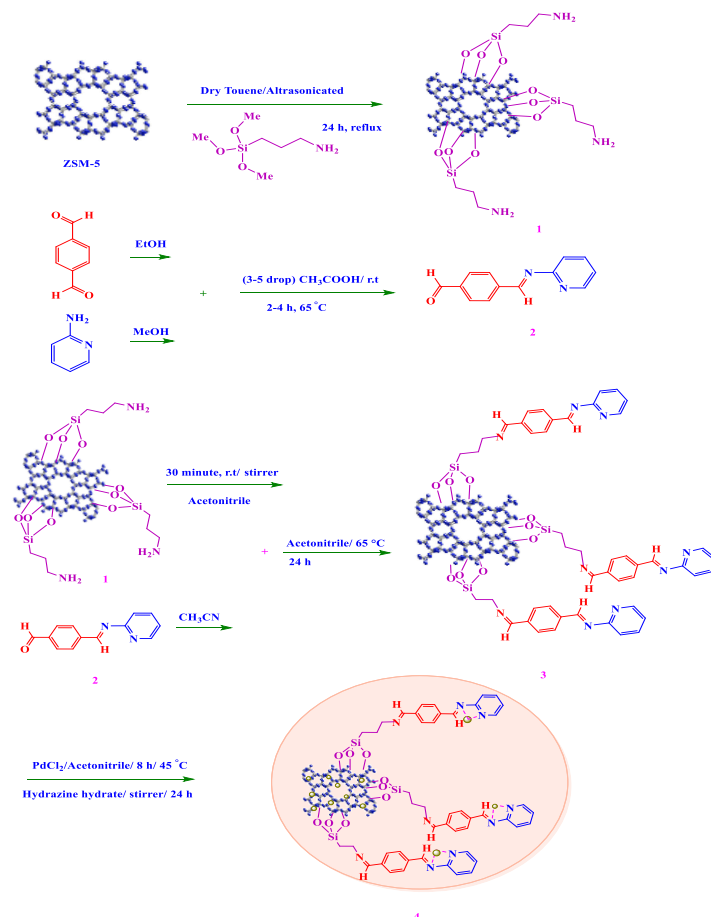


Fig. 3. Schematic synthesis of Palladium nanoparticle immobilized on ZSM-5@APTMS@ (E)-4-((pyridin-2-ylimino) methyl) /Pd-NPs

Results and discussion:

FT-IR spectra

The FT-IR spectra for ZSM-5@ APTMS and the final synthesized catalyst ZSM-5@ APTMS @ (2-Aminopyridine-terephthalaldehyde) @Pd-NPs are illustrated in Figure 4. The spectrum reveals absorption bands at 3396 cm^{-1} and 3429 cm^{-1} , which are indicative of O-H stretching vibrations. Additionally, a band within the range of $3350\text{--}3650\text{ cm}^{-1}$ is observed, corresponding to the stretching vibration of hydroxyl groups. The symmetric and asymmetric stretching vibrational bands are noted at 798 cm^{-1} and 1076 cm^{-1} , respectively, which are attributed to the silanol group vibrations (Si-O-Si). Furthermore, distinctive bands at 2297 cm^{-1} and 2928 cm^{-1} are associated with C-H vibrations, along with a notable absorption band at 2939 cm^{-1} that corresponds to CH₂ stretching. A notable band observed at 1589 cm^{-1} and another at 1627 cm^{-1} are attributed to the (C=C) bond, while the bands detected at 1156 cm^{-1} and 1155 cm^{-1} are associated with (C-O) groups, each playing significant roles in the molecular architecture. Furthermore, the detection of an asymmetric stretching vibration band near 1225 cm^{-1} serves to validate the zeolite structure within the final synthesized catalyst. Additionally, the bands located in the ranges of 1100 cm^{-1} and 1400 cm^{-1} correspond to internal tetrahedral asymmetric stretching vibrations and bending vibrations, respectively. A band observed at 1400 cm^{-1} is indicative of the bending vibrations associated with the N-H group. The band located at 3439 cm^{-1} reflects the stretching modes of NH₂ groups, which have been successfully modified, providing compelling evidence for the functionalization of ZSM-5. Additionally, the band that appears at 1532 cm^{-1} corresponds to the stretching vibration of the C-N bond in the amine component of the ZSM-5@ APTMS compound. These findings further substantiate the effective attachment of APTMS to the surface of the ZSM-5 substrate. Furthermore, the overlapping of other characteristic band from various components of the composite necessitated the application of additional characterization techniques to validate the formation of the catalyst (Figure 4) [50]

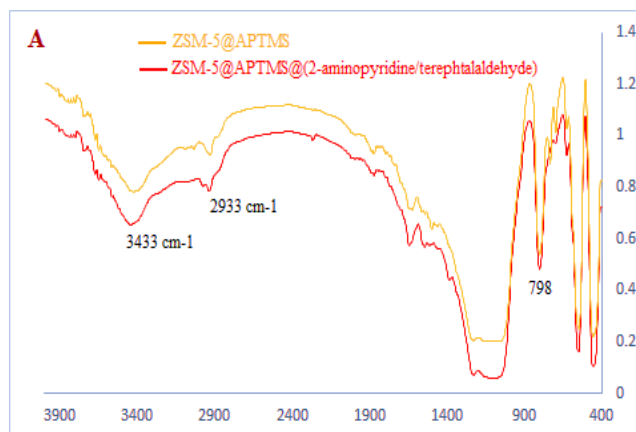


Fig. 4. Infrared spectrum (FT-IR) analysis of ZSM-5@ APTMS and ZSM-5@ APTMS @ (2-Aminopyridine-terephthalaldehyde) @ Pd-NPs

X-ray Diffraction (XRD) Analysis

The crystalline architecture of ZSM-5@ APTMS @ (2-Aminopyridine-terephthalaldehyde) integrated with Pd-NPs has been analyzed using X-ray diffraction (XRD) techniques, as illustrated in Figure 5. The XRD pattern reveals the emergence of new peaks associated with the composite of ZSM-5@ APTMS @ (2-Aminopyridine-terephthalaldehyde) and Pd-NPs, which align with the standard Bragg reflections at indices (111), (200), (220), and (311) for Pd-NPs, thereby confirming their successful synthesis [51].

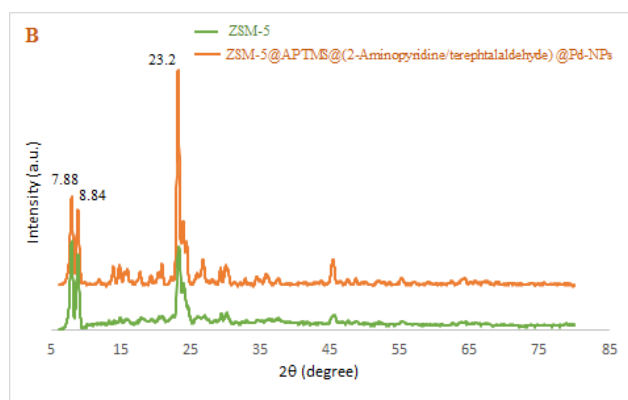


Fig. 5. XRD pattern of ZSM-5@ APTMS @ (2-Aminopyridine-terephthalaldehyde) @ Pd-NPs,

In this study, hydrazine hydrate was employed as a reducing agent, leading to the synthesis of larger nanoparticles (NPs) in comparison to alternative reductants like sodium borohydride (NaBH₄), with the objective of generating palladium nanoparticles (Pd-NPs) on the surface of modified ZSM-5. The transmission electron microscopy (TEM) images reveal a uniform distribution of Pd NPs across the ZSM-5 surface, as illustrated in Figure 6A-D. Further analysis through

scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and elemental mapping was conducted to assess the elemental composition and the spatial arrangement of elements within the final composite, as shown in Figures 6A-C, 6D, and 5E. The SEM-EDS results validate the presence of aluminum, sulfur, silicon, sodium, oxygen, carbon, nitrogen, and palladium in the ZSM-5@ APTMS @ (2-Aminopyridine/terephthalaldehyde) @Pd-NPs, which exhibited a palladium loading of 9.14 wt.%. Additionally, the SEM elemental mapping demonstrates a consistent distribution of elements throughout the sample matrix, confirming the successful synthesis of the composite (Figure 6A-C).

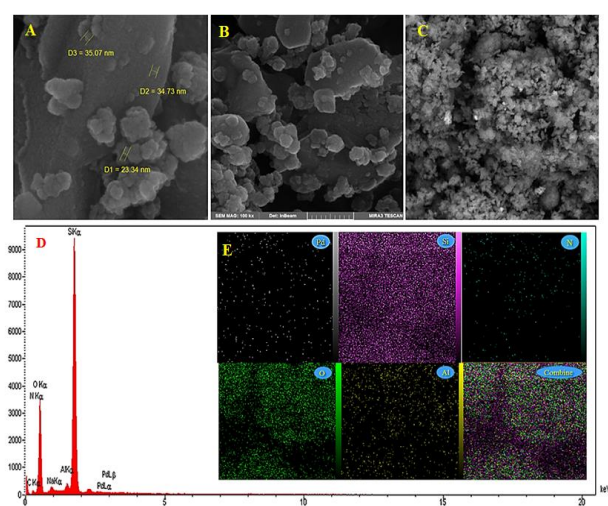


Fig. 6. A, B, C) the SEM images, D) EDS, and E) the mapping spectra of ZSM-5@APTS@ (2-Aminopyridine-terephthalaldehyde) @ Pd-NPs

The investigation into the morphology and surface characteristics of ZSM-5@ APTMS @ (2-Aminopyridine / terephthalaldehyde) @Pd-NPs was conducted using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques, as depicted in Figures 6A-C and 7A-D. As illustrated in Figure 6A, the SEM analysis reveals that the nanoparticles exhibit a diameter ranging from approximately 23.34 to 35.07 nm. Furthermore, the TEM images demonstrate a uniform distribution of Pd-NPs across the surface of the modified ZSM-5 nanocrystals, which possess both intra- and inter-crystalline porous structures, as shown in Figure 7A-D. The elemental composition and the spatial distribution of elements within the ZSM-5@ APTMS @ (2-Aminopyridine/terephthalaldehyde) @Pd-NPs were analyzed using energy-dispersive X-ray spectroscopy (EDS) and mapping techniques, as illustrated in Figures 6D and 6E. The EDS results reveal an atomic ratio of silicon to aluminum (Si/Al) of 42, thereby confirming the

effective immobilization of palladium (Pd) nanoparticles onto the newly developed ZSM-5@ APTMS @ (2-Aminopyridine/terephthalaldehyde) @ Pd-NPs catalyst. The ZSM-5 catalyst exhibits a high Si/Al ratio exceeding 10, which suggests an increase in crystal size and surface area, ultimately enhancing the physicochemical characteristics of the catalyst.

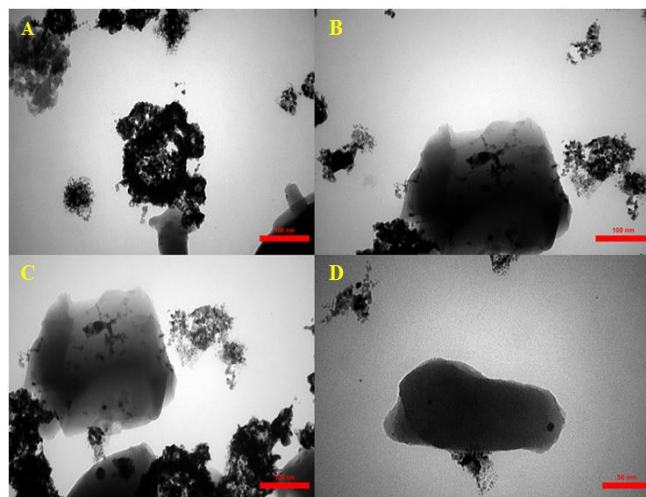


Fig. 7. The transmission electron microscope (TEM) images of ZSM-5 @ APTMS @ (2-Aminopyridine/terephthalaldehyde) @ Pd-NPs

The transmission electron microscope (TEM) images of the newly developed catalyst ZSM-5 @ APTMS @ (2-Aminopyridine/terephthalaldehyde) @ Pd-NPs reveal a hierarchical arrangement of modified ZSM-5 nanocrystals characterized by both intra- and inter-crystalline porous structures, as depicted in Figure 7A-D. The low-magnification TEM images validate the presence of ZSM-5 modified zeolite @Pd-NPs, showcasing uniform crystallites measuring 50 and 100 nm, which aligns well with the results obtained from scanning electron microscopy (SEM). Importantly, the images display bright spots indicative of intra-crystalline mesoporosity, with numerous brighter regions corresponding to the identified mesoporous structures, making them easily distinguishable.

General procedure for the Suzuki reaction

In a typical procedure, 1 mmol of the designated aryl halide was combined with 1.1 mmol of aryl boronic acid in 3 mL of distilled water, serving as an environmentally friendly solvent, within a 10 mL single-neck flask. To this solution, 0.025 g of the synthesized ZSM-5@ATPMS/2-aminopyridine/terephthalaldehyde/PdNPs catalyst and 2 mmol of K_2CO_3 were introduced and stirred. The specific temperature and duration of the reaction were contingent upon the precursor utilized. The reaction's progress was monitored using thin-layer chromatography (TLC) with a

solvent system of n-hexane and ethyl acetate in a 7:3 ratio. Upon completion of the reaction, the catalyst was removed by filtration, the mixture was allowed to cool to 25°C, and the organic phase was extracted using diethyl acetate. The extract was subsequently dried over magnesium sulfate (MgSO₄), which was later removed by filtration. The organic solvent was then evaporated, and column chromatography was employed for product purification, utilizing a solvent ratio of n-hexane to ethyl acetate at 1:5. The identification of the products was confirmed through physical data such as melting points, as well as Fourier-transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) techniques, as detailed in the supporting information.

General procedure for the Heck reaction

In a 10 ml round-bottomed flask, a reaction mixture was prepared by combining 1 mmol of the selected aryl halide, 1.1 mmol of olefin, 2 mmol of potassium carbonate (K₂CO₃), 3 ml of distilled water, and 0.03 g of the newly synthesized ZSM-5@ATPMS/2-aminopyridine/terephthaldehyde/PdNPs catalyst, all maintained at a temperature of 60°C. Upon completion of the reaction, the catalyst was separated by centrifugation. The mixture was then allowed to cool, and ethyl acetate was employed to extract the resulting products. Following the extraction, the organic solvent was removed through evaporation after drying the mixture with MgSO₄. To achieve product purification, column chromatography was performed using a solvent system of n-hexane and ethyl acetate in a 1:5 ratio. The identification of the products was confirmed through physical data such as melting points, as well as FT-IR and NMR techniques, with supporting information provided.

General procedure for the Sonogashira reaction.

In a typical procedure, 1.2 mmol of acetylene was combined with 1 mmol of the corresponding halobenzene in a one-neck balloon containing 3 mL of distilled water. To this mixture, 20 mg of a catalyst composed of ZSM-5@ATPMS, 2-aminopyridine, terephthalaldehyde, and PdNPs, along with 2 mmol of K₂CO₃, was introduced. The reaction temperature was then elevated to 50°C while maintaining stirring for a designated duration, as outlined in Table S4. The reaction's progress was monitored using thin-layer chromatography (TLC) with a solvent system of n-hexane and ethyl acetate in a 6:1 ratio. Upon completion of the reaction, the catalyst was removed through filtration, followed by washing with ethanol and drying at 60°C for 20 minutes. The resulting filtered solution was allowed to cool to room temperature, after which the organic components were extracted using pure diethyl ether (Et₂O). Product purification was achieved through column chromatography employing a solvent mixture of n-hexane and ethyl acetate in a 1:4 ratio. The

identification of the products was confirmed through physical data such as melting points, as well as FT-IR and NMR techniques, with additional details provided in the supporting information.

Catalytic performance

Following a thorough characterization of our proposed catalyst, we evaluate its catalytic performance in various coupling reactions, specifically focusing on ZSM-5@ATPMS /2-aminopyridine/terephthaldehyde/PdNPs in the context of Heck, Sonogashira, and Suzuki reactions. Our investigation commences with an analysis of the catalyst's effectiveness in facilitating the Suzuki reaction, utilizing the interaction between iodobenzene and phenylboronic acid in the presence of ZSM-5@ATPMS /2-aminopyridine/terephthaldehyde/PdNPs as a model reaction. We systematically examine the influence of several parameters, including reaction time, temperature, solvent choice, base type, and catalyst quantity, on the reaction kinetics, with the results presented in Table 1. In order to identify the most effective solvent for the Suzuki-coupling reaction involving the proposed catalyst, the reaction's progress was assessed across a range of solvents, including water, toluene, DMSO, DMF, CH₂Cl₂, MeCN, a mixture of ethanol and water, ethanol, tetrahydrofuran. The findings indicate that ethanol yields the most favorable results. The reaction temperature was elevated to 80°C, with optimal outcomes observed at 60°C; further increases in temperature did not enhance the reaction yield. Utilizing thin-layer chromatography (TLC) to monitor the reaction, it was established that at 60°C in water, equilibrium was reached after 60 minutes. The optimal catalyst quantity was ascertained by evaluating the reaction's progress with varying catalyst amounts. The study concluded that 25 mg of the proposed catalyst is sufficient for the Suzuki reaction to proceed effectively. Consequently, these investigations demonstrate that the highest yields are obtained with 25 mg of the ZSM-5@ATPMS/2-aminopyridine/terephthaldehyde/PdNPs catalyst at 60°C in water after a duration of 60 minutes. The optimization tests were conducted for both the Heck and Sonogashira reactions utilizing the proposed catalyst. The findings of this investigation are encapsulated in Tables S1 and S3, which detail the results for the respective reactions. For the Heck reaction, the combination of iodobenzene and styrene was employed as the model reaction, while the iodobenzene and phenylacetylene reaction served as the model for the Sonogashira reaction. The study revealed that the optimal conditions for the Heck reaction were achieved by employing H₂O as the solvent, K₂CO₃ as the base, and 30 mg of ZSM-5@ATPMS/2-aminopyridine/terephthaldehyde/PdNPs as the catalyst, conducted at 60°C for 120 minutes, yielding the highest results. Conversely, the ideal conditions for the

Sonogashira reaction were determined to be 20 mg of catalyst in H₂O with K₂CO₃ at 50°C for a duration of 20 minutes.

Table 1. The findings of the Suzuki coupling reaction optimization experiments

Entrance	Catalyst (mg)	Solvent	T (°C)	Base	Time (min)	Yield (%)
1	-	EtOH absolute	r.t	K ₂ CO ₃	60	-
2	5	EtOH absolute	80	K ₂ CO ₃	60	40
3	10	EtOH: H ₂ O	80	K ₂ CO ₃	60	75
4	20	EtOH: H ₂ O	80	K ₂ CO ₃	60	99
5	20	EtOH: H ₂ O	80	K ₂ CO ₃	40	99
6	20	H ₂ O	80	K ₂ CO ₃	40	99
7	25	H ₂ O	65	K ₂ CO ₃	60	99
8	25	H ₂ O	60	K ₂ CO ₃	60	99
9	25	H ₂ O	55	K ₂ CO ₃	60	92
10	25	H ₂ O	60	KOH	60	90
11	25	H ₂ O	60	K ₃ PO ₄ .3H ₂ O	60	78
12	25	H ₂ O	60	CH ₃ COONa	60	25
13	25	H ₂ O	60	Et ₃ N	60	50
14	25	H ₂ O	60	Piperidine	60	30
15	25	H ₂ O	60	Na ₂ CO ₃	60	68
16	25	DMSO	60	K ₂ CO ₃	60	-
17	25	DMF	60	K ₂ CO ₃	60	35
18	25	1,2-dichloroethane	40	K ₂ CO ₃	60	35
19	25	MeCN	60	K ₂ CO ₃	60	10
20	25	PhCH ₃	60	K ₂ CO ₃	60	30
21	25	NMP	60	K ₂ CO ₃	60	35
22	25	THF	60	K ₂ CO ₃	60	20

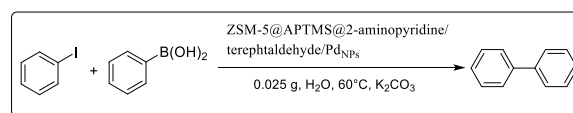
Conditions for the chemical reaction: 1 mmol of Iodobenzene and 1 mmol of phenylboronic acid.

Following the identification of the optimal reaction conditions, we evaluated the versatility of our proposed methodology by synthesizing a variety of biphenyl derivatives from an array of precursors. In this investigation, multiple aryl halides and aryl boronic acids were subjected to reactions facilitated by the proposed catalyst under the established optimal conditions. The findings of this research are summarized in Table 2, which illustrates that the reactions yield high product quantities when aryl halides are utilized, regardless of whether these halides occupy the ortho, meta, or para positions on the aromatic ring. Furthermore, the data indicates that even the use of an aliphatic halide results in a substantial yield. The efficacy of the proposed catalyst is underscored by its

successful facilitation of the Suzuki coupling reaction with various iodo, bromo, and chloro derivatives of aromatic compounds, highlighting its broad applicability and effectiveness.

The broad applicability of the method we proposed for the Heck and Sonogashira reactions was also investigated, with the results detailed in Tables S2 and S4, respectively. This research demonstrated that the combination of ZSM-5@APTMS/2-aminopyridine/PdNPs effectively facilitates these reactions, yielding products in good to excellent quantities; however, it is noteworthy that the yields for certain products in the Sonogashira reaction were comparatively lower.

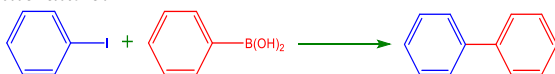
Table 2. Preparation of various organic compounds by Suzuki coupling reaction under optimum conditions.



Entry	Aryl halide	Aryl boronic acid	Product
1			
2			
3			
4			
5			
6			

The catalytic efficacy of the Suzuki cross-coupling reaction utilizing ZSM-5@ATPMS /2-aminopyridine /terephthaldehyde/PdNPs is evaluated in comparison to various catalysts documented in the literature, as presented in Table 3. The findings reveal that the catalyst we propose achieves one of the highest yields recorded to date. This remarkable performance may be attributed to the careful post-synthesis modification involving an N-rich organic ligand, which effectively alters the electronic structure of the ZSM-5 framework. The incorporation of 2-aminopyridine modifies the electronic characteristics of ZSM-5, thereby enhancing the catalytic activity of the palladium nanoparticles within the composite. Furthermore, as indicated in Table S6, a similar trend is observed for our proposed catalyst in the context of the Heck reaction.

Table 3. Comparison of the catalytic performance of the proposed catalyst with some related reports in the literature.



Entry	Catalyst	Reaction condition	Yield (%)	Time (h)	Ref.
1	Pd@Mag-MSN (1)	K ₂ CO ₃ , CH ₂ Cl ₂ , 80 °C	85	6	52
2	Xerogel g1-MNPs (1)	Na ₂ CO ₃ , CH ₃ OH, 60 °C	99	2	53
3	Pd/NiFe ₂ O ₄ (0.1)	Na ₂ CO ₃ , DMF, 90 °C	50	2	54
4	Pd-Fe ₃ O ₄ (1)	K ₂ CO ₃ , DME: H ₂ O 3: 1, reflux	71	24	55
5	C/Co@PNIPAM -PPh ₂ -Pd (3)	K ₂ CO ₃ , toluene: H ₂ O 2: 1, 85 °C	99	16	56
6	Co@C@Pd (1.1)	Na ₂ CO ₃ , THF: H ₂ O 1: 2, 65 °C	96	2	57
7	Pd/Fe ₃ O ₄ @C (0.3)	K ₂ CO ₃ , EtOH, reflux	100	1	58
8	Pd@Fe ₃ O ₄ (0.816)	K ₃ PO ₄ , CH ₃ OH, 40-65 °C	90	18	59
9	Fe ₃ O ₄ @PUNP ^a -Pd (0.1)	K ₂ CO ₃ , H ₂ O, 90 °C	98	1	60
10	GA-FSNP@Pd (0.28)	K ₂ CO ₃ , solvent free, 90 °C	92	0.25	61
11	Pd-IPG (0.1)	NaOH, EtOH: H ₂ O, 60 °C	99	1	62
12	GO/NHC-Pd (1)	Na ₃ PO ₄ .12H ₂ O, H ₂ O, 100 °C	91.6	6	63
13	Pd NPs on polymer (0.08)	K ₂ CO ₃ , H ₂ O, 25-100 °C	83	5	64
14	Pd-HoMOF (0.4)	KOH, DMF, 100 °C	99	1	65
15	(Pd (II)-NHCs) _n @nSiO ₂ (0.27)	K ₂ CO ₃ , DMF: H ₂ O (2:1), 60 °C	97	6 min	66
16	Pd (II)-NiFe ₂ O ₄ (0.5)	K ₂ CO ₃ , EtOH: H ₂ O, 80 °C	96	3	54
17	GO-CPTMS@Pd-TKHPP (10)	K ₂ CO ₃ , EtOH: H ₂ O, 80 °C	99	15 min	67
18	ZSM-5@APTMS@2-aminopyridine/terephthaldehyde@Pd-NPs (0.025)	H ₂ O, K ₂ CO ₃ , 60 °C	99	60 min	This study

Recyclability

The ability of the catalyst to be reused is a crucial aspect of its application on a larger scale, as it facilitates the execution of multiple iterations of the same chemical reaction. To evaluate the recycling efficiency of our proposed catalyst, we extracted it from the reaction mixture and subjected it to several washes with ethyl acetate. Subsequently, we assessed the performance of the recycled catalyst in the model reaction over a total of ten

cycles. As illustrated in Figure 9, the catalyst maintained its efficacy after three cycles, demonstrating over 80% of its initial performance even after ten applications. This remarkable reusability can be attributed to the robust water resistance exhibited by ZSM-5 in aqueous conditions. Additionally, the pore structure of ZSM-5 effectively limits the penetration of water molecules to the secondary building unit (SBU), thereby enhancing the stability of the material. Figure S1 further demonstrates that the ZSM-5@APTMS/2-aminopyridine/terephthaldehyde/PdNPs catalyst exhibits outstanding reusability in both the Heck and Sonogashira coupling reactions, sustaining its performance across ten cycles.

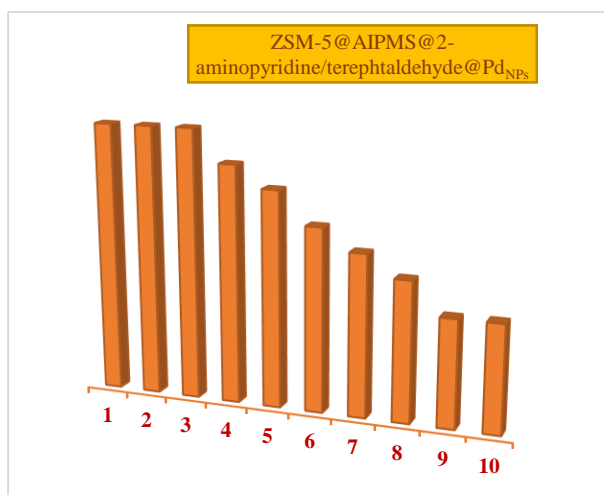


Fig. 9. The recyclability of ZSM-5@ APTMS @2-aminopyridine/terephthaldehyde@Pd-NPs catalyst.

ICP Results After Recycling

ICP analysis of the recycled catalyst was performed after 7 times of catalyst use, after each use cycle to check the amount of Pd, and the results are summarized in Table 1. As shown in this table, only a very small amount of Pd, less than 0.03%, was leached.

Catalyst	%mol palladium
1	0.8
2	0.79
3	0.79
4	0.78
5	0.77
6	0.76
7	0.75

Conclusion

In this research, ZSM-5 was selected as a support for the heterogenization of palladium nanoparticles (Pd NPs)

owing to its significant surface area and intrinsic structural stability. The composite material, designated as ZSM-5 @ATPMS/2-aminopyridine/terephthaldehyde/Pd-NPs, underwent comprehensive characterization through techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and elemental mapping, confirming its successful synthesis. This catalyst was subsequently employed to facilitate three types of carbon-carbon coupling reactions: Suzuki, Heck, and Sonogashira, all of which exhibited enhanced catalytic performance. The findings of this investigation suggest that the remarkable efficiency observed can be attributed to the modulation of the microenvironment surrounding the palladium nanoparticles (NPs). In this research, ZSM-5 was selected as the support for the heterogenization of the Pd NPs, owing to its significant surface area and inherent structural stability. The catalyst demonstrated exceptional recycling capabilities, which can be linked to both the intrinsic resistance of ZSM-5 and the additional resistance conferred by its high surface area, unique channel architecture, thermal stability, resistance to corrosion, shape selectivity, and the porous characteristics of ZSM-5. Furthermore, the catalyst was shown to be reusable for up to eight cycles. A critical aspect of employing this catalyst in aqueous solvent conditions pertains to its effectiveness in facilitating the Suzuki, Sonogashira, and Heck reactions under very mild conditions.

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Author contributions

L.M. synthesized catalyst, identified and synthesized the desired C-C Coupling reactions, L.M. wrote the paper, M. V edit the paper.

Conflicts of interest

There are no conflicts to declare.

Data Availability

All data generated or analyzed during this study are included in this published article (and its Supplementary Information files).

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