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CeO_2/Pd Nanoparticles Incorporated Fly Ash Zeolite: An Efficient and Recyclable Catalyst for $C_{sp}{}^2$-$C_{sp}{}^2$ Bond Formation Reactions

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The catalytic activity of CeO_2 and palladium nanoparticles supported fly ash zeolite (CeO_2/Pd@FAZ) for $C_{sp}{}^2$-$C_{sp}{}^2$ bond formation was studied. CeO_2/Pd@FAZ was characterized by FTIR, XRD, EDAX and TEM studies. In the Suzuki-Miyauracross-coupling reaction, biphenyl derivatives with excellent yields were obtained, and the reaction conditions were optimized. The catalytic activity was explored using a wide variety of diversely substituted aryl bromides and chlorides with aryl boronic acid under optimized reaction conditions. The recyclability of the catalyst was established for three cycles, with the conversion rate from 99 to 40%, which gained the advantage of heterogeneous catalysis.

KEYWORDS

CeO_2 nanoparticles, Pd nanoparticles, Suzuki-Miyauracross-coupling, zeolites

1 | INTRODUCTION

Coal fly ash is a solid waste generated from thermal power plants, which consists of crystalline aluminosilicates, mullite, and metal oxides in trace amounts. The utilization of fly ash is a matter of global concern from an environmental and economic point of view. Owing to the high silica and alumina content, fly ash can be converted into zeolite by hydrothermal treatment, which finds a wide range of applications. Recently, metal nanocatalysts have been extensively studied as model catalysts for industrially significant reactions. The high surface-to-volume ratio of nanomaterials makes their role significant in catalysis. Homogeneous catalysts get dissolved in the reaction medium, thus rendering all catalytic sites accessible to reactants in solution, which leads to high activity. However, separation, handling efficiency, and reusability of homogeneous catalysts need to be addressed, which opens scope for heterogeneous catalysis. Anchoring nanocatalysts to fly ash zeolite (FAZ) offers the advantage of heterogeneity, thereby exploring the possibility of reusability of the catalytic system.

Literature reports reveal that the incorporation of metal ions and metal complexes in zeolite enhances the catalytic activity of zeolites. The Advanced Oxidation Process (AOP), especially photocatalysis, has been reported

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by loaded metal nanoparticles in zeolites to degrade contaminants in wastewater to stable inorganic compounds such as carbon dioxide and water.[1]

Of the rare earth oxides, ceria is most widely used as catalyst,[2,3] polishing materials[4,5] and so on. The catalytic performance of supported metal nanoparticles enhances due to specific interactions with CeO_2 due to stabilization.[6] Ru/CeO_2 catalyst has been reported to show excellent activity for the addition of sp^2 C-H bonds of aromatic ketones to vinyl silanes.[7] Pt/CeO_2 catalyst has been reported for CO oxidation,[8] hydrogenation,[9] methanol decomposition,[10] *etc.* Hydrosilylation of organic substrates has been reported using CeO_2 supported gold catalysts.[11] The properties of cerium oxides have been reported to be strongly dependent on their microstructures, including size, morphology, and specific surface area.[12] The dispersion of CeO_2 on porous materials could generate small oxide particles and increase the number of active sites. The incorporation of CeO_2 nanoparticles in FAZ increases its thermal stability and availability of active sites for catalysis.[13] Zeolites have been reported as efficient catalysts for several organic reactions. Transition metals have been used as catalysts with potential advantages. Metal nanocatalysts have been extensively studied as model catalysts in fundamental research and involve practical applications in catalysis. Palladium nanocatalysts have been proved to have effective catalytic activity for hydrogenation[14,15] and carbon–carbonbond-formingreactions,[16,17] which find significant applications in pharmaceutical and fine chemical industries. In particular, the formation of $C_{sp}{}^2$-$C_{sp}{}^2$ bonds through coupling reactions has been demonstrated to have a broad scope. A coupling reaction is a process of forming a carbon–carbon bond through the use of a metal catalyst. Adolphe Wurtz has explored coupling reactions in which sodium metal reacted with an alkyl halide via metal-halogen exchange followed by nucleophilic substitution of a second equivalent of the alkyl halide.[18] Subsequent works involving other metals in coupling reactions have been reported, including copper, nickel, and palladium.[19] Strong interactions between metal and metal oxide nanoparticles and that with the support induce changes in the valence band structure of the metal nanoparticles, thereby enhancing their activity.

Cross-coupling reactions of aryl halides (chlorides or bromides) with aryl boronic acids, known as Suzuki-Miyaurareaction,[20,21] have been reported as an efficient and less toxic method to form $C_{sp}{}^2$-$C_{sp}{}^2$ bonds. Owing to their high selectivity and functional group tolerance, the palladium catalysts have been used extensively for Suzuki-Miyauracross-coupling reactions. However, separation of palladium metal catalysts from the desired products and its recyclability are complicated issues that can be overcome by using solid supports for the catalytic process. In this context, CeO_2 and Pd loaded nanoparticles supported in fly ash zeolite (CeO_2/Pd@FAZ) have been used as catalysts for $C_{sp}{}^2$-$C_{sp}{}^2$ bond formation. This work aims at studying the activity of CeO_2/Pd@FAZ towards cross-coupling reactions for the formation of $C_{sp}{}^2$-$C_{sp}{}^2$ bonds, establishing the scope of substrate and recyclability of the catalyst.

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

Coal fly ash was collected from the electrostatic precipitators of Tuticorin Thermal Power Station. $(NH_4)_2Ce(NO_3)_6$ manufactured by E. Merck (99.0% assay) was used for preparing CeO_2 nanoparticles. Na_2PdCl_4 and $NaBH_4$ of 99.5% assay manufactured by E. Merck were used for the synthesis of Pd nanoparticles. All reagents and solvents used for studying the catalytic activity were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, and Avra Synthesis) and used without further purification. IR spectra were recorded from 4000 to 400 cm^{-1} using JASCO 4600 Infrared spectrometer. X-Ray Diffraction patterns were recorded on the XPERT-PRO diffractometer using Cu-Kα radiation of wavelength 1.54 Å. TEM studies were carried out at SAIF, IIT, Mumbai using PHILIPS, CM 200, TEM microscope operated at 200 kV with a resolution of 2.4 Å. GC analyses were performed on Agilent 7820A GC fitted with an FID detector and capillary column. EDAX analysis was carried out on Bruker Nano GmbH using XFlash 5010X detector. Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents at room temperature on a Bruker Avance 300 spectrometer operating at 300 MHz. Deuterated solvents were dried by storage over 4 Å molecular sieves. Chemical shifts (δ) are expressed in ppm using TMS as internal standard, and coupling constants (J) are given in Hz. Surface area and pore size distribution were analyzed using Quantachrome Autosorb iQ2 surface area & pore volume analyzer. X-ray photoelectron spectroscopic analysis was performed using an XPS K-Alpha surface analysis, Thermo Fisher Scientific.

2.2 | Synthesis of FAZ

Fly ash collected from Tuticorin Thermal Power Station (TTPS) was subjected to hydrothermal treatment to synthesize FAZ, as reported in the literature.[22,23] The cation exchange capacity was determined and was found to be in accordance with the reported value.[24]

2.3 | Loading of CeO_2 nanoparticles in FAZ

The prepared fly ash zeolite was loaded with CeO_2 nanoparticles through the cation exchange process followed by calcination. The typical procedure is as follows, 2.0 g of $(NH_4)_2Ce(NO_3)_6$ and 1.0 g of fly ash zeolite were dispersed in 30 ml of double distilled water and gently stirred at 60 °C for 2 h. The Ce (IV) loaded zeolite was washed (three times with double distilled water and one time with ethanol) and dried at 80 °C overnight. The sample was calcined at 550 °C for 4 hr to obtain CeO_2 loaded fly ash zeolite.

2.4 | Synthesis of CeO_2/Pd nanoparticles loaded FAZ (CeO_2/Pd@FAZ)

100 mg of CeO_2 loaded FAZ is transferred to a 100 ml beaker and 8 ml of double-distilled water was added. The dispersed solution was stirred well at room temperature for 30 min. To this well-dispersed solution, Na_2PdCl_4 (13 mg in 2 ml of double-distilled water) was added dropwise under vigorous stirring and continued for one hour at room temperature. Finally, a solution of $NaBH_4$ (10 mg in 3 ml of double-distilled water) was added into the solution and stirred at this temperature for further 3 h. Over the period of reaction time, the initial brown colored solution turned to black, indicating the reduction of Pd(II) to Pd(0). The material CeO_2/Pd@FAZ was repeatedly washed with double distilled water and dried under vacuum for 24 hr.

2.5 | Typical procedure for the Suzuki-Miyaura reaction

A glass vial was sequentially charged with appropriate amounts of aryl bromide (0.5 mmol), phenylboronic acid (0.55 mmol), and K_2CO_3 (1 mmol) and catalyst in methanol (5 ml). The reaction mixture was stirred at 60 °C under aerobic condition for required time and then diluted with water (10 ml). Extraction was carried out with ethyl acetate (3 x 5 ml), dried over anhydrous sodium sulfate and the solvent was stripped off under vacuum. GC analysis was performed by dissolving the solid residue in 2 ml of dichloromethane, and an aliquot from the solution was injected into the injector port.

3 | RESULTS AND DISCUSSION

The FAZ prepared by the hydrothermal treatment of fly ash was characterized by BET, FTIR, XRD, and XRF and reported to be X-type zeolite. During the hydrothermal treatment, amorphous aluminosilicate deposits on the particle surface of coal fly ash gradually, thereby progressing towards the formation of FAZ. The cation exchange capacity of the prepared zeolite has been found to be 457 meq/100 g, which indicates the possibility of exchanging metal ions, which can be further reduced to the corresponding metal/metal oxide nanoparticles.[22]

3.1 | Characterization of CeO_2/Pd@FAZ

The XRD pattern of CeO_2/Pd@FAZ is presented in Figure 1. In addition to the XRD peaks of FAZ, characteristic peaks corresponding to that of CeO_2 nanoparticles are located at 2θ values 29, 33, 47, 56, 64, 79, and 88 which correspond to (111), (200), (220), (311), (400), (420), and (422) respectively (JCPDS card no. 34–0394).[25] The broad nature of the XRD patterns indicates that the crystallite sizes of the samples are tiny. Peaks due to Pd nanoparticles are feebly located at 2θ values 46, 68, 81 and 86, which correspond to (200), (220), (311), and (222) planes respectively (JCPDS card no 75–8371).[26] The XRD pattern indicates that the framework of the zeolite is intact, and the major peaks of FAZ correspond to a higher intensity compared to that of the incorporated nanoparticles. The loading of CeO_2 and Pd nanoparticles in the framework of zeolite has been confirmed by matches with the fluorite structure of CeO_2 and the fcc structure of Pd nanoparticles, and the

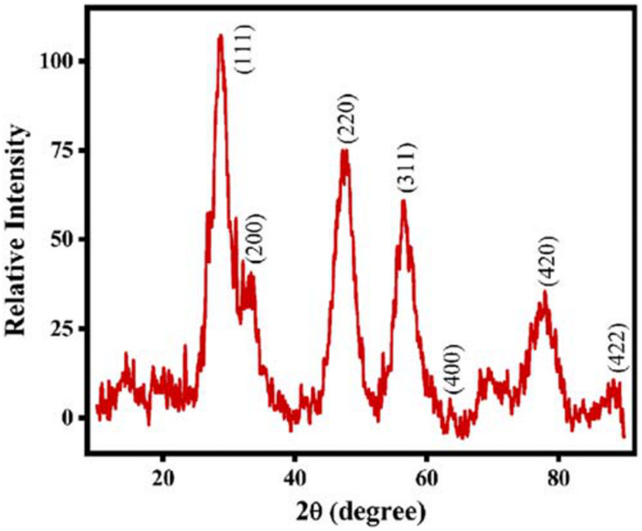


FIGURE 1 X-Ray Diffraction pattern of CeO_2/Pd@FAZ

framework of FAZ remains unaffected after the incorporation of nanoparticles.

The FT-IR spectrum of CeO_2/Pd@FAZ is presented in Figure 2. The most intense band at 991 cm^{-1} corresponds to the asymmetric stretching of Si-O-Al. The peak at 1341 cm^{-1} represents the presence of substituted Al atoms in the tetrahedral forms of silica frameworks. The band at 3406 cm^{-1} represents the asymmetric and symmetric –OH stretching vibrations suggesting the presence of possibly hydrated aluminum silicates. The band at 1631 cm^{-1} corresponds to the bending mode of water molecules. All these observations correspond to that of FAZ.[27] In addition to the stretching and bending modes to that of FAZ, Ce-O stretching frequency is observed at 676 cm^{-1} showing the loading of CeO_2 nanoparticles in FAZ.[28]

The morphological studies of the synthesized CeO_2/Pd@FAZ have been carried out by TEM analysis. Figure 3 displays the TEM images of CeO_2/Pd@FAZ, which consists of agglomerated nanoparticles comprised of nanostructures in the range of 1–100 nm. The SAED pattern indicates a lack of crystallinity owing to the poor loading of nanoparticles in the porous framework of FAZ. The loading of CeO_2 and Pd in the pores of zeolite is confirmed by EDAX analysis, which is presented in Figure 4. The Elemental Analysis spectrum confirms the presence of Pd at 0.25 keV and 2.8 keV[29,30] besides for Ce at 0.95 keV and 2.8 keV, which is in accordance with the EDAX spectrum of CeO_2 nanoparticles.[31] Peaks corresponding to Al and Si present in the FAZ matrix are located in the EDAX spectrum.[32] To further confirm the presence of palladium in the CeO_2/Pd@FAZ, the sample was subjected to X-ray photo electron spectroscopy (XPS) (Figure 5). The presence of peaks at 335.7 and 340.9 eV confirms the existence of palladium in zero oxidation state and the peaks corresponding to 882.69, 889.11, 898.40, 901.15, 907.15 and 917.07 eV confirm the presence of cerium in +4 oxidation state.[33] From the XPS survey spectrum the amount of palladium is found to be 10.29 at%. Both adsorption and desorption isotherms presented in Figure 6 exhibit typically type IV pattern with the relative pressure (P/P_0) range between 0.2–0.9, shows a gradually increased nitrogen adsorption. Both isotherms of CeO_2/Pd@FAZ shows the mesoporous nature and the surface area is found to be 152.23 m^2/g with the average pore diameter is 10.67 nm.

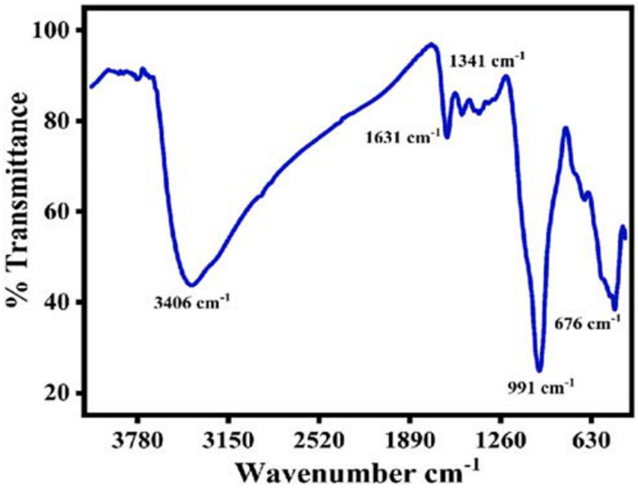


FIGURE 2 FT-IR spectrum of CeO_2/Pd@FAZ

3.2 | Catalytic activity of CeO_2/Pd@FAZ towards Suzuki-Miyauracross-coupling reactions

Suzuki-Miyaura cross-coupling reaction is one of the attractive and highly demanding reactions in synthetic organic chemistry because of its robust functional group tolerance. Notably, palladium is an expensive metal but well known for its transmetalation property, and palladium mediated coupling reactions are successively well utilized in industrial and academic research for targeted synthetic methodologies.

Herein, we investigated the catalytic efficiency of the CeO_2/Pd nanoparticles incorporated FAZ towards the cross-coupling reaction of the aryl halides with boronic acid derivatives. Initially, a model reaction was performed to optimize the appropriate catalyst for the Suzuki-Miyaura reaction. FAZ, Pd loaded FAZ (Pd@FAZ), and CeO_2/Pd loaded FAZ (CeO_2/Pd@FAZ) were screened for their activities. A preliminary reaction with phenylboronic acid, 4-bromoacetophenone, K_2CO_3 (as base), methanol (as solvent) and catalyst was carried out at room temperature (Table 1, entries 1–3). At a time interval of 2.5 h, the catalyst CeO_2/Pd@FAZ exhibits good catalytic conversion to 48% of the cross-coupled product (Table 1, entry 3). CeO_2/Pd loaded FAZ was identified as a better catalyst and attracted attention to study its activity towards Suzuki-Miyauracross-coupling reactions.

CeO_2 assists the formation of well-dispersed and smaller Pd nanoparticles, which results in a larger surface area of the catalyst. Apart from size effect, CeO_2 improves the catalytic activity of Pd as CeO_2 modifies the electronic structure of Pd through its synergic interaction.[34] This correlates with the observation that CeO_2/Pd loaded FAZ has better activity compared to FAZ and Pd loaded FAZ.

To further explore as an efficient catalyst to perform the Suzuki-Miyauracross-coupling reaction, the base plays a vital role.[35] To optimize the choice for the base, the model reaction was further examined by varying the

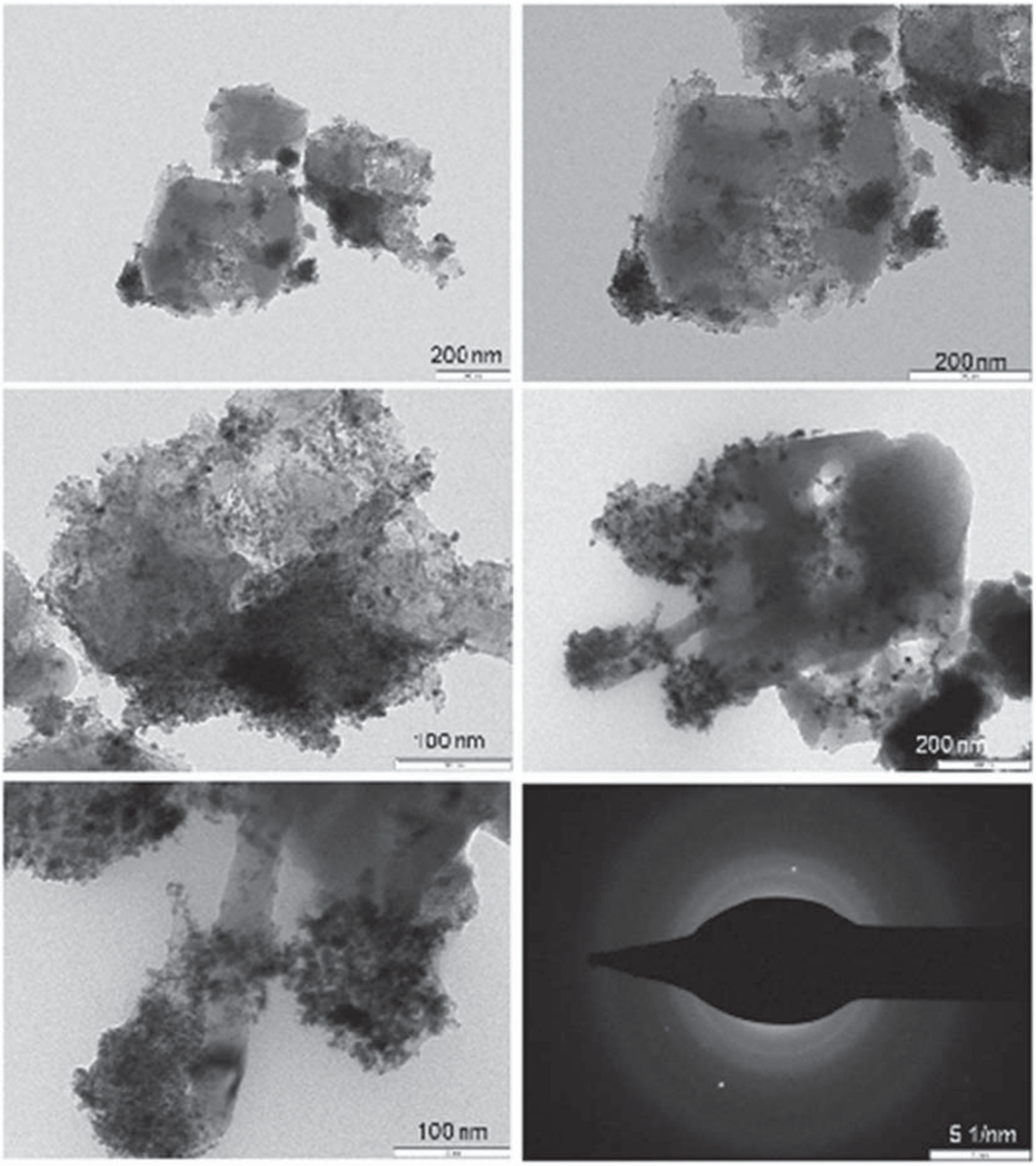


FIGURE 3 TEM images of CeO_2/Pd@FAZ

bases under the optimized reaction conditions. A wide range of inorganic bases, including K_2CO_3, NaOAc, $LiOH{\cdot}H_2O$ and Cs_2CO_3, and organic bases including triethylamine and DABCO (1,4-diazabicyclo[2.2. 2] octane) have been used under standard reaction conditions (Table 1, entries 3–8). K_2CO_3 furnished a conversion of 48% (Table 1, entry 3) and hence was chosen as the base for subsequent reactions. In the absence of base, there is no evidence for the formation of cross-coupling reaction (Table 1, entry 19). To evaluate the suitable solvent for the optimization, various polar and non-polar solvents like H_2O, MeOH, DMF, THF, CH_3CN and toluene were examined to choose the best solvent for the reaction (Table 1, entries 3, 9–13). The result shows that both methanol and DMF facilitate significant conversion among the different solvents used for optimization (Table 1, entries 3 and 13). The solubility of the substrate and interaction between CeO_2/Pd@FAZ and substrate is very poor in water medium. Hence, the reactions are not progressing in water.

The effect of catalyst loading was studied by varying the weight percentage of catalyst (5 to 20) as the amount of catalyst used in catalytic reaction plays an imperative role. Under optimized reaction conditions, the catalytic activity of CeO_2/Pd@FAZ was accomplished by varying the loading of catalyst, reaction temperature, and the results are summarized in Table 1. It is observed that a decrease in the catalyst loading (20 to 5 wt.%) increases the catalytic activity, along with increase in reaction temperature (Table 1, entries 3, 14–18) and in the absence of

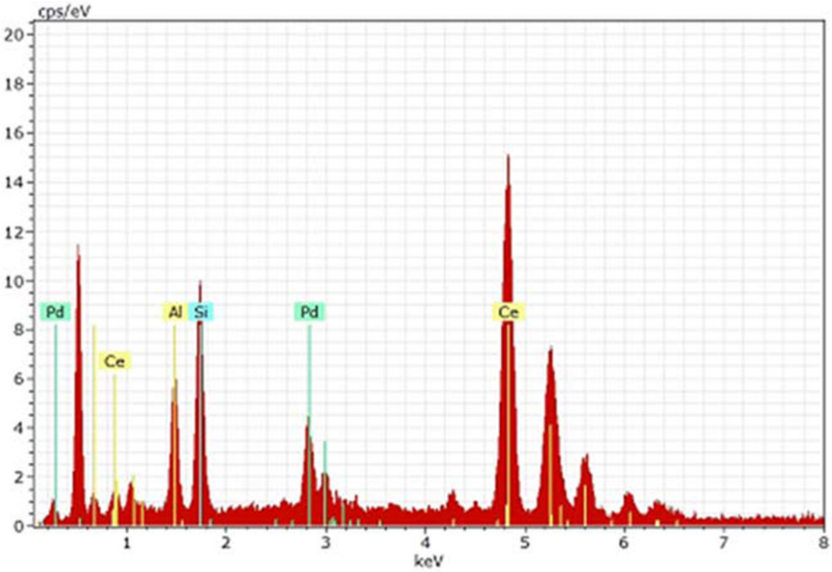


FIGURE 4 EDAX spectrum of CeO_2/Pd@FAZ

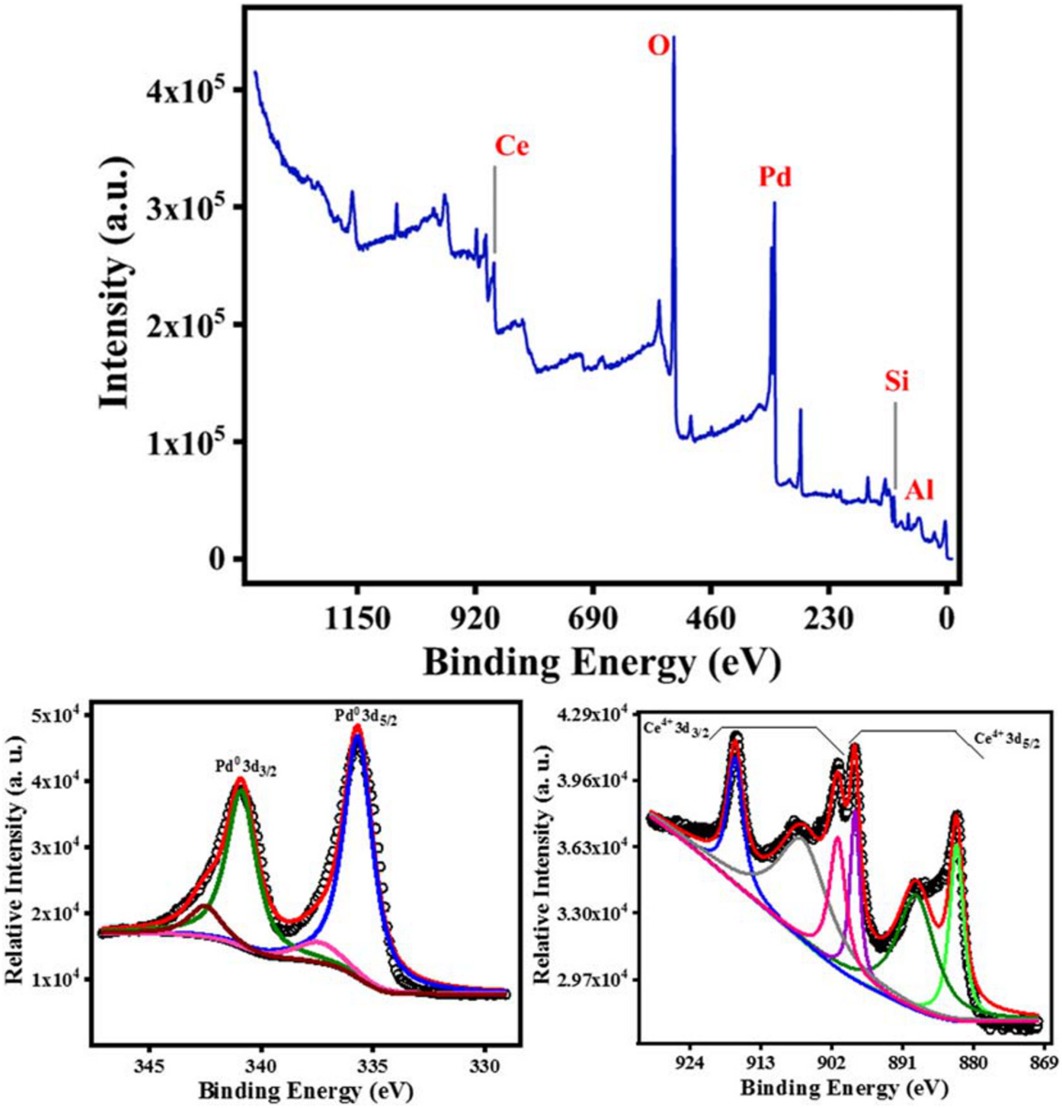


FIGURE 5 X-ray photoelectron spectrum of CeO_2/Pd@FAZ

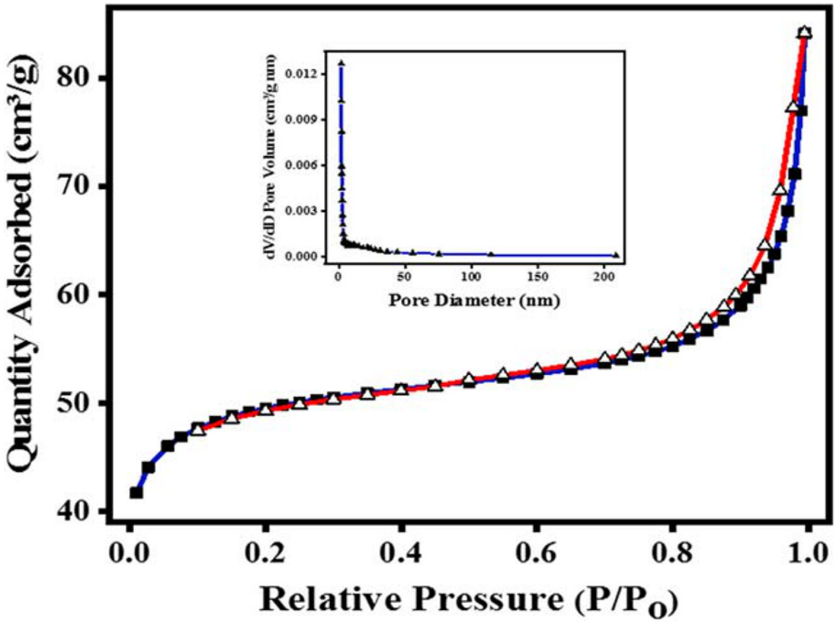
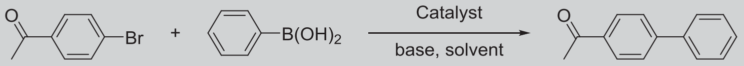


FIGURE 6 BET adsorption isotherm of CeO_2/Pd@FAZ

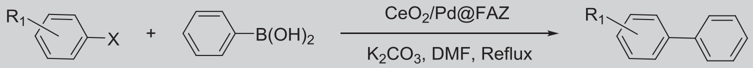
TABLE 1 Screening of catalysts, bases, and solvents for Suzuki-Miyauracross-coupling



Entry	Base	Catalyst	wt%	Solvent	Temp (°C)	Time (h)	Yield (%)
1.	K_2CO_3	FAZ	20	MeOH	30	2	-
2.	K_2CO_3	Pd@FAZ	20	MeOH	30	2	39
3.	K_2CO_3	CeO_2/Pd@FAZ	20	MeOH	30	2	48
4.	NaOAc	CeO_2/Pd@FAZ	20	MeOH	30	2	40
5.	$LiOH{\cdot}H_2O$	CeO_2/Pd@FAZ	20	MeOH	30	2	40
6.	Cs_2CO_3	CeO_2/Pd@FAZ	20	MeOH	30	2	19
7.	DABCO	CeO_2/Pd@FAZ	20	MeOH	30	2	35
8.	TEA	CeO_2/Pd@FAZ	20	MeOH	30	2	-
9.	K_2CO_3	CeO_2/Pd@FAZ	20	CH_3CN	30	10	3
10.	K_2CO_3	CeO_2/Pd@FAZ	20	Toluene	30	10	9
11.	K_2CO_3	CeO_2/Pd@FAZ	20	THF	30	10	3
12.	K_2CO_3	CeO_2/Pd@FAZ	20	Water	30	10	-
13.	K_2CO_3	CeO_2/Pd@FAZ	20	DMF	30	10	47
14.	K_2CO_3	CeO_2/Pd@FAZ	20	MeOH	65	10	91
15.	K_2CO_3	CeO_2/Pd@FAZ	10	MeOH	30	10	63
16.	K_2CO_3	CeO_2/Pd@FAZ	10	MeOH	65	10	92
17.	K_2CO_3	CeO_2/Pd@FAZ	5	MeOH	30	10	69
18.	K_2CO_3	CeO_2/Pd@FAZ	5	MeOH	65	10	97
19.	-	CeO_2/Pd@FAZ	20	MeOH	65	10	-
20.	K_2CO_3	-	-	MeOH	65	10	-

Reaction condition: 4-bromoacetophenone (1 equiv), phenylboronic acid (1.1 equiv), base (1 equiv), solvent (3 ml). Using 4-bromoacetophenone as an internal standard and the coupled product was determined by GC.

TABLE 2 Substrate scope in Suzuki Miyaura cross-coupling using CeO_2/Pd@FAZ



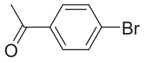
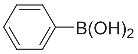
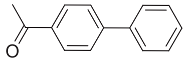
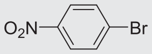
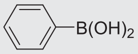
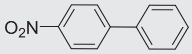
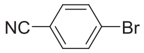
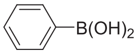
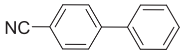
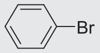
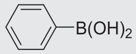
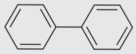
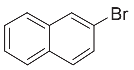
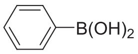
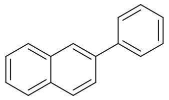
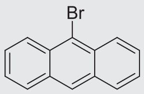
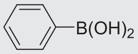
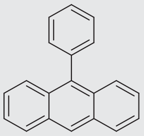
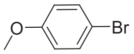
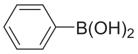
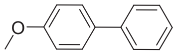
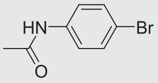
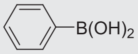
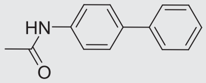
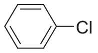
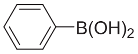
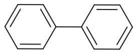
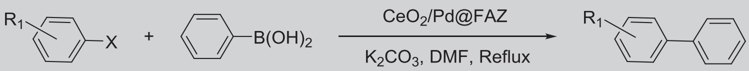
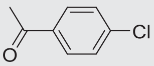
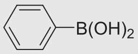
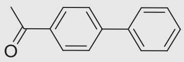
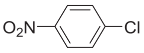
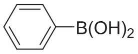
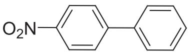
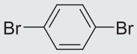
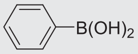
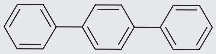
S.No	Aryl Halide	Boronic acids	Product	Time (h)	Yield (%)[a]
1.				2	97
2.				21	68
3.				22	88
4.				20	82
5.				22	91
6.				4	91
7.				24	51
8.				21	71
9.				24	71
10.				21	35

TABLE 2 (Continued)



S.No	Aryl Halide	Boronic acids	Product	Time (h)	Yield (%)[a]
					
11.				29	69
12.				22	78[b]

[a] Reaction condition: aryl halides (1 equiv), phenylboronic acid (1.1 equiv), K_2CO_3 (1 equiv), (5 wt%) CeO_2/Pd@FAZ, DMF (3 ml). [b] phenylboronic acid (2.1 equiv).

CeO_2/Pd@FAZ, (Table 1, entry 20), cross-coupling reaction did not proceed. The CeO_2/Pd@FAZ with 5 wt. % loading afforded the coupled product in excellent conversion (Table 1, entry 18).

Likewise, significant efforts were made to examine the substrate scope by reaction of phenylboronic acid with a wide variety of diversely substituted aryl bromides/chlorides under the optimized reaction condition, and the results are compiled in Table 2. The coupling reaction between 4-bromoacetophenone and phenylboronic acid using MeOH as solvent affords a conversion of 91% coupled product under reflux condition (Table 1, entry 14), whereas in the case of other all substrates, MeOH as solvent shows lesser catalytic conversion compared to DMF (data not shown). In this regard, DMF is fixed as optimum solvent for the further reactions to study the substrate scope of the aryl halides. All the reactions progressed efficiently to afford the biaryls in good to excellent yields. The electronic nature of aryl halides has significant effects on catalytic conversion. Aryl bromides with electron withdrawing groups proceed much faster with high conversion (Table 2, entries 1–3) compared to that of electron releasing groups in the aryl bromides (Table 2, entries 7 and 8). In addition, the electronically neutral substrate also incurred excellent yields (Table 2, entries 4–6).

Further, the scope of the reaction was extended to less reactive aryl chloride derivatives. Under optimized reaction conditions, chlorobenzene, 4-chloroacetophenone, and 4-chloronitrobenzene were coupled with phenylboronic acid. 4-chloroacetophenone gave only 35% of the coupled product (Table 2, entry 10) while 4-chloronitrobenzene afforded 69% (Table 2, entry 11) of the cross-coupled product under similar reaction condition. In addition to that, the reaction of 1,4-dibromo benzene with two equivalents of phenylboronic acids afforded the corresponding bis-coupled product in good yields (Table 2, entry 12). The GC yields for the coupling reactions have been presented in Figures S1-S5. The products have been confirmed by ^{1}H-NMR and the results are listed in Figures S6-S8.

To check the recyclability of the catalyst, a series of reactions were carried out under optimized reaction conditions of 4-bromoacetophenone (0.5 mmol) as reactant, phenylboronic acid (0.6 mmol) as coupling counterpart, K_2CO_3 (0.5 mmol) as base and DMF (3 mL) as solvent using CeO_2/Pd@FAZ (5 wt. %). The results indicate their conversion rate from 99 to 40% (Figure 7) though there is considerable leaching of catalyst from cycle I to III. The catalyst has been efficiently used for three cycles, with an activity of 40% conversion in the third cycle. In this study, up to 97% conversion has been observed in ten hours with recyclability up to three cycles by loading CeO_2 and

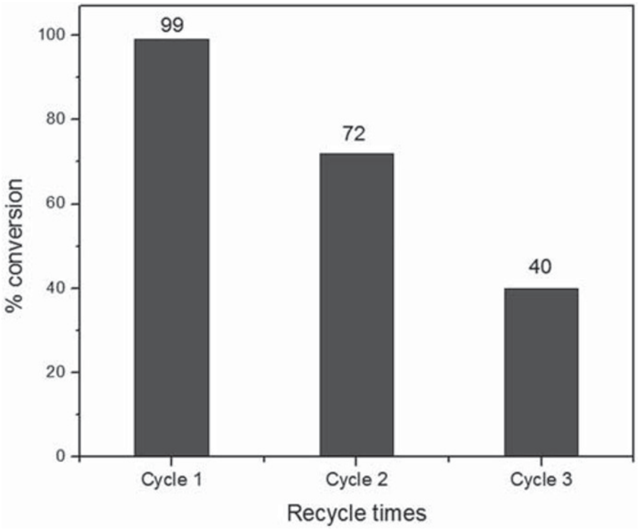
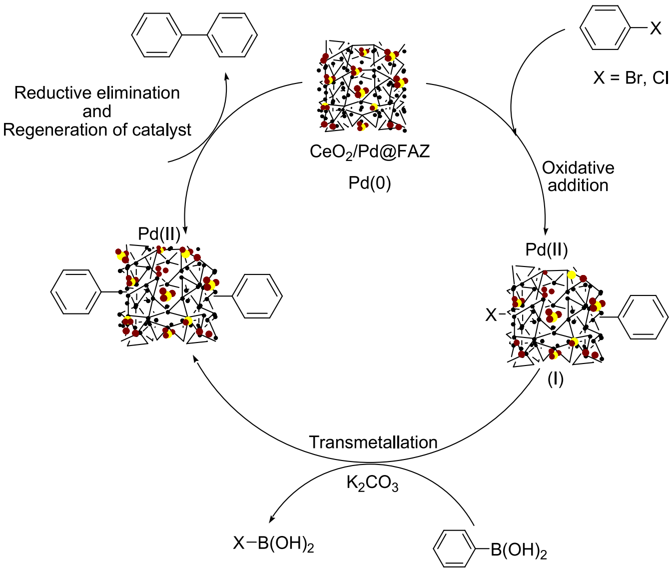


FIGURE 7 Recyclability test of catalyst CeO_2/Pd@FAZ

Pd nanoparticles in FAZ, which is at par with the yields reported in literature with commercial zeolites.[36,37]

Though the mechanistic details are not ascertained, a plausible catalytic cycle for the Palladium-catalyzed cross coupling reaction of aryl halide and aryl boronic acid using K_2CO_3 as base is shown Scheme 1. The aryl halide undergoes oxidative addition reaction with Pd(0) (I) in the catalyst CeO_2/Pd@FAZ. Presence of CeO_2 in the catalyst enhances the easier oxidation of Pd(0) to Pd (II) during the oxidative addition reaction with aryl halide. The in-situ formed chlroboronic acid facilitates transmetallation reaction to afford intermediate II which on reductive elimination affords the coupled biaryl product and regenerates the catalyst.



SCHEME 1 Plausible mechanism for the formation of biaryls catalyzed by CeO_2/Pd@FAZ

4 | CONCLUSION

CeO_2/Pd nanoparticles incorporated in FAZ has been proved as an efficient heterogeneous catalyst towards cross-coupling reactions involving $C_{sp}{}^2$-$C_{sp}{}^2$ bond formation reactions between aryl halides and phenylboronic acid. Reaction conditions including the catalyst, base, solvent and substrate scope have been optimized. The presence of electron-withdrawing groups in the aryl halides enhances the rate of the reaction with good conversion while the electron releasing groups affect the rate of reaction with reasonable yields. Further, the catalyst has been recycled and reused up to two times. Apart from postulating a sophisticated method for the utilization of fly ash, this work suggests a cost-effective catalyst for Suzuki Miyaura cross-coupling reaction.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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