

A new air and moisture stable robust bio-polymer based palladium catalyst for highly efficient synthesis of biaryl compounds

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The designs of robust natural polymer based catalysts are important for catalytic systems in the view of industrial purposes and green chemistry. In this study, a new air and moisture stable robust starch-based Pd(II) catalyst was designed and characterized with different analytical techniques. Catalytic behavior of the prepared robust palladium(II) catalyst was investigated in the Suzuki coupling reactions of aryl iodides, aryl bromides and aryl chlorides with phenyl boronic acid under microwave irradiation using very short reaction time. Sustainability and reusability of the catalyst was also explored under benign conditions. As a result of the catalytic tests, the green catalyst gave excellent biphenyl yields, TONs and TOFs with very low catalyst loading. More importantly, the robust catalyst has showed that it can be reused several times without important loses from its activity in the coupling reactions. The study showed that the robust starch-based Pd(II) catalyst had more advantages than other catalysts reported in the literature due to its economic, sustainable, thermal durable, environmentally friendly and practice properties.

KEYWORDS

biphenyl, ninhydrin test, robust catalyst, starch, TOF

1 | INTRODUCTION

Transition metal-catalyzed carbon–carbon formation reactions are an effective process for synthesis of biaryl compounds via coupling reaction. Suzuki C(sp²)-C(sp²) reactions among the coupling reactions such as, Stille,^[1] Heck,^[2] Negishi,^[3] and Kumada,^[4] are one of the most important and has been widely used in on a academic lab scale and industrial fields.^[5] Also, Suzuki C-C reaction is advantageous over the other coupling reactions thanks to their stability of temperature, moisture, air as well as tolerance to broad range of functional groups on the substrate.^[6] In literature, many researchers developed different homogeneous and heterogeneous catalysts and their catalytic behaviors were investigated

in Suzuki coupling reactions.^[7] It was reported that heterogeneous catalysts were more beneficial than homogeneous catalysts because of their high catalytic activity and ease of separation from reaction media.^[8] However, the biggest problems in catalytic systems are (1) low recycle performance due to leaching from the support (2) difficult recovery of the used catalyst (3) and expensiveness of synthesis of catalyst.^[9] These factors are very important for catalysts because of economical and practical demands in industrial applications. So, for the last few years, both robust bio-based heterogeneous catalysts and magnetically recoverable catalysts have been drawn considerable attention because they retain the catalytic activity of catalyst for a long time and prevent leaching of the metal ions.^[10] Besides these, to fabricate catalysts

which are cheaper and easily synthesizable, researchers have frequently tended to synthesis biopolymer based catalysts and one-step synthesis methods.^[11]

Polysaccharide-supported heterogeneous catalysts such as cellulose and chitosan derivatives have played an important role in different catalyst systems and catalytic reactions due to green nature, low cost, mechanical stability and ease of source, in recent years.^[12] Among the polysaccharides, starch is versatile solid polymeric material because of its unique properties such as the abundance in nature, nontoxicity, biodegradability, and easy chemical modification.^[12c] Therefore, starch has great potential for catalytic systems as a support material due to its mentioned superior properties.

In the current article, to overcome leaching from the support and improve reusability performance of the catalyst, a novel heterogeneous Pd(II) catalyst was designed using starch which is robust biopolymer for catalytic systems. Briefly, amine functionalization of starch was done with using 3-aminopropyl triethoxysilane (APTES). Then, Schiff base formation of starch was performed by refluxing with 2-thiophenecarboxaldehyde in ethanol. Finally, palladium catalyst was prepared by stirring with Na₂PdCl₄ in water. The chemical structure of catalyst was illuminated by using FTIR, TGA, XRD, ICP-OES, SEM and EDAX. Catalytic behavior of high thermally stable Pd(II) catalyst was investigated in synthesis of biaryls via microwave irradiation under benign reaction conditions. Catalytic tests revealed that the bio-based palladium catalyst produced excellent biphenyl yields in short reaction time (6 min). Noticeably, the catalyst yielded higher TONs and TOFs. The catalyst also showed superior reusability in Suzuki reactions.

2 | MATERIAL AND METHODS

2.1 | Materials

Starch from potato, APTES, 2-thiophenecarboxaldehyde, Na₂PdCl₄, KOH, NaHCO₃, NaOH, Cs₂CO₃, Na₂CO₃, K₂CO₃, MgSO₄, phenyl boronic acid, aryl halides toluene,

ethanol and ninhydrin were purchased from Sigma-Aldrich.

2.2 | Instrumentation

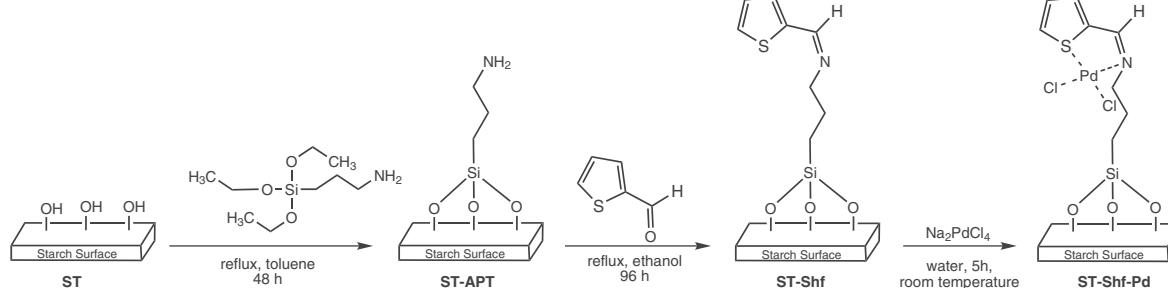
FT-IR spectra of the ST, ST-APT, ST-Shf and catalyst were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. X-ray spectra were obtained on a Rigaku smart lab system (at 40 kV, 30 mA, and 2θ with a scan angle of 10–60°). Thermal and mechanical durability of ST, ST-APT, ST-Shf and catalyst were studied on an EXSTAR S11 7300 (nitrogen atmosphere; 30–650 °C heating range). The surface properties of samples were obtained on a QUANTA-FEG 250 ESEM. The analyses of Pd, Cl and Si ions on the catalyst were determined using an EDAX-Metek. Palladium ion content of the robust starch based catalyst was detected by using Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). Characterization of biaryl compounds were done on GC-MS Agilent GC-7890 A- MS 5975. A domestic microwave oven was used in the catalytic performance tests.

2.3 | Amino functionalisation of starch (ST-APT)

2 g of starch and 3-aminopropyl triethoxysilane (4 ml) were transferred into 40 mL dry toluene and refluxed at 100 °C for 48 h. After the end of the reaction, amino functionalized precipitate of starch was filtered and dried at room temperature (Scheme 1).

2.4 | Preparation of starch Schiff base (ST-Shf)

Schiff base formation of starch was prepared by refluxing NH₂-functionalized starch (1 g) with 2-thiophenecarboxaldehyde (3 ml) in ethanol for 96 h. Formation of imine groups was followed by using FT-IR ATR technique. After the Schiff base reaction completed, the product was filtered and rinsed hot ethanol. Then,



SCHEME 1 Production of robust starch based Pd(II) catalyst

yellowish Schiff base product was dried in an oven at 60 °C for 24 h (Scheme 1).

2.5 | Synthesis of robust starch-based Pd(II)catalyst (ST-Shf-Pd)

ST-Shf (0.3 g) and Na₂PdCl₄ (0.45 g) were stirred in water (25 ml) at room temperature for 5 h. Then, brownish precipitate was filtered and washed with water. Robust starch-based catalyst was dried at room temperature (Scheme 1).

2.6 | Catalytic performance experiments

To a dried Schlenk tube, the aryl iodide, aryl bromide or aryl chloride (1.12 mmol) and phenyl boronic acid (1.87 mmol), K₂CO₃ (3.75 mmol) and robust ST-Shf-Pd catalyst (2×10^{-3} mol %) were added and irradiated in microwave oven for 6 min at 50 °C under a solvent-free medium. At the end of the reaction time, the mixture was extracted with water-toluene (1:2). Then organic phase, which is containing biphenyl compounds, was sent to GC/MS analysis.

3 | RESULTS AND DISCUSSION

3.1 | Characterization studies

3.1.1 | FT-IR analysis

FT-IR analysis gives rapid and enough information to illuminate chemical characterization of samples. To determine the chemical structural changes of the samples following the chemical modifications, FTIR spectra of ST, ST-APT, ST-Shf, and ST-Shf-Pd were recorded and they are presented in Figure 1. The characteristic bands were observed for ST: -OH stretching at 3287 cm⁻¹, -C-H stretching at 2923 cm⁻¹, -O-H bending at 1634 cm⁻¹, -CH₂ bending at 1456 cm⁻¹, and -C-O stretching at 761–1457 cm⁻¹ (Figure 1a).^[13] In the spectrum of ST-APT, -OH and -NH stretching bands were observed at 3291 cm⁻¹. Also, bending vibration of N-H was observed at 1642 cm⁻¹ (Figure 1b). These important bands showed that immobilization of the APTES onto starch were achieved. On the other hand, strong band attributed to imine bonds (-CH = N) was observed at 1633 cm⁻¹ in the spectrum of ST-Shf following condensation reaction of ST-APT with 2-thiophenecarboxaldehyde (Figure 1c). This important peak gave a good evidence of successful preparation of Schiff base of ST-APT. In the case of ST-Shf-Pd, this band was shifted lower frequency (1624 cm⁻¹) because of coordination of Pd(II) ions with the nitrogen of imine (Figure 1d).^[10c]

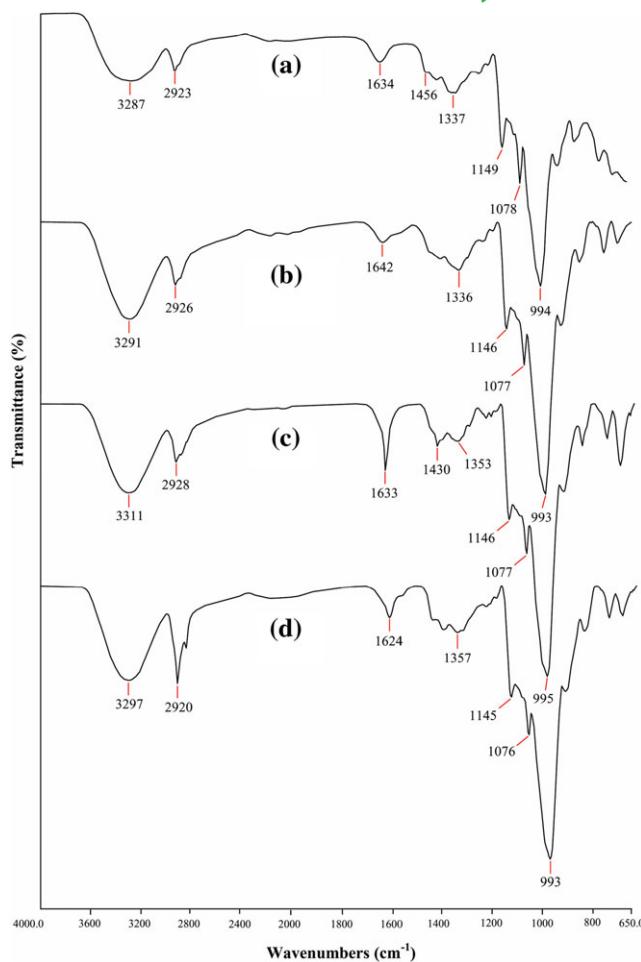


FIGURE 1 FT-IR spectra of a) ST, b) ST-APT, c) ST-Shf, and d) ST-Shf-Pd

3.1.2 | Ninhydrin test

Ninhydrin test was performed to confirm free primer amino groups on the surface of starch following the treatment of APTES with starch (Figure 2). This test was carried out by refluxing the ST-APT with ninhydrin in ethanol. After the test, immediately, it was observed that the colour of the reaction solution turned into purple (Figure 2b). This obvious color conversion showed that APTES was attached on the starch surface. In addition, the electronic spectrum of this solution was analyzed and strongly transition at 580 nm was observed in the spectrum (Figure 2b). This absorption band also revealed presence of -NH₂ groups on the starch chain.^[14]

3.1.3 | Thermal analysis (TG/DTG)

Thermal durability is one of the most effective property for retain catalytic performance of catalyst under harsh reaction conditions. Thermal degradation behaviors of

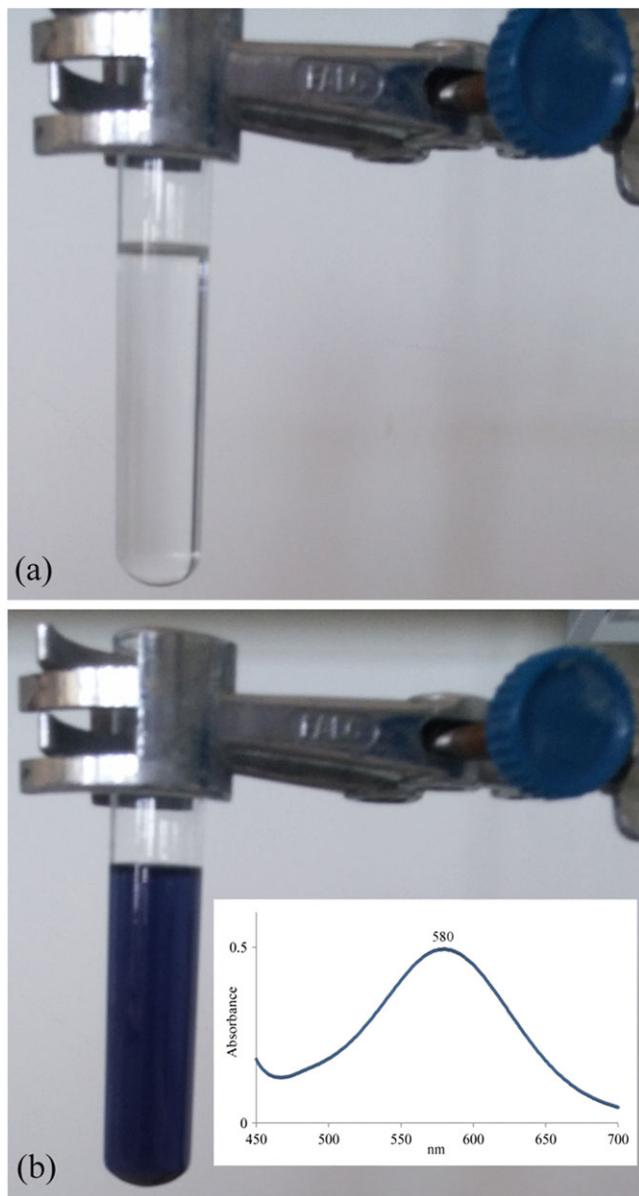


FIGURE 2 Ninhidrin test of a) solution of ST-APT, b) solution of ST-APT containing ninhydrin

ST, ST-APT, ST-Shf, and ST-Shf-Pd were studied by TG/DTG analysis and their curves are given in Figure 3. When thermal stability of ST was examined, it was detected ST had high thermal durability ($303\text{ }^{\circ}\text{C}$). Thermal degradation temperature of ST-APT and ST-Shf were determined as 301 and $302\text{ }^{\circ}\text{C}$, respectively. These results showed that chemical stability of the starch was conserved after the chemical modifications. On the other hand TGA diagram of the ST-Shf-Pd indicated that it was durable up to about $357\text{ }^{\circ}\text{C}$. This high decomposition temperature has shown that catalyst has good mechanical and chemical strength. All these obtained results showed that robust starch based palla-

dium catalyst can be a potential candidate for catalytic systems due to its mechanical and chemical durability capacity.

3.1.4 | Powder X-ray diffraction analyses

Crystalline and purity natures of ST, ST-APT, ST-Shf and ST-Shf-Pd were explored by powder X-ray and their diagrams are presented in Figure 4. The characteristic peaks of starch were observed at 5.5° , 14.84° , 17.12° , 19.14° , 22.22° , 23.68° , and 24.02° in the spectrum of ST (Figure 4a). After the chemical modification of ST, peaks were widened and crystallinity structures of ST-APT (Figure 4b) and ST-Shf (Figure 4c) were decreased compared to ST. These findings can be attributed to decrease of the number of OH groups of ST following the chemical modifications. On the other hand, after the palladium attachment to the ST-Shf, two new peaks are observed at 42.72° and 48.98° which can be assigned palladium space in the spectrum of the catalyst^[10d] (Figure 4d). These peaks revealed that catalyst was successfully prepared.

3.1.5 | SEM-EDAX analyses

Surface morphological characters of ST, ST-APT, ST-Shf and ST-Shf-Pd were studied using SEM-EDAX. When SEM images showing surface structure of ST were examined, it was seen that the surface was nearly smooth and contains different sizes granules (Figure 5a-b). After amino functionalisation of starch, granules were covered with particles (Figure 5c-d). On the other hand, we observed that numbers of the particles on the surfaces of granules were increased following the Schiff base formation of ST-APT (Figure 5e-f). These clear differences in the images showed that the chemical modifications of ST were achieved. In the case of the catalyst, partially regular surface structure was observed following the coordination of palladium to ST-Shf (Figure 5g-h). In addition, to confirm chemical modifications of ST, the structural compositions of the samples were examined with EDAX analysis (Figure 6). In the EDAX spectrum of the ST-APT, clearly Si peak was observed, verifying that APTES was attached on the starch surface (Figure 6a). On the other hand, Pd and Cl peaks were obviously appeared along with Si in the spectrum of the catalyst (Figure 6d). These peaks indicated that catalyst was successfully prepared. In addition, to determine amount of palladium in the catalyst, ICP-OES analysis was carried out and the palladium content was detected as 17.5% by mass.

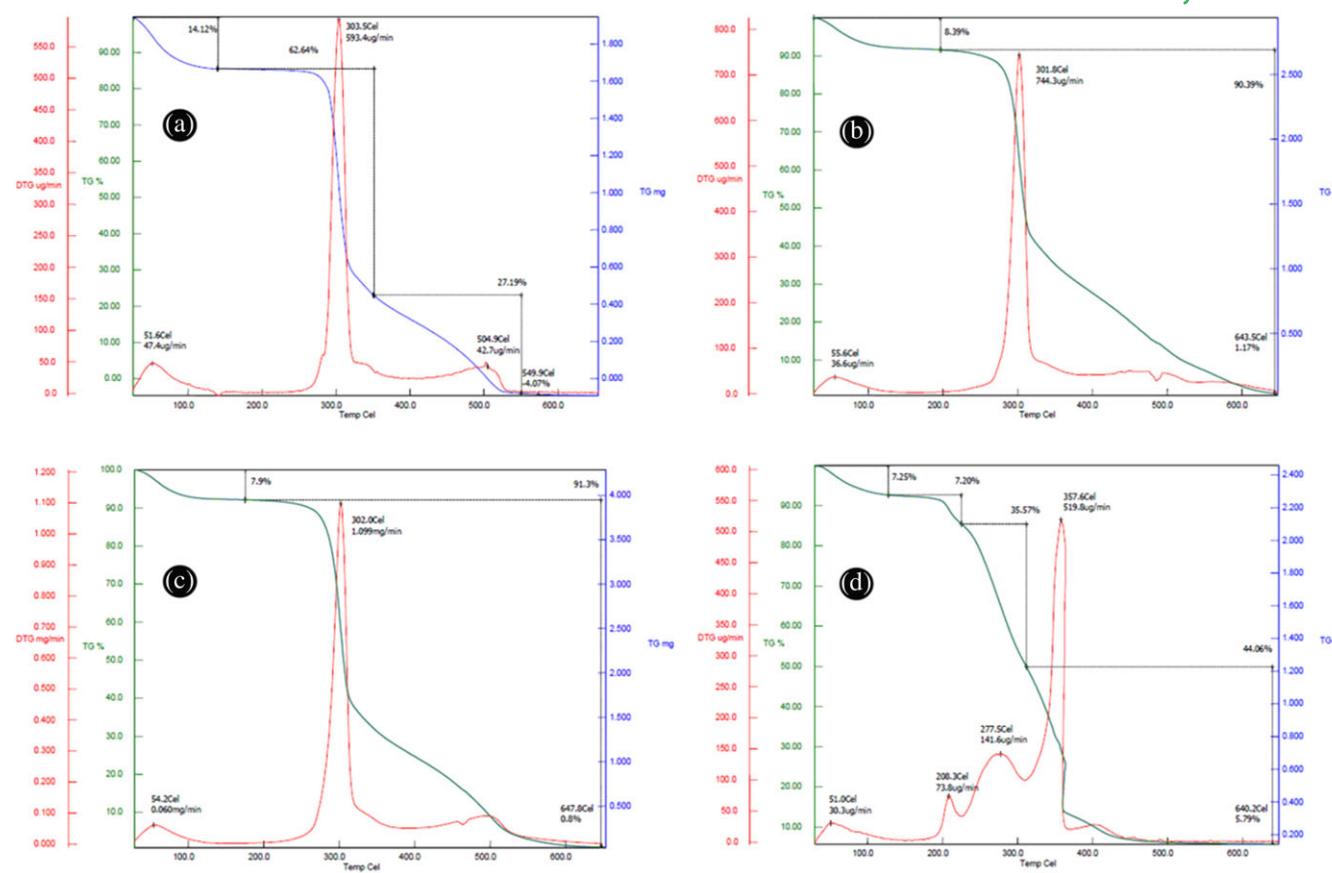


FIGURE 3 TG/DTG spectra of a) ST, b) ST-APT, c) ST-Shf, and d) ST-Shf-Pd

3.2 | Investigation of catalytic performance of the catalyst

3.2.1 | Optimization studies

The catalytic activity studies were performed using microwave irradiation under solvent-free media to provide more effective, more economical and practical advantages than conventional heating systems. Optimization studies were carried out on the coupling reaction of 4-bromoanisole with phenyl boronic acid which was selected as a represent reaction. The influence of base system on biphenyl yield was studied using different bases and K_2CO_3 was determined to be the most effective base system (KOH, 45%; $NaHCO_3$, 22%; NaOH, 39%; Cs_2CO_3 , 81%; Na_2CO_3 , 58%; and K_2CO_3 , 99% yield). The effect of reaction time on the product yield was also investigated and obtained biphenyl yields were recorded as follows; 1 min (20%), 2 min (45%), 3 min (60%), 4 min (78%), 5 min (89%), 6 min (99%) and 7 min (99%). From the results optimum reaction time was selected as 6 min. In order to determine optimum catalyst loading in Suzuki coupling reaction, preliminary experiments were carried out using different catalyst loading as follows: 2.5

$\times 10^{-4}$ mol% catalyst (15%), 5×10^{-4} mol% catalyst (45%), 1×10^{-3} mol% catalyst (%85), 2×10^{-3} mol% catalyst (99%), 3×10^{-3} mol% catalyst (99%). We selected optimal catalyst loading as 2×10^{-3} mol%.

3.2.2 | Catalytic performance of ST-Shf-Pd catalyst in Suzuki coupling reaction

Catalytic activity of robust starch-based Pd(II) catalyst was investigated in the coupling reaction of different aryl bromides (Table 1, entries 1–10), iodides (Table 1, entries 11–15), or chlorides (Table 1, entries 16–22) with phenyl boronic acid under mentioned above optimum reaction conditions. Catalytic activity tests showed that ST-Shf-Pd catalyst gave excellent biphenyl product yield in the coupling reaction of aryl iodide. The catalyst also produced high reaction yields with aryl bromides using very small catalyst loading. On the other hand, it is known that aryl chloride is less active than aryl iodide and aryl bromides in the Suzuki cross coupling reaction.^[15] Therefore, aryl chlorides are expected to give lower yields in the coupling reactions. However, good reaction yields were obtained with aryl chlorides in the presence of robust starch-based

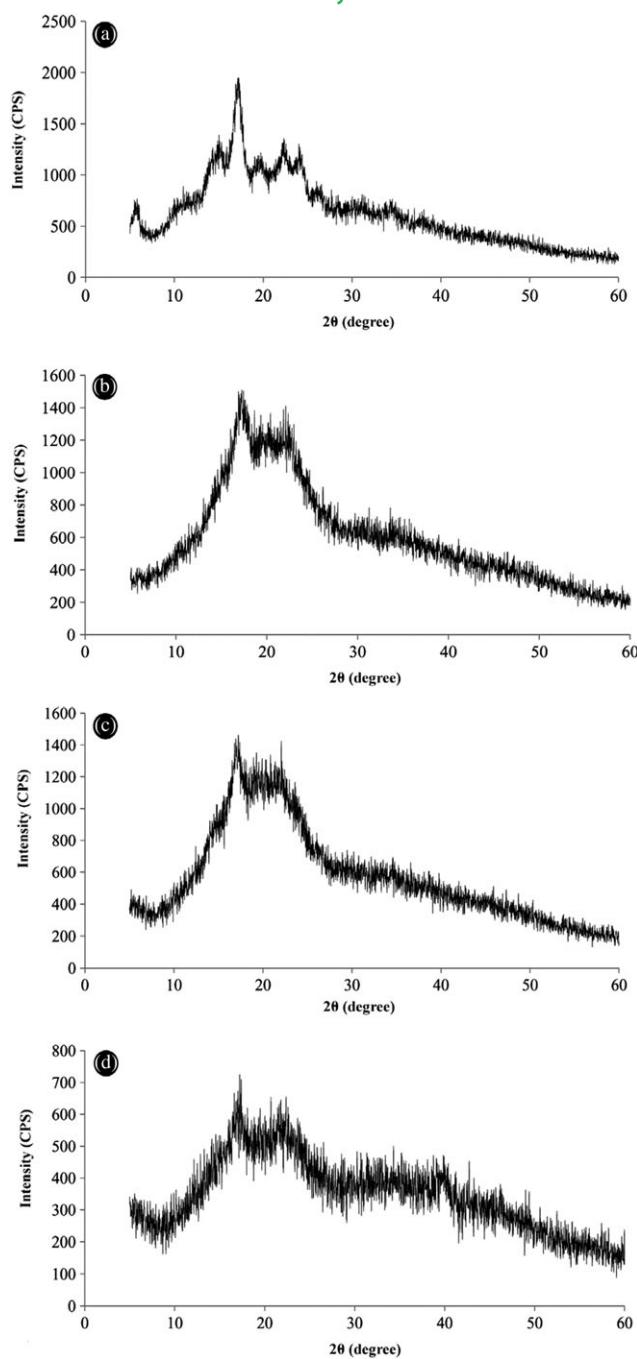


FIGURE 4 XRD diagrams of a) ST, b) ST-APT, c) ST-Shf, and d) ST-Shf-Pd

Pd(II) catalyst in the present study (Table 2, entries 16–22). These findings indicate that ST-Shf-Pd catalyst is suitable for Suzuki C(sp²)-C(sp²) reactions. In addition, the effect of the electronic properties of the substrate on the biphenyl yields were studied in the coupling reaction of different -ortho, meta-, or para-substituted aryl halides with phenyl boronic acid. These tests exhibited that -para substituent groups on the substrate gave higher reaction yield compared to -ortho and -meta substituent groups.

In addition, the catalytic activity studies showed that electron withdrawing groups ($-NO_2$ or $-CN$) were more reactive than electron-donor groups ($-CH_3$) in the coupling reactions. For example, the coupling reaction of 4-bromobenzonitrile with phenyl boronic acid produced 94% biphenyl yield (Table 1, entry 6). In addition, TON and TOF values, which are the key parameters for industrial applications such as pharmaceuticals and fine chemicals,^[32] were calculated for all Suzuki cross coupling reactions and the findings are given in Table 1. As seen from the Table 1, robust starch-based Pd(II) produced excellent TONs and TOFs.

3.2.3 | Comparison with other reported catalyst

To show the superior catalytic performance of robust starch-based Pd(II) catalyst, biphenyl yields, reaction time, TON and TOF values obtained in the present study were compared to different catalysts in the literature and the results are presented in Table 2. As seen from Table 2, robust starch-based Pd(II) catalyst gave higher reaction yields, TON and TOF values with very small of the catalyst and very short reaction time than other catalysts. In addition, in the view of low cost, high thermal stability, green nature, reusability and sustainability, robust starch-based Pd(II) catalyst are advantageous than previously reported studies.

3.2.4 | Sustainability and reusability of robust starch-based Pd(II) catalyst

The sustainability and reusability of any catalyst is one of the most significant feature for an industrial and academic point of view. Therefore, reusability of robust starch-based Pd(II) catalyst was investigated on the represent coupling reaction under optimum conditions. After each of cycle experiment, the ST-Shf-Pd catalyst was removed from reaction media with filtration and regenerated by washing with hot methanol and water. After drying, the same ST-Shf-Pd catalyst was reused for the next runs under similar conditions. As a result of the longevity tests, robust starch-based Pd(II) catalyst showed superior reusability in the Suzuki C(sp²)-C(sp²) reactions. Following the 10 cycles, biphenyl yield decreased from 99% to 80%. These tests showed that ST-Shf-Pd catalyst could be reused for 10 cycles without important change in its activity. These findings reveal that robust starch-based Pd(II) catalyst can be used in different industrial applications thanks to its recoverable and reusable potential.

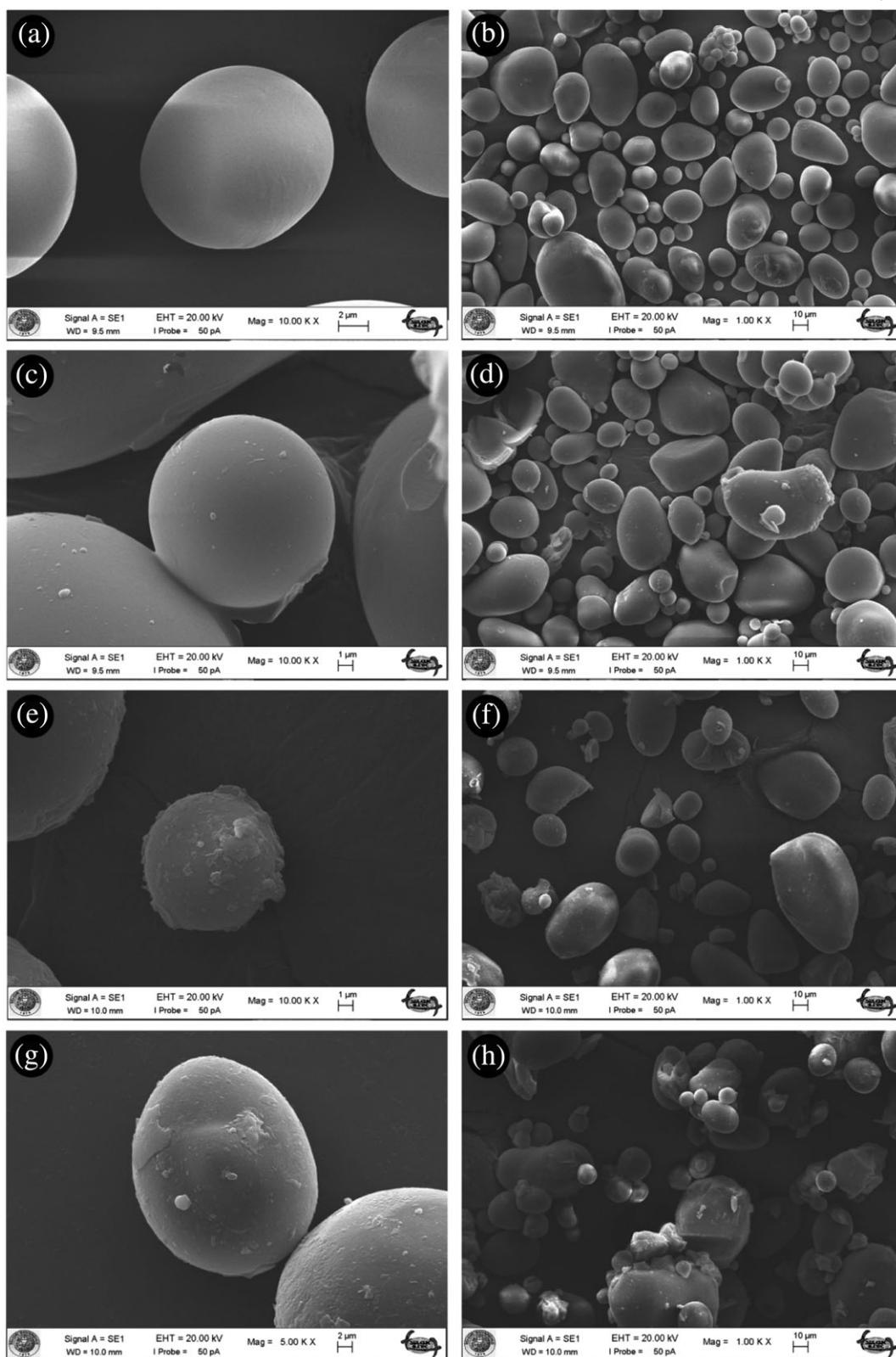


FIGURE 5 SEM images of a-b) ST, c-d) ST-APT, e-f) ST-Shf, and g-h) ST-Shf-Pd

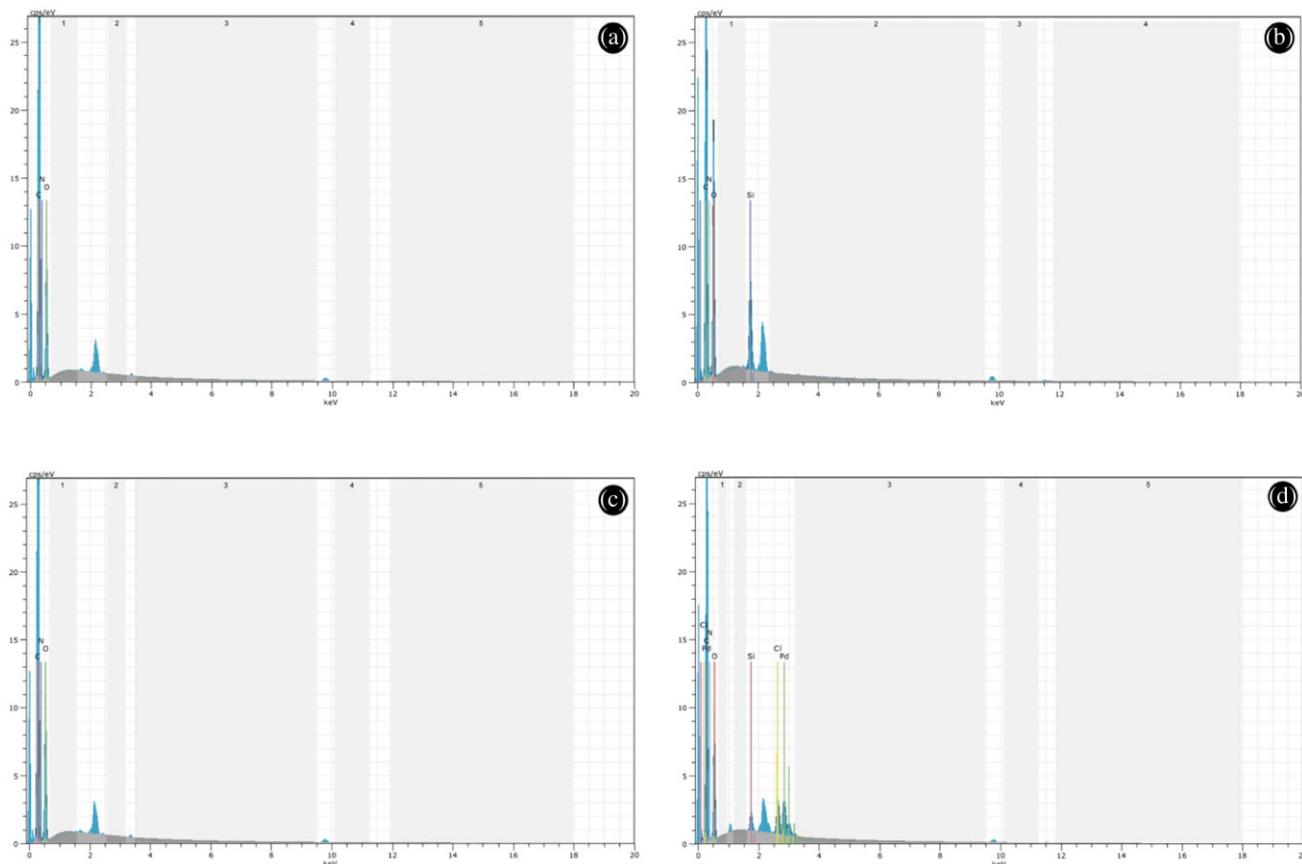


FIGURE 6 EDAX spectra of a) ST, b) ST-APT, c) ST-Shf, and d) ST-Shf-Pd

TABLE 1 Suzuki C-C reactions of different aryl halides and phenyl boronic acid in the presence of robust starch based palladium(II) catalyst

Entry	Phenyl boronic acid	Aryl halide	Product	Biphenyl Yield (%)	TON	TOF
1	<chem>c1ccccc1B(O)2</chem>	<chem>Br-c1ccccc1OCH3</chem>	<chem>c1ccccc1-c2ccccc2OCH3</chem>	99	49.500	495.000
2	<chem>c1ccccc1B(O)2</chem>	<chem>Br-c1ccccc1OCH3</chem>	<chem>c1ccccc1-c2ccccc2OCH3</chem>	97	48.500	485.000
3	<chem>c1ccccc1B(O)2</chem>	<chem>Br-c1ccc(CO)c(c1)C</chem>	<chem>c1ccccc1-c2cc(CO)cc(c2)C</chem>	86	43.000	430.000
4	<chem>c1ccccc1B(O)2</chem>	<chem>Br-c1ccccc1N</chem>	<chem>c1ccccc1-c2ccccc2N</chem>	88	44.000	440.000
5	<chem>c1ccccc1B(O)2</chem>	<chem>Br-c1ccccc1N</chem>	<chem>c1ccccc1-c2ccccc2N</chem>	85	42.500	425.000
6	<chem>c1ccccc1B(O)2</chem>	<chem>Br-c1ccccc1C#N</chem>	<chem>c1ccccc1-c2ccccc2C#N</chem>	98	49.000	490.000
7	<chem>c1ccccc1B(O)2</chem>	<chem>Br-c1ccccc1N#O2</chem>	<chem>c1ccccc1-c2ccccc2N#O2</chem>	91	45.500	455.000

(Continues)

TABLE 1 (Continued)

Entry	Phenyl boronic acid	Aryl halide	Product	Biphenyl Yield (%)	TON	TOF
8	<chem>c1ccccc1B(O)2</chem>	<chem>c1ccc(Br)c([N+](=O)[O-])cc1</chem>	<chem>c1ccccc1-c2ccc([N+](=O)[O-])cc2</chem>	90	45.000	450.000
9	<chem>c1ccccc1B(O)2</chem>	<chem>c1ccc(Br)c(C)ccc1</chem>	<chem>c1ccccc1-c2ccc(C)cc2</chem>	56	28.000	280.000
10	<chem>c1ccccc1B(O)2</chem>	<chem>c1ccc(C)c(Br)cc1</chem>	<chem>c1ccccc1-c2ccc(C)cc2</chem>	55	27.500	275.000
11	<chem>c1ccccc1B(O)2</chem>	<chem>Ic1ccc(O)cc1</chem>	<chem>c1ccccc1-c2ccc(O)cc2</chem>	97	48.500	485.000
12	<chem>c1ccccc1B(O)2</chem>	<chem>Ic1ccc(N)cc1</chem>	<chem>c1ccccc1-c2ccc(N)cc2</chem>	87	43.500	435.000
13	<chem>c1ccccc1B(O)2</chem>	<chem>Ic1ccc([N+](=O)[O-])cc1</chem>	<chem>c1ccccc1-c2ccc([N+](=O)[O-])cc2</chem>	91	45.500	455.000
14	<chem>c1ccccc1B(O)2</chem>	<chem>Ic1ccc(C)ccc1</chem>	<chem>c1ccccc1-c2ccc(C)cc2</chem>	72	36.000	360.000
15	<chem>c1ccccc1B(O)2</chem>	<chem>Ic1ccc(C)ccc1</chem>	<chem>c1ccccc1-c2ccc(C)cc2</chem>	67	33.500	335.000
16	<chem>c1ccccc1B(O)2</chem>	<chem>Clc1ccc(O)cc1</chem>	<chem>c1ccccc1-c2ccc(O)cc2</chem>	70	35.000	350.000
17	<chem>c1ccccc1B(O)2</chem>	<chem>Clc1ccc(O)cc1</chem>	<chem>c1ccccc1-c2ccc(O)cc2</chem>	65	32.500	325.000
18	<chem>c1ccccc1B(O)2</chem>	<chem>Clc1ccc([C+](=O)[O-])cc1</chem>	<chem>c1ccccc1-c2ccc([C+](=O)[O-])cc2</chem>	62	31.000	310.000
19	<chem>c1ccccc1B(O)2</chem>	<chem>Clc1ccc(C#N)cc1</chem>	<chem>c1ccccc1-c2ccc(C#N)cc2</chem>	80	40.000	400.000
20	<chem>c1ccccc1B(O)2</chem>	<chem>Clc1ccc([N+](=O)[O-])cc1</chem>	<chem>c1ccccc1-c2ccc([N+](=O)[O-])cc2</chem>	75	37.500	375.000
21	<chem>c1ccccc1B(O)2</chem>	<chem>Clc1ccc(C)ccc1</chem>	<chem>c1ccccc1-c2ccc(C)cc2</chem>	45	22.5000	225.000
22	<chem>c1ccccc1B(O)2</chem>	<chem>Clc1ccc(C)ccc1</chem>	<chem>c1ccccc1-c2ccc(C)cc2</chem>	38	19.000	190.000

Reaction conditions: 1.12 mmol aryl halides, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3 , 2×10^{-3} mol % robust starch based palladium(II) catalyst, 50 °C, 0.1 h under MW.

TON, turnover number; TOF, turnover frequency (mol product mol $^{-1}$ catalyst h $^{-1}$).

TABLE 2 Comparison results of robust starch-based Pd(II) catalyst with other catalysts in the Suzuki coupling reactions

Entry	Catalyst	mol % of Pd	Time	Temperature	Yield (%)	TON	TOF	Ref.
1	Polyaniline-anchored palladium catalyst	2.2	4 h	95	91	41	10	[16]
2	PdNPs catalyst	1.0	12 h	100	96	96	8	[17]
3	Pd-SMU-MNPs catalyst	0.92	30 min	50	96	104	208	[18]
4	Cis-chelated Pd(II)-NHC complex	1.0	24 h	100	99	99	4	[19]
5	Tridentate NHC-Pd(II) complex	1.0	12 h	80	88	88	7	[20]
6	Fe ₃ O ₄ /DAG/Pd catalyst	0.2	9.6 min	Room temp.	98	490	3062	[21]
7	CpNiBr(NHC) complexes	3.0	2 h	90	87	29	14	[22]
8	Fe ₃ O ₄ /SiO ₂ -DTZ-Pd.	0.5	30 min	80	98	198	396	[9]
9	N-heterocyclic carbene complexes	0.2	12 h	100	97	485	40	[23]
10	PdNP-NMe ₂ @SiO ₂ catalyst	0.5	4 h	50	98	196	49	[24]
11	X-Pd ₃ L catalyst	0.005	2 h	70	99	19.800	9.900	[25]
12	Chitosan supported Pd catalyst	0.01	4 min	50	100	10.000	151.515	[26]
13	O-carboxymethyl chitosan Schiff bases and its Pd(II) complex.	0.02	12 h	100	100	5000	417	[27]
14	Pd@NH ₂ -MIL-125 catalyst	0.9	22 h	100	86	95	4	[8]
15	CS-g-mPEG Pd (0) catalyst	0.5	3 h	150	95	190	63	[28]
16	Fe ₃ O ₄ /P(GMA-AA-MMA)-Schiff base-Pd.	0.1	1 h	80	99	990	990	[10d]
17	Binuclear Pd(II) complexes	0.01	2 h	75	99	9.900	4.950	[29]
18	Pd(II)-SBA-16 catalyst	0.5	2.5 h	80	100	200	80	[30]
19	Silica gel-supported N-heterocyclic carbene-Pd catalyst	0.1	0.3 h	85	100	1.000	3.333	[31]
20	Robust starch-based Pd(II) catalyst	2x10 ⁻³	6 min	50	99	49.500	495.000	Present study

3.2.5 | Leaching and mercury poisoning tests

We carried out leaching test by analyzing hot filtrate with ICP-OES following the 10th run to determine amount of Pd lost on the support. The test revealed very low leaching (~1%) of palladium ion from bio-based palladium(II) catalyst. Additionally, this value is consistent with biphenyl yield decreased from 99% to 80% after the 10 cycles. On the other hand, we performed mercury poisoning test on the model coupling reaction according to our previous study and the test indicates that robust starch-based Pd(II) catalyst has heterogeneous nature [33].

4 | CONCLUSIONS

In this paper, a new high thermally stable bio-based palladium(II) complex containing starch Schiff base ligand was synthesized and its chemical structure was illuminated with different analytical and spectral methods. Catalytic behavior of designed robust palladium catalyst was examined against Suzuki cross coupling reactions. The starch supported palladium catalyst showed

remarkable catalytic activity towards the synthesis of the biaryls in a Suzuki coupling reaction by producing excellent TONs and TOFs values as high as 49.500 and 495.000 after very short reaction time. In addition, sustainability and reusability tests showed that the catalyst could be used several times. These findings indicate that starch is suitable as support material for Suzuki coupling reactions and in different catalytic systems. In addition, this paper has revealed that robust starch based palladium catalyst can be also potential candidate for various catalytic systems due to its superior catalytic performance than other catalysts in the literature.

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